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Physics and Biophysics

Silicon Versus Carbon

Fundamental Nanoprocesses, Nanobiotechnology and Risks Assessment

Edited by
Yuri Magarshak
Sergey Kozyrev
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PREFACE

Even though there is no generally accepted definition of nanotechnologies to be defined as distinct discipline there is an emerging consensus that their advent and development is a growing in importance factor of the contemporary and future technological civilization.

One of these most fundamental issues we are confronted with is the compatibility with life itself. From single cell organisms to humans, carbon is a key building block of all molecular structures of life. In contrast the man created electronic industry to build on other elements, of which silicon is the most common. Both carbon and silicon create molecular chains, although different in their internal structure. All life is built from carbon-based chains. As long as the man built technological products do not directly interfere with the physiology of life the associated risks from them are relatively easy to identify. They are primarily in the environmental pollution and the possibility of upsetting the natural balance of biocoenosis, on a planetary scale. The basic life functions are still not directly subverted. We can use TV, computers, drive cars and use other technological utilities without fear of direct interference with our cellular functions. This is in particular because all these technological utilities are many orders of magnitude larger than typical scales of biological activity. Most of biological activity, from fermentative catalysis to DNA replication takes place on nanoscale.

The situation is radically different when the technological goals are building nanoscale size products. All biological processes take place on nanoscale. From fermentative catalysis to DNA replication, alien and potentially hostile nanoscale structures can directly interfere and in the worst case subvert the biological processes. It is reminded that DNA double helix is ~2 nm, the fermentative globules, biological regulators and fermentative complexes is ~1–10 nm, and live cell is about 100 nm and more. The concept of using nanoproducts, such as medical nanorobots for purposeful interference with physiological functions of organisms is on the drawing boards. Where is the border between benign interference and damaging invasion and corruption of fundamental bio-functions on a cellular and molecular level? Clearly the risk assessment must become a fundamental aspect of any scientific and business feasibility study while creating and developing of one or another nanotechnology and nanoproducts. Michael Crighton's book "Prey" describing the swarm of nanorobots recklessly released by irresponsible company into atmosphere may be a grim science fiction but potential hazards are definitely there.

These and other issues should not only be considered in the context of particular nanotechnologies but rather on a strategic level of visualizing the technological clusters and general principles upon which the nanotechnologies of the future will be operating.

Some of the basic issues are the principles of computations, communications and other intelligent functions upon which the future nano-devices will be built. The first-generation computers were built on lamps. Then followed a revolutionary transition to semiconductors and microchips at the heart of which was massive use of silicon. A question I would like to pose is the following. Is it not necessary to make a break with silicon in and plan a carbon revolution in nanotechnologies? There are at least two aspects to this question. (a): If the risk assessment will convincingly confirm that silicon based nano-products represent danger for live organisms on a fundamental level than the transition to carbon seems to be imperative. (b): If such transition will be assessed as imperative whether there are scientific and technological possibilities for substitution of silicon.

No unambiguous answers exist at this time. I would like to remind that silicon is one of the most common chemical elements on Earth, for instance usual sand is 50% silicon. Carbon of which we made to a large extent is one of the most widespread elements in Universe. On the other hand there is practically no silicon in us. And this is not really surprising because of silicon ability to form chains and this can be dangerous to carbon based chains. Practically every silicone molecule in live cells, if there are such, is under strict control not to get loose. And now imagine swarms of silicon nanoprobes invading our blood flow, brain, cells. Even if they were designed for benign purposes would it be possible to clean the organisms of their presence when their targeted functions are accomplished? And might they not inadvertently affect the immune system of which our knowledge is so far from being complete. Life had avoided contact with silicon on a molecular level for billions of years. Is it accidental?

We know that atmospheric pollution before 20th century had been primarily organic based. What will happen if we start inhaling silicon based nanorobots? This is a large-scale scientific and intellectual problem. Military faced a somewhat similar problem at the dawn of thermonuclear era when it was not totally clear that a thermonuclear reaction would not ignite a chain reaction in atmospheres hydrogen. But this was a relatively straightforward physical problem that could be resolved theoretically and unfortunately practically when large hydrogen bombs were exploded. The hazards that we are facing with uncontrolled invasion of silicon-based nanodevices is much more subtle, involves multitude of particular technologies, and the consequences may become apparent only over a span of time. Military in our time are seriously developing various futuristic nanodevices for military purposes. We on the other hand want to see the development of nanotechnologies in a way that is conducive for the good of our civilization and not destructive.

Interaction of life with nanotechnologies of the future raises additional ethical problems. By the end of 20th century technological civilization reached the stage when in certain areas our technological creations are many times more than what we really need. Indeed, a large part of our current inventions and new products are gadgets and consumer goods. On the other hand the fundamental for our survival development of alternative energy sources and environment protection have little to boast. Wrong prioritizing of objectives can skew the evolution of our civilization in a way that will be difficult to fix in the future. The usual argument that the free market unencumbered by pressures and regulations will determine itself the harmonious paths for technological development is not incontestable; especially it is hollow at the time when we are all passing through a truly gigantic economic upheaval.

In this context defining of general principles upon which the progress of nanotechnologies should proceed, with particular attention to 'silicon vs. carbon' paradigm, is high on the list of priorities. Theoretical deductions, experiment, sociological, ecological and economical aspects should be all inclusive for integrated approach to the problems that are posed to us by nanotechnologies. It seems right if we all biologists, physicists, computer scientists, engineers, societal sociologists, doctors and philosophers would attempt together to chart what we believe may be really necessary and useful to do for making nanotechnologies a harmonious aspect of our civilization.

Such was more or less the spectrum of participants that took part in ARW in St. Petersburg. The program was split into four sessions:

1. Environmental friendly nanotechnologies and risk assessments
2. Environmental and biological risks of nanobiotechnology, nanobionics and hybrid organic-silicon nanodevices
3. Fundamental nano-processess: from theory to technological applications and Risk assessments
4. The social aspects of nanotechnological revolution

Obviously it is not possible to solve the problems posed above in one workshop. The Organizing Committee intends to hold regularly similar events dedicated to these problems. Also more specialized workshops with attention to particular aspects of the general issues will be held. The lecturers and participants of poster sessions showed high motivation and the size of submitted to us material exceeded the limit allowed by our Springer publishers. Under the circumstances some of the participants kindly cooperated with us and reduced the size of their essays, or united two into one to accommodate the required regulations. Unfortunately some of the interesting papers were not included at all because of their size.

In total, approximately 50% of submitted material and at least one paper by each participant were included in the publication. The rest will be published in a special issue of "New and Old Concepts in Physics" in 2009.

The Organizing Committee is especially grateful to NATO for the generous support of the workshop. We are also indebted to Navy Global and Navy USA for extending additional grants enhancing the quality of the workshop, making more efficient the preparation of the manuscripts for publication and facilitating collaborative work of international groups that were formed in the aftermath of the meeting.

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IS “SILICATE LIFE” POSSIBLE?

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Abstract. The simplest theory of chemical reactions (including also structural isomerisation reactions) is based on the model of potential barrier overcoming which separates combining states (chemical forms) of molecular objects. In a more complicated model not only the zero but other oscillation level positions are taken into account that in the theory of temperature reactions leads to the statistical sum changes on the states. In all traditional models only energetic factors are taken into consideration. A close structural similarity of some organic and silicon organic compositions (for example, paraffins and silans) and similarity of electron building of carbon and silicon atoms, that also reflects in the similarity of their atomic orbitals, were noticed by researchers long ago. These options cause an idea of a possibility of what can be called “the silicate life”. In connection with new visions at the mechanism of the elementary act at chemical reactions there was an opportunity to consider some chemical factors which influence the run of the reactions that earlier had slipped out from the attention.

Keywords: valence, carbon, silicon, Schrödinger equation, silicate life

1. Introduction

A close structural similarity of some organic and silicon organic compositions (for example, paraffins and silans) and similarity of electron building of carbon and silicon atoms, that also reflects in the similarity of their atomic orbitals (AO), were noticed by researchers long ago. These options cause an idea of a possibility of what can be called “the silicate life”. In connection with new visions at the mechanism of the elementary act at chemical reactions there was an opportunity to consider some chemical factors which influence the run of the reactions that earlier had slipped out from the attention. Of course, it was well known that for the explosion of the methane and oxygen mixture it was required to have a sufficient local increase of the temperature, and the analogous

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oxygenizing reaction SiH_4 in the mixture with O_2 goes already at rather lower temperatures. Nevertheless, the idea of “the silicate life” again and again has been discussed in the literature. Let us consider this problem.

2. Chemical Transformation as a Resonance Non-Irradiative Transition

The simplest theory of chemical reactions [1–4] (including also structural isometrisation reactions) is based on the model of potential barrier overcoming which separates combining states (chemical forms) of molecular objects. The way of the reaction corresponds to the geodesic curve connecting the minima of energetic “holes” of two quant substructures (structural isomers). The excitation energy (activation) of the reaction is determined by the distance on the energy scale from the “hole” minimum of the initial molecular structure till the saddle point of the potential barrier. It is seen that in this model the mass effect is totally absent.

The simplest method of counting this effect lies in counting the activation energy not from the energy “hole” minimum but from the energy of zero oscillations. Now note that the substitution even of one atom for the heavier one even at fully unchanged electron state will result in the following: the oscillation frequencies will either reduce or remain unchanged (some of them).

In the result the zero oscillation level always decreases while this substituting and that is why the reaction activation energy must always increase in comparison with the case of “light” modification, and the reaction velocity – decrease.

In a more complicated model not only the zero but other oscillation level positions are taken into account that in the theory of temperature reactions leads to the statistical sum changes on the states. For the models which take tunnel transitions into account it can lead to disappearance or appearance of the quant state resonance and, correspondingly, also to the change of the reaction velocity.

In all traditional models only energetic factors are taken into consideration. Let us take one more very important factor.

The main statements of the theory of chemical transitions will be taken for the basis which has been developed in monograph [5] and several pervious several publications.

According to this theory a chemical transformation is rendered as a resonance non-irradiative transition between combining levels of subsystems different in structure whose general state is described by a wave packet for which the module of the wave function square has the following form [5]:

$$|\Psi(t)|^2 = |\Psi_1|^2 \cos^2 \omega t + |\Psi_2|^2 \sin^2 \omega t \,. \tag{1}$$

In expression (1) Ψ_1 and Ψ_2 are wave functions of stationary resonance electron-oscillation states of the subsystem (with energy E_{ev}), and ω is the frequency of quant beating of these states in the wave packet. This value determines the probability of the non-irradiative transfer, i.e., chemical transformation. In its turn, $\omega = E_{ev}\, S_{ev}$, where S_{ev} is an overlap integral its own electron-oscillation functions of these resonance states of the reacting chemical objects. In a rather good approximation while calculating ω it is possible to be limited by the calculation of only oscillation content S_{vv} of the total integral S_{ev}, which obtains the Herzberg–Teller form [6]. Methods of the corresponding calculations have been developed [6]. It allowed one to carry out modeling for a big number of concrete molecular structures. In all the cases the electron-oscillation levels and their corresponding wave functions were calculated, the resonance states were determined as well as their overlap integrals and ω, meaning which are included into the expressions for probability of chemical transformations (non-irradiative resonance transfers) and into the coefficients of the corresponding kinetic equations while defining the kinetics of the processes under consideration.

To visualize and demonstrate only the effects related with the change of the atom mass, let us consider examples of monomolecular reactions of isomerization at different deutero-substitutions.

The results illustrating the changes at isotope substitutions of non-irradiative transfer probabilities, are given in Table 1. Symbols of isomer transformations of a row of molecules are the following: allen↔methylazetyllen (AM), buten-1↔buten-2 (BU12), gexen-1↔gexen-2 (HE12), buten-1↔buten-3 for «linear» (BU13) и «curved» (BUc13) forms and their isotope substitutes (BU12-D_3, BU13-D_6, BUc13-D_6, AM-D_1, AM-D_2, AM-D_3, AM-^{14}C). It is seen that values ω can change very much, sometimes by orders, and the isotope substitution can result in "differently directed" effects. So, for example, for the structural transformation BU12 the deutero-substitution (BU12-D_3) leads to reducing value ω by the order and for BU13 and BUc13 (BU13-D_6 and BUc13-D_6) – to increasing analogous on meaning. We should also stress that there is no direct dependence of the effect value on "the degree" of isotope substitution, that is seen very well, for example, for the transformation AM, when one-and- twofold deuterising leads to a very strong and quantitatively the same effect ($\sim 10^3$), but at a threefold deuterising this effect is practically absent. As it was earlier shown by computer methods of the experiment, at these changes of the values of molecular parameters the kinetics of the chemical process of the structural transformation can substantially alter resulting not only in quantitative but also qualitative changes – "inversions" of the ratio of the obtained products quantities in the result of photochemical transformations [6].

Isotopic effects in the reactions with deutero-substitution H→D are, of course, significantly larger than while substituting $^{12}C \rightarrow ^{14}C$, but in this case they reach the order of the values on quant beating frequency of the resonance levels, and consequently, of the probabilities of non-irradiative transfers. The obtained effects in some cases are significantly bigger than those which appear when only the factors related with the changes of the energy level positions, are taken into account.

Now consider the physical origin of the results under discussion.

Any chemical transformation is related with substitutions of atoms in the initial molecular system. These substitutions can happen only in the result of oscillations having a big amplitude and excite them, the external energy is required to be introduced into the system.

If to consider a chemical process as a non-irradiative transfer between two combining states at the quant resonance of the energy levels of the subsystems and mixing of the corresponding wave functions, it is clear that the probability of this transfer will be determined by the mutual relation of normal oscillations of atoms in subsystems, in this case – by the oscillation forms of isomers. A quantitative characteristic of this mutual relationship is the value of the overlap integral S_{vv} of the oscillation wave functions of resonance vibron states participating in the reaction of isomer structures. In its turn the value of integral S_{vv} is determined by the ratio of the normal coordinates of combining isomers which has the following form:

$$Q_1 = AQ_2 + b, \tag{2}$$

where Q_1 and Q_2 are normal coordinates corresponding to the isomer structures, normalized on the zero oscillation amplitudes, A – is a squared matrix of the axes turn and scale change for normal coordinates at the transfer of the second isomer to the first one, and b – is a vector of the shift of the coordinate systems beginning, i.e., of the position of the "hole" minimum for the isomers whose geometry is described in the system of normal coordinates and characterized by the point in the corresponding multi dimensional space. The shift of vector b, defined by the expression [6]

$$b = Q_0^{-1}\tilde{L}_p \Delta s \tag{3}$$

(Δs – is a vector of geometry changes in natural coordinates (change of distances between atoms, valent angles, and etc.) and Q_0, L_p – matrices of the zero oscillation amplitudes and the corresponding impulses of the first isomer [7, 8]), characterizes the degree of difference of geometrical configurations of the combining molecular structures and is the main parameter determining the value of the overlapping integral S_{vv}, especially at significant molecule deformations [6]. Rather important is not only the norm (length) of vector b ($\|b\|$), which is a quantitative characteristic of the difference degree of the geometries of the combining molecular structures, but also the distribution of value on its components b_i, i.e., its structure since this very distribution characterizes the degree of localization (delocalization) of the special deformation of the molecule while structural transforming. It is necessary to emphasize that the locality of the structural transformations which refers mainly to a relatively small atomic grouping of the molecule (its fragment) is one of the key factors defining an opportunity of the given inter-isomer transfer and introduction of the notion of the reaction centre itself as one of the basics in chemistry [6, 7].

To illustrate the influence of vector b for the meaning of the matrix element S_{vv} being searched for that is for the value ω, we'll give the data of concrete calculations (Table 1). For example, while transition from the isomer transformation BU12 to BU13 the structure of vector b, which will be characterized by the quantity of its elements b_i, having their values in the given intervals of the meanings, changes very slightly but the length of vector $\|b\|$ alters significantly (due to increase of b_i values for the coordinates corresponding to big deformations; $b_i^{\max}$ changes from 7 to 14).

TABLE 1. Ratios of norms of vector b ($\|b\|$), its structure (N – number of elements b_i of the given value), integrals of overlapping of the oscillation wave functions S_{vv} and quant beating frequencies ω for different isomer transformations of molecules

Isomer transfer*		$\|b\|_A \leftrightarrow \|b\|_B$	$N_A \leftrightarrow N_B$		$\frac{(S_{vv})_A}{(S_{vv})_B}$	$\frac{\omega_A}{\omega_B}$
A	B		$1 \le b_i < 5$	$b_i \ge 5$		
BU12	BU13	20↔22	8↔7	7↔7	10^4	10^4
BU12	HE12	20↔20	8↔15	7↔5	10	10
BU12	BUc13	20↔18	8↔12	7↔6	10^2	10^2
BU12	BU12-D_3	20↔23	8↔8	7↔6	10	10
BUc13	BUc13-D_6	18↔21	12↔10	6↔6	10^{-1}	10^{-1}

This results in decreasing values S_{vv} and, respectively, ω by the order. Comparing structural transfers BU12 and HE12, it is seen that the length of vector b does not change in this case, but its components alter significantly (deformation for transfer HE12 is much less localized than for BU12; the number of elements b_i important on value for the given process grows from 15 till 20), that finally also results in changing S_{vv} by more than one order of the value. A simultaneous change of the norm and component of vector b is possible as it takes place, for example, while comparing transfers as it takes place, for example, in BU12 and BUc13. It is noticeable that relative delocalization of the deformation in BUc13 compared with BU12 is so big that even decreasing of the length of vector b cannot compensate this influence and the probability of transforming BUc13 in comparison with BU12 reduces by two orders.

The reasons of the difference of shift vectors b for different isomer transformations are quite understandable from expression (3) – this is the difference of either the values of geometrical changes Δs or the forms of oscillations characterized by matrix L_p, or of the both simultaneously. In case of isotope substitution when vector Δs does not change in general, the second reason of changing vector b and as a consequence of the transfer probability, is the only one.

It is well known that at the isotope substitution the forms of normal oscillations (especially while substituting H→D) can change very much [6]. It results in changing vector b and, thus, altering value of the vector of oscillation functions overlapping S_{vv}, quant beating frequency ω and the probability of structural transformations (in particular, for the examples given in Table 2).

Actually, (see Table 1) for the structural molecular transformation BU12 deutero-substitution (BU12-D3) results in such changes of the oscillation forms that the first mechanism mentioned above is realized – the length of vector b changes, and it leads to decreasing ω by the order. For molecular transformation BUc13 at deuterising (BUc13-D6) a differently directed action simultaneously of the both mechanisms is characteristic: though the norm of vector b grows significantly that should result in decreasing the overlapping integral. The change of the components of vector b due to the change of the oscillation forms, is so significant that in the result S_{vv} and ω grow by the order. This complicated influence of changes of the normal oscillation forms on the quantitative characteristics determining the probability of the process of the molecule structural transformations results in the following: the changes of the process characteristics may have a different sign and the kinetic isotope effect can be “differently directed”. It is necessary to stress that due to the same reasons the change of the probability can be negligibly small even at significant isotope changes in the molecule as, for example, it takes place for the isomer transfer AM while substituting three atoms H for D (see Table 2).

TABLE 2. Influence of isotope substitution on the values of quant beating frequencies ω determining probabilities of isomer transformations of molecules

Isomer transfers*		$\frac{\omega_A}{\omega_B}$
A	B	
BU12	BU12-D_3	10
BU13	BU13-D_6	10^{-1}
BUc13	BUc13-D_6	10^{-1}
AM	AM-D_1	10^{-3}
AM	AM-D_2	10^{-3}
AM	AM-D_3	1
AM	AM-^{14}C	10^{-1}

It goes without saying that the effect in general decreases at isotope substitution with insignificant changes of the masses of atoms due to the smaller changes of the oscillation forms, for example, 12C→14C in comparison with H→D though in this case it also may be significant (see above).

The performed analysis has shown that in the theory of structural transformations of the molecules when studying even the simplest isotope effect, it is necessary to take into account not only the energetic factor which influences on it but also the probabilistic one conditioned by the changes of the probabilities of non-irradiative transfers due to the changes of the normal oscillation forms. The second factor can lead to rather significant on value effects since the transfer probability can change by the orders of values that, in its turn, can result in significant and not only quantitative but also qualitative changes of the kinetics of the structural transformation process.

Now we are coming back to the question at the very beginning of the article. Let us compare the forms of oscillations of molecule C4H10 and model structure Si4H10, which differs from C4H10 only by the substitution of the masses of atoms C with Si at totally unchanged geometrical and electron construction of the first molecule (all the oscillation coordinates and power constants are preserved).

The results of corresponding calculation shows that at a simple substitution as C by Si the forms of normal oscillation are changing drastically, i.e., also the wave functions.

Ab initio IR spectra of molecules C4H10 and Si4H10 demonstrate differences also in the distribution of electron density that is reflected in the meanings of the power constants and frequency shifting X − H and H − X −H oscillations.

If now to take into account everything mentioned above on the probabilities of chemical reactions and their dependences on the forms of oscillations transforming at the reactions of the structures, and the fact that the reduplication process basic for all the phenomenon of life, is multi staged and self-coordinated [5] in the high degree, then the conclusion that appearance of "the silicate life" is an extremely low probability, becomes unavoidable.

3. To the Problem of the Possibility of Silicate Life

Our considerations are the following:

First of all, the key point underlying the phenomenon which is conventionally called "life" should be defined. It is often considered that everything reduces itself to self-organization, i.e. to emergence of the complex from the simple. This is necessary but not sufficient! In polymerization, a complex structure emerges from the simple too, but this is not life! Life is, first of all, reproduction. On the molecular level it is reduplication.

The reduplication process itself is a multi-structural one, it is a sequence of elementary acts of reactions. The correspondent physics is expounded in the book on molecular processes [5]. It is important that all stages should be concerted. Death, that is, self-destruction of replicas, must take place. This leads to biological rhythm. Only as a result of all this the time arrow appears, manifesting itself in the growing stream of information that is transferred from the donor molecule to the replica, which itself becomes the source of reduplication.

Nature has selected organics. The similarity with siliceous compounds should not be misleading. Firstly, these compounds are considerably less stable. It may lead to untimely "dying" of the matrix, which will cease the reduplication process. Secondly, the fluctuation frequencies in organics and in silicates are substantially different. The masses of C and Si are significantly different too. Therefore the conditions of the course of similar reactions at the transfer from C to Si must be completely different. Thirdly, processes in complex molecules are impossible without intermolecular energy transfer. A simple example with C is migration of the double bond over the chain of singular ones. Nothing comes out with the Si atom.

4. Conclusion

To construct anything similar to life is not likely with Si.

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NANOCARBON TECHNOLOGIES: PROSPECTS AND RISKS

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Abstract. In this paper we review the current state and prospects of carbon nanotechnologies as a new emerging point for atomic-molecular manipulation, design and discovery connected with fullerenes, carbon nanotubes and biology. The merging nanoscale interface between carbon and biology structures are shortly discussed in terms of fundamental insights and possible applications encompassing nanobionics as lessons from animate nature, artificial modifications of living systems as well as multicomponent molecular structures for biology, physics, chemistry, engineering, and medicine. Protein-based as well as carbohydrates-, lipids-, or DNA-based molecular assemblies loaded with nanocarbon are addressed in the context of the engineering systems design. Several examples from our collaborative work are used to demonstrate connections between points of nano and bio and to show how such an interdisciplinary approach has led us to new ideas and applications. Nanocarbons have little similarity with the well-known biologically active substances. There is no oxygen, nitrogen, phosphorous-containing or other typical moieties, such as common pharmacophoric anchors or groups. In the same time fullerenes demonstrated a wide spectrum of biological activity. Mechanisms of their biological action are still unknown. For this reason our work was focused on the computer-based molecular modeling of the action of nanocarbon structures on the well-known biological structures: proteins, DNA, carbohydrates, and lipid molecules. Possible biological hazards, fundamental questions and prospects associated with nanocarbon technologies are highlighted.

Keywords: nanocarbon, nanotubes, fullerenes, biological structures, molecular modelling, nanobionics, bionanotechnology, nanobiotechnology, biological hazards

1. Introduction

The general subject of this paper is the prospects and risks of nanocarbons technologies connected with nanobionics on the one hand and possible toxicological risk on the other. The first researches of biological activity and toxicity of nanocarbons (fullerenes and carbon black) in Russia have been undertaken in 1994 (group of Yakutseni P.P.) in

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frame of the first All-Russian national nano-program “Fullerenes and Atomic Clusters” under the direction of Lemanov V.V. and Kozyrev S.V. [1].

What we want from nanotechnology? We want a new good nanostructured material or a nice nanodevice but these are just some of the possibilities. In asking what we want from nanotechnology, we must put the question in its broadest form. We must ask not for the goals we form as we go about our daily activities but for the greater goal. In other words, what is the most valuable thing in nanotechnologies? It is quite clear that man-made fullerenes and nanotubes are promising materials in nanocarbons technologies with very hopeful properties [2–4]. Biological molecules are considered as great tools in nanobiotechnology that have very attractive properties and allow many technology applications.

The main question of our consideration is whether a hybrid world of man-made nanocarbons and biological structures is possible? And another question – is it dangerous?

2. Nanocarbon Prospects

Nanocarbons technologies deal with many forms of carbon (balls, tubes, sheets, diamonds, graphenes, etc.), among which fullerenes and nanotubes are most widely used. The world of biomolecules is presented by four classes of substances but the number of species is huge. More than 100,000 proteins play the role of structural elements of living and mass transport, substances and energy conversation, switchers, receptors and sensor controls. Different types of nucleic acids like DNA, RNA, including artificial systems and regular 2D, 3D-lattices. A lot of carbohydrates molecules play a significant role in energy conservation, assembling and information transfer. Lipid membranes consist of many tens lipids and carry out functions of structuring and isolating cell compartments, matrixes for different proteins. There are no such molecules as fullerenes or carbon nanotubes in living.

Is a new hybrid world possible?

2.1. NEW WORLD POSSIBILITY

It is well-known that biological molecules selectively co-operate with each other. For this purpose the rules demanding complementarity between non-polar hydrophobic groups and polar interactions such as hydrogen bonds or interaction of opposite charges should be observed. Nanocarbons have very unusual spatial structure and do not contain any polar groups. At first sight the probability of biomolecular recognition for fullerenes or, for example, tubes appears as low.

As a result of our long study [5–7] it has appeared that nanocarbons can co-operate with other molecules in a very unusual manner.

One of the important factors of intermolecular interactions is van der Waals forces. In the case of usual molecules, there is an important interaction of the most closely located atoms hydrogen–hydrogen and rare hydrogen–carbon. This energy makes about 0.015 kcal/mol for each hydrogen–hydrogen and about 0.04 for carbon–hydrogen interaction. In usual molecular systems without nanocarbons, the close contact probabilities for these two interactions are about 40% and 18% correspondingly. For nanocarbon-containing systems, they are 0% and greater than 60%. It means that enthalpy driven van der Waals binding for nanocarbons with other organic molecules is three times larger than usual.

Another important factor for molecular interactions is hydrophobicity. Diameter of fullerenes or nanotubes molecules is about the size of most known bioactive molecules and drugs (0.7–1.5 nm). It means that there is no controversy in size to bind with different hydrophobic pockets of biological macromolecules in general. Entropy driven effect of hydrophobicity of nanocarbons is due to their monoelemental composition (pure hydrophobic carbon).

The third factor is the π-interactions. Nanocarbons demonstrate intensive π–π interactions with other aromatic systems, e.g., such as some amino acids, all nucleic bases, etc., π–n interactions with lone pairs, and even π-cationic interactions with charged moieties localized on the surface of biological molecules or with biological ions, which form bridges for binding between nanocarbons and organic molecules of living.

The last but not the least is high spherical (fullerenes) or cylindrical (nanotubes) symmetry of nanocarbons. Usually, formation of an intermolecular forces network demands for stopping the rotation of molecule round its centre of gravity. It is energetically unfavorable with more than a 3–4 kcal/mol per each axe of rotation. For fullerenes, such energy losses do not arise because of indiscernible rotations of the quasi-spherical structure. For nanotubes, these odds are moderate but still present.

Summarizing these four factors, one can speculate that nanocarbons might form hybrid bimolecular complexes nanocarbon–biomolecule or heterogenic multicomponent atomic-molecular nanostructures: nanocarbons–water–ions–biomolecules with different types of atoms and molecules, including main type proteins, nucleic acids, carbohydrates and lipids.

2.2. MAPPING THE NEW WORLD

Simple calculation gives us enormous variety of combinations for creation of atomic-molecular ensembles that consist of nanocarbons with different proteins, nucleic acids, carbohydrates, lipids and other additions (ions and other small molecules). Due to their unique physical and chemical properties, nanocarbons have attracted considerable interest in wide fields of research including material science, photonic, electronic and biomedical applications [4].

Each of thousand biological molecules has a certain functional role, which has got used to execute sensing, switching, energy storage or transformation etc. in perfection. A lot of possible combinations of species or corresponding properties demand first of all not experimental but a theoretical map.

Step 1. At the initial stage, the numerical modeling of the interaction of nanocarbons with typical elements of some micromolecules of natural origin has been performed and compared with the experimentally obtained data for water solutions.

Step 2. At the second step, the numerical modeling of more complex objects was performed, with fullerenes on the one side, and amino acids, nucleic basis, sugars, single phospholipids and cations on the other side, interacting in the vacuum or the water environment.

Step 3. After that some typical secondary structures of proteins RNA and DNA molecules, polysaccharides and phospholipids layers were analyzed for interaction with fullerenes. The theoretical results obtained were tested experimentally by using NMR spectroscopy and other techniques (lipid bilayers) and photospectrometric studies of proteins fermentative activity, dependently from fullerenes concentration and photo-exitactions conditions.

Step 4. The models developed have been used for the well-directed design of appropriate nanostructures, nanotubes and forecasting the biological hazards of nanocarbons for health and environment.

The detailed description of the used methods of molecular modeling and experimental results will take a lot of place. Here we would rather concentrate on the results of the performed work and the following prospects of nanocarbon technologies connected with biological objects.

2.3. NANOCARBONS – PROTEIN

From the point of view of the nanotechnology, many thousands of proteins can be divided into four functional classes: the structural proteins used in the structural skeleton or the mechanical amortization of living (1); the molecular machines such as ferments or muscles (2); the chemical, optical, electrical and other sensors (3); the different switchers for energy conversations, ion currents and regulation (4).

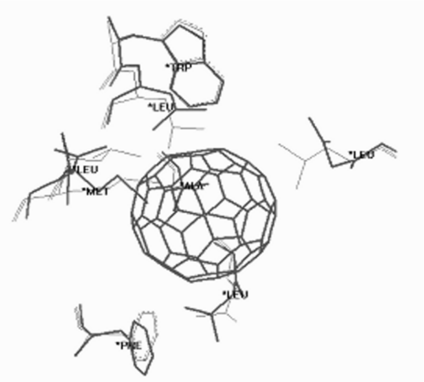

Figure 1. The nearest environment of the molecule C_{60}, in protein recognition site. An example of estrogenic receptor. For comparison, usual positions of the nearest amino-acid residues are marked with thin lines

To establish a model of interactions of fullerenes with proteins, it is essential to evaluate the fullerenes binding points. In the result of molecular simulation it was found that fullerenes C60 can interact with a single polypeptides chain (enthalpy 4–9 kcal/mol), with the protein surface (especially, with a positive charged amino acids residues), and with inner cavities of protein like hydrophobic pockets and recognition sites of ferments and receptors with a free energy up to 20 kcal/mol (Fig. 1).

Interaction of fullerenes with typical elements of structure of proteins is no less interesting. It means that α-helixes, parallel and anti-parallel β-sheets are common positions for binding of fullerenes (Figs. 2 and 3).

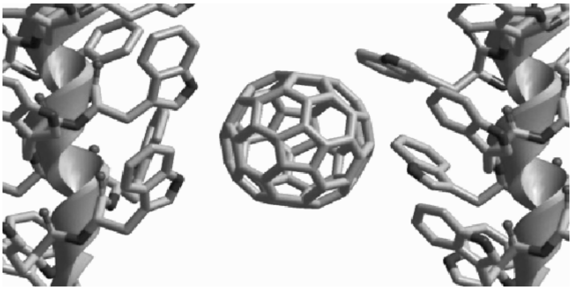

Figure 2. The nearest environment of the molecule C_{60}, in interacting with amphipathic α-helixes typical for most proteins

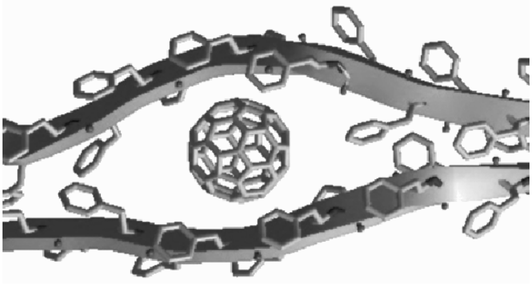

Figure 3. Molecule C_{60} in interaction with hydrophobic β-sheets of silk protein. It is easy to see that energetically favorable binding disturbs protein structure in the nearest environment

Due to the unique molecular architecture, fullerenes appear to be capable of entering intensive interaction with binding sites of receptors, enzymes, structural or other proteins. Obtained results have general character and can be reproduced for a number of others fullerenes (C_{20}, C_{24}, C_{70} were tested in simulation) and even for carbon nantotubes (Fig. 4).

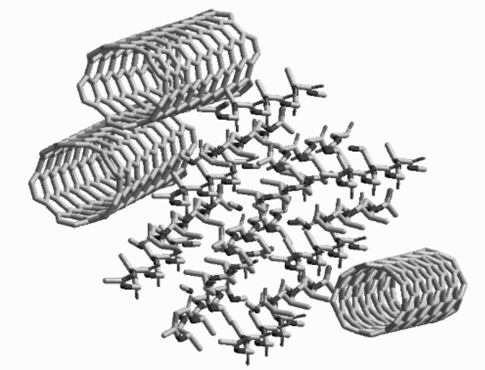

Figure 4. Three carbon nanotubes with hydrophobic β-sheets. Binding with silk proteins structure create parallel orientation of nanotubes

Binding with proteins leads to a very general result. In live systems, proteins function under control of regulatory networks. In artificial systems there are no such regulation available. Application of nanocarbons lead to a opportunity to manipulate the function of a protein by changing the concentration of the nanocarbon. Due to the optical properties of nanocarbons, the activation or the inhibition of proteins is possible also by an ultraviolet and this is important.

In the result of the interaction, the fullerenes form a complex with receptor ferment or other protein. Contrary to the selective structurally specific chemicals, which are capable to act only on proteins corresponding to them, fullerenes can interact with many different proteins, which is unusual.

First, it is well known that an interaction means binding. This means a discovery of the new world of the systems that combine the unique properties of nanocarbons and proteins.

Second, the occupations of any recognition site regulate proteins and change activity of proteins function up/down depending on concentration.

Third, after photoexitation nanocarbons change properties for some time. Attributes of connected proteins also vary. It means that nanocarbons are the first useful tool not only for production of a wide set of protein-based devices like switchers, sensors and molecular machines but also for programming them in a concentration and/or photodynamically depending manner.

The same holds true for structural proteins and protein-based materials. As a result of modeling pair elements of α-helixes (Fig. 2) or β-sheets (Fig. 3) it is easy to see that C_{60} plays the role of the binding “bridge” between peptides chains and strengthens the interaction. In the case of α-helixes, the intensity of interaction depends on amino-acids residues, whereas for β-sheets, this dependence is less specific. Nanocarbon increases a distance between α-helixes or β-sheets. The occurrence of the local defects indicates that it is capable of increasing porosity of a material and changing its elasticity, longitudinal and cross-section stretching, depending on the concentration and the illumination.

Parallel nanotubes orientation presented by Fig. 4 is interesting not only for material design but also for electronics. The model developed demonstrated that:

- There is a possibility of creation of the hybrid systems uniting functional properties of nanocarbons with proteins.
- Changes in the concentration of carbon allow one to alter the functioning of the hybrid systems.
- Photoexcitation of the carbon-bearing systems allows one to carry out their dynamic programming.
- Available methods of numerical modeling allow one to conduct the well-directed nanodesign of systems with the desired physical and physico-chemical attributes.

2.4. NANOCARBONS – NUCLEIC ACIDS

Results of modeling of nanocarbons and gene molecules (single stranded RNA, single and double stranded DNA) allow one to assert that fullerenes, unlike carbon nanotubes, co-operate intensively with nucleic acids with free energy of binding up to 20 kcal/mol. It was demonstrated that fullerenes produce a complex where DNA/RNA strands are seemingly coated with C_{60} molecules (low concentrations of fullerenes) or with C_{60} threads (highest concentrations). The results of a molecular dynamics and Monte Carlo computer simulation have demonstrated that fullerenes drastically change the spatial organization and the functions of gene molecules.

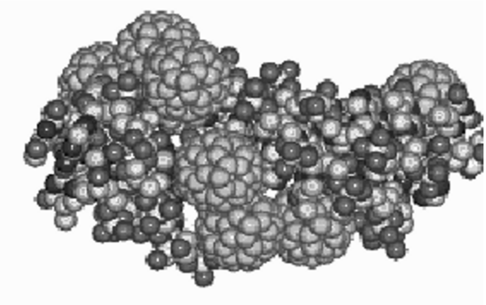

Figure 5. Fullerenes C_{60} cover gutter at the surface of double stranded DNA. There is no intercalation in DNA inner space

For technological applications, the sensor controls and the regular two- and three-dimensional lattices of DNA are especially interesting. The latter is used for producing of special (e.g., optical) crystals, base plates as matrixes bearing guest molecules or nanoparticles arrays (e.g., elements of memory), and other operated 2D, 3D-lattices with controlled step till 0.34 nm.

First, carbon changes the DNA properties. Thus, as well as in the case of proteins, there are possibilities of changing mechanical, electric and other physical characteristics of nucleic-based nanosystems, e.g., via fullerenes concentration or photodynamic management of DNA lattices or sensors controls. Second, fullerenes covering a gene surface can connect with gene molecule and a wide range of another substances. Triple complexes like DNA-fullerene-guest are possible for loading of gene-based systems with a wide set of such molecules that usually don't bind with DNA or RNA.

Third, nanocarbons possess the expressed water repellency that allows one to carry out hydrophilic DNA/RNA structures to nonpolar phases.

2.5. NANOCARBON – LIPIDS

As a result of modeling of fullerenes and nanotubes in lipid membranes, it was estimated that the binding free energy of nanocarbons exceeds 14 kcal/mol. So, nanocarbons were shown to be absolutely special agents capable of contacting a wide range of membranes with various lipid or protein–lipid composition, modifying the spatial organization and phase state of membrane, including dynamic defects in membranes structure, permeability for small molecules, association of different guest molecules, electrochemical potential, surface tension and microviscosity, electronic, physical and chemical properties and so forth. This opens new possibilities of changing the characteristic of a membrane by loading it with nanocarbons and/or photodynamic excitation for well-directed design and programming of such membrane based nanosystems as:

- Designed nanocarbobs-lipids nanoparticles (e.g. micelles or vesicles) with desired physico-chemical, optical and drug-delivery properties
- Well-modified nanocarbons-lipids structural bases for assembling of different active molecules or their aggregates
- Nano-thin membranes for high performance gas/liquids filtering or separation of chemicals

2.6. NANOCARBON – CARBOHYDRATE

Another prospect of nanocarbons technology applications is the creation of artificial complexes of nanocarbons with saccharides of different size. As a result of conducted molecular simulations, the new hybrid structures were predicted, such as fullerenes and carbon nanotubes with monosaccharides, polysaccharides, including ring and tube like polysaccharide molecules [8].

In translational and rotation movement of molecules, free energy of interaction amounts to 8–13 kcal/mol. In the course of simulation conformations of saccharides were changed. The most preferable variants of binding assumed that fullerenes were located near the centre of a polysaccharide ring or a polysaccharide tube end face. Interesting complex is also available where the nanocarbon play the role of an axe and one or more saccharides rings can rotate around the axe.

At present glycobiology nanotechnology is still at the beginning and it is difficult to speculate about applications of nanocarbons-sugars systems except for new nanoaggregates as details for molecular mechanics engineering, nanocarbons interruption in processes for energy transformations, partitioning in polar/nonpolar volumes, and molecular self-recognition and self-assembling processes.

2. Nanocarbons Risks

Fullerenes have no structural prototypes among well-known regulatory or signaling biomolecules. As a result of computer simulation of C_{60} with proteins and other biological important molecules, it is shown that because of the compact carbon structure, fullerenes could demonstrate an exceptionally intensive interaction with a variety of cavities, which usually forms the most regulatory important part of biological macromolecules – binding sites. In spite of absence of any typical pharmacophoric moieties, the energies of C_{60} and nanotubes binding are comparable with the usual energy of drug-receptor interaction. It means that nanocarbons and especially fullerenes must possess remarkable and wide spectrum biological activity, which agrees with the existing experimental data [5, 9]. During the simulation of nanocarbons with lipids molecules, it has been demonstrated that fullerenes and carbon nanotubes can easily be deposited in a fatty phase. Are nanocarbons potential drugs or toxic agents?

The toxic properties of fullerenes C_{60}/C_{70} mixtures and fullerenes site were studied for the first time in 1995 on hydrobionts, white mice and rats under conditions of acute and repeated impact [10]. The data obtained in dark conditions allow for a classification of fullerenes as virtually non toxic chemical formations. The same holds true for the newer results that show that the unmodified fullerenes C_{60} themselves have no negative effect. In contrast to this, under the ultraviolet irradiation or to light conditions chemically-modified fullerenes (either covalently or noncovalently), some C_{60} derivatives can be highly toxic [11]. Exposure to carbon nanotubes is associated with effect on DNA, pulmonary toxicity, fibrotic lesions, skin toxicity [12].

Therefore, many further studies on well-characterized materials are necessary to determine the safety of carbon nanotubes as well as their environmental impact. Herewith extreme hydrophobicity of nanocarbons structures significantly complicates every experimental studies of toxicity or no toxicity. In the same hydrophobicity can lead to retention or accumulation in living and it is not so good.

Generally, the health and environmental risk of fullerenes can be presently estimated as low or moderate. Fullerenes and most of its chemical derivates don’t demonstrate negative effects and are more likely considered as drugs. Carbon nanotubes risk may be considered as moderate. Practically, the question about nanocarbons risks claims for the further work in molecular modeling of nanocarbons structures risk assessments and well-directed experimental evaluations of every new derivate.

3. Conclusion

The technology is a combination of only three main operations: composition or assembling (1); decomposition or disassembling (2), and measurement or analysis (3). The main goal of any technology is qualitative changing of the subject of work.

Nanocarbons interact with all major types of biological macromolecules in unusual manner that involves intensive van der Waals forces, π-interactions, high symmetry preferences, and remarkable hydrophobicity. Basing on the molecular simulation results and the experimental data concerning biological activity of fullerenes in dark and light in connection with the problem of the nanocarbons–biomolecules interaction, we proposed a model for nanocarbons–biomolecules assembling.

Interaction of nanocarbons with proteins, gene molecules, carbohydrates, and lipids have attracted considerable interest in many fields of research and development including material science and biomedical applications. This creates two direct challenges based on possibility to create novel dry and wet combined nanostructures [6, 7].

First challenge is the discovery of the new world of composed structures uniting unique functional properties of fullerenes or carbon nanotubes with biological molecules having various specialization. This prospect opens many novel opportunities for the development of (a) new nanoscale materials and devices for broad banded applications with useful optical, electronically, mechanical, physico-chemical and other attributes, and (b) smart structures operated by nanocarbons, the third chemicals, photo- and electro excitations and ability to propagate changes of properties. Second challenge is defined by the interaction of nanocarbons with a wide set of biomolecules. Any such interaction can be considered as a factor of the biological action that defines prospects for the development of new medical applications or risks for potential biological hazards.

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ADVANCED ENVIRONMENT FRIENDLY NANOTECHNOLOGIES

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Abstract. The economic, security, military and environmental implications of molecular manufacturing are extreme. Unfortunately, conflicting definitions of nanotechnology and blurry distinctions between significantly different fields have complicated the effort to understand those differences and to develop sensible, effective policy for each. The risks of today's nanoscale technologies cannot be treated the same as the risks of longer-term molecular manufacturing. It is a mistake to put them together in one basket for policy consideration – each is important to address, but they offer different problems and will require far different solutions. As used today, the term nanotechnology usually refers to a broad collection of mostly disconnected fields. Essentially, anything sufficiently small and interesting can be called nanotechnology. Much of it is harmless. For the rest, much of the harm is of familiar and limited quality. Molecular manufacturing, by contrast, will bring unfamiliar risks and new classes of problems. The advanced environment friendly nanotechnologies elaborated by Israel Company Polymate Ltd. – International Research Center are illustrated.

Keywords: nanotechnology, nanomaterials, composites, environmental risks

1. Introduction

Desktop nanofactories will use vast arrays of tiny machines to fasten single molecules together quickly and precisely, allowing engineers, designers, and potentially anyone else to make powerful products at the touch of a button. Although such a contraption has been envisioned in some detail for almost two decades, and although the basic concept goes back to 1959, when the physicist Richard Feynman first articulated it, it's only in recent years that technology has advanced to the point where we can begin to see the practical steps that might bring it into reality. Materials with features on the scale of nanometers often have properties different from their macroscale counterparts. The prospect of a new materials technology that can function as a low-cost alternative to high-performance materials has, thus, become irresistible around the world. By this

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means nanotechnology presents a new approach to material science and engineering as wall as for design of new devices and processes. Figures 1 and 2 can give some imagine of the global tendency of nanotechnology development.

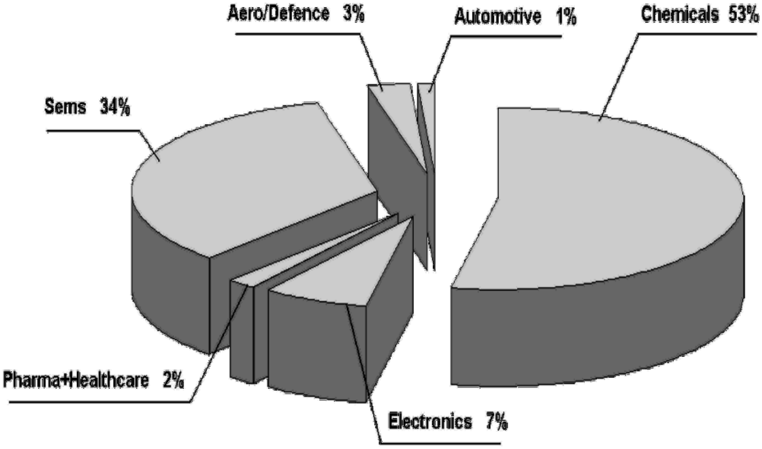


Figure 1. Global nanotechnology

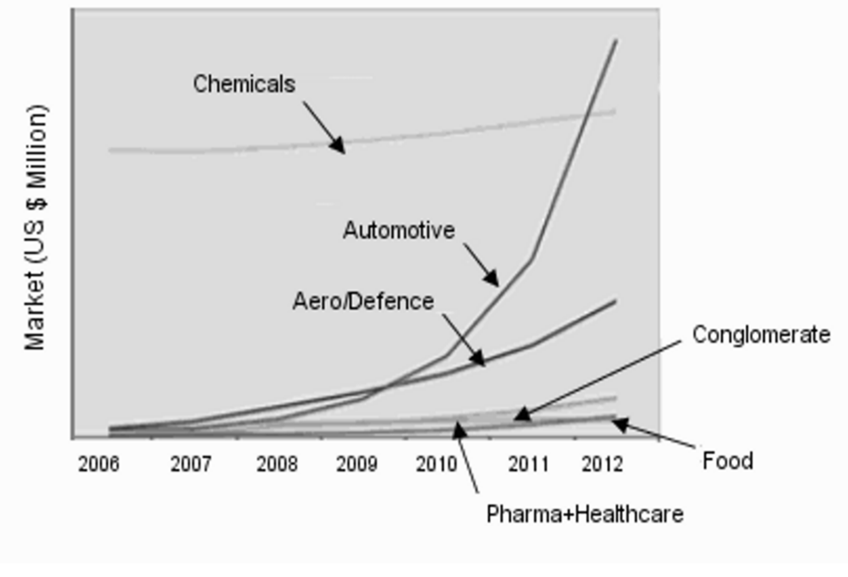


Figure 2. Nanotechnology market opinion 2006–2012

Nanomaterials may be categorized depending on the location of the nanoscale structure in the system (Fig. 3). This leads to a division of nanomaterials into three main categories, which then can be further divided into subcategories:

- Materials that are nanostructured in the bulk
- Materials that have nanostructure on the surface
- Materials that contain nanostructured particles

After an initial literature review, and when considering the information needed in order to describe a nanomaterial from a physical and chemical perspective when estimating the hazard of nanomaterials, we propose the following nine properties as being important: (1) Chemical composition, (2) size, (3) shape, (4) crystal structure, (5) surface area, (6) surface chemistry, (7) surface charge, (8) solubility, and (9) adhesion, defined as the force by which the nanoparticles and it components are held together. The Danish researchers then went ahead and combined their categorization framework from above with this list of properties to construct a hazard identification scheme (Table 1).

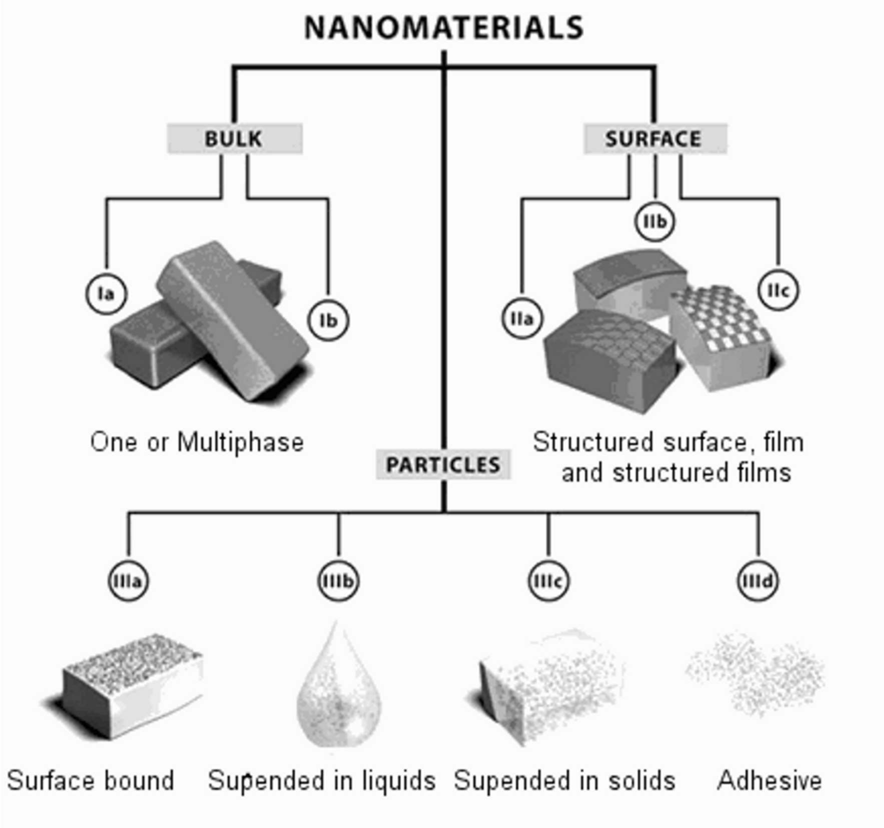


Figure 3. Classification of nanomaterials

Israel is one of leaders in nanotechnology, not only in fundamental academic researches but mainly in industrial researches and founding start-up companies. Figure 4 presents the new elaboration in the field of environment friendly nanotechnologies one of the leader Israeli companies: International Nanotechnology Research Center Polymate with a branch in Berlin, Germany.

TABLE 1. Properties of nanomaterials with point of view their hazard

Materials	Properties	Chemical composition	Size	Shape	Crystal structure	Surface area	Surface chemistry	Surface charge	Solubility	Adhesion
Bulk	Ia	+	−	−	−	±	±	±	+	+
Multiphase	Ib	+	+	+	−	+	+	−	+	+
Structured surface	IIa	+	+	+	−	+	+	−	+	+
Film	IIb	+	+	+	−	−	+	−	+	+
Structured film	IIc	+	+	+	−	−	+	−	+	+
Structured boundNPs	IIIa	+	+	+	+	+	+	+	+	+
NPs suspended in liquids	IIIb	+	+	+	+	+	+	+	+	+
NPs suspended in solids	IIId	+	+	+	+	+	+	+	+	+
Airborn NPs	IIIe	+	+	+	+	+	+	+	+	+

2. Nanostructured Composites Based on Interpenetrated Polymer Network

This project is oriented to prepare nanocomposites based on interpenetrated polymer network (IPN), such as polyurethanes, epoxies and acrylate by way of creating nanoparticles of SiO_2, TiO_2 and other metal oxides during a technological stage from a liquid phase. Using as interpenetrating polymer networks principle in production of composite materials provides a unique possibility to regulate their both micro-and nano-structured properties Formulation of a new class of nanocomposite materials is characterized by the absence of contaminants for a network polymers technology. As a main component of such technology we are using branched (dendro)-aminosilanes that at the first stage are curing agents for many oligomers.

The proposed dendro-aminosilane hardeners give the possibility to introduce the siloxane fragments into aromatic structure of diphenylolpropane based epoxy-amine network polymers. Additional hydrolysis of aminosilane oligomer creates the secondary nano-structured network polymer that improves the service properties of the compound. Branched (dendro) polyamine hardeners are novel direction in epoxy and cyclocarbonate and acryl resins chemistry.

The new hardeners give rise to formation of IPN of a polymerized resin with a polysiloxane network by the hydrolytic polycondensation of silane groups. IPN network may be formed on the base of epoxy- cyclocarbonate oligomers. It was found that at least 0.1 eq wt of silane per epoxy resin equivalent weight may result in IPN formation. It has been known that epoxy resin has low resistance to acetone and methanol attack. IPN film provides increasing the resistance.

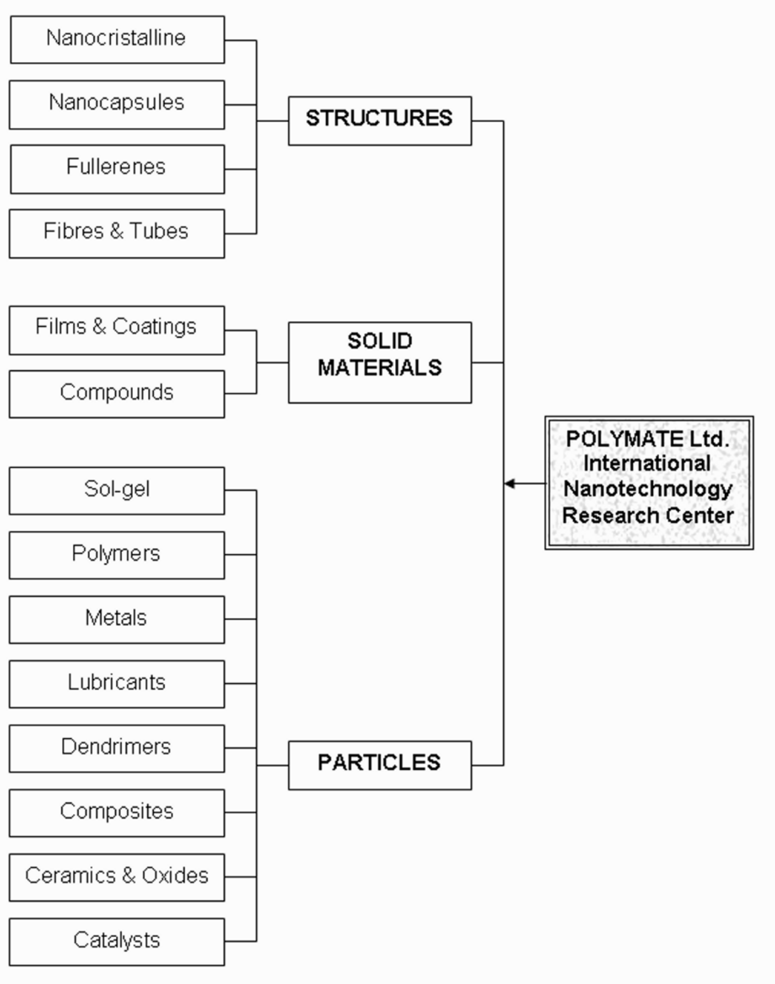
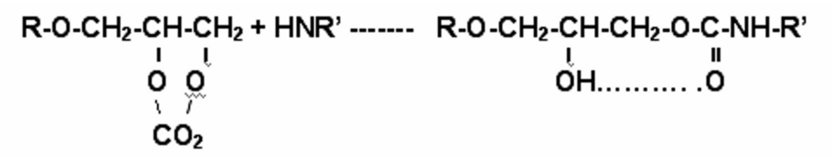


Figure 4. Nanotechnology material engineering field of activity of Polymate Ltd. – INRC

Novel hybrid nonisocyanate polyurethane based nanocomposites (HNIPU) was received by the following reaction:



$$R\text{-}O\text{-}CH_2\text{-}\underset{\underset{\underset{CO_2}{\backslash\;\;/}}{O\;\;\;O}}{CH\text{-}CH_2} + HNR' \text{-------} R\text{-}O\text{-}CH_2\text{-}\underset{OH\ldots\ldots\ldots}{CH}\text{-}CH_2\text{-}O\text{-}\underset{.O}{C}\text{-}NH\text{-}R'$$

Pilot production of two component paints, top coatings, adhesives and floorings are obtained. Figure 5 illustrated industrial application of the IPN flooring. The two-component compounds have unique properties that combine the best mechanical properties of polyurethane and chemical resistance of epoxy binders.

Figure 5. IPN flooring (Tosaf Compaunding Co., Israel)

3. Nanocomposites Based on Hybrid Organo-Silicate Matrix

By using a principle of forming nanostructure by creating nanoparticles during a technological process from a liquid phase, Polymate has elaborated a few of composites based on different kinds of soluble silicates. Significant increasing of silicate matrix strength and toughness was reached by incorporation of special liquid additives, such as TFS, which effect as a microcrystallizing nucleator on the technological stage and later they colmatage the pores of silicate matrix. Our last elaborations are mainly applying a novel type of soluble silicate contained organic cations, for example, the DABCO ()-based organic alkali soluble silicate.

4. Polymer Nanocomposites with Very Low Permeability and High Resistance to Aggressive Environments

Novel chemically resistant polymer materials were elaborated with adding nano-size inorganic active fillers that react with aggressive medium into which they are introduced, forming a new phase of high-strength hydrate complexes. This enhanced bonding occurs upon the penetration of aggressive media into active nano-fillers containing polymer material. The chemical resistant properties of the forming polymer materials are activated by harsh environmental conditions where polymer systems without additives remain defenseless to chemical corrosion.

Polymate Ltd., INRC has developed an extensive product range of such active nano-fillers for upgrading the most common polymers against a wide variety of aggressive media including acids, sea water, fluorine, alkalis and more.

5. Novel Metallic Matrix Nanoreinforced Materials Produced by Method of Super Deep Penetration

Technological process on the basis of new physical effect "superdeep penetration" allows to make from the known tool steels (e.g., HSS) new composite materials (Fig. 6). These materials possess the increased level of properties, can be used for replacement base steels in metal-cutting and stamp tool. In some cases new materials can be used for replacement of a hard metal (on the basis of WC) in the tool for mining (e.g., cutters of coal and mining machines, Fig. 7). The application of technology developed allow to increase the service life of tools up to 1.5–5.0 times compared to the common used tools. The technology can be applied for the volume strengthening practically any type of instrumental steels.

Use of new physical effect "super deep penetration" (SDP) allows to receive composite materials on the basis of aluminium, with the set anisotropy of physical and chemical properties.

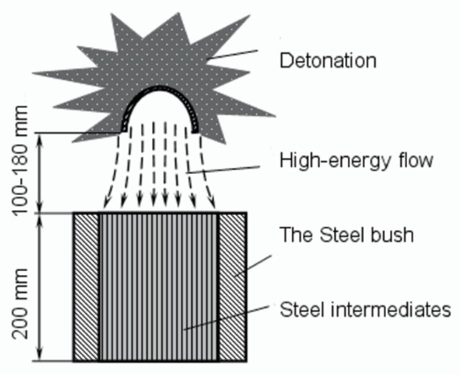


Figure 6. Principal scheme of superdeep penetration of micro-particles into metal body

Figure 7. The tools for coal cracking strengthened by SDP method

Use of features of process SDP allows to change properties of a material qualitatively. In microvolume electroconductivity of aluminium can change in several times. In preparation it is received electroconductivity, in mutually perpendicular directions differing in two times. These materials are intended for new electric and electronic devices. The effect from use of a new aluminium material in electric installations and electronic control systems will make, due to reduction in expenses for expensive materials, hundred millions and billions dollars USA. Cost of process of rearrangement of structure of aluminium preparation does not exceed $40/kg. By industrial production of such material its cost can be decreased in 2–3 times. From individual preparation can be made tens electric and thousand electronic devices. Process SDP is high-efficiency and does not demand the expensive equipment. The new technology of volumetric reorganization of aluminum, creation zones of nano-structures, the materials received on this basis, will find wide application by manufacture of electric installations and electronic devices.

6. Water-Dispersion Paint Composition with Biocide Properties Based on Silver Nano-Powder

We have elaborated advanced bioactive coating with using silver nanoparticles. As found in numerous studies during the last two decades, particles with dimensions in nanometer scale ($10^{-9} - 10^{-8}$ m) possess peculiar properties, different from those of atoms and ions on the one hand and of bulk substance on the other. These silver nanoparticles was received by the novel BAR-synthesis. The biological activity of varnish-paint materials modified by silver nanoparticles was estimated on the following microorganisms:

- *Escherichia coli* (*E. Coli* 1257) as a conventional model of bacterial contamination of the environment

- Coliphage (RNA-phage MS-2) as a model of viral infection, including influenza A and B, hepatitis A, et al
- Mold fungi (*Penicillium chrysogenum*) as a typical representative of microflora of the dwellings and a model of fungicidal contamination
- Spores as a model of spores and other microflora

The data of the testing confirms the significant advantages of elaborated waterborne acrylic bioactive coatings.

7. Nanocellulose and Biodegradable Composite Materials

The new nano-scale cellulose product (NanoCell) with CI crystalline modification was prepared using advanced, environmentally friendly, resource-save and cheap technology. The developed technology permits producing NanoCell in pilot and industrial amounts. NanoCell product can be manufactured in the form of dispersions, high solid paste and dry powder.

The FDA-approved aqueous polymer nanostructured composition CreenCoat is applied for protective covering of paper and board. The coating layer imparts to material barrier properties against permeation of water, grease, oxygen and some other substances. Waste of coated material can be repulped and used in paper industry or decomposed in nature due to its biodegradability (Fig. 8).

The GreenCoat emulsion is coated on cardboard surface by means of bar-coater and dried at temperature 150–170°C for 30–60 s. Then the GreenCoat glazing hot melt composition is coated on first layer by means of bar-coater at temperature 130–135°C and air cooled.

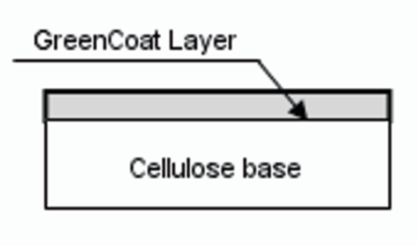


Figure 8. The new nano-scale cellulose product

Waste of coated material can be repulped and used in paper industry or decomposed in nature due to its biodegradability (Fig. 9).

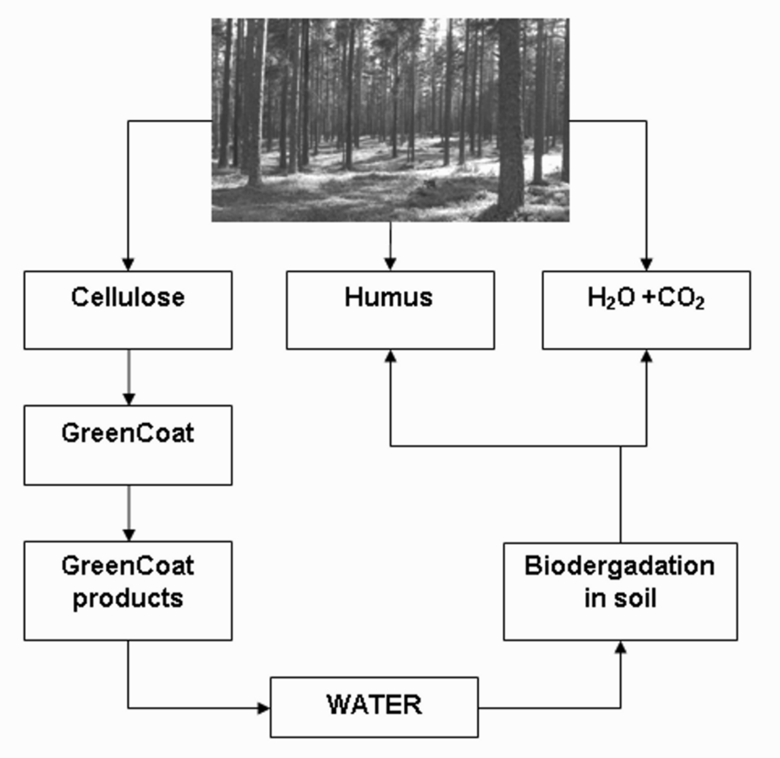


Figure 9. Recycling of the biodegradable coatings

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NOVEL ENVIRONMENT FRIENDLY METHOD OF PREPARING NANOREINFORCED COMPOSITES BASED ON METALLIC, CERAMIC AND POLYMER MATRIXES – SUPERDEEP PENETRATION

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Abstract. At superdeep penetration (SDP) process of penetration of discrete microparticles and stitching of metals, ceramics and polymers by the synthesized filaments, on depths in tens and hundreds millimeters is realized. Contrary to the basic models at SDP intensive energy release is observed: local melting, synthesis, radiation and forming of massive composite materials. Process of SDP occurs in the boundaries of the closed system. Products of interaction for example, carbon and silicon are saved in volume of preform and don't organize harmful waste at manufacture. The massive composite material is formed in a pulse regime and modified in volume by nano and micro structural elements. Manufacture of a durable material does not demand traditional process of sintering.

Keywords: stitching, SDP, chemical compounds, structure reorganization

1. Introduction

Technological processes on the basis of interaction of carbon and silicon materials should guarantee ecological safety. Usually using a complex of the equipment which ensures localization of waste of manufacture of composite materials and products. However, using of the additional equipment essentially increases expenditures for production. Traditional powder metallurgy demands significant expenditures of energy. Therefore creation of the new techniques that allow to minimize expenditures of energy and harmful waste is an actual problem.

The objective reason of leading development of techniques which are based on static or low-speed processes is the opportunity of visual inspection in real-time mode. Development of the engineering's that based on dynamic and high-speed processes is

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defined by occurrence of the devices registering high-speed processes. Besides, the probability of appearance of technology depends on an observability of the basic physical and chemical effects creating a basis of technology in nature conditions. Therefore study of process of shock interaction of bunches of dust particles with a solid bodies a long time was not effective. The subjective reason that braked researches in this area of science was excessive concentration of efforts in military applications.

As the basic dimensionless factor at impact it is used ratios of depth and the cross-section size of a crater to the main size of a striker (caliber). In the 20th century steady representations were generated, that at high-speed impact it is impossible to realize process of penetration with depth over six main sizes of a striker. Therefore long time high-speed dynamic processes were considered as the physical tool only for surface or near-surface changes of solids bodies (details).

Basis of dynamic volumetric reorganization of an usual material into a composite material is the unusual physical effect. Superdeep penetration (SDP) is naturally realized at impact of bunches of a space dust with envelopes of aircraft. Only in 1975 the complex of physical conditions at which the bunch of a space dust penetrates into solid barriers on depths in 100–10,000 initial sizes of dust particle [1] has been certain. At SDP dust microparticles get into solid body as if the material of the barrier is gas or plasma. Process of weaving metals, ceramics and plastic materials is observed. This process has similarity to weaving process of a fabric. Discrete particles are simultaneously needles and cords. Reinforcing filaments arise at interaction of entered substance with a matrix material. The matrix material compresses reinforcing filaments.

Numerous models of superdeep penetration explain this unusual process by sharp reduction of expenditures of energy on driving of particles into solid body due to specific mechanisms of penetration [1]. Hence the physical effects realized at SDP, should happen practically without expenditures of energy, i.e. without intensive interaction of entered substance and a matrix material. However results of researches have shown that SDP leads to intensive interaction of entered materials with a matrix material, including realization of processes of synthesis of new chemical compounds. Such unusual interaction in real-time mode at penetration of powder particles into a barrier realizes volumetric reorganization of structure of a matrix material and creation of nanoreinforced composite materials on depths in tens and hundreds millimeters [1].

In the industry powders of carbon, silicon and their chemical compounds are used widely. In a space dust such materials are often met. Therefore study of interaction of these materials in SDP condition with solid bodies in the form of metals, alloys, ceramics and plastics is interesting, both for a science, and for the industry.

The purpose of the given research is study of features of interaction of materials in condition of SDP.

2. Brief Review of Known Models of Superdeep Penetration

In the first cycle of experimental investigations (1974–1978), the proofs of the existence of superdeep penetration of a clot of particles into the barrier have been obtained. It has been confirmed, that it is impossible to explain the results of SDP on the basis of the known models of macro-impact. The known models can be divided into four types.

Basically, these models describe the SDP process as interaction of an individual striker with a zone of its movement in the barrier.

The models, in which the energy was expended due to the elastic reaction from the barrier material, are included to the first type of the models. The hypothesis, that freezing of plastic deformation occurs at SDP has been given in Refs. [2]. Grigorjan have assumed that superdeep penetration is realized through a system of cracks. The energy during penetration is spent only on elastic deformation. To explain the experiment results which contradicted to the model described in Refs. [2], the additional assumptions have been taken [3]. New hypothesis saying that non-planar cracks appear is offered. On the basis of this hypothesis it was assumed that after the collapse of hundreds thousand unusual cracks, the matrix material can be strengthened and the tops of cracks are melted and deformed. The author has stated a static resistance at SDP [2]. At present, the hypothesis about cracks is used for qualitative explanation of unusual results [4]. For example, this hypothesis explains strikers penetration into the steel at the temperature of 196°C.

It is possible to include the models, in which the particles transfer into the barrier occurs in the special transport elements "solitones" (whirlwinds), to the second type of hypotheses. The hypothesis says that unusual transport of the elements and strikers proceeds with no energy expenditure. In 1998, the hypothesis was offered, that superdeep penetration of the particles it is a process of an exchange in mass and energy due to the developed instabilities in material [5]. The degree of non-equilibrium at SDP is described by dependence of entropy change from deformation of a matrix material. The hypothesis on hydro-dynamical instability in local areas of the barrier surface, loaded by a stream of micro-strikers, is known [6]. At micro-cumulation, transport whirlwinds are created at the front of a shock wave, initiated by the background shock wave. The striker material is carried by the transport whirlwinds into the barrier. According to the author, recrystallization and amorphisation of the matrix material, as well as the traces of micro-particles material transfer can be explained by high pressures and temperatures in the zones of micro-cumulation. A hypothesis on creation of volumetric "soliton", in which the striker at SDP moves without the expenditure of energy, has been offered for the first time by Cherepanov [7]. "Soliton" carrying the micro-strikers are similar to the transport whirlwinds [6].

The third type of hypotheses is based on the assumption that there are special mechanisms of a flow, crushing, and a loss of strength that were not known earlier. At implementation of special mechanisms, strength of the barrier material is reduced. Thus, as a rule, the static and dynamic strength, macro-deformations of the barrier, crushing of grains, and emission are neglected. For example, the hypothesis on the existence of a specific flow of the micro-striker by a stream from a matrix material is offered [8]. Material destruction in the penetration zones is assumed under various conditions of the stress produced in the elasto-plastic medium [9]. In a regime of free oscillations, in the target, the standing wave is formed with invariable phase and amplitude varying with time. The kinetic energy is thus expended only for crushing of the barrier material. The analogous hypothesis is presented in Refs. [10, 11]. The authors assume that in a volume of the matrix material at SDP, long and narrow zones of tensile stress appear, into which the micro-strikers are propagated. In Ref. [12], the SDP model, based on a typical mechanism for a cumulative jet is offered. According to the authors, new mechanisms of the penetration 10-fold diminish the known expenditures of the kinetic energy.

The authors have developed the concept based on the fourth type of hypotheses. The hypothesis is based on a conception, that at the barrier hit by a clot, variable pressure fields are created. In the barrier, the pressure attains the magnitude that is necessary for the dynamic phase transition. In Ref. [13], for the first time, the hypothesis was presented that penetration of the particles from a clot into the metal barrier at SDP occurs during the period when the dynamic phase transition is not completed. Special features of such a hypothesis were: barrier material has no long-distance connections, process duration is limited, size and striker velocity and boundaries between various phases are limited too [13]. To confirm this hypothesis, special experiments have been carried out and the time of a dynamic phase transition in the barrier material has been defined. The dynamic losses of the kinetic energy of the strikers were considered. Experimental demonstrations of the implementation of the dynamic phase transition at SDP have been presented much later [14]. The mechanism of the additional energy supplied to the striker [15]. has been offered which increases efficiency of the used kinetic energy. In Andilevko work [16], the hypothesis on the losses of the static strength at the dynamic phase transition was not rejected. In Refs. [1, 13, 17, 18], the deficiency of the kinetic energy of a clot for superdeep penetration and the possibility of existence of an additional source for energy generation were observed. The possibility of generation of additional energy from the chemical reaction between the introduced substance and the matrix material is reported in Ref. [19]. The reviews on various attempts to modernize the SDP mechanisms are considered can be found in Refs. [1, 13, 16, 17].

3. Investigations of Superdeep Penetration (SDP)

The first experimental *condition* of superdeep penetration process was formulated. The craters with a depth-to-striker size ratio of above 6–10 are recorded at collision of the barrier with a stream of strikers having the sizes less than 500 μm [1, 17, 20].

The second experimental *condition* of SDP is the presence of a band of impact velocities. Impact velocity cannot be lower than the velocity of superficial perturbations at the barrier's surface. For the impact velocities higher than the velocity a shock wave passing in the barrier material, the strikers, at first, are broken according to the known mechanism and only then they are in the SDP regime.

The third experimental *condition* of SDP is the existence of a stage of preliminary formation of a compressing pressure in the barrier material.

Consideration of qualitative, semi-quantitative and quantitative aspects of SDP allows us to analyze this unusual process.

Figure 1 shows the schemes of various craters.

For SDP, the hardness of the striker material does not affect essentially the penetration depth. In Fig. 2, the zone of retardation of a striker, made of highly plastic material (Pb), is shown. By comparison with usual and abnormal craters it becomes obvious that for SDP, the visible diameter of the channel is always smaller than the initial size of striker (Figs. 1 and 2).

The diameter of the channel is called the transverse dimension of a penetration trajectory (penetration zone), which can be seen after polishing and etching processes of a metallographic specimen.

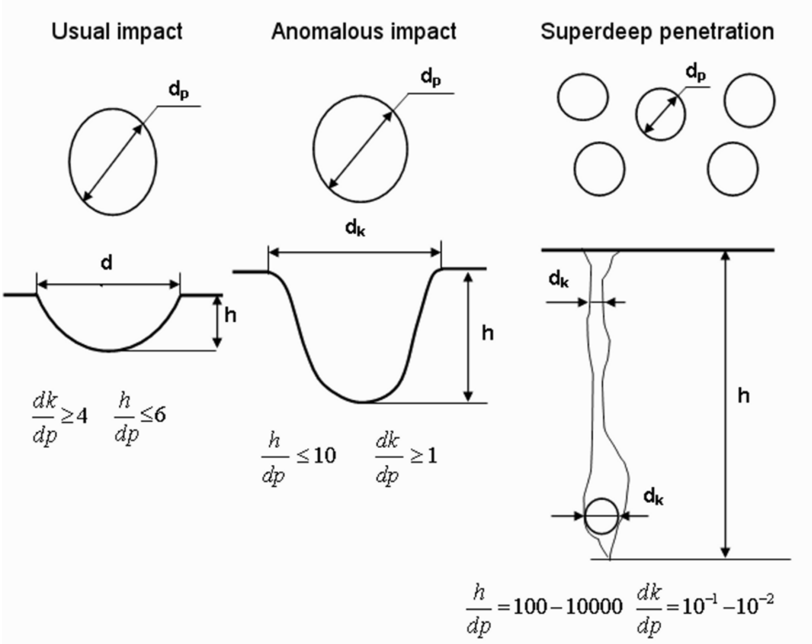


Figure 1. Comparison of characteristic features of various impacts with a barrier, d_p – diameter of a striker, d_k – diameter of a crater, and h – crater depth

Figure 2. Rest of a lead particle in a steel barrier, ×5,000

Using the solutions of acids and alkalies of different concentrations, it is possible to gain various diameters of a puncture zone (channel). Traces of a bullet (copper or iron) in rubber after its penetration are displayed only on the axis of its movement. On the basis of this similarity, it is possible to explain experimental results of micro-alloying of the barriers at SDP.

At SDP, the channel collapses (closes). It is possible to confirm this assertion in the experiments with lead dust. Lead (Pb), injected into the channel zones, at SDP, during preparation of a specimen for investigation, reacts with the etching solution. However, the products of a chemical reaction do not leave the surface.

The trajectory of motion of lead particles in a barrier in the form of white strings can be seen at a metal surface of a barrier (Fig. 3). Only those sections of a trajectory which are at the plane of a longitudinal cross-section of a barrier are visible.

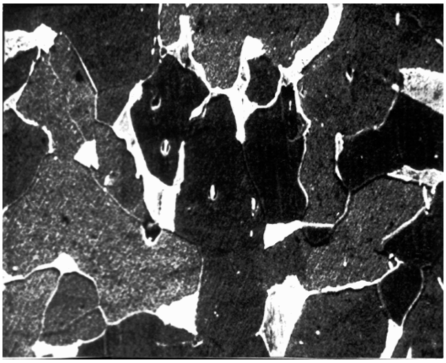


Figure 3. Trajectory of motion of lead particles in a steel barrier, ×1,000

We treat similarly the process of punching a rubber barrier by bullets. On this basis, we try to answer the question: what causes a collapse of a channel at SDP? Strong compressing stresses appear in the volume of barrier's material at SDP. What is the reason for these stresses? At usual impact, compression forces (pressure) are not significant and the crater diameter exceeds the striker calibre more than four times. An individual striker cannot give such results.

It is obvious that when a clot of dust particles affects a barrier, the pressure fields appear. The pressure fields in a barrier originate due to the kinetic energy of the impact. Emergence of a variable pressure field explains the presence of velocity gradients and density in the volume of a clot (stream) of separate strikers. After the striker starts to create a channel element, just in this zone the reduction of a pressure field occurs. The channel element closes. Therefore the presence of a pressure field in the volume of a barrier is a necessary condition of superdeep penetration [1, 17].

Studying these questions has led to a formulation of the second condition of SDP implementation. Superdeep penetration of strikers into a barrier can occur only at the impact of a clot (stream) of micro-strikers. SDP process never occurs for a single particle.

4. Effects Appearing at Superdeep Penetration

When a clot of strikers hits the barrier, a variable background pressure is generated in the barrier's material. During the interaction between the strikers and the barrier, separate strikers penetrate into the medium, loaded preliminarily by the hit of other strikers which did not penetrate the barrier but they transferred their energy (pressure) into it. Thus, when the depth of striker penetration is bigger than the striker size, the crater cavity, behind a striker, collapses under influence of the generated background pressure. Since this moment, a qualitative change of the energy reduction has started. During the interaction process lasting 10^{-8}–10^{-5} s, the power consumption of the closed system sharply increases. As a result, the unusual effects that are characteristic for the SDP conditions should occur.

4.1. INTERACTION CONDITIONS DETERMINING A CRATERING TYPE

The first effect of penetration at the SDP, due to the presence of a background pressure, is closing of the crater (channel cavity) on the whole distance of the striker movement in the barrier. As a result, the formation of a superdeep channel does not cause the loss of air-tightness of the metal barrier.

The second effect is no direct dependence of the initial hardness of the striker material on the penetration depth. It means that hardness of the barrier material, in the SDP zone, is always lower than that of the striker hardness made of any known material. Such an effect proves, that SDP transfers the barrier's material, in a local zone (during interaction $-\Delta\tau < \tau_c$), into a dense plasma state. The striker's material, which is affected during the penetration for the long time τ_c, is in a solid or in a liquid state [1, 17, 20, 21].

The third effect is non-uniform distribution of the pressure fields in the barrier's material. Penetration of the strikers occurs in these zones of the material when the pressure is at least of the order higher than the background pressure in the barrier. The pressure fields are mainly in long and narrow zones on the whole barrier thickness. At the beginning of the SDP investigations, this effect has been formulated as a modelling assumption [1, 17, 20] and then it has been confirmed experimentally [13].

The fourth effect, which directly results from the third effect, it is strong local deformation in the zones of the barrier material [1, 20, 21].

As a result of such a set of interaction conditions, *the fifth effect* appears, i.e., the loss of the striker's mass at the increasing depth of the striker penetration into the barrier. During the striker passage through the barrier, its initial size decreases by hundreds times. Decrease in size and mass of the striker is non-uniform along the penetration depth, what proves the changes of SDP conditions in the barrier [1, 15, 20].

Additional effects arising at SDP, as a result of the collective action of all before determined conditions are: *occurrence of electric charges* at the interaction of materials of the striker and the barrier and occurrence *of a wide spectrum of electromagnetic fields* during the movement of a clot of strikers in the metal barrier [14, 22].

Simultaneously, in the volume of the barrier material, in the point sources the *flows of massive charged particles*, apparently ions, occur. The energy of such particles is so high that they can pass (starting from "a hot point") through the barrier material. The experiments employing additional filters (protection screens situated at the particles exit from the barrier) have shown that the energy of the particle at the barrier's surface (after its passage through the barrier material) was 100 MeV [23].

On the back surface of the barrier, at the strikers exit, *microjets of dense plasma* appear. These jets possess high penetrating power. Their velocities attain hundreds meters per second. A diameter of such a jet is not larger than 1–2 μm, and a length does not exceed some millimetres [23]. The jets have the charges and interact with the electromagnetic fields.

Interaction between the striker and the barrier materials, in local zones (channel elements), leads *to occurrence of chemical elements* [20], which were absent earlier in this material, and it causes *a synthesis of metastable compositions* [20, 21, 24] which are not shown in the known constitution diagrams. It can be explained by simultaneous action of high pressure, intensive deformations, and radiation in the interaction zone [21]. Neither mechanical, nor hydrodynamical factors of SDP have essential influence on a situation inside the metal barrier.

5. Expenditure of Energy in a Process of Superdeep Penetration

The energy expended in the process of superdeep penetration was estimated using a principle of minimization of energy expenditures. Within this approach, at each analysis' stage, the minimal possible estimation of the energy expenditures was accepted. When the energy expenditures were too high, even using a minimization principle, the assumptions for re-use of the spent energy were offered. For the calculations we have used the results obtained experimentally. To compare the introduced and the spent energy, the following approach has been accepted. For calculation of the kinetic energy, injected by a clot of high-speed particles, the overestimated assumptions were taken, and for the calculation of the expenditures of the energy, implemented during the loading – only the assumptions obviously underrating the energy values were accepted. Such approach, allows us to focus on qualitative aspects of the SDP process.

5.1. ESTIMATION OF THE KINETIC ENERGY OF THE CLOT OF HIGH-SPEED MICRO-PARTICLES

For calculation of a quantity of the energy gained by the metal barrier as a result of the shock-wave loading with a high-velocity stream of micro-particles, the following values of parameters were used: the mass of the ejected (driven) material m_1=0.1 kg, the mass of the explosive charge m_2=0.2 kg, the velocity of the micro-particles clot – 1,000 m/s. For these parameters, the kinetic energy of the ejected (driven) material was 1.5×10^5 J.

At the macro-impact, restriction of a relative depth of the penetration is caused by the fact that the impact energy is expended for overcoming the static impact resistance (90–98%) and the dynamic component of the resistance causes the energy loss of 2–10%. The dynamic expenditures of the energy originate at the transfer of the striker and barrier materials with some velocity, during ejection of the barrier material from the crater and during the movement of the material of the cavity walls and its bottom [1, 13, 17]. In addition, the dynamic expenditures of the energy at usual impact include the energy expenditures for the dynamic settlement and macro-crater formation [18].

In Ref. [18], the energy expenditures on macro-changes of the barrier are estimated. The observable changes of the barrier's geometry are shown in Fig. 4.

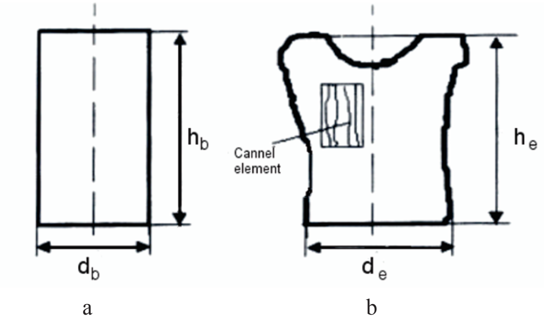


Figure 4. Changes in the metal barrier, arising as a result of its impact with a clot of particles: (a) initial cylindrical barrier (h_b, d_b) and (b) the barrier after the dynamic loading (h_e, d_e)

As a barrier material, the cylindrical samples, made from the alloy of iron with 0.4% of carbon, having the diameter of 50 mm and the height of 100 mm have been taken. As the striker materials, the micro-particles of SiC powder of the fraction of 63–70 μm were used. For this case, the energy expenditure for the macro-crater formation was E_κ = 2,548 J and the energy expenditure for the dynamic settlement was of the minimum value E_d = 401,821 J.

5.2. FORMATION OF A CHANNEL STRUCTURE DURING THE SUPERDEEP PENETRATION PROCESS

In a steel sample, the zones (channel elements) with the changed structure have appeared. Figure 5 shows the scheme of such a channel element (zone). In the channel element zone, the number of defects in the material sharply increases. The maximum number of the structure defects is observed in the central zone of the channel element (Fig. 5).

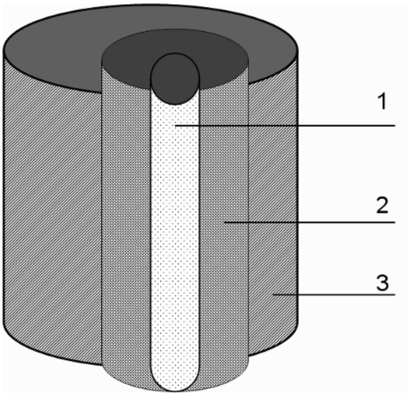


Figure 5. Scheme of a channel zone, 1 – amorphous material, 2 – microcrystalline material, 3 – defective material

When the special alloying additions are not used, the activated central zone completely disappears (is etched) during metallographic examinations. However, with the decreasing intensity of chemical or electrochemical effect, this zone is filled with a specific material. This specific material it is the product of interaction between the injected substance and the matrix material of the barrier.

Two kinds of channel elements can be observed. The first kind represents an element of a crack type with the striker fragments fixed in it. These fragments can be also observed far from an axis of the channel element. As a rule, such kind of the channel element is observed when the striker's substance is fragile ceramic material. For example, silicon carbide (SiC) undergoes fragmentation in a pulse regime when it is heated to high temperatures. Penetration of the fragments from the central zone of the channel element to other zones of the barrier material occurs in a pulse regime, i.e., it has explosive character.

The second kind of the channel element is characterised by the maximum number of defects in the central zone. As a rule, the material injected by a clot of separate strikers has higher plasticity when compared with the ceramics plasticity and it intensively interacts with a matrix material. In this case, the material of the central zone of the channel element was a metastable composite of various concentrations of both injected and matrix substances. For such kind of the channel element, the traces of intensive plastic deformation can be observed. Amorphous state of a thin structure of the central zone was stated due to studying this structure by means of a transmission electron microscope.

In a lot of experimental investigations, nano- and micro-structures were recorded in the central zone of the channel element. It is logical to assume, that the higher number of defects appear in the narrow zone of the channel material. In our opinion, the existence of various channel elements testifies on various regimes of superdeep penetration.

In such approach, the difference between two kinds of the channel elements appears because of various regimes of the removal of the central zone material from the channel element. Basing on the study of the first kind of the channel element, it is possible to observe that owing to the relaxation processes in a macro-volume of the barrier material, the number of defects decreases. However, it is necessary to consider a real time of implementation of the process of the channel element formation (10^{-8}–10^{-5} s) and intensity of the process of energy reduction in a volume of the barrier material (metal hardening). In our opinion, more logical is assumption, that the part of defective material, being formed in the narrow central zone of the channel element, is ejected with the direct and return jets from a solid macro-body. Thus, the difference between the first and the second kind of the channel elements formation results from the mass and velocity of the jets of the ejected defective material. On this basis, it can be stated that the closing (collapse) process of the channel elements is of significant meaning.

For estimation of the energy expenditures on the formation of a zone with the channel micro-structure, the standard assumptions are used: static resistance of the barrier material is equal to null and velocity of the moving walls of the channels is equal to the velocity of an individual micro-striker.

As a result of the channel elements formation, the energy is spent on disclosing of the channels, in the direction perpendicular to the axis of micro-strikers movement, and on their collapsing (collapse of cavitation bubbles) after the particles passage.

Let us estimate the SDP process with employing the energy of the dynamic phase changes. We will consider a case of the injection of a clot of TiB_2 particles in the iron barrier. Also, we will estimate the minimal volume V_{iz} of the channel element of the barrier, in which the change of a phase proceeds. It results from the experimental data, that the residual part of the striker (striker rest) has the size smaller or equal to 0.05 d_p. The experimentally obtained limiting depth is h = 0.3m. We will assume that the minimal channel volume of the barrier has the cone form. A cone diameter equals 66.5×10^{-6} m (a cross-section of the striker) and its height is 0.3 m. In this case, the mass of the barrier material which moves in a dynamic regime will be also underrated because, in a deformation process, the collapse of nearby layers are not taken into account. Then:

$$V_{iz} = \pi h d_p^2 \frac{1.0525}{12}, \qquad (1)$$

where h is the barrier (zone) thickness and d_p is the striker diameter.

The cone volume is $V_{iz} = 0.347 \times 10^{-9}$ m^3. The material volume, in which a dynamic change of a phase proceeds, will be determined by a relationship of the kinetic energy E_p and the pressures of initiation of the dynamic change of the phase P_i:

$$V_f = \frac{E_p}{P_i} = 12.5 \times 10^{-6}\,\mathrm{m}^3 \qquad (2)$$

Essential non-uniform distribution of the pressure fields in local zones of the metal barriers and behaviour of the phase changes in them have been proved. In particular, $\alpha \rightarrow \varepsilon \rightarrow \alpha$ transformations are shown using low-alloy steel as an example. The high-pressure phase in them is the ε-phase. The pressure for initiation of $\alpha \rightarrow \varepsilon$ transition is 12 GPa [14]. The phase ε is not kept after the loading removal but the traces of $\alpha \rightarrow \varepsilon \rightarrow \alpha$ cycle are registered after the micro-structure change. The transverse size of the zones, being tested in a cycle of transformation, changes in a wide range, from a fraction to 1–2 μm.

The quantity of the calculated high-pressure zones, formed due to the impact energy of a strikers clot, is $N = \frac{V_f}{V_{iz}} = 36000$ pcs. However, the channel elements are not distributed uniformly along the crater depth.

For the determined conditions, the penetration velocity u_p is $\upsilon_p = \upsilon_s \frac{\lambda}{1+\lambda}$, where $\lambda = \sqrt{\frac{\rho_s}{\rho_m}}$; λ=0.73535. Then, υ_p=127…1,271 m/s. The average penetration velocity is $\upsilon_{p.m}$ = 423 m/s.

The minimal movement velocity in the metal barrier is v_p=127 m/s and the length of a clot of discrete strikers (distance for acceleration) is ≈0.15 m. The strikers clot moves to the barrier with the velocity of 300–3,000 m/s. Due to it, the loading by a jet is realized in the time interval 5.0×10^{-5}–5.0×10^{-4} s, i.e., during $\tau_l \approx 450$ μs. As a clot material we use TiB_2 (titanium boride) particles of the density of 4.38×10^3 kg/m^3 at the melting temperature of 2,790°C and the micro-hardness $H\mu = 3{,}370 \pm 60$ kg/mm^2 [13].

The striker moving with the maximum velocity penetrates into the cylindrical barrier during $\tau_{p1} = 2.36 \times 10^{-4}$ s. The striker with the minimum velocity could penetrate (but it is impossible) during $\tau_{p2} = 23.60 \times 10^{-4}$ s. The striker, driven with the average velocity ($\upsilon_{pm} = 423$ m/s), could penetrate into the barrier only during the time $\tau_{pm} = 7.0 \times 10^{-4}$ s. Hence, the strikers having the average and lower velocities during the loading can penetrate the barrier only to the depth of 0.2 m. It corresponds to the experimental results (Table 1) obtained for the tested steel barrier (HSS) with TiB_2 particles. With the increasing barrier depth, a part of structure defectiveness has decreased by 246 times. The most intensively has decreased the density of the channel elements (2.8 times) and the average (visible) diameter of the channel has increased.

The quantity of channel elements on the penetration depths from 0 up to 0.2 m is $N_{0\text{–}2} = 4.8 \times 10^5$ pcs and $N_{2\text{–}3} = 1.7 \times 10^5$ pcs. The volume of the calculated individual channel element on the penetration depths from 0 up to 0.2 m is $V_{z(0\text{–}3)} = 0.347 \times 10^{-9}$ m^3 and the volume of the calculated channel element on the depths from 0.2 up to 0.3 m is $\Delta V = V_{z(0\text{–}3)} - \mathrm{V}_{z(2\text{–}3)} = 0.192 \times 10^{-9}$ m^3. The volume of the high-pressure zones is $V_{zc} = \mathrm{N}_{0\text{–}3}\mathrm{V}_{iz} + (\mathrm{N}_{0\text{–}2} - \mathrm{N}_{0\text{–}3})\Delta V = 0.119 \times 10^{-3}$ m^3 and the number of cycles of the high-pressure zones appearance $N_{cf} = \dfrac{V_{zc}}{V_f} = 9.5$. Then, a part of the kinetic energy injected during one cycle into the barrier material amounts ≈10% of the energy which is required for the loss of static strength (for creation of the high-pressure zone) $E_{\sum f} = \sum E_p = 1.42 \times 10^6$ J. This unusual result was obtained without taking into account the energy expenditures on the channels collapse and on other processes.

From a principle of minimization, it is accepted that the high-pressure regions originate 9.5 times in a pulsing regime of the metal cylinder volume.

TABLE 1. Parameters of a structure of the barrier material (HSS steel)

Barrier zone	Striker size (d_p)	Structure defectiveness	Average (visible) diameter of a channel (d_k)	Density of channel elements	Volume of defective structure (V_d)	Mass of defective structure (M_d)
[m]	[10^{-6} m]	[10^{-3}%]	[10^{-6} m]	[mm^{-2}]	[10^{-8} m^3]	[10^{-3} kg]
Depth 0–0.2 m	0–60	6.3800	0.576	245	2.504	0.2028
Depth 0.2–0.3 m	0–60	0.0259	0.616	87	0.508	0.0411

However, the time of the barrier loading at the impact with a clot of separate strikers $\tau_l \approx 4.5 \times 10^{-4}$ s cannot be neglected. The SDP process can be realized only during the barrier loading with a particles clot. Therefore the particles with the minimal velocity cannot penetrate through the whole barrier thickness during the loading process. Then, the time of an individual cycle of a high-pressure action can be estimated as $\tau_{imp} = \dfrac{\tau_{loading}}{N_{cf}} = 47.2\times10^{-6}$ s.

For this penetration time, the penetration depth is $H_{i1}=\upsilon_p\times\tau_{imp} = 6.0\times10^{-3}\ldots60.0\times10^{-3}$ m. The average penetration depth for one pulse is $H_{medium} = 20.0$ mm.

During the first pulse, it is impossible to create the channel elements on the whole depth of a metal cylinder. Thus, on the basis of the gained estimations of an average velocity, a number of the channel elements on the depths up to H_{medium}, formed during the time τ_{imp} can be determined. A volume of an individual channel's element, from a surface up to the depth H_{medium}, is defined from a difference of two cone volumes. The first cone has the base diameter $D_1 = 66.5$ μm and the height $h_1 = 0.3$ m. The second cone has the base diameter $D_2 = 62.0$ μm and the height $h_2 = 0.280$ m. Then, if $V_f = 12.5\times10^{-6}$ m^3, the exact quantity of the channel elements of the first cycle is $N_{amend} = \dfrac{E_f}{\Delta V_{1-2}} = 190840$. The quantity of the channel elements, registered experimentally is $N_{0-2} = 480{,}812$. During the first cycle, the high-pressure zones, corresponding to the channel elements number N_{amend} are formed on the depth of a metal cylinder. Other channel elements are formed in the next cycles. During ≈2.5 cycles, all the channel elements are formed on the distance between the surface and 20-mm crater depth. What will happen next? Will the channel elements exist (pulsate) after $\tau_{imp} = 47.2\times10^{-6}$ s?

If the channel elements are closed after the striker passage and the further pulsation stops, the return jet is sharply broken. Correspondingly, the blocking of the outlet holes cannot affect the mass transfer process in the SDP regime. Such an assumption contradicts the known experimental results [21, 25].

We accept the underrated assumption that opening of the channel elements proceeds with the velocity equal to the penetration velocity of the strikers into the barrier. In this case, the energy is spent only on the movement of the mass of high-pressure zones with the penetration velocity. Static resistance of the striker material equals null. Then, energy expenditure for the channel elements opening E_{op} can be defined from Eq. (3):

$$E_{op} = \frac{M_f\upsilon_{pm}^2}{2}, \tag{3}$$

where $M_f = N_{\exp}V_{iz}\rho_m$. Estimating this expenditure, with the average values, we will gain $E_{op} = 49{,}366$ J.

Let us estimate the dynamic expenditures of the energy on the channels closing. We accept a mass of the barrier material, which moves at the opening and a collapse of the channel, as equal to the cone mass. In this case, a magnitude of the barrier material mass which moves in a dynamic regime will be also underrated if the dynamic mass transfer of a cone material, without involving the nearby layers to a cone, is supposed in the collapsing process. A collapse velocity of the channel element can be calculated according to Eq. (4) [28, 34]:

$$\upsilon_{com} = \sqrt{\frac{2E_S}{3M_f - 2M_{d1}}}, \tag{4}$$

where E_s it is the energy spent on the channels collapse.

As the barrier can be divided, along its thickness, into two zones, i.e., from 0 up to 0.2 m and from 0.2 up to 0.3 m, the data can be divided into two parts. The volume of an individual cone of the high-pressure zone is $V_{z(0-3)} = 0.347 \times 10^{-9}$ m^3 (the zone 0–0.3 m). A part of the cone in the zone 0.2–0.3 m (diameter 44.33 μm, length 0.1 m) will have the volume $V_{z(2-3)} = 0.154 \times 10^{-9}$ m^3 and $\Delta V = V_{z(0-3)} - V_{z(2-3)} = 0.192 \times 10^{-9}$ m^3.

To neglect the influence of the static strength of the barrier material, we have made an assumption that in the cone volume, the high-pressure $\sum E_p = 1.42 \times 10^6$ J is produced. For the channel elements opening, the energy E_{op} = 49,336 J is spent. Hence, the residual energy is $\Delta E = \sum E_p - E_{op} = 1.37 \times 10^6$ J. Taking into account characteristic properties of the zone structures, this energy is distributed proportionally to the volumes of the high-pressure zones $\Delta E = \Delta E_{0-2} + \Delta E_{2-3}$.

The estimated parameters of the collapsing channel elements are shown in Table 2. The energy expenditure on the channel elements collapsing in the barrier is E_{com} = 459,245 J and $E_{com} + E_{op}$=508,611 J.

TABLE 2. Parameters of a collapsing process of the channel elements

Zone depth	Mass of material under high-pressure (M_f)	Mass of defective residual (M_d)	Collapsing velocity (υ_{com})	Energy (E_{com})	Quantity of channel elements
[m]	[kg]	[10^{-3} kg]	[m/s]	[J]	[pcs]
0–0.2	0.751	0.2028	824	254,955	480,812
0.2–0.3	0.213	0.0411	1,385	204,290	170,737
0–0.3	0.964	0.2439	976	459,245	–

5.3. CHANGE OF THE BARRIER MICRO-STRUCTURE

In the barrier volume, a dislocation pattern characteristic for usual explosive loading appears. The changes of geometry and sizes of the grains and their twinning are observed. We have accepted that the energy spent on the twinning, change of geometry and sizes of the grains was only 5% of the total compression energy $E_{com.ex}$. Thus, the energy spent on these micro-structural changes is $E_{ex} = 29.7 \times 10^4$ J [18].

5.4. OTHER FACTORS CAUSING THE ENERGY EXPENDITURES

Other factors causing the energy expenditures are: formation of micro-jets of dense plasma at the back surface of the barrier [23], pulse electromagnetic radiation [25], and formation of the streams of high-energy ions [24]. Because now there are no reliable quantitative data on these processes so, according to a principle of minimization, the energy expenditures on these processes were neglected.

6. Energy Balance

The introduced and spent energies will be compared:

$$E_p = E_a, \tag{5}$$

where E_p is the energy introduced during superdeep penetration and E_a is the energy spent on the SDP process.

We considered the expenditures of energy on:

- Formation of the macro-crater ($E_k = 2{,}548$ J)
- Barrier settlement ($E_d = 401{,}821$ J)
- Changes of a structure of the barrier material ($E_{ex} = 97{,}000$ J)
- Production of the high-pressure zones ($E_{\Sigma f} = 1.42 \times 10^6$ J)
- Opening of the channel elements ($E_{op} = 49{,}336$ J)
- Collapse of the channel elements ($E_{com} = 459{,}245$ J)

and other expenditures of energy, e.g., on radiation E_{ad} and jets formation.

The sum of the rated expenditures $E_a = E_k + E_d + E_{op} + E_{com} + E_{ex} + E_{\Sigma f} \approx 2.63 \times 10^6$ J. However, we will apply a principle of minimization of energy expenditures. According to this principle, it is possible to neglect the expenditures of energy: on formation of the macro-crater E_k, settlement of the barrier E_d, and the changes of a structure of the barrier material E_{ex} since the energy generated in these processes could be repeatedly used in the processes of the channel formation ($E_{op} + E_{com}$). Accordingly, $E_{op} + E_{com} > E_k + E_d + E_{ex}$. However, as it has been shown earlier, the processes of the channel elements formation can occur as a result of transformation of the energy of high-pressure fields ($E_{\Sigma f} \geq E_{op} + E_{com}$). We accept that E_{ad} results from the transformation of the energy $E_{op} + E_{com}$. Therefore minimal necessary energy expenditure for the process of superdeep penetration is accepted as $E_a = E_{\Sigma f} = 1.42 \times 10^6$ J.

Thus, in dependence on the extent of the use of a minimization principle $\frac{E_p}{E_a} = (5.6...10.5) \times 10^{-2}$, i.e., 5–10%.

Because for estimation the approach of under-stating of the expenditures of the energy and over-estimation of the power consumption has been accepted, the possible mistakes in the given approach cannot be significant. It is obvious, that even 5–10 times mistake in calculation of the energy expenditures does not change qualitatively the energy balance at the SDP. The probability of the following equation is high:

$$E_p + E_{unk} = E_a, \tag{6}$$

where E_{unk} is the additional energy emitted during the interaction process.

In this case, even the additional expenditures of the energy for radiation, heating and emission of the barrier material in form of micro-jets can be compensated:

$$E_p + E_{unk} = kE_a, \tag{7}$$

where k is the coefficient which does not include the energy losses during the superdeep penetration process.

7. Features of Interaction of a Stream of Particles with Ceramics

Let's consider specificity of interaction of carbon and its chemical compounds with silicon. As a subject of research used a plate of a monocrystal of silicon and a micro-devices on their basis. Structural specific changes which observed on a surface of a plate from monocrystal of silicon are examined. Conditions of interaction allow to realize stably effect of superdeep penetration in metal barrier. It have wide experience in such researches. Plates of a monocrystal of silicon have high hardness and high fragility. Nevertheless in experiments with using of rigid regimes plates crushing was observed. The example of destruction of a microdevice, in rigid regime at direction perpendicular to action of a stream of particles is shown on Fig. 6.

Damages of a plastic envelope of the microdevice also have not been detected at use of visual and x-ray methods. Damages have been detected after removal of a protective envelope. Cracks have arisen between knots of an inflection in a plane of section of a plate of a silicon monocrystal. Knots of an inflection have been investigated (Fig. 7) and zones of impact are detected.

In a silicon plate the zone of punching with a diameter in a cross-section less than 1 μm and depth ≈ 180 μm was generated. As a barrier was the fragile material then it is possible to consider that the cross-section size striker does not exceed the size of a zone of punching. Striker represents long and thin body [24].

In work [24] it is shown that in a metal barrier there are microjets with a speed in longitudinal direction υ_t = 1,482 m/s and in a cross-section direction of a jet are compressed with speed υ_{com} = 1,048 m/s. In such conditions ($P = 11.3 \times 10^{11}$ N/m^2) the material of a jet exists in a condition of dense plasma. At processing the container with a microdevice the plasma jets pass through gaps. Such gaps are existing in system: between an internal surface of a cover and an ampoule, between an ampoule and a cover of a microdevice, between an internal surface of a cover and a surface of a plate from a monocrystal of silicon. Driving of a jet in gaps is realized in interval of time 0.67×10^{-6}–3.37×10^{-6} s. During this period of time there is a unloading of a jet in a cross-section and pressure in a point of contact varies in a range: 11.3×10^{11} N/m^2 – 1.1×10^9 N/m^2– ~10^7 N/m^2. If hardness of Si monocrystal no more than 10^9 N/m^2 then at pressure decrease up to 10^9 N/m^2 the penetration of a jet into a chip stops. Executed calculations [25] show: speed of driving of a jet in a silicon plate is U = 961 m/s, and the length of a jet is L ≥ 98 μm. If to execute transition from rigid to soft regime of operation of microjets then punching of a plate stops. Affecting of plasma jets on silicon plates gets other kind. Operation in a soft regime is shown on a Figs. 9 and 10.

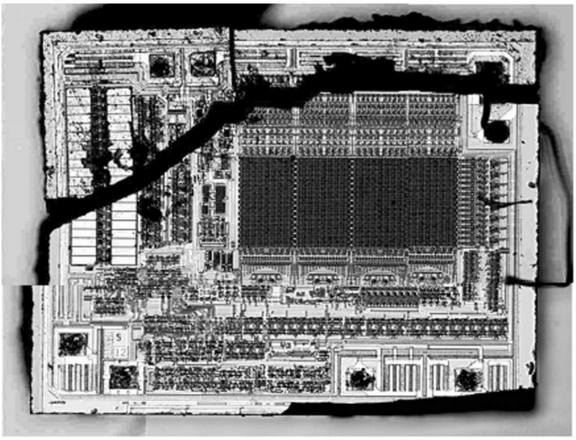


Figure 6. A view of the damaged monocrystal of silicon, ×75

In a soft regime the jet acts on a local area and heats up it. Such action evaporates from a surface of a plate a covering – the circuit of the microdevice. In this zone it is possible to see numerous small holes.

Heating of a local area depends on microjet parameters. The temperature of local heat can be above temperature of fusion for silicon (Fig. 8). At intensive heating there are bubbles of melt (Fig. 8a). Significant overheating of a local area of a silicon plate initiates growth of new monocrystals (Fig. 8b).

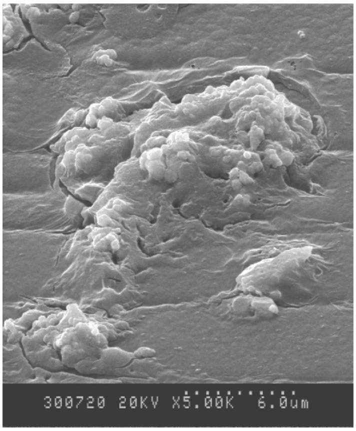


Figure 7. A zone of damage of a silicon plate in a soft mode

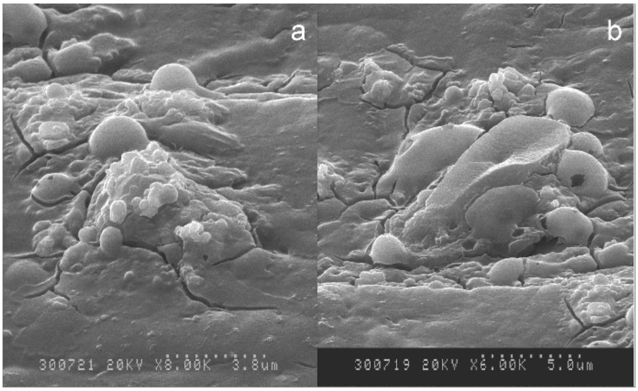


Figure 8. Segments of local melting on a surface of a silicon plate: (a) a zone of formation of bubbles of melting; (b) a zone of initiation of growth of new monocrystals of silicon

Bubbles of the fused silicon have traces from punching by microjets. Hence, these microjets acted on a barrier after formation of bubbles. Bringing in SDP mode particles of carbon and its chemical compounds, interaction of elements of a stream and a barrier (silicon plate) will be always realized at high temperature and high pressure. The spectroscopic analysis of a surface of a plate before and after processing shows interaction of carbon and silicon. The thick-walled container allows to keep products of interaction in the set atmosphere and also to protect the working personnel from radiation.

Conditions of interaction ensure synthesis of chemical compounds. We observe heat removal into silicon plate. By using of a barrier from carbon (diamond) on its surface it is possible successfully to synthesize a wide gamma of metastable chemical compounds. Qualitative difference of process of synthesis in SDP mode from other known processes is its low energy capacity at a stage of creation of a high-speed stream of discrete particles [13]. Anomaly of this process is the fact that despite of rather low level of initial kinetic energy at synthesis the high pressure and high heat are realized.

At using microchips as samples specific processes on metal surfaces are found out (Fig. 9). From volume of a metal solid body under action of high pulse pressure the microtubes are squeezed out: lengths of 5–25 μm and diameters of 5–10 μm (Fig. 9a). It is obvious, that process of an extrusion happens due to energy from microexplosion inside of metal. The electroplating can be removed from a surface of a metal element only due to evaporation of a covering (Fig. 9b). The cross-section size of pinholes which punching is not accompanied by the microexplosion is ~1 μm (Fig. 9c). Zones with cracks, apparently, arise during a relaxation of residual stresses (Fig. 9d). The received experimental results have shown presence of significant additional expenditures of energy at synthesis. These energy expenditures were not considered earlier at calculation of balance of energy of superdeep penetration.

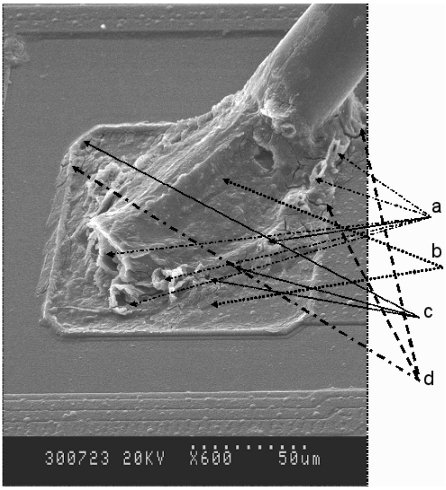


Figure 9. Features of interaction of a metal element of the microchipe with a plasma jet at SDP: a – zones of dynamic extrusion of metal micropipes (microexplosions); b – a zone with the removed electroplating; c – zones with microholes; d – zones of microcracks

8. Features of Interaction of a Stream of Discrete Particles with Plastic

Interaction of discrete streams of microparticles with plastic in SDP mode was investigated for definition of properties of protective shells. So studying of plastic shells of microchips has shown that such shells in SDP mode do not lose hermeticity. At small magnifications by visual observations it was not possible to find out results of interaction. Therefore in work [26] traces of interaction between stream of Ni particles and a plastic foil were examined. The shape of traces that strikers have created in a foil is shown on Fig. 10.

Traces of inclusions contain material of particles and barrier in different percentage. Observable holes have been received only after etching by an acid solution. Selective etching of zones of puncture proves local activation of plastic in this zone. For definition of the fact of superdeep penetration and efficiency of particles penetration in composite barrier we had been used so-called “foil method” [27]. The choice of this technique explains simplicity of its application. This technique registers traces of penetration. There are traces that leave particles in nonmetallic materials. If to use such materials for a composite barrier as a fluoroplastic and a cardboard, then the analysis of changes of their structure will be difficult for executing. The channel, that the particle creates, “slams” and has diameter from 1 μm up to 1 Å. Open cavity can be absent completely then only a track – the deformation area with inclusions of a material of penetrating particle is conserved. Etching of this deformation zone of a track till the size when the track is well visible using of an optical or scanning electronic microscope is necessary. Teflon has high chemical resistance, the cardboard inversely easily etching. In carried out researches were used three kinds of barrier. The barrier in the first container was made from steel 45 and had thickness 50 mm. The second barrier was two-component "steel – fluoroplastic". Thickness of layer of the steel located on the side of collision with a stream of particles was 20 mm and following layer – fluoroplastic (teflon $(CF_2 - CF_2 - \ldots)_n$,) was 25 mm. The three-component barrier consisted from layers in sequence: steel (thickness 20 mm), four sheets of a dense cardboard with common thickness ≈6 mm and layer of fluoroplastic (25 mm). Definition of efficiency of penetration of particles into barriers on the determined depth (equal to thickness of a barrier) was made by amount of traces in a foil after penetration. Traces (inclusions) which were qualitatively differed from the initial defects of foils were [27] calculated. The foils were analyzed on optical microscope. The second, the fourth and the tenth foils from the back side of the barrier were in addition investigated on a scanning electronic microscope "Com - Scan" (England) with the micro x-ray spectrum analyzer. Typical traces of interaction of strikers with a barrier, it is possible to divide into three kinds. On Fig. 11a the characteristic trace from "through" punching of a foil is visible.

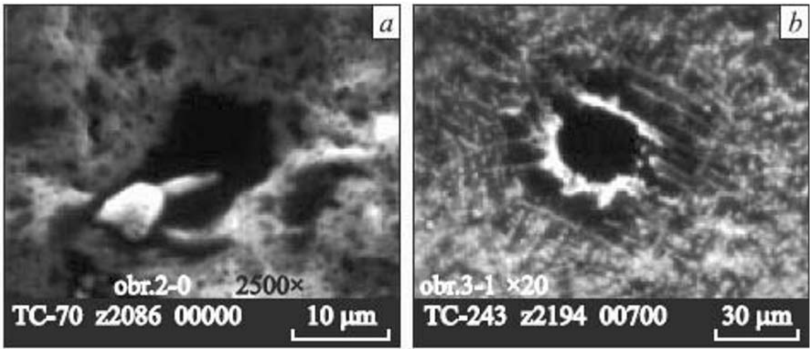
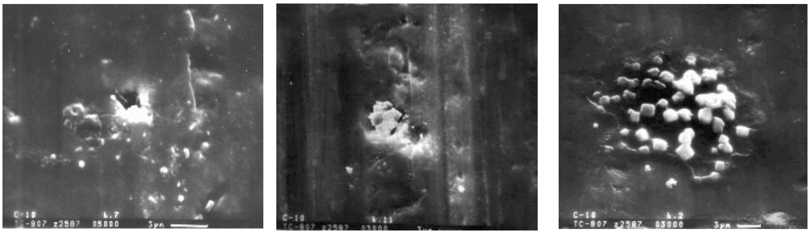


Figure 10. Tracks of damages in plastic films, received in a mode of superdeep penetration at processing in the protective container: (a) thickness of a barrier of 200 mm, 2 foil; (b) thickness of a barrier 50 mm, 31 foil

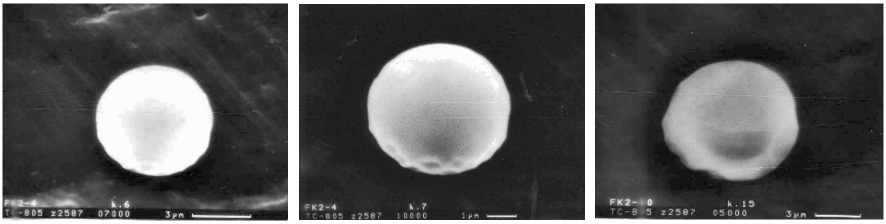
On a Fig. 11c "cork" from the beaten out material of the previous foil after punching of striker is visible. It confirms results of the point analysis of the inclusions that show presence aluminium into cork – a material of foil.



a b c

Figure 11. Variants of tracks from interaction of striker with the tenth foil: (a) through punching of foil, ×5,000; (b) rest from striker, ×3,000; (c) beaten out "plug" from the ninth foil, ×3,000

For two and three-component barrier on foils the new elements of structure with the spherical form are recorded. Under action of a scanning electronic microscope there is a strain of a surface of a sphere. The surface of a sphere seems to be "spreading". Dynamics of change is displayed on a Fig. 12 where inclusion through different time intervals from the beginning of action of scanning electronic microscope is displayed.



a b c

Figure 12. Inclusion on a foil behind the barrier consisting from three layers "steel – cardboard – Teflon": (a) after its detection, ×7,000; (b) in 10 s, ×10,000; (c) in 20 s, ×5,000

The analysis has shown that spheres consist of light elements. It is natural to assume, that this material – fluoroplastic (elements of fluorine-carbonic chain (CF_2) of polymer). Fluoroplastic congeals from liquid state taking form with a minimal surface. As at temperature above 260°C fluoroplastic is softening (melts at 327°C) then this assumption well explains occurrence of new spherical inclusions.

Composite barrier regulate process of penetration in SDP mode [26]. During interaction discrete stream of particles with plastic in SDP mode intensive processes of mass carry are observed. The intensive irradiation of electromagnetic fields and streams of high-energy ions in addition changes properties of plastic.

9. Features of Creation of New Porous Materials

SDP processing is taking place in the isolated volume as penetration of particles occurs even through thick barrier. Creation of a particle flux and processing of specimens is carried out separately. But because of features of SDP interaction the additional dynamic loads inside of a specimen occur. Changes of interacting materials and SDP regime are changing the process of synthesis of a carcass material. During synthesis inside of a solid body there is a reinforcing carcase material. The matrix material and a material of a carcase (skeleton) have various physical and chemical properties. Due to this it is possible to delete selectively any element of a construction of a composite material. Let's consider a variant of such technological approach. For this purpose in SDP regime we synthesize a skeleton which material has the increased chemical activity in comparison with a matrix material. As a matrix material we took a glass.

Glass sample etched at different dwell time in a solution of hydrofluoric acid. On Fig. 13 change of structure of a glass sample is shown at various conditions of etching.

Figure 13. Structure processed in SDP mode of glass sample after various modes of etching ×1,000: (a) 30 s, (b) 60 s, (c) 120 s

The analysis of experimental results has shown, that at SDP regime in fragile nonmetallic materials there are specific defects [28]. Specific damages arise in fragile materials (glass, silicon) by action of microjets inside of a protective envelope. Microjets have high penetrating ability. Interaction of a jet with glass has high-energy character, leads to occurrence of tracks and change of properties of glass. It is expressed in amplification of activity of defective zones in a glass specimen.

Processing of glass materials it is expedient to execute for the purpose of shaping details in glass with volumetric porous structure. Change of regimes of chemical and electrochemical etching in a range of real time allows to create from a composite material a new porous material with the cross-section size of through pores from nanometers up to tens micrometer.

10. Conclusion

On the basis of complex theoretical and experimental researches of the interaction of materials in a condition of superdeep penetration the opportunity of dynamic reorganization of a massive solid body into a composite material is shown. It is possible to do following basic conclusions from the received results:

1. Interaction of working substance and matrix material in SDP conditions is realized in the enclosed system which the solid body is. Therefore products of interaction, including interactions of silicon and carbon among themselves and with other materials, do not represent danger to an environment.
2. Feature of the processes based on effects of superdeep penetration, is the rather low level of expended energy. Though SDP effects are accompanied by high and superhigh pressure, an intensive strain, local heat-up and microexplosions, an intensive electromagnetic and ionic irradiation, but necessity for use of powerful power sources is absent.
3. Superdeep penetration is realized inside of a solid body in automodelling regime. Process of superdeep penetration is well combined with other technological decisions, and new industrial products are effectively realized at complex effect.

4. In a regime of superdeep penetration at conditions of multifactorial impact the new composite material is made from a massive solid body by modified nano- and microelements. Presence of nano and microelements in a skeleton of a composite material are the reason of significant changes of physical and chemical properties. The material on these levels of structure has physical and chemical properties which considerably differ from properties of this material on mezo- and macrolevels.

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SDP TECHNOLOGY FOR "GREEN" TECHNOLOGY OF METALLIC REINFORCED NANOCOMPOSITES

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Abstract. New "green" technology is based on using an unusual physical phenomenon – superdeep penetration (SDP). Synthesis of a skeleton and formation of nanostructure is realized in metals. Influence of chemical compounds of an injected substance and a metal matrix on SDP process is considered. Features of behavior of steel and aluminum are defined by the parameters of dynamic phase transitions in these materials. Superdeep penetration is used for manufacturing of special composite metal materials with an unusual complex of properties.

Keywords: SDP, synthesis, dynamic phase transition, influence zone

1. Introduction

The competitive technology is created only with using new physical and chemical effects. The important factors for competitiveness definition are ecological safety and power consumption of technological processes. Competitiveness of technology for production of a new material is defined by technical possibilities of processing.

The big interest is shown to create complex materials. In such materials, various macrocells of a design have a considerable difference between physical and chemical properties [1]. A process of manufacturing of composite fiber materials can be divided into three basic stages. The first stage is preparation of a massive matrix. The second stage is manufacturing of fibers for reinforcing of a composite material. The third stage is a process of assemblage of a composite material of the constructional elements made at the first two stages of a process. Some specific problems appear at each stage of a process. The basic problem is the contradiction between the engineering decisions made at various process stages.

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It is possible to create a composite fiber material, in which the fibers are made of a matrix material but the size of structural elements of fibers differ from the size of structural elements in a matrix material [2]. In micro and nano conditions, the material has physical and chemical properties which differ from the properties of the same material on meso and macro level. The earlier used materials with nano- and micro-structures were produced using traditional technologies. Now, new methods, employing new physical tools, appeared.

As a rule, the third stage of manufacturing of a composite material is a thermal process. Such a process at diffusion provides durability of a contact between the elements of a composite material. The base problem at production of a massive material from nano and micro powders is that increase in intensity of thermal processing really increases durability of connections between the elements of a composite material. But thermal processing also initiates increase in the sizes of elements of a structure of a reinforcing component. Therefore the solutions that are efficient for particular stages of the process are not efficient for a composite material technology.

Increase in wear resistance of details of working bodies and the tools is basically reached by application of protective coatings and by reinforcing tools with hard alloys. As a result of ecological research in Europe, it has been proved that for consumers and manufacturers, hard alloys on the basis of WC and Co are cancerogenic. All attempts, on the basis of traditional powder metallurgy, to find alternative were inefficient. For 80 years of searches, the alternative to these hard alloys (WC + Co) has not been found [3].

Hard alloys represent a massive composite material. The combination of firm carbide and layers of plastic metal creates high level of wear resistance, durability on a bend, impact strength. These hard alloys can be replaced only by new composite materials. The possibilities of traditional powder metallurgy for changing a structure and additional alloying hard alloys and steel alloys are practically exhausted.

Shortcoming of traditional methods of volume hardening is that increase in wear resistance of the products is accompanied by reduction of bending durability and impact strength [4]. It causes interest in nonconventional technologies of metal hardening, for example, hardening of details by explosion. At the impact of shock waves on various steels, unusual physical effects are observed, i.e., rise in temperature, shock compression, and dynamic phase transition. Hardness distribution on a depth of metal depends on the form of an area of a high pressure. The maximum increase in wear resistance (in 1.65 times) at high-manganese steels is reached at complex action: additional alloyings and hardening by explosion.

It is possible to raise a level of properties of tool steels by transformation into a composite material. For example, the material can be modified in a volume by the elements of micro and nano structure.

The massive composite material can be made at the action on the base steel with intensive sign-variable deformations, high gradients of pressure and temperature. For this purpose, intensive plastic deformation and electric discharges in melts are used [5].

High pressure in a solid body is not a primary factor of structure crushing. The higher gradients of pressure and higher heterogeneity of a solid body material, the higher probability of local material deformations and its structure's crushing. The factor influencing the material structure crushing is the time of a process. As a rule, in a solid body, at the impulse processes there are fluctuations (gradients) of energy, pressure, temperatures, deformations etc. These dynamic processes differ from static processes [6].

The maximum changes in material properties can be received using physical tools which simultaneously provide multifactorial action on a material. At the movement through a substance, high-energy ions brake and destroy a material along a movement trajectory. When the experiment with irradiation in time is combined with loading of the graphite sample with a high pressure, then the structure reorganization in a narrow zone of graphite (phase transition) is observed [7]. Thus, graphite became amorphous. The experiments with metallic zirconium have confirmed that at the joint action of irradiation and a high pressure, structural transformation occurs. If the substance is under the pressure, then the irradiation with heavy ions serves as the catalyst of a phase transition. Due to this unusual physical effect it is possible to create micro-and nano elements of a structure in a solid body.

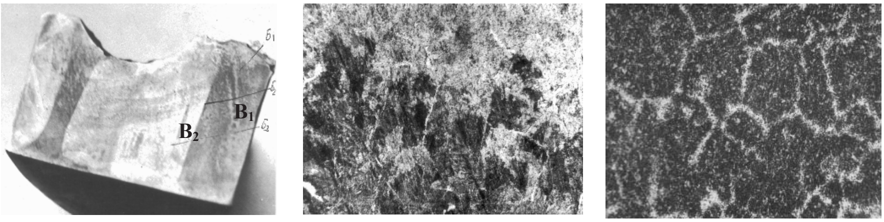
The physical phenomenon at which the following physical effects simultaneously occur are: high pressure, intensive deformation, electromagnetic fields, ion streams, dynamic alloying and synthesis. This phenomenon is known as superdeep penetration (SDP) or “Usherenko” effect. The dust clot, in SDP conditions, penetrates into barriers on the depths in tens and hundreds millimeters. At usual impact, the ratio of a penetration depth to a striker caliber (determined by a particle diameter) does not exceed 6–10. At SDP, the resistance of a barrier material at the movement of particles clot in it as though decreases in hundreds and thousand times [8]. In the conditions of superdeep penetration, the dust particles penetrate into barriers, form in them lengthy (tens millimeters) channel elements of structure with cross-section section of channels in a range 10^{-4}–10^{-1} from a caliber of the striker. Local reorganization of the structure of a solid body allows us to form massive composite materials. Strengthening fibers in such a composite material are lengthy zones of the reconstructed structure. In a skeleton of a composite material, the matrix structure is crushed at micro or nano level.

The purpose of the presented work is to define the features of green technology for creation of the metal reinforced nano composite materials.

2. Features of Dynamic Reorganisation in Steel at Superdeep Penetration

Qualitative difference of production of composite materials at the use of superdeep penetration from traditional powder metallurgy is that the basic physical tool is the high-speed clot of discrete particles (powder). At SDP, a matrix is the massive high-strength material. At a loading in static conditions in a solid body, a uniform field of pressure is produced. Pressures in static conditions are created up to $\leq 10^5$ N/m^2. On the basis of this information it was assumed, that at the distribution of shock waves and deformation waves into a solid body, approximately uniform field of pressure ($\leq 10^9$ N/m^2) will be produced [4].

Let us consider a real experiment on shock interaction. Registration of an area of a high pressure we will execute due to the changes of a structure and physical and chemical properties of a barrier material. For the approach to a real geometry at blow, the surface of the steel sample was deformed preliminary by a steel sphere with a diameter of 30 mm. Clots of powder particles were used as strikers. After the pulse processing of steel preparation (concentration C ≤ 0.45%) a barrier cut in a longitudinal plane, a cut surface polished and etched with a nitric acid solution. The photo of areas of a high pressure (B_1) is shown in Fig. 1a. A background level of the pressure in a massive steel barrier (B_2) was ≤0.2–1.0 GPa (Fig. 1a). Thus, in a dark area of a section of the barrier (B_1), the level of pressure of more than 8–12 GPa (Fig. 1a) is obtained.



a b c

Figure 1. Distribution of different fields of pressure at impact: a – ×0.5; b – boundary between sections of high and low pressure, ×200; c – crushing of structure elements into area of the high pressure of steel barrier at heat (1,000°C, 1 h), ×200

Between the macroareas of high and low pressure (B_1–B_2), the sharp border is visible, Fig. 1b. Therefore in a metal solid body, at the action of clots of dust particles (in SDP mode), simultaneously there are the macroareas of both, low and high pressure. The high pressure area in a solid body volume is surrounded by an area of low pressure. In Ref. [9], it is foretold that at SDP in a solid body there is a steady wave – a soliton. Experimentally such soliton corresponds to the pulsing area of high and ultrahigh pressures. The length of the area of a high pressure (soliton) corresponds to a thickness of a barrier. Tracks have been found out in the areas with various levels of pressure. It, apparently, proves, that the narrow area of a high pressure (soliton) arises, as an independent object.

Wide area of the high pressure (B_1) was formed at combination of a considerable quantity of high pressure narrow oscillating solitons. Therefore the area – B_1 has high level of defectiveness. For the proof, after SDP processing, a metal solid body was heated up at the temperature of 1,000°C within 1 h. After that, the changes in structures of areas of high and low pressures were compared. In a high pressure zone, at the subsequent heating, the set of dot defects has arisen, grains were split up, and numerous centers of recrystallization were appeared, Fig. 1b and c. Growth of grains (Fig. 1c) occurred only after an additional stage of allocation of new structural defects (recrystallization). Therefore for increase in the sizes of grains, in a high pressure zone at the subsequent heating, additional time is required. In the field of low pressure, the grains of a barrier material at heating increase in a size faster because there is no stadium of additional structural defects. Therefore stability at heating (red-hardness) of the steel processed in the field of a high pressure is higher, than the same steel processed in the field of low pressure.

Cavities on a cross-section of the preparation are formed after chemical etching by a nitric acid solution. Formation of visible defects is explained by removal, at etching, the activated zones of structure (Fig. 2a). Specificity of these defective zones is also high resistance of the activated material to thermal influence (Fig. 1b). The experiments have shown that defects in steel, created at SDP, do not disappear even after heating for ten hours at the temperature of 1,000°C. After thermal processing in HSS matrix, the borders of grains section are formed and the cross-section size of the activated zones decreases in 10–25 times, Fig. 1c.

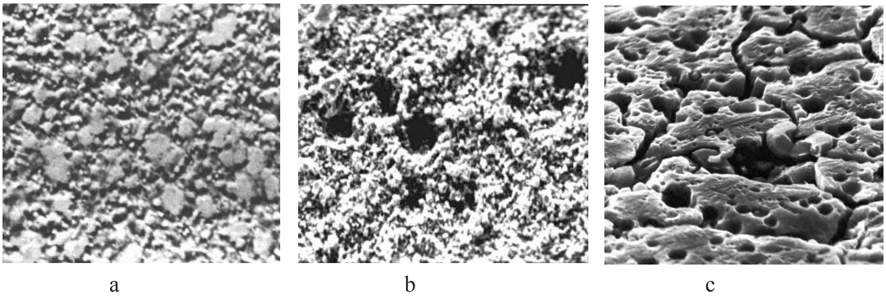


Figure 2. HSS steel at different stages of processing: a – before processing, ×1,000; b – after SDP, ×1,000; c – after SDP and heat treatment, ×5,000

Qualitative difference of some new elements of structure, i.e., the zones of strikers movement (channel zones), are local sections of overheated and quenched metal (Fig. 3).

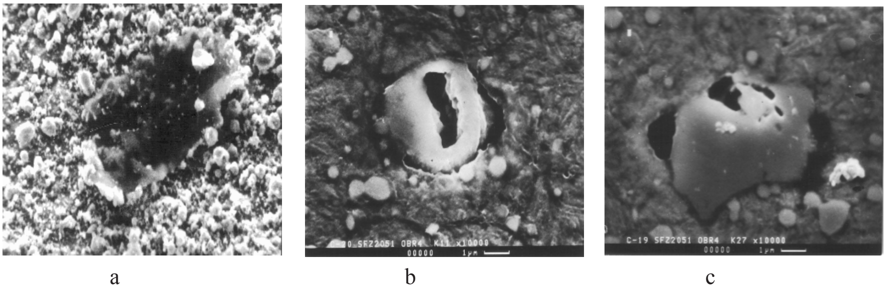


Figure 3. Zones of local fusion into HSS steel: a – ×2,200; b – ×10,000; c – ×10,000

Such elements of a structure are not present in an initial material. These elements can be used for identification of a process of superdeep penetration. Zones of local fusion can be formed round several, closely located “channel” zones (Fig. 3a). Rather large zone is observed when the thermal energy from an individual channel element is insufficient for fusion. But at the big magnifications (≥ 10,000) individual channel elements with overheated elements (Fig. 3b and c) are observed. Such elements of a structure have different reflective ability and reaction to etching than a matrix material.

In a longitudinal direction inside HSS matrix, the channel sections in a plane do not exceed 0.5 mm. These results are explained due to the fact that in combined steel there are available high gradients of hardness and density in a volume. During the movement into a steel matrix, the strikers oscillate around the axis of their penetration (Fig. 4).

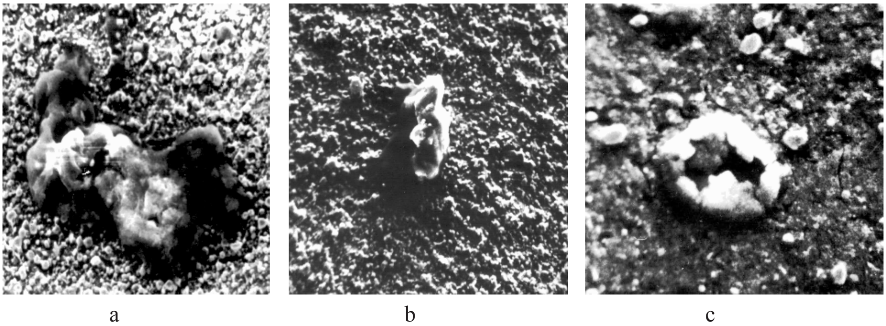
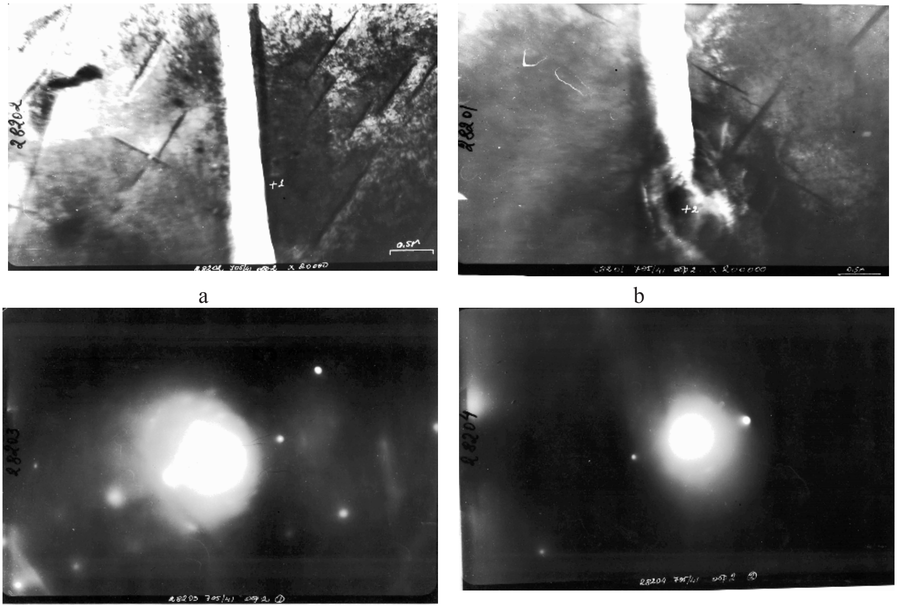


Figure 4. HSS steel – fusion zones: a – trail from driving of microparticles, ×2,000; b – trail from driving of microparticles, ×1,000; c – zone after heating (1,200°C, 1 h), ×4,000

Because of microparticles oscillation, the way of powder particles considerably exceeds the length of the strengthened preparation. The strengthened elements form a skeleton similar to a spring. By using special etching it can be seen that a diameter of a zone of interaction between moving particles and a matrix has a variable size, Fig. 4a. Chemical and physical properties of a material from the synthesized channel zone essentially differ from the matrix properties. The channel section, which after chemical etching on 4–5 µm projects from HSS matrixes, is shown in Fig. 4b. Intensive heating of channel zones causes occurrence of smaller structural elements, Fig. 4c. The complex consisting of the synthesized fiber elements and the plates from matrix steel, bound with them, creates zones of "influence" which, depending on a mode of superdeep penetration, constitute 3–20% of a volume of a composite material.

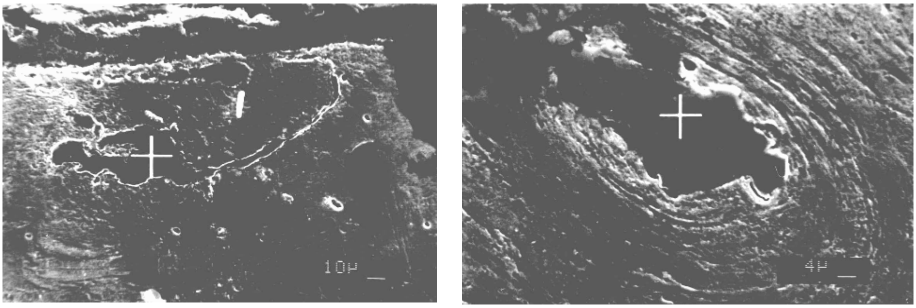
During the movement of a particle in a barrier, the whole complex of physical processes is realized: deformation of materials of a particle and a matrix, friction, pulsation of a field of a high pressure (oscillating soliton), radiation, and heating [8]. After the striker penetration into a skeleton material, the processes of relaxation occur. As a result, the thermal energy from zone interactions (channel) is rejected to a matrix material. At heat rejection (heat-sink cooling), the synthesized material is quenched in a steel matrix. Depending on the total thermal energy and intensity of a heat-removing, various structural conditions can be received in a channel material. The channel element created in the steel ($C \leq 0.45\%$) with a particle from Si_3N_4, is shown in Fig. 5. Materials of a channel zone and the braked striker are electron amorphous (Fig. 5c and d). In a mode of superdeep penetration, Si_3N_4 particles intensively interact with an iron matrix and synthesize metastable compounds in an interaction zone (Fig. 6).



a b

c d

Figure 5. Solid-phase amorphization of a material inside a zone of penetration, ×20,000: a – the top part of a channel element (length ≈1.5 μm) with a zone of diffraction (+1); b – a zone of braking and the braked striker with a zone of diffraction (+2); c – diffraction picture (diffraction pattern) zones (+1); d – diffraction picture in the braked striker (+2)



a b

Figure 6. Zones of interaction of Si_3N_4 particles inside an iron barrier: a – a new structural element to a depth of ≈70μm, ×300; b – a new structural element on a depth of ≈4.3 mm, ×750

The material (Fig. 6a) – O = 8.34%, Al = 7.67%, Si = 58.70%, Fe = 25.30% was synthesized in an iron barrier along a trajectory of strikers (Si_3N_4) movement. The form of a new structural element specifies that the metastable material was in liquid or in quasi-liquid condition. Braking of a liquid striker (Fig. 6b) is realized in the conditions of an intensive plastic deformation. The microanalysis of the braked striker has shown its structure: Al = 0.69%, Si = 62.89%, Fe = 26.42%. Reduction of concentration of oxygen in a striker on the depth of penetration is explained by oxidation of walls of the channel along a movement trajectory. Interaction of a striker and an iron matrix is accompanied by additional release of heat. At quenching of the overheated liquid material from an interaction zone in iron, the synthesized material became amorphous one (Fig. 5).

To check this assumption, in the SDP mode, we will enter silicon particles into an iron matrix. Initial particles of silicon had approximately a cubic form. Interaction of the particles of silicon with an iron barrier is shown in Fig. 7.

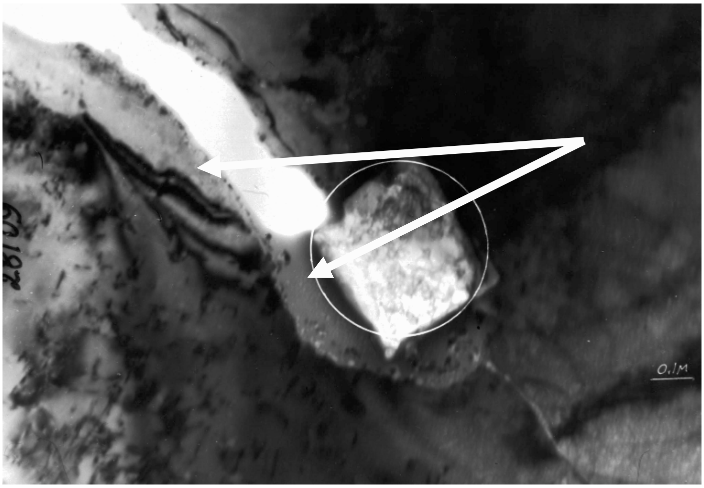


Figure 7. Zone of braking of Si striker of the cubic form, ×60,000

Round the etched long aperture and the braked striker, the remains of a material of a channel zone (white arrows) were situated. This material has more light shade and differs from a matrix material (Fig. 7). The structure of a material of a channel zone is nano and micro crystalline. The striker has decreased in size approximately in 100 times, but it has kept the cubic form.

Superdeep penetration proceeds in the time shorter than 1 s. This time is not enough to finish steel reorganization in a composite tool material. The increase in speed of a mass transition in a solid body volume leads to increase in the energy consumption of a process. Therefore it is purposeful to finish formation of a composite material at thermal processing.

3. Changes Structure of Aluminium and Its Alloys at Superdeep Penetration

The basic problem in studying the changes of a structure of aluminum and its alloys after SDP is creation of techniques of samples preparation from the activated material.

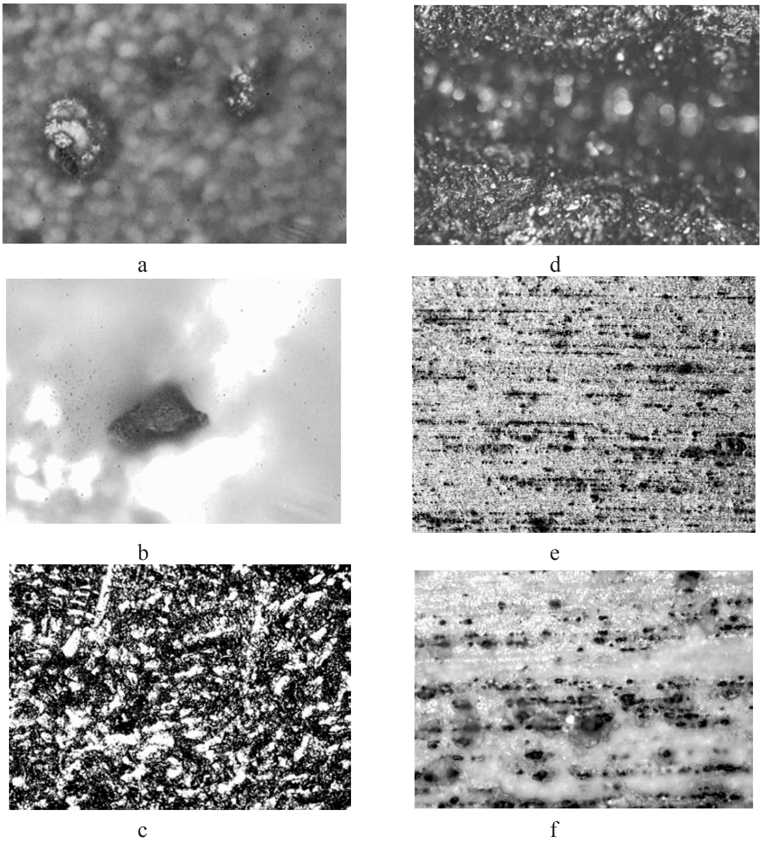
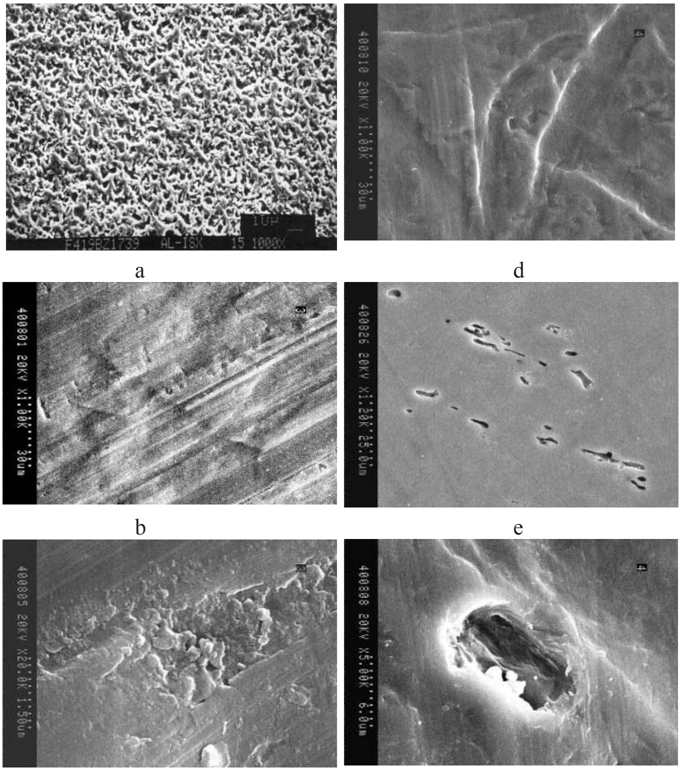


Figure 8. Structure of the aluminum processed in SDP mode: a – SiC→Al (cross-section), ×3,000; b – Pb→Al (cross-section), ×3,000; c – an initial alloy - Al-12% Si, ×100; d – SiC→Al-12% Si (longitudinal section), ×100; e – Pb→Al-12% Si (longitudinal section), ×100; f – Pb→Al-12% Si (longitudinal section), ×400

Because of high plasticity of aluminum there is puttying a surface of samples. Definition of an etching mode is carried out taking into account the specific activation of a material. The correct technique for preparation of samples reveals small structural elements (Fig. 8) with using an optical microscope. After introduction of SiC powder in Al matrix, strong activation of zones of "influence" occurs (Fig. 8a and d). During electrochemical processing, these zones are dissolved faster than Al (Fig. 8a and d). We can see these zones, as the cavities on a surface of the sample. The zones saturated by Pb, have the lowered etching ability (Fig. 8b, e, and f). These zones project over a surface of the aluminum sample. In Al-12% Si alloy, the zones of "influence" include the whole system of tracers (channel microzones). The matrix material is stitched by tracers. The share of zones of "influence" reaches 8–10 vol%. Various powders introduced into aluminum and its alloys at SDP allow us to change etching ability of a received material. It is possible to raise etching ability of the activated zones or to lower this etching ability at the expense of introduction of inhibitors. In relation to a matrix, the aluminum etching ability of zones of "influence" can be changed in several times.



a d b e c f

Figure 9. Structures of aluminum samples after processing in SDP mode: a – initial Al after etching; b – Al (SDP) without etching, ×1,000; c – Al (SDP) without etching, ×20,000; d – Al (SDP) etching, ×1,000; e – tracks in Al (SDP) with etching, ×1,200; f – defective (channel) zone in Al (SDP) with etching, ×5,000

Using a scanning electronic microscope for investigations does not reduce significance of an etching process of a sample surface. In Fig. 9, the features of a structure of aluminum materials are shown.

When the samples of aluminum without etching are studied (Fig. 9b), it is impossible to observe new elements in a structure. Therefore, the scientists have considered for a long time that the phenomenon of superdeep penetration in aluminum does not occur. Even at considerable magnifications (Fig. 9c, ×20,000), on a surface of the sample is not possible to reveal specific structural defects. Even due to weak etching, single (Fig. 9d and f) and collective (Fig. 9e) structural elements have been shown. It is obvious, that studying these defects at small magnification (×1,000) does not give the information about their specific character. The defects studied at magnification ×5,000 (Fig. 9f) has allowed to find out the deformed structure of a new microzone. The technique facilitating revealing of defective (channel) zones in aluminum is application, at SDP, the powder materials which do not interact with Al matrix. In Fig. 10, the lengthy (longitudinal) elements of a structure received at SDP are shown.

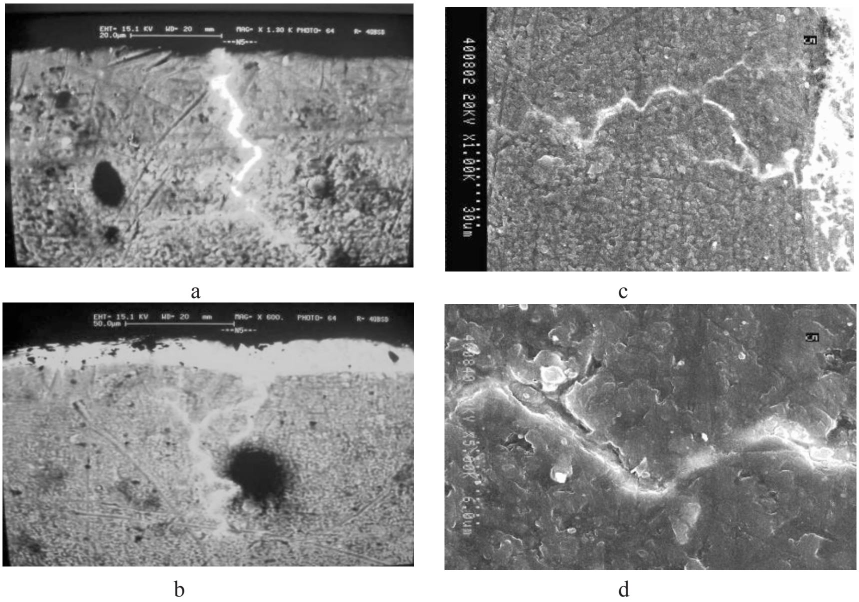


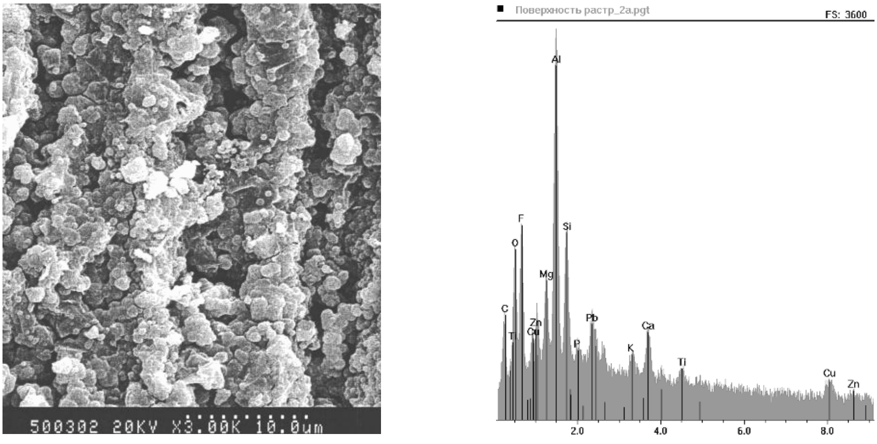
Figure 10. The channel longitudinal elements of structure created in aluminum at Pb introduction: a – 1 defective zone (luminescence); b – 2 defective zone (luminescence); c – 2 defective zone, ×1,000; d – a track, ×5,000

Using lead (Pb) allows us to inhibit an interaction zone in aluminum and to show this zone on a surface of a microsection. Besides, introduction of Pb as a heavy element, allows for revealing a channel structure by electronic methods. Lead in the penetration process is in a liquid condition. However, the lead striker moves in a solid body as it does not meet the resistance from solid aluminum. Whether lead interacts with a matrix at this time?

4. Features of New Elements of Structure into an Aluminum Barrier

The modern equipment allows us to define special zones in a volume of an aluminum matrix. In these zones, there is interaction of an entered substance and a metal matrix. For investigations of this phenomenon, the microanalysis can be effectively used. Al-12% Si alloy and also the technically pure aluminum for pouring of samples, prepared in the induction crucible furnace with the graphite crucible, because of induction heating provides uniform hashing and excludes liquation of alloying elements in a melt volume.

As the object of research we use Al-12 % Si alloy. This material, after introduction of Pb particles, has been subjected to electrochemical processing (Fig. 8d, e, and f). The results of scanning and the microanalysis are presented in Fig. 11.



a b

Figure 11. Structure of Al-12% Si alloy after superdeep Pb penetration and electrochemical processing: a – structure of zones of influence; b – the raster analysis of an aluminum matrix (200 × 300 μm)

However, such a form of demonstration of the information is inconvenient for the numerical analysis. Therefore one uses the concentration results collected in the tables. The received information about the changes in a structure of the zones of influence is presented in Table 1.

In the influence zones, there is a considerable quantity of alloying elements. Alloying elements which were absent in an initial material are found out. For example, potassium and calcium (K and Ca) have been found out. These elements in the process of manufacturing (moulding) for the technological reasons are removed from a material. Concentration of Ca in various points of a zone changed from 0.05 to 7.5 mass%. Concentration of K varied from 0.00 to 3.64 mass%. At the given analysis, the possible error does not exceed 0.4 mass%. Concentration of Pb in an influence zone in all analyses is 0.60–10.54 mass% that exceeds the background concentration in an initial alloy (0.03 mass%). In a number of points of a zone of “influence”, the concentration of Mg varied from 0.00 to 2.24 mass%. In initial Al-12% Si alloy, Mg concentration (average concentration) did not exceed 0.01 mass%. Concentration of Fe in a zone varied over a wide range 0.1–76.8 mass% and, as a rule, exceeded background value in an initial alloy (0.13 mass%). The change of Mn concentration is less appreciable. Manganese changed concentration from 0.00 to 7.48 mass%, and background concentration was 0.06 mass%. The titan was not in an initial alloy. Concentration of Ti in an influence zone fluctuated from 0.01 to 1.84 mass%. Zinc was in an initial alloy as an impurity – 0.05 mass%. In an influence zone, in four points of analysis, Zn has not been found out. However, the concentration of Zn in two points of the analysis has appeared considerably higher than the background value of 2.71–24.08 mass%. It is impossible to explain these results as an instrument error.

TABLE 1. Concentration of chemical elements in influence zones (mass%)

No	Al	Si	Ca	K	Pb	Mg	Fe	Mn	Ti	Zn
1[a]	61.41	12.44	7.50	3.64	10.54	2.24	0.88	0.50	0.80	–
2	94.64	1.41	0.05	0.06	1.19	2.17	0.10	0.35	0.01	–
3	69.87	13.43	4.54	3.22	5.49	2.08	0.24	0.00	1.11	–
4	79.49	0.33	0.24	0.07	0.60	0.00	7.65	0.05	1.84	–
5	75.72	2.26	0.27	0.00	1.66	0.00	9.82	7.48	0.06	2.71
6	1.94	14.8	0.49	3.14	2.35	0.25	76.86	0.25	0.06	0.15
7	51.30	3.92	0.63	0.00	5.36	0.00	9.93	4.62	0.14	24.08
8[b]	86.90	12.75	0.00	0.00	0.03	0.01	0.13	0.06	0.00	0.05

[a] Averaging on a surface 200 × 300 μm.

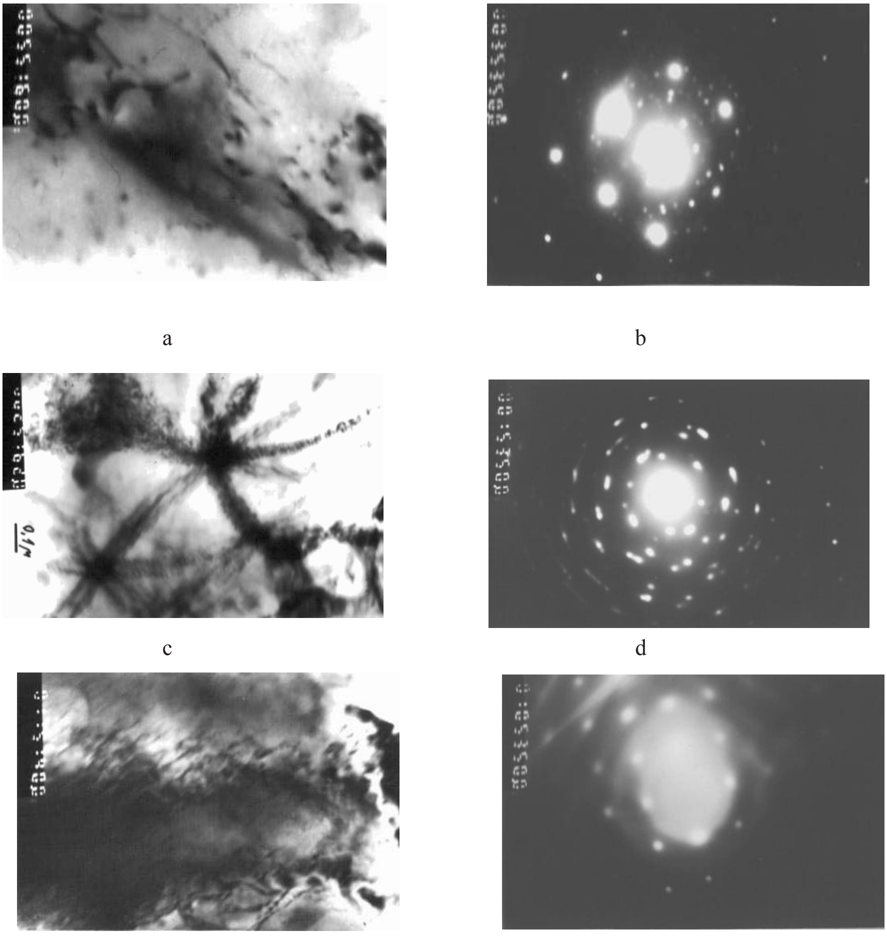
[b] Initial analysis after preparation moulding.

The stitching of an aluminum matrix with stream particles should lead to strong distortions in a penetration zone. Results of this research are shown in Fig. 12.

When in a mode of superdeep penetration the powder particles with the sizes less than 100 μm were used, then the size of a channel zone in a cross-section was much less than an initial size of a striker [10]. Such objects can be effectively studied using a transmission electron microscopy. It is shown in Fig. 11 and Table 1 that lead strikers not only penetrate into solid aluminum, but also intensively interact with it. At interaction, not only new metastable chemical compounds are synthesized but also new chemical elements are synthesized, too. For example, K and Ca not only are absent in an initial material, but because of technological features of a foundry process even at introduction in melt they do not remain in a definitive material. Therefore there are no bases to assume that penetration of particles at SDP is realized with the minimum expenses of energy.

5. Creation of Composite Materials on the Basis of SDP Technologies

Using unusual physical features of SDP method for the decision of a practical problem - creations of metal composite materials, is a current problem for a modern science. The basic features of this method, allowing to predict high competitiveness of technology, following the factors are: high speed of a process of change of a structure of a massive metal material, ecological safety of a processes of synthesis of reinforcing materials (synthesis in the closed system of a massive matrix), low power consumption of technology, modifying a massive metal body in a solid state with special micro and nano structural elements. The decision of technological problems we will consider on the examples of production of composite materials on the basis of aluminum and iron matrix.



a b

c d

e f

Figure 12. Thin structure in aluminum after SDP: a – a zone of high concentration of dislocations, ×60,000; b – a section electron diffraction pattern “a”; c – the bending extinction contours going from edges of channels, formed by the introduced particles, ×60,000; d – microdiffraction of a section of structure “c”; e – structure of the central channel microzone, ×40,000; f – a dim ring electron diffraction pattern in the form of halo dispersion from a section “e”

Using SDP for reception of new tool materials allows, during 10^{-3}–10^{-7} s, to introduce into a solid body volume (steel of type HSS) alloying elements on the depths in tens and hundreds millimeters [8]. At formation, into of steel preparation, of the fibers having nano- and a microstructure, a composite tool material is received. The material of channel zones (fibers) is alloyed by the introduced substance. There is anisotropy of mechanical properties, characteristic for a composite material. In the process of production, it is possible to use relatively cheap impulse accelerators on which the streams of powder particles with speeds ≈1,000 km/s are obtained.

The important mechanical property of tool steel is wear resistance. Usually, increase in a level of wear resistance at production of tool steels is reached at the expense of a substantial growth of concentration of alloying elements (from 5 to 40 mass%). At a dynamic alloying, the concentration of introduced alloying elements does not exceed 0.01–0.1 mass%. Therefore it is possible to explain increase in wear resistance of tool steel on tens and hundreds percent only by a specific structure of material.

Preparations from a tool composite material are easily processed. The increase in a level of mechanical properties occurs after definitive thermal processing. It was assumed that the structural defects arising at the pulse processing in metals and alloys are eliminated at the diffusion processes. Heating of metal preparations, subjected to explosive hardening, leads to fast decrease in a level of hardness of a defective structure of surface layers. SDP does not lead to increase in hardness of surface layers before thermal processing. If steel preparations with the raised level of hardness are exposed to a dynamic alloying, then SDP leads to appreciable reduction of hardness by depths to 10 mm. The investigations showed that the new structural elements resulting from SDP are very steady thermally. For elimination of these defects it is necessary to anneal composite material at a high temperature (≥1,000°C) for many hours [11]. Quenching of the tool from steels of HSS type lasts minutes and does not destroy a composite structure. In the process of tempering of the processed steel there is the possibility of additional hardening due to a low-temperature synthesis of strengthening threads (whiskers). The maximum level of mechanical properties of the tool steel, exposed to a dynamic alloying, is reached at the complex approach, including the development of the introduced alloying composition, SDP modes, and optimization of modes of thermal processing.

Composite materials have anisotropy of properties in various directions. Anisotropy of physicomechanical properties increases after thermal processing. In a direction of introduction of a stream of powder particles in HSS preparation, it was possible to raise wear resistance in 1.8 times, and in a cross-section direction on 14%. If the tool basically wears out along the length, its service durability increases repeatedly. Use of this feature in the strengthened tool steel, characteristic for composite materials, allows us to solve successfully the questions of creation of new constructions of the tool for processing of metals and cutting of rocks. Such approach has been realized at manufacturing of the rotating tool of mining machine for salt extraction. Unexpected results have been obtained at the use, as a criterion of the change of mechanical properties, such parameters as shock durability (viscosity). Reception, in steel preparations, the strengthened and activated zones should lead to wear resistance increase. Such elements of a structure should reduce a level of shock strength (impact resistance) and bending durability. The skeleton material could be a source for formation of cracks. The increase in specific density of these elements of a structure could lower the level of physico-mechanical properties. However, SDP processing has raised the shock durability (viscosity) of a composite material in comparison with initial steel to 20–40% and bending durability to 50%.

Interesting technological problem is a process of zone hardening of large-sized details and a change of a thickness of a zone of high hardness at heat treatment. At volumetric dynamic alloying of large-sized products, changes the structure of large zones (to 200 mm) of a large-sized tool. Thus, service durability of stamps has been increased by 20–60% [11].

The metal-cutting tool made of this material, at the processing of high-strength titanium alloys, has shown the resistance in 1.8–3 times higher than a similar tool made of initial tool steel. The rotating tool has been made of composite steel for mining machines for rock salt extraction (Fig. 13). The tool was used in salt mines in Italy and Belarus. Service durability of the tool has appeared in 1.5–5 times higher than for similar tool with cutting inserts from hard alloy on the basis of tungsten carbide [11].

Figure 13. Self-sharpened mining tool and metal blocks from the composite tool material

Aluminum and aluminum alloys are effectively used as the elements of electric machines and electric schemes [10]. In this area, the competition to aluminum is made only by copper and silver. It is important to receive additional possibility of management of its physical properties.

Penetration of powder microparticles in Al and Al-12% Si alloy forms a composite material with anisotropic structure (Fig. 14). Electrochemical properties of a composite material are anisotropic (Figs. 10–12). Unusual result of the reorganization of a structure at SDP is considerable intensification of an alloying of the channel zones. Especially, high concentration of some chemical elements was stated, which in an initial metal matrix were impurities or were absent (Table 1). It has allowed us to predict essential influence of these zones on the properties of producing composite aluminum materials.

Superdeep penetration causes strong distortions in a material structure on macro, micro and a nano levels (Figs. 10–12). The bending extinction contours going from the edges of channels, amorphisation of microzones, high concentration of dislocations in narrow and long elements of structure (channel elements) were observed earlier at SDP investigation in iron and its alloys [3, 9, 11, 12]. Specific defects are a characteristic structural sign at SDP. Now, such structural elements cannot be received in a metal solid body with other methods.

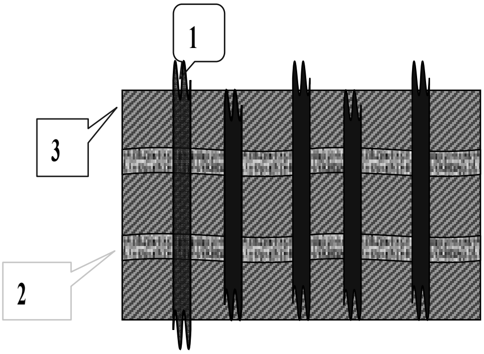


Figure 14. Scheme of structure of composite: 1 – "channels" along an axis of introduction of particles, 2 – "channels" across introduction of particles, 3 – matrix material

The reinforced skeleton of this material consists of fiber zones of the reconstructed structure. The scheme of such material is shown in Fig. 14. Occurrence of the zones, reinforcing a material in a cross-section direction, is apparently connected with a microstriker turn at braking in a barrier material. The share of cross-section channel elements in aluminum and its alloys is 20–30% of the quantity of longitudinal zones.

The composite material, on the basis of technical aluminum, received by processing with a dust clot in SDP mode, has been used for the change of electric resistance. Because it is known that composite materials possess anisotropy of properties, an electric resistance was determined in mutually perpendicular directions: in longitudinal section (along a direction of a powder stream) and in a cross-section section (Fig. 15). Samples were cut for investigations by means of electrospark processing. From each sample, in a cross-section and longitudinal direction, four to five plates were cut out. Electric resistance was defined as an average value from the made measurements. The electric resistance of the processed sample was compared with this obtained from the measurements on an initial material [10].

In direction 1. The value of electric resistance of technical aluminum $\rho_{Al1} = 5.27 \times 10^{-6}$ Ω·s·m. The composite has $\rho_{K1} = 4.41 \times 10^{-6}$ Ωs·m. Then, $\rho_{K1}/\rho_{Al1} = 0.835$. It is experimentally established, that electric resistance (ρ_1) after processing has decreased for 16.4%. In direction 2. The initial average $\rho_{Al\text{-}2} = 6.42 \times 10^{-6}$ Ω·s·m. The composite has $\rho_{K2} = 9.08 \times 10^{-6}$ Ω·s·m. Then, $\rho_{K2.}/\rho_{Al\text{-}2.} = 1.41$, i.e., the electric resistance has increased by 41.2% after processing.

The change of electric resistance in a cross-section occurs non-uniformly. Whether there is anisotropy of electric resistance in initial technical aluminum? For this purpose $\rho_{Al\text{-}2b.}/\rho_{Al\text{-}1b} = 1.21$ times. Thus, due to moulding, the difference of electric resistance in a longitudinal direction concerning transverse on 21% is provided. Electric resistance in the transverse direction is $\rho_{K1} = 4.41 \times 10^{-6}$ Ω·s·m. Then, $\rho_{K2} = 9.08 \times 10^{-6}$ Ω·s·m. Anisotropy in a composite material is $\rho_{K1}/\rho_{K2} = 2.05$ time. Electroconductivity in a transverse direction, in the processed sample, is getting more than 105% than in a longitudinal direction.

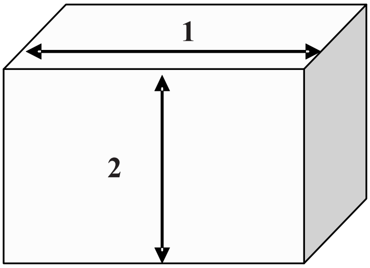


Figure 15. Scheme to take measurement for electric resistance of composite: 1 – across, 2 – along

The received results have allowed us to assume that electric properties of preparation essentially differ among themselves on the zones. Therefore the plates were tested by means of scanning Calvin's device. The results of scanning are presented in Fig. 16. The central zone, which is designated by red color, corresponds to the lowest work of electron exit. Scanning is executed on the scale of 2:1. The relation of an electrical conductivity of the zones, designated by different colors in Fig. 16, makes 4–5 times.

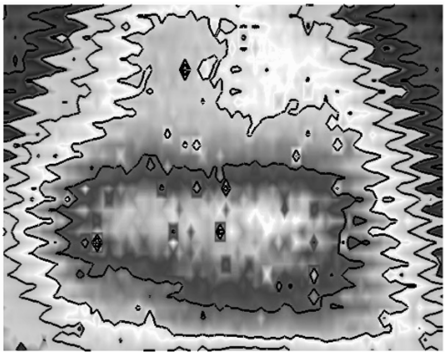


Figure 16. Change of electric resistance into across section of composite

6. Conclusions

The process of reorganization of a massive firm metal body in a composite material is considered. Occurrence in a metal barrier of a skeleton is shown on iron and aluminum examples. The skeleton represents the zones of influence which are formed of fibers of a synthesized material and surrounding volumes with strongly deformed structure of matrix metal or alloy. In the closed system, the complex of high-energy processes is realized. Interaction products, for example, carbon and silicon, remain in a solid body. Interaction products, including silicon and carbon interactions among themselves and with other materials, are not dangerous for environment. It allows us to formulate the following basic conclusions:

1. At superdeep penetration, in a steel barrier there is a system of solitons. The oscillating soliton has narrow and long field of high and ultrahigh pressure (≥8–20 GPa). The soliton is situated in a field of the lower pressure (≤1 GPa). Interaction of solitons creates the fields of a high pressure in a metal body and borders between the fields of high and low pressures.
2. At SDP, in solitons, high-energy effects occur. Carbon and silicon particles co-operate with a matrix material in the conditions of combination of high pressure, intensive deformation, electric and magnetic fields, heating, streams of high-speed ions. The level of thermal emission in local zones depends on a chemical compound of particles and a metal matrix. At this interaction, in the closed system, the exo - and endothermic effects are possible.
3. At the limited speed of heat removal in high-alloy steel, local sections of melting are produced. In a superdeep penetration mode, depending on a composition of an introduced substance, modification of a metal solid body with amorphous, nano and micro elements of structure is realized. New elements of a structure in an iron matrix are steady at heating.
4. Using a hypothesis about an intermediate dynamic phase transition has allowed to execute a quantitative estimation of defectiveness of a structure of a composite material and to predict changes of structure depending on a material of initial steel. Estimation of the energy density is executed at blow of a steel barrier which under other conditions of SDP is necessary for initiation of a process of channel elements formation $\rho_E = \frac{E_p^1}{\Delta V_f} = 0.64 \cdot 10^9$ J/m^3.
5. In comparison with a steel feature of the processes in aluminum, a level of spent energy is lower. Calculation of experimental results shows that a level of the pressure P_u, necessary for initiation of dynamic phase transition in aluminum, is ≈5 GPa. The high pressure phase in aluminum has the density less than at an initial phase at the low pressure $\rho_l/\rho_i = 0.702$ (70.2%). This feature explains the difficulties with definition of dynamic phase transition in aluminum with usual methods.
6. In an alloy of aluminum and 12% silicon (AK12), the high pressure phase has the density less than at an initial phase of the low pressure – $\rho_l/\rho_i = 0.534$ (53.2%). The relation of a density of initial phases in aluminum and aluminum alloy AK12 is $\rho_{Al}/\rho_{AK12} = 1.02$. The relation of density of phases of high pressure is $\rho^1{}_{Al}/\rho^1{}_{AK12} = 1.34$. The obtained results explain increase in a depth of penetration into high-alloy aluminum alloys in comparison with a depth of penetration into technical aluminum.
7. For aluminum alloy AK12, the influence of additives of various modifications of carbon on a share of the activated (synthesized) material after superdeep penetration is shown. In a number of modifications: soot, fullerene, graphite, with other things being equal a share of the activated material varies in 42:29:1.

8. Superdeep penetration into aluminum is accompanied not only by synthesis of chemical compounds in a zone of a skeleton of a composite material, but also by the occurrence in this zone of chemical elements which in initial materials were absent. From this point of view, occurrence of K and Ca after SDP is convincing. If K and Ca were introduced into an initial matrix, at a stage of usual foundry process, then these chemical elements would not remain in a solid state in aluminum preparations because of specificity of a foundry process.
9. Though SDP effects are accompanied by high and ultrahigh pressure, intensive deformation, local heating and microexplosions, intensive electromagnetic and ionic irradiations, dynamic phase transitions, synthesis of chemical compounds and chemical elements, there is no necessity to use powerful energy sources.
10. The presence of nano - and micro elements in a skeleton of a composite material is a reason of considerable changes of physical and chemical properties. Presence of a skeleton substructure in a composite material is the reason of considerable anisotropy of physical and chemical properties.
11. Manufacturing of a tool composite material on the basis of a high-alloy tool steel has allowed to rise of a level of properties of matrix steel by tens and hundreds percent and to produce the ecological and competitive metal-cutting and mining tool without hard alloy.
12. Manufacturing of a composite material on the basis of technical aluminum has provided anisotropy of electrochemical and electric properties up to 2 times and regulation of electron work function in the given zones of a product.

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SUBSTANTIATION OF INTERNATIONAL NANOMATERIALS SECURITY GROUP CREATION

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Abstract. Nanotechnology has achieved the status as one of the critical R&D area. Scientists use the unique properties of atomic and molecular assemblages built at the nanometer scale. The ability to manipulate the physical, chemical, and biological properties of molecules and particles affords to design agents with set up properties. But the technology allows creating not only useful agents. Possible accidental or deliberate creation of new nanoparticles (NPs) with dangerous properties is highly probable minor product of progress in the new area. The article briefly describes some pathways in development and implementation of NPs for medicinal and the similar purposes. Some of NPs can effective facilitate and mask transport of various agents in various environments. Possible creation of new dangerous NPs (e.g. conjugates based on combination of extensively use NPs and chemical, biological and radioactive agents) as well as creation of brand new NPs and nanodevices with unique properties needs creation of international multidiscipline community for security evaluation of nanomaterials and technologies. The community will forecast possible dangerous unexpectedness in the field of nanoscale materials and devices and suggests rational pathways for prevention of the threats.

Keywords: nanoparticles (NPs), toxicology, biosafety, toxicant, airborne distribution, criminal, international cooperation

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1. Introduction

Recently scientists have started to identify, create, purposefully modify and widely apply objects from 1 to 100 nm (i.e. from macro molecules to viruses). This new scientific line of investigation has been called nanotechnology (Fig. 1).

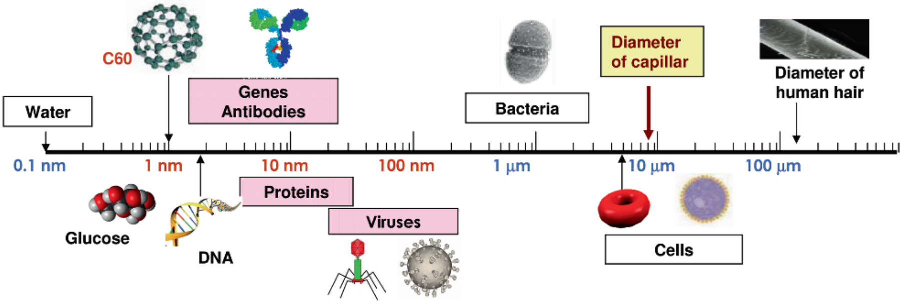

Figure 1. Comparative sizes of natural nanoparticles

In the course of this investigation new molecular nanoparticles (NP) have been synthesized, including fullerenes, nanotubes, nanocones, nanowire, dendrimers, derived clusters, complex molecular nanodevices, derived conjugates with well-known bioactive compounds, and so on. The above mentioned research has enabled to create substances and systems with given biological properties [1–4].

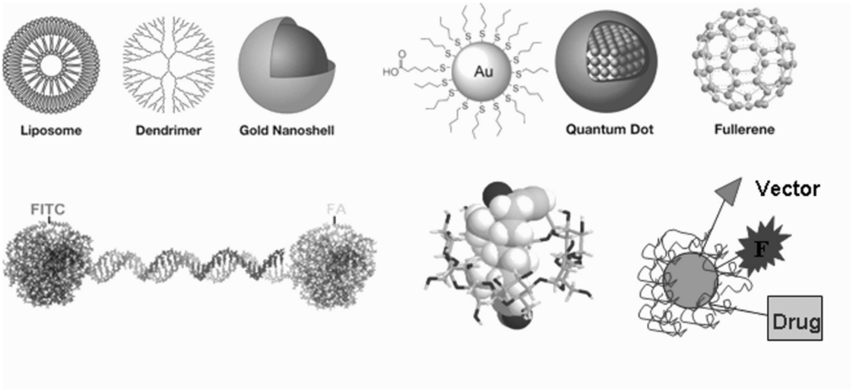

Figure 2. Some NPs and NP-based drug delivery systems

Bio applications of NP includes: drug delivery systems, sensors, imaging and diagnostic means and devices, catalysts, absorbents, new delivery systems for agrochemicals, nanofibers and nanomaterials, materials for implants, cosmetics and skin protection creams, hygienic means and so on (Fig. 2).

It's worth mentioning that unique transport properties of some NP results from more than a lot greater (3-exponent) increase of bioactive compounds' water solubility and ability to overcome biobarriers in the direction of biotargets (from skin to blood-brain barrier) [5–10].

This feature together with NP's ability to prolong different effects, to protect compounds from metabolism, and to form stable aerosols can result in the appearance of new NP which may drastically affect human organisms and environment.

2. Proposed Approach

Creation of NP with unknown or dangerous characteristics can become quite common. The main reason would be the development of combinatorial ways of new NP synthesis based on commercially available samples, on the one hand, and chemical, biological and radioactive agents, on the other hand.

The essential part of biosafety control includes instrumental analytical and toxicological investigations of newly synthesized nano-objects [11]. These investigations should be based on the following:

- Development of effective standard methods of NP identification and quantitative analysis
- Analysis of toxicology of molecular NP, their conjugates and more complicated derived systems
- Development of effective standard methods of NP toxic properties detailed investingations *in vitro* and *in vivo*
- Forecast of NP possible modifications, e.g. universal (multi-purpose) systems of drug delivery which would significantly increase water solubility, and creation of NP from 5 to 100 nm which would be able to form stable aerosols, etc. (Fig. 3).

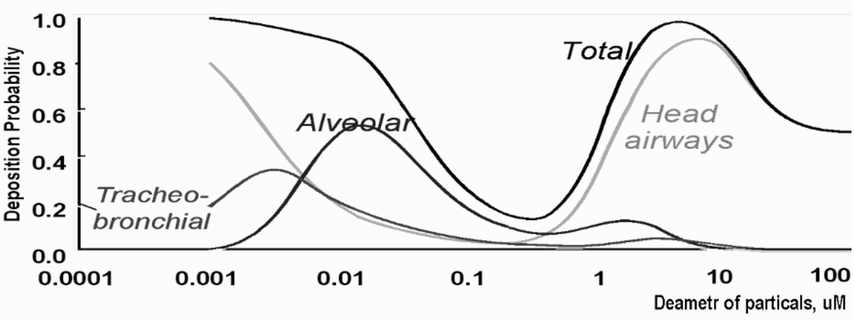

Figure 3. Adsorption depends on particles size (ICRP 1994 model: adult, nose breathing, at rest). Particles in the range of 5–100 nm are effectively adsorbed in alveoluses and trachea that provides their maximal bioavailability [12, 13]

Biosafety evaluation system should enable to clearly recognize dangerous NP at the early stages of scientific research.

It’s worth mentioning that by now toxic properties of only 10 NP have been studied more or less in detail (including metal oxide nanoparticles, several quantum dots, Au NP, fullerene C60). This information is certainly not sufficient enough to create nano-objects biosafety concept.

General approach for NP properties estimation is released at national organizations like Nanotechnology Characterization Laboratory NCI at Frederick [14] (Fig. 4).

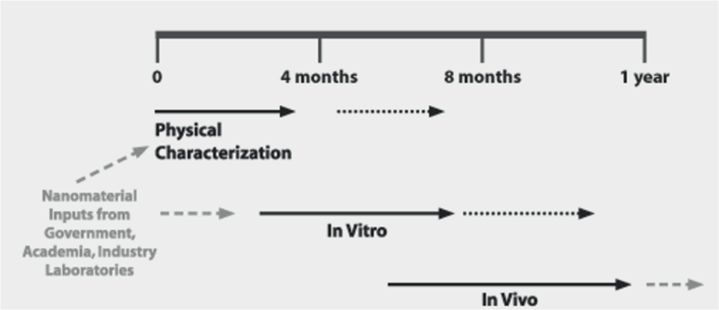

Figure 4. Cascade for Nanomaterial Characterization at NCL/NCI [15]

Standard set of nanoparticles should be validated by laboratories worldwide and made available for benchmarking tests of other newly created nanoparticles [11] (Fig. 5).

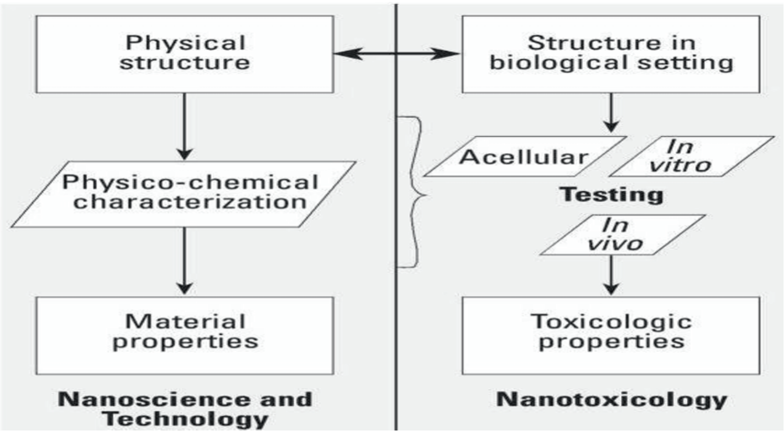

Figure 5. The parallel relationship between material design and material testing (nanotechnology and nanotoxicology) [11]

But problems of NP safety can’t be solved only as a safety estimation of initial NP and nanosystems for civil purposes. For example, some researches showed NPs opportunity to facilitate transport of toxic materials (heavy metals, pesticides, dioxins, etc.) in the environment. Classical example – toxicants transportation on diesel car combustion products (carbon particles contain hydrocarbons, sour inorganic impurity, metals salts, nitrates, nitrites, etc.). It is one of major risk factors of cancer diseases development at megacities inhabitants. Typical urban atmosphere contains approximately 10^7 particles/cm^3 of air less than 300 nm in diameter.

Also there is a hypothesis of effective airborne distribution of toxic thermo-stable materials on combustion products (incl. NPs) formed at fires (for example, plant or depot fire) and other anthropogenic disasters or warfare [17]. Estimation of the phenomena needs joint effort of multidiscipline researchers and engineers [18] (Fig. 6).

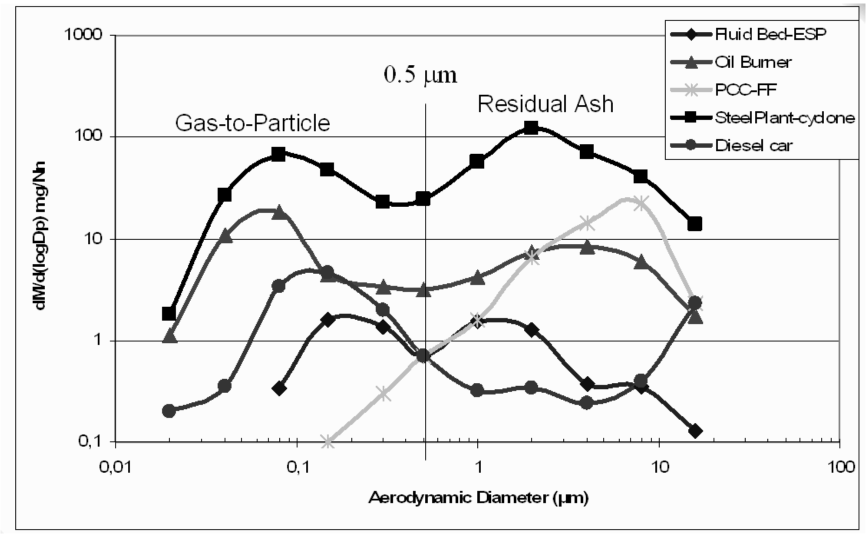

Figure 6. Mass distributions of fine particles emitted from various processes [16]

In order to implement the NPs and nanotechnology biosafety evaluation system in the world the current issue to be considered is the foundation of instrumental analytical and biological laboratories network which would carry out scientific research in accordance with the ISO TC 229 “Nanotechnology” standard [19] (Fig. 7).

TC 229 working areas include three pathways for development: Terminology and Nomenclature (JWG 1), Measurement and Characterization (JWG 2), Health, Safety and Environment (WG 3) [20].

Another issue of current importance is the creation of information system which would register and forecast NPs’ properties and derived objects [21].

Also international community has to take into consideration possibilities of criminal use of volatile or high water soluble nanomaterials. Even safe nanomaterials can be used as carriers of toxic materials. For example, volatile nanomaterials can be used for criminal actions in confined crowded spaces (incl. big buildings, underground systems and so on). Toxic effect may be increased due to NPs penetration via simple protection equipment; more effective adsorption in airways or in gastrointestinal tract, more effective skin penetration, masking effect against analytical and medical investigations, and so on [12, 13, 22–26].

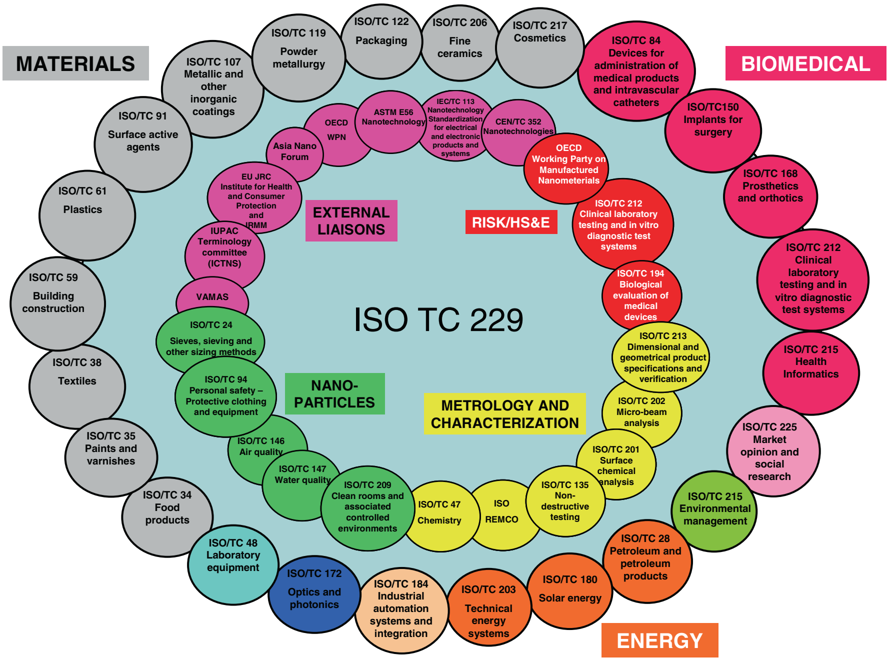

Figure 7. Map of current and potential liaisons for ISO/TC 229 [19]

Possible accidental or deliberate creation of new dangerous conjugates based on conjugation of extensively use NPs and chemical, biological and radioactive agents as well as creation of brand new NPs and nanodevices needs creation of international multidiscipline community for security evaluation of nanomaterials.

3. Summary

We propose to organize NanoMaterials Security Group (NMSG) as a collaborative mechanism of interaction of scientists, engineers and other professionals; national and international organizations for preparation of concrete forecasts, recommendations, rules, methods, techniques and so on in security and safety of new nanoscale materials and devices. The activity will prevent possible dangerous unexpectedness in the field of nanoscale materials, devices and related technologies.

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MATTER STRUCTURING IN NANO SCALES AND FUNDAMENTAL CONSTANTS OF PHYSICS

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Abstract. It is generally believed that all fundamental constants are the same everywhere. The experience with the variable velocity of light suggests however that such a belief may not be justified. In spite of that the possibility that the Planck constant may be different at different scales and at different places of our universe never was discussed. Since the constancy in space of the Planck constant cannot be checked in direct experiments the only way of proving its constancy or variability is to consider theories which allow to vary this fundamental constant. The comparison of the derived results with the corresponding results of standard quantum mechanics solves then the problem. In the talk we present an approach to quantum mechanics which allows to vary the Planck constant. Due to troubles with exact solutions our results have approximate character only. The possible consequences for practical nanotechnology, for theories of many-electron atoms and for large scale structures of the universe are discussed.

Keywords: foundation of physics, matter structure, fundamental constants

1. Introduction

Our world manifests different properties at each level and scale of investigation. This is reflected in the existence of many physical theories which are applied to different parts of our knowledge. It seems therefore that physics is divided into many particular domains which sometime has very little in common. But we believe in the unity of physics. It is therefore worth to ask the question whether physics indeed is a unified intellectual technology of investigating and understanding the surrounding world. Or is it a collection of different theories for each scale of our knowledge? To find the answer to this question we first should specify the starting point of our consideration. It should be as much universal as possible and therefore it cannot be restricted to any particular branch of physics. Since each branch of physics is characterized by specific sets of

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physical constants we must analyze the role of these constants in physical description of the world. Let us observe that the most universal physical theories like Newton's mechanics and Maxwell's electrodynamics in their basic equations do not contain constant at all. This is one of the reasons of their universality and generality. All customary mechanical and electrodynamical physical constants appear only at the stage of applying these theories to particular phenomena. Technically it is done by using different constitutive relations for different physical situations. On the contrary, quantum mechanics and Einstein theory of gravity contain physical constants in their basic equations. We must therefore decide whether the basic and primary equations of physics should contain physical constants or not? Our answer to that question is: *physics on its very primary and most fundamental level should not be based on any physical constants irrelevant how fundamental they are thought!* So, we must look for physics without physical constants! [1] Universality and generality of any theory may be achieved only after adequate choice of its basic concepts. But how do choose the basic concepts? To answer such question we must find some guiding principle. All branches of physics have one common feature: they all describe the symmetries observed in physical systems. The numerical coincidence of theoretical results with experimentally observed data is a secondary requirement and depends on the required and achieved degree of accuracy. *The most general and powerful guiding principle therefore must be related to the symmetry principles of physics.*

2. Spacetime Symmetries

As it is well-known we have spacetime symmetries and higher symmetries. Among spacetime symmetries we have the Galilean low energy symmetry and the Lorentz high energy symmetry. So, it seems that the situation with respect to the choice of spacetime symmetry should be sufficiently clear. It is customary to choose only one from these two possibilities. But neither for very small sizes like nanosystems nor for very large sizes like cosmic scales we do not know what the spacetime symmetry is. Therefore, instead of making a definite choice we may proceed in a different way which joins smoothly both Galilean and Lorentz symmetries. In fact, in Galilean physics it is known that the proper symmetry is described by the so-called one-parameter extension of the Galilean group [2]. It acts in the five dimensional extended spacetime with five coordinates x^μ where $\mu = 0, 1, 2, 3, 4$, with $x^0 = ct$, $x^1 = x$, $x^2 = y$, $x^3 = z$ and x^4 with different physical interpretations [3]. For example, we may look on x^4 either as on some control parameter or as on the action integral in Jacobi–Hamilton formalism. The change of the inertial reference system is described by the transformations

$$\vec{x} \to \vec{x}\,' = R\vec{x} + \vec{\upsilon}t + \vec{a} \,,$$

$$t \to t' = t + b \,, \tag{1}$$

$$x^4 \to x^4{}' = x^4 + \vec{\upsilon} \cdot R\vec{x} + \frac{1}{2}\vec{\upsilon}^2 t + \varphi ,$$

where R is the rotation orthogonal 3 × 3 matrix. These transformations leave invariant the extended spacetime interval

$$(\Delta s)^2 = 2\left(\Delta x^4\right)(\Delta t) - (\Delta \vec{x})^2 + c^2 (\Delta t)^2 , \tag{2}$$

where c is an arbitrary constant with the dimension of velocity. If we ask for the most general linear transformations which leave the expression (2) invariant we shall get the result

$$\vec{x} \to \vec{x}' = R\vec{x} + \gamma\vec{\upsilon}t + \frac{\lambda}{c^2}\vec{u}x^4 + \vec{a}$$

$$t \to t' = \gamma t + \frac{\vec{u} \cdot R\vec{x} - \varepsilon\vec{\upsilon}R\vec{x}}{c^2(1-\varepsilon\alpha)} + \frac{\lambda}{c^2}\varepsilon x^4 + b , \tag{3}$$

$$x^4 \to x^4{}' = c^2\alpha\gamma t + \frac{(1+\varepsilon)\vec{\upsilon} \cdot R\vec{x} - (1+\alpha)\vec{u} \cdot R\vec{x}}{1-\alpha\varepsilon} + \lambda x^4 + \varphi$$

where

$$\gamma = \left(1 + 2\alpha - \frac{\vec{\upsilon}^2}{c^2}\right)^{-\frac{1}{2}}$$

$$\lambda = \gamma\left[(1+\alpha)\sqrt{1+\frac{\vec{u}^2}{c^2}} - \left(\alpha + \frac{\vec{\upsilon} \cdot \vec{u}}{c^2}\right)\right]^{-1}$$

$$\varepsilon = \sqrt{1+\frac{\vec{u}^2}{c^2}}$$

and R is a 3 × 3 matrix which satisfy the generalized orthogonality relation

$$R^T V R = I ,$$

where the matrix elements of V are given by

$$V_{ls} = \delta_{ls} + \frac{(1+2\alpha)u_l u_s - (1+\alpha\varepsilon+\varepsilon)(u_l\upsilon_s + \upsilon_l u_s) + \varepsilon(2+\varepsilon)\upsilon_l u_s}{c^2(1-\alpha\varepsilon)} , \tag{4}$$

Here we have altogether 15 free parameters and from mathematics we can learn that our group of transformations is the de Sitter group *SO* (4, 1). The de Sitter group contains as subgroups the Galilean group – specified by the relations

$$\alpha = \frac{\vec{\upsilon}^2}{2c^2}, \quad \vec{u} = 0$$

the Lorentz group – specified by the relations

$$\alpha = 0, \quad \vec{u} = (1+\varepsilon)\vec{\upsilon}$$

and the four-dimensional Euclidean group – specified by

$$\alpha = 0, \quad \vec{\upsilon} = 0$$

So, having a theoretical description invariant under the de Sitter group we always may reduce it to either Galilean or Lorentz covariant descriptions. It is also possible to write down a general differential equations covariant under the de Sitter group [4] using the invariant differential operator

$$2\frac{\partial}{\partial t}\frac{\partial}{\partial x^4} - \Delta - c^2 \frac{\partial^2}{\partial^2 x^4}, \tag{5}$$

or a square root of it in the case of Dirac like theories [5]. Concluding this part we may say that there exists a common symmetry group unifying all possible spacetime symmetries. In each particular case we may pass to some subgroup of this unified group either by intentional choice of the subgroup or by some procedure of spontaneous breaking of the original symmetry on the level of the choice of non-covariant solutions of the covariant starting equations. In covariant description of phenomena each set of physical quantities carries some representation of the spacetime symmetry group. Having unified these symmetries into one de Sitter group we may start from the Galilean symmetry whose representations by a well-known mathematical procedure can induce the representation of the whole de Sitter group and after finding the induced representations of the whole de Sitter group any such representation may be restricted to another subgroups as, for example, the Lorentz group. In such a way we have the possibility of transferring the non-relativistic information into the relativistic world and vice versa.

3. Higher Symmetries

Each higher symmetry needs some physical carrier. Usually in fundamental physics the carriers of higher symmetries are physical fields defined on spacetime because the symmetries are local. More exactly, the fields are carriers of a given representation of the symmetry group. As long as the higher symmetries will not be unified into one universal group we cannot speak on one symmetry group as we did for spacetime symmetries. This is exactly the reason why we must consider so many different symmetry groups. But the principle is unique: we always have to choose a set of some basic fields which completely reflects the symmetries of the system. These fields in each particular case may have additional physical interpretation. But this is a secondary feature. Let us denote the basic fields by $\Psi_\alpha(x)$, where the index α stands for all indices needed in the theory. The basic fields propagate in spacetime and in order to describe their propagation we introduce a second collection of fields denoted by $\Phi_{\mu,\beta}(x)$. Here the index μ is a spacetime index while all other indices are denoted by. Having the Ψ and Φ fields we may relate them by the first set of basic equations in the form

$$K^{\alpha,\upsilon}_{\beta,\mu}\nabla_\nu\Psi_\alpha(x)=\Phi_{\mu,\beta}(x), \tag{6}$$

where $K^{\alpha,\nu}_{\beta,\mu}$ are some numerical factors and the summation over repeated indices is understood. The numerical factors vary for each particular case. However the general structure of all kinematical equation of physics is just contained in equation (6). They have exactly the same structure as the first Newton equation which relates the trajectory function with the velocity. To formulate the dynamical laws of physics we introduce a third collection of fields denoted by $\Omega_\gamma(x)$ which describe the influence of the external environment on the studied systems of matter or fields (here γ denotes a set of indices necessary to describe such influence). The fields $\Omega_\gamma(x)$ define the balance equations expressed in terms of a collection of fields $\Pi^\mu{}_\gamma(x)$. These balance equations have the familiar form

$$\nabla_\mu\Pi^\mu_\gamma(x)=\Omega_\gamma(x), \tag{7}$$

Equations (6) and (7) are the basic primary equations of physics. They have to be completed by suitable set of constitutive relations. This is exactly the place where physical constants enter physics. We shall now show that equations (6) and (7) indeed contain all known equations of physics.

For all evolution equations of matter we have

$$K^{\alpha,\nu}_{\beta,\mu}=\delta^\alpha_\beta\delta^\nu_\mu, \tag{8}$$

and in flat spacetime the derivatives $\nabla\mu$ reduce to the ordinary partial derivatives $\partial\mu$. In the Newton equations of a single material points all fields depend only on the time variable. Choosing the basic fields ψ as the trajectory functions $x(t)$, $y(t)$, $z(t)$ and the Φ fields as the components of the velocity $\upsilon_x(t)$, $\upsilon_y(t)$, $\upsilon_z(t)$ we easily can check that our equation (6) exactly coincides with the Newton equations

$$\frac{d\vec{x}(t)}{dt}=\vec{\upsilon}(t), \tag{9}$$

Similarly, choosing the fields Π as the three components of momentum and the Ω fields as the components of the acting force we shall get the Newton dynamical equation

$$\frac{d\vec{p}(t)}{dt} = \vec{F}(t), \tag{10}$$

The theory will be complete provided the momentum (the Π fields) will be connected to the velocity (the Φ fields) by the standard relation

$$\vec{p}(t) = M\vec{\upsilon}(t), \tag{11}$$

and the acting force (the Ω fields) will be given by some force law (expressed in terms of the Ψ or/and Φ fields). For Schroedinger equation of a scalar field $\Psi(x)$ we should assume the following constitutive relations

$$\Pi^0(x) = i\hbar\Psi(x), \tag{12}$$

$$\Pi^j(x) = -\frac{\hbar^2}{2M}\Phi_j(x), \tag{13}$$

$$\Omega(x) = -V(x)\Psi(x), \tag{14}$$

where $V(x)$ is the usual non-relativistic potential. It is easy to check that such constitutive relations indeed lead to the Schroedinger equation for the field $\Psi(x)$. Similarly, for the Klein–Gordon equation for a scalar field with self-interaction we must assume the following constitutive relations:

$$\Pi^\mu(x) = g^{\mu\nu}\Phi_\nu(x), \tag{15}$$

where $g^{\mu\nu}$ is the Minkowski metric tensor and

$$\Omega(x) = -\frac{M^2c^2}{\hbar^2}\Psi(x) + F(\Psi(x)), \tag{16}$$

where F describes the self-interaction of the field $\Psi(x)$. The Dirac field equations are also obtained from our basic equations through the suitable constitutive relations [4]. The Maxwell field equations for electrodynamics and Einstein equations for gravity may be obtained as well.

In the first case we have to choose the following kinematical factors

$$K^{\lambda\varepsilon\nu}_{\omega\eta\mu} = \delta^{\lambda}_{\omega}\delta^{\varepsilon}_{\eta}\delta^{\nu}_{\mu} + \delta^{\lambda}_{\eta}\delta^{\varepsilon}_{\mu}\delta^{\nu}_{\omega} + \delta^{\lambda}_{\mu}\delta^{\varepsilon}_{\omega}\delta^{\nu}_{\eta}\,, \tag{17}$$

The basic fields of the type Ψ are here the components of the electromagnetic skew symmetric tensor $F_{\mu\nu}$, the fields of the type Π are the components of the skew symmetric tensor $H^{\mu\nu}$, the external influence on the system is the current fourvector j^{ν} (the fields of the type Ω) and the fields of the type Φ vanish. In the second case we have to choose

$$K^{\beta\eta\lambda\varepsilon\nu}_{\alpha\omega\kappa\xi\mu} = \delta^{\beta}_{\alpha}\delta^{\eta}_{\omega}\left(\delta^{\lambda}_{\kappa}\delta^{\varepsilon}_{\xi}\delta^{\nu}_{\mu} + \delta^{\lambda}_{\xi}\delta^{\varepsilon}_{\mu}\delta^{\nu}_{\kappa} + \delta^{\lambda}_{\mu}\delta^{\varepsilon}_{\kappa}\delta^{\nu}_{\xi}\right), \tag{18}$$

The basics fields (of the type Ψ) here are the components of the curvature tensor and the fields of the type Φ vanish. The famous Einstein equations cannot however be obtained from our basic primary equations. The only equation of general relativity which has the form of equation (7) is the conservation law for energy and momentum

$$\nabla_{\nu}T^{\nu}_{\mu}\left(x\right) = 0\,, \tag{19}$$

The Einstein equations are non-differential relations between the Ricci tensor field $R_{\mu\nu}$ (x) (constructed from the basic curvature tensor) and the dynamical energy-momentum tensor field $T_{\mu}^{\ \nu}$ (x) and this relation contains the gravitational constants. According to our approach the basic equations should not contain physical constants. These are the non-differential constitutive relations which introduce all the necessary constants into consideration. Therefore, Einstein equations should be treated as constitutive relations and not as basic equations which describe Nature!

4. Advantages of the New Approach

The approach presented here has at least two big advantages over the standard approach. First, our approach shows that all quantum mechanical wave equations have a common root with classical mechanics. The connection of classical and quantum physics is on the level of basic evolution equations [6] and is independent from the canonical formalism widely used in the passage from classical to quantum physics. All these theories differs only by different choices of basic fields and constitutive relations and not by different laws of physics. Second, the basic equations (6) and (7) of any physical theory do not contain physical constants. All constants are introduced by constitutive relations. However, only for very simple physical systems these relations operate solely with physical constants while for more complicated and non-uniform systems the constants are always replaced by some functions of spacetime variables. In the case of classical mechanics in such a way we get the possibility to describe bodies with changing masses. In electrodynamics such a replacement allows to take into account the influence of impurities of the medium on the electromagnetic processes and we may consider media whose physical properties change (polarize and magnetize) under the influence of external electromagnetic interactions. Similarly, in the case of gravity we may consider gravitational systems whose properties change under the influence of external gravitational fields. The standard Einstein theory in analogy to electrodynamics must then be treated as the "vacuum" version of the theory of gravity. It is clear that all that considerably extends the range of applicability of known theories. We may generalize this by saying that physical phenomena at each scale are governed by the same physical laws but by different (sometimes very drastically different) constitutive relations. The constitutive relations reflects the structuring of matter at each scale. In particular, in the presented approach we may consider the consequences of the possible different values of the Planck constant $\hbar$ at each scale level. What we really know is that the Planck constant has its experimental value at the level of atomic phenomena. Has it the same value in nuclear physics, for subnano scales or at the cosmological scale? These are examples of questions which up to now were impossible to ask due to the lack of a suitable formalism. Now we can attack such problems. The problem is relatively simple when the Planck constant changes with jumps. In such a case it is sufficient to consider the quantum mechanical wave equations in each domain of constancy of $\hbar$ separately and at the end to match the solutions with suitable boundary conditions. The results then crucially depend on the boundary conditions. In quantum mechanics it is customary to consider only one type of boundary conditions for which the wave functions and/or their first derivatives are continuous. Such boundary conditions are not enough physically justified. The existing arguments are purely mathematical. Meanwhile already in classical physics, particularly in electrodynamics, we have to do with discontinuous wave quantities like the electrostatic potential. The continuity or discontinuity depends on the physical nature of the boundary. In classical physics we may have passive or active boundaries (in electrostatics it means charged slabs or consisting from dipoles) while in quantum physics all boundaries or barriers are always considered to be passive. The introduction of active quantum mechanical barriers means that the barriers may produce or annihilate quantum mechanical probability. In this way we may speak on amplifiers of probability [7] which were first introduced by Stanislaw Lem in his science fiction writings. It is strange that up to now nobody was trying to incorporate this notion into the rigorous science. The amplification or annihilation of probabilities at boundaries may also be connected with sudden change of the values of the Planck constant in very narrow domains of space. The discontinuity of wave functions can be discussed only for problems defined in restricted domains of space. For, for example, the hydrogen atom it is vague because the only boundary conditions are put at infinity. For problems with barriers, so widely considered in solid state physics and in nanotechnological problems, the discontinuous boundary conditions lead to shifts in the wave number spectrum and correspondingly to the rearrangements of the energy spectrum. The shift of the ground state energy means the appearance of some new kind of vacuum energy because the only way to explain the emerging of the ground state energy is to treat it as some kind of the quantum mechanical vacuum energy. The case with smoothly changing Planck constant is much more complicated. So, we restrict ourselves only to the simple example.

5. Simple Example

From the constitutive relation (12)–(14) with variable Planck constant instead of the Schroedinger equation we get the equation

$$-\frac{1}{2M}\partial^k\left[\hbar^2(\vec{x},t)\partial_k\Psi(\vec{x},t)\right]+V(\vec{x},t)\Psi(\vec{x},t)=i\frac{\partial}{\partial t}\left[\hbar(\vec{x},t)(\vec{x},t),\right], \tag{20}$$

which may be rearranged into the form

$$-\frac{\hbar^2}{2M}\left[\partial_k-(\partial_k\ln\hbar)\right]\left[\partial_k-\partial_k(\ln\hbar)\right]\Psi+\mathbf{V}\Psi=i\hbar(\partial_t-\partial_t\ln\hbar)\Psi\,, \tag{21}$$

where

$$\mathbf{V}=V+\frac{\hbar^2}{2M}\left[\Delta\ln\hbar+\left(\vec{\nabla}\ln\hbar\right)^2\right], \tag{22}$$

This form shows that the changing Planck constant introduces both new interaction (the expression in the square bracket) and a special gauge field with vanishing classical electromagnetic field. We have therefore to do with some kind of the Aharonov–Bohm effect induced by the variation of Planck constant. Unfortunately, at the moment we do not know what the variation of the Planck constant is. Therefore, we must go to some particular models which however will spoil the universality of our consideration. Another way of proceeding is to consider the Planck constant as a dynamical field with its own field equation. The Schroedinger theory is the only case for which we know how to introduce variable Planck constant. For relativistic equations arising from the constitutive relations (15) and (16) the primary location of the Planck constant is not clear. But due to our unification of all spacetime symmetries into one de Sitter symmetry we may start from the Schroedinger equation and end up with Lorentz covariant theory.

6. Conclusions

We have shown that basic equations of all fundamental physical theories can be derived from one universal and simple set of primary equations which do not contain any physical constants. All necessary constants appear through constitutive relations which define the concrete physical situation to which the primary equations have to be applied. Our scheme allows the unification of all particular theories into one more elegant and simple supertheory. In the framework of such theory we may vary the fundamental physical constants replacing them by functions of spacetime coordinates. This leads to a significant extension of possible physical systems which may be subjected to theoretical description.

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SIZE EVOLUTION OF NANOCLUSTERS: COMPARISON BETWEEN THE PHASE DIAGRAM AND PROPERTIES OF Mo–S AND CARBON NANOPARTICLES

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Abstract. In this article a comparison between inorganic nanoparticles with hollow closed structure and the carbon fullerenes and nanotubes is undertaken. First, the structural evolution of inorganic fullerene-like (IF) nanoparticles of MoS_2 as a function of their size is examined in some detail and compared to that of carbon and BN fullerenes. It is shown that hollow closed structures of MoS_2 are stable above 3 nm (app 10^3 atoms). In the range of 3–8 nm (10^3–10^5) nanooctahedra with metallic character are the most stable form of MoS_2 Semiconducting nanotubes and quasispherical IF nanoparticles become the stable-most form beyond that size and the bulk (platelets) are stable above about 0.2 μm. The stability of inorganic nanotubes is also discussed. The scaling-up of the synthesis of IF-WS_2 and the very recent successful synthesis of large, amounts of pure WS_2 nanotubes are briefly described. The stability of IF and INT of MoS_2 (WS_2) under pressure and that of carbon is also discussed. Applications of the IF-WS_2 as superior solid lubricants, which lead to their recent commercialization, is demonstrated.

Keywords: fullerenes, nanotubes, inorganic fullerene-like, inorganic nanotubes

1. Introduction

WS_2 nanoparticles with inorganic fullerene-like structures (IF) and inorganic nanotubes (INT) were reported first in 1992 [1]. They were followed by IF-MoS_2 [2] and MoS_2 nanotubes [3]. These works opened a new chapter in the study of clusters of layered compounds and a new field of inorganic materials. Subsequently, the growth mechanism of the IF-MS_2 (M = W, Mo) from the respective oxide nanoparticles was elucidated in a series of studies [4]. This understanding permitted the scaling-up of their synthesis and paved the way for the detailed study of some of their properties. It was found for example, that such nanoparticles can serve as superior solid lubricants [5]

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and can also improve the mechanical properties of various nanocomposites [6, 7]. Further scaling-up of the process to industrial level was undertaken by "NanoMaterials" (www.apnano.com) which recently commercialized the first of a large series of lubrication fluids under the brand name NanoLub^{TM}.

The present paper presents the size-evolution of nanoclusters of Mo(W)-S. Some analogies and the differences with carbon clusters and nanotubes are also shown. The final section is devoted to a short discussion of the applications of the IF nanoparticles.

2. Discussion of the Results

2.1. NANOCLUSTERS

The chemistry of hollow closed nanostructures has started developing quite recently, although hydro-borane polyhedra are known for many years. Naturally occurring framework structures with built-in hollow spaces, like zeolites, are also investigated for many years and are used as, e.g. specific catalysts in the oil refining industry for many years. Intuitively the chemical bond is unstable beyond 3 Å, and other long range interactions, like the van der Waals (vdW) forces operate at distances of up to 7 Å. Not surprisingly therefore, the search for stable nanoparticles with hollow spaces beyond 1 nm started only after the discovery of the C_{60} and carbon nanotubes.

One of the most important questions which arise from these studies is the size evolution of Mo-S clusters and those of layered compounds in general. It is intuitively clear that the hollow nanostructures are unstable in species having either small or large number of atoms (N). Thermodynamically in the macroscopic limit van der Waals stacking of the molecular S-Mo-S layers forming the known platelets crystals is the stable form. Such planar structures are completely unstable in the small N limit due to the occurrence of a large number of dangling bonds in the prismatic (*hk*0) edges of the crystal. Moreover the S-Mo-S bonding is in general unstable for nanoclusters of say $N < 100$ atoms. This is true also for small carbon nanoclusters, which are not stable in the graphitic (sp^2) lattice. Instead, ubiquitous stable moieties with C–H bonds become the cornerstone of organic chemistry for small N.

Taking the analogy of C_{60} and the fullerene series, it is clear that in the case of IF nanoparticles and INT the size (diameter-D) scales with N in a different mode (N^2) compared with bulk compounds (N^3), like CdSe. This property entails lower specific gravity for the IF clusters, an important fact for several applications, including armored nanocomposites. C_{60} is the smallest stable closed cage form of carbon (D-0.7 nm). It was felt early on that the thick S-M-S sandwich layer suffers from appreciably larger strain effects and cannot fold into closed structures below a given radius of curvature. Therefore, it became evident that the smallest MoS_2 clusters must be appreciably larger than that of C_{60}. Furthermore, careful examination of the MoS_2 structure indicated that pentagonal rings, which exist in carbon fullerenes, are energetically an unfavorable structural moiety for such clusters. Contrarily, rhombi (rectangles), which make a genuine part of the MoS_2 lattice [2], could become a stable moiety in the vertices of such nanoclusters. Indeed, an intensive search for multiwall MoS_2 nanooctahedra with six rhombi in their corners concluded that such clusters exist but they are only rarely observed in the high temperature synthesis of IF-MoS_2 [8]. Remarkably though, ablating a MoS_2 target with a pulsed Nd-YAG laser produced numerous MoS_2 nanooctahedra [9]. In retrospect, pulsed laser ablation provides the ideal conditions for the growth of such nanooctahedra. The short laser pulse forms hot and dense plasma of atoms. The rapid quenching of this ablated plasma does not permit sufficient time for diffusion of the atoms and arrangement into large clusters. Therefore, the small groups of atoms arrange in a local minimum energy state of a symmetric nanocluster, preferably as nanooctahedra. Further attempts in using solution based arc-discharge to synthesize such nanoclusters met with partial success, only [10]. Unfortunately, the synthesis of a few milligrams of the pure MoS_2 nanooctahedra phase, which would allow its physical characterization, could not be realized thus far. One of the most remarkable observations in this context is the size evolution of BN nanoclusters. BN is isoelectronic with C_2 and indeed BN crystallizes in two phases which are analogous to carbon: hexagonal (graphitic) BN and tetragonal BN which is analogous to diamond. Notwithstanding this analogy, $(BN)_{30}$ nanoclusters are unstable because they must contain 12 pentagonal rings. Each such ring would have at least one B–B or N–N bond, making the pentagons energetically unfavorable. Instead, the $(BN)_2$ square moieties are energetically preferable because they contain B–N bonds. Thus, $(BN)_{12}$ nanooctahedra which are made of six disjoint squares and eight hexagons, are the smallest stable BN clusters [11].

Some progress in the research of these nanooctahedra has nevertheless been recently realized by combining *ab-initio* density functional tight binding (DFTB) calculations with careful experimental observations of laser ablated MoS_2 samples[12]. However, much more experimental and theoretical work is needed to elucidate the entire "phase diagram" and the properties of such nanoclusters. Figure 1 shows a transmission electron microscope (TEM) image of three such MoS_2 nanooctahedra varying in size from 3–5 nm.

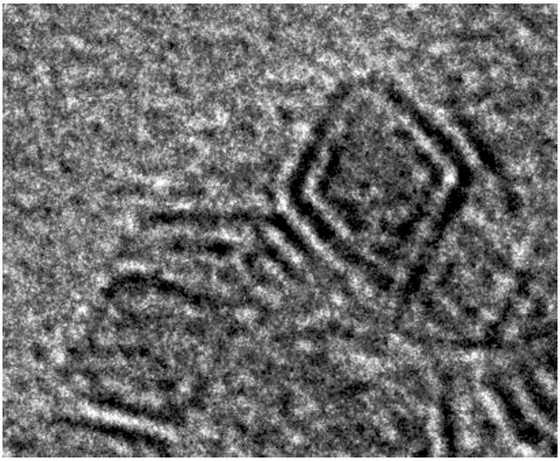
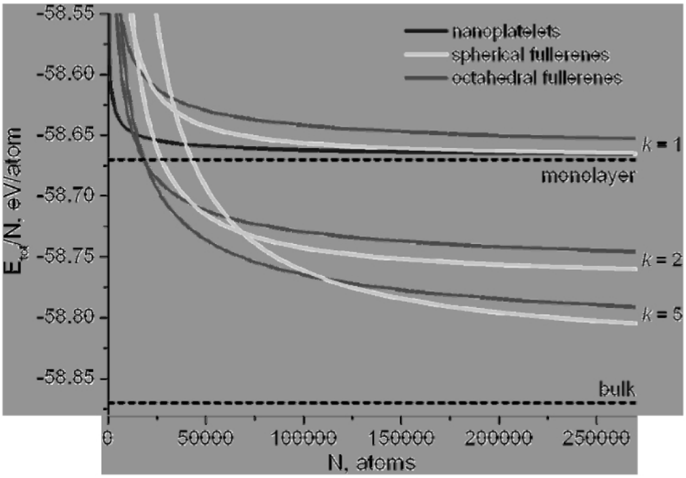


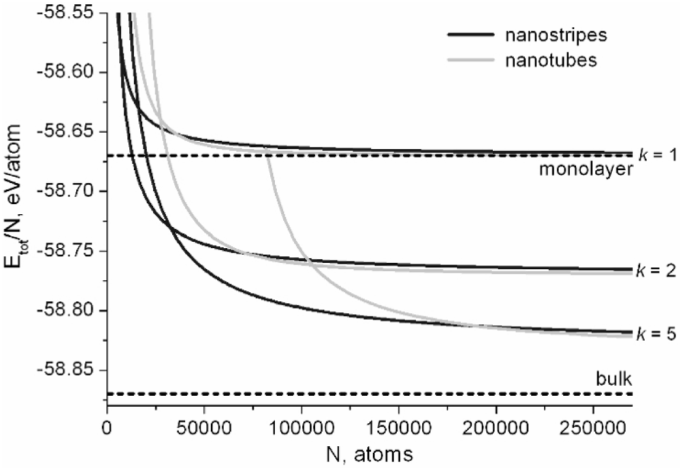
Figure 1. Transmission electron microscopy (TEM) image of three MoS_2 nanooctahedra. The distance between each two fringes is 0.62 nm

Characteristically they have a nested structure and are made of 2–5 MoS_2 layers. DFTB calculations combined with molecular dynamics (DFTB-MD) were used in the framework of a semi-empirical model for different kinds of MoS_2 nanoparticles.

Figure 2a shows the energy/atom calculations as a function of the nanoparticle size (number of atoms) [12]. Most remarkably, multiwall nanooctahedra with 2–5 layers (red curves) become the lowest energy (stable) state at sizes between about 3–10 nm (app. N = 10^3–10^5). Careful analysis of the experimentally observed MoS_2 nanooctahedra produced by laser ablation showed indeed quite good agreement with these results.



a



b

Figure 2. Calculations of the energy/atom for different kinds of MoS_2 nanoclusters: a. 0D and b. 1D nanoparticles (the nanotubes and nanostripes are taken with constant length of 500 atomic units)

Among the abundant stable nanooctahedra the largest one had 25,000 atoms. Larger nanooctahedra were also observed, however rather rarely [13] (see also Fig. 3). Above about 8 nm nanotubes and quasi-spherical fullerene-like nanoparticles become the stable form of MoS_2 (app. $N = 10^5–10^7$).

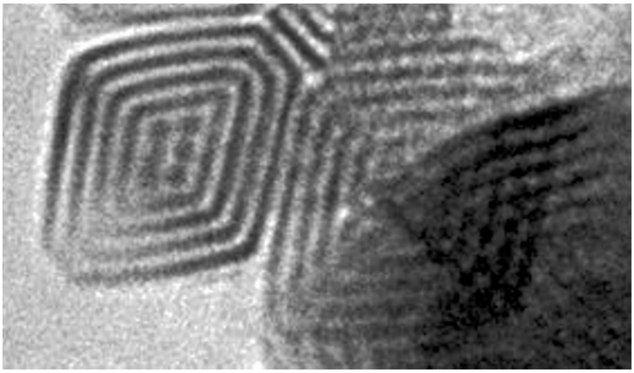


Figure 3. TEM image of two MoS_2 nanooctahedra with five layers. The distance between each two layers is 0.62 nm

Folding of the MoS_2 layers into closed structures becomes practically impossible below 3 nm. For $N < 30$ (Mo + S) atoms clusters of the kind Mo_4S_6 and Mo_6S_8 with Mo-Mo bonds are found to be the stable form [13]. For larger species with more than 10 MS_2 units, stable triangular clusters of the form $Mo_{15}S_{42}$, become stable [14–16] (see Fig. 4). These planar clusters are characterized by having a MoS_2 core (with Mo–S bonds) flanked by S_2 pairs with S–S bonds in the rim. The S–S rim pairs were shown to endow the nanoclusters a metallic character. All these small clusters are characterized also by strong adsorption to gold surfaces [17], which is a hallmark for protruding sulfur atoms with non-saturated chemical bonds. Contrarily, the fully bonded sulfur atoms on the basal (0001) surface of bulk 2H-MoS_2, or IF- and INT of MoS_2 do not exhibit particular affinity to gold surfaces.

Figure 4. $Mo_{15}S_{42}$ triangular cluster (adopted from Ref. [13]). Grey and black balls represent sulfur and molybdenum atoms, respectively

MoS_2 is a well known catalyst for hydrodesulfurization of gasoline. It is well accepted that the reactive dangling bonds at the prismatic (*hk*0) edges of the MoS_2 lattice are the active sites for this catalytic reactivity. Recently, the electrocatalytic splitting of water by the triangular Mo_nS_{2n+m} clusters which possess a metallic character was demonstrated [18]. Given their metallic character it is expected that the MoS_2 nanooctahedra will exhibit also a strong catalytic character for various reactions. Moreover, imperfect hollow and closed MoS_2 nanoparticles exhibited strong hydrodesulfurization catalytic behavior [19]. These observations suggest that in order for the basal surface of the IF-MoS_2 nanocrystal to become catalytically reactive, it must contain defects which expose imperfectly bonded metal atoms. Some evidence for the catalytic effects of MoS_2 nanotubes does exist [20]. It is not known at this time where is the border line between the MoS_2 nanoparticles with strong catalytic reactivity and those which are non-reactive and to what extent it is associated with the metallicity of the nanocluster.

Another difference between carbon and IF-MoS_2 (IF-WS_2) is the pressure dependence. The phase diagram of carbon shows that the sp^2 bond (graphite) is unstable beyond 1.7 GPa in ambient conditions and transforms into sp^3 bonding (diamond). No high temperature/pressure phase exists in the case of MoS_2 (WS_2). These observations explain the high compression strength of the IF nanoparticles under isotropic pressure [21]. The remarkable shock wave resistance of the IF nanoparticles is another manifestation to this fact [22]. These findings and the demonstrated compatibility of the nanoparticles with regards to polymer processing [6, 7] offer numerous applications for the IF nanoparticles.

2.2. NANOTUBES

A semi-empirical model, which is based on *ab initio* (DFTB) calculations has been employed also in order to evaluate the stability of MoS_2 nanotubes and compare them to stripes of the same material and the same number of atoms. Comparison with the experimentally synthesized WS_2 nanotubes was done as well [23]. Figure 5 shows a TEM image of a typical multiwall WS_2 nanotube. Summary of the calculated data is shown also in Fig. 2b. While the nanotubes are less stable than the narrow stripes at small sizes, they become more stable when the diameter of the nanotube exceeds about 10 nm. The elastic energy of bending of the MoS_2 nanotubes was found to be more than an order of magnitude larger than for carbon nanotubes. This difference explains the one order of magnitude difference in the diameter of carbon and inorganic nanotubes. Whereas the diameter of singlewall carbon nanotubes is about 1–1.5 nm, MoS_2 (WS_2) multiwall nanotubes with inner diameter of 10–15 nm and outer diameter of between 20 and 30 nm are obtained *en-mass.* The energy per atom of the MoS_2 nanotubes is some 0.02 eV/atom lower than that of a spherical and multiwall (IF) nanoparticles of the same size (see Fig. 2a and b). The greater stability of the nanotubes as compared to the fullerene-like nanoparticles would give hope that their large scale synthesis by the fluidized bed reactor (FBR) could be accomplished. So far however, multiwall WS_2 nanotubes were obtained as a small fraction (ca. 5%) of the total IF–WS_2 product [24].

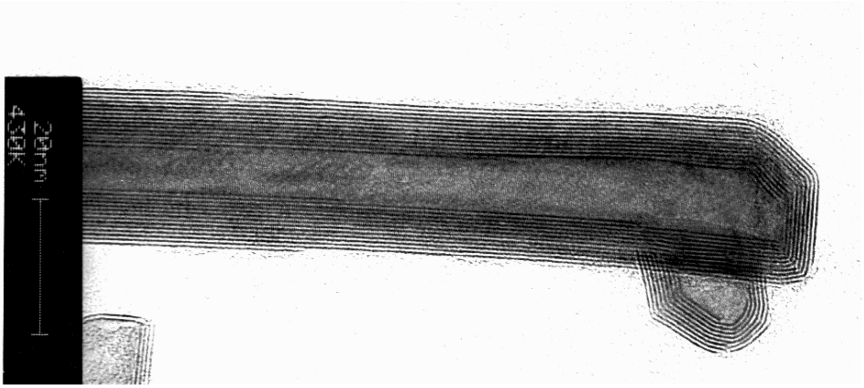


Figure 5. TEM image of a six-wall WS_2 nanotube. The distance between each two fringes is 0.62 nm

The reason for this phenomenon might be related to the detailed kinetics of the reaction and in particular the nucleation step. Indeed for small IF and INT the energy per atom is larger for the latter (see Fig. 2a and b), suggesting that the nanoparticle topology is determined in the early stages of the growth. While this idea is generally true, a few exceptions are also known. For example $H_2Ti_3O_7$ nanoscrolls are obtained by exfoliation of monomolecular layers of large such crystals [25]. It is strongly believed that future optimization of the reaction parameters will lead to much higher yields for the INT paving the way for their large scale synthesis and their eventual commercialization. Indeed, recently significant progress has been accomplished in this regards and 100 g/batch of almost pure WS_2 nanotubes are routinely obtained (see www.apnano.com). It is noteworthy that, while the synthesis of high-quality carbon nanotubes necessitates a catalyst, this is not the case for many of the INT reported so far. Another distinguishing point between carbon and INT is the fact that the synthesis of singlewall INT has been rarely reported [26]. Given the energy/atom relationship shown in Fig. 2 it is rather obvious to see why multiwall rather than singlewall nanotubes are preferred in the case of MoS_2. It is likely that in the case of carbon nanotubes synthesis, the energetic would also be favorable for multiwall nanotubes. However, the catalytic reaction promotes the singlewall nanotube growth in this case.

3. Applications of IF-MS_2

The efforts to find genuine applications for the IF nanoparticles and INT have been discussed in a number of review articles. In particular, the progress in using the IF-WS_2 as superior solid lubricants, have been recently discussed [27]. Figure 6 shows the friction coefficient of a sample coated with a thin film of electroless cobalt impregnated with IF-WS_2 nanoparticles, in comparison to the stainless substrate and the Co coating [28]. The low friction coefficient of the Co + IF coated surface offers numerous applications for self-lubricating coatings and for the IF nanoparticles as additives to lubricating fluids. The increased strength, thermal stability and glass transition of polymers to whish tiny amounts of the IF-WS_2 nanoparticles were added [6, 7] offers numerous other applications for these nanoparticles. Research into the use of various IF nanoparticles for catalysis and materials for rechargeable batteries is in its infancy. Different toxicity studies have indicated that the IF-WS_2 nanoparticles are benign.

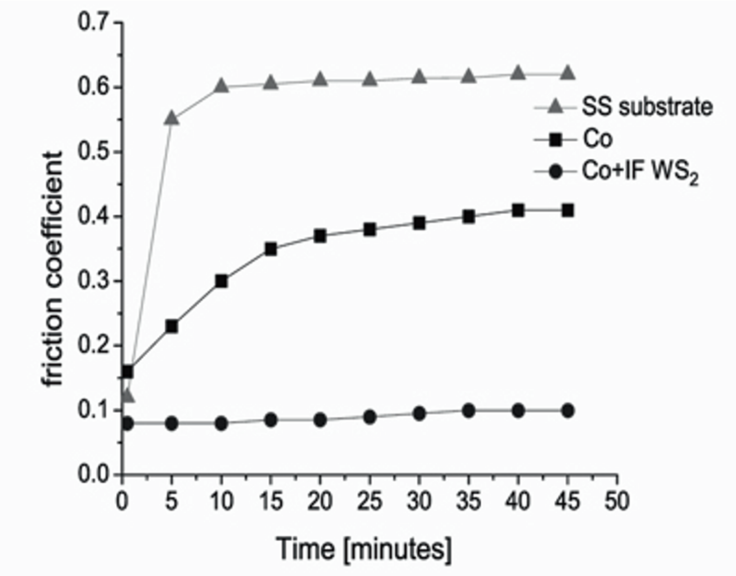


Figure 6. Friction coefficient of stainless substrate coated with cobalt film with and without IF-WS_2 nanoparticles

In conclusion, notwithstanding the progress and the initial successful efforts to commercialize IF and INT of MS_2 compounds, much more work is needed to perfect their synthesis and the study of their properties. The chemistry of IF and INT of various layered compounds have to be studied in detail in order to explore new properties which can lead to enabling applications, in fields like catalysis, rechargeable batteries and more.

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NANOMATERIALS NEXUS IN ENVIRONMENTAL, HUMAN HEALTH, AND SUSTAINABILITY

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Abstract. Three interconnected and underpinning aspects of nanotechnology viz.: environment, human health, and sustainability are discussed. Sustainable development using nanomaterials by employing responsible manufacturing, principles of "green chemistry"; by drastically reducing waste discharge and emission by-products; generation and storage of energy; development of lightweight yet mechanically strong components; development of bio-degradable goods – for medicine, waste disposal, containers, etc. and to monitor, detect, and remediate the environmental pollution are discussed. A brief discussion of fate and transport of nanomaterials in air, water, and soil; life-cycle analysis, and methodologies to conduct risk-assessment in the context of source reduction and conservation is introduced. It is expected that such emerging and potentially transformative studies will make a major contribution to improving the quality of the life of citizens worldwide, in particular in sectors such as environment and health care.

Keywords: nanomaterials, pollution, biodegradable, energy, sustainability

1. Introduction

From the Malthusian doctrine of "The principle of population" to Rachel Carson's congressional testimony, debates on pollution resulting from anthropogenic activities has been a challenging theme for policy-makers, researchers, and industrialists. An increase in population and consumption of fossil fuels to sustain transportation and energy demand has led to increased pollution worldwide. Although the correlation between environmental pollution and global warming is debatable, the effects of pollution and its impact on human health are irrefutable. Pollution in large cities has reached an alarming level and is widely perceived to be a leading contributor to chronic and deadly health disorders and diseases affecting millions of people each year. In a recent study, the World Health Organization (WHO) reported that over 3 million people suffer from

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the effects of air-borne pollution. Furthermore, reports from the World Energy Congress (WEC) suggest that continued fuel usage at its current rate will result in pollution creating irreversible environmental damage by 2025. Furthermore, increased urbanization and use of fossil fuels contribute to pollution and emission of green house gases (GHG), widely believed to be responsible for global warming. A large sector of the world's population have no access to fossil fuels, yet suffer from the adverse effects of pollution due to transport through air, water, and soil. Of the group of pollutants that contaminate urban environment are fine suspended PM, Nitrous Oxide (NO_x), sulphur dioxide (SO_2), volatile organic compounds (VOCs), and ozone (O_3) that pose the most widespread and acute risks. Environmental pollution in developing countries has reached an alarming level, thus necessitating studies and measures, such as cap-and-trade, carbon credit, purchasing pollution credit, efforts to sequester CO_2, use of alternate energy sources, etc., to limit emission of GHG. Figure 1 illustrates pollutions footprint of various sources of energy and a proposed "future distributed-source energy solution", while the right panel shows pollution pathways and a prototype to monitor pollution [1, 2].

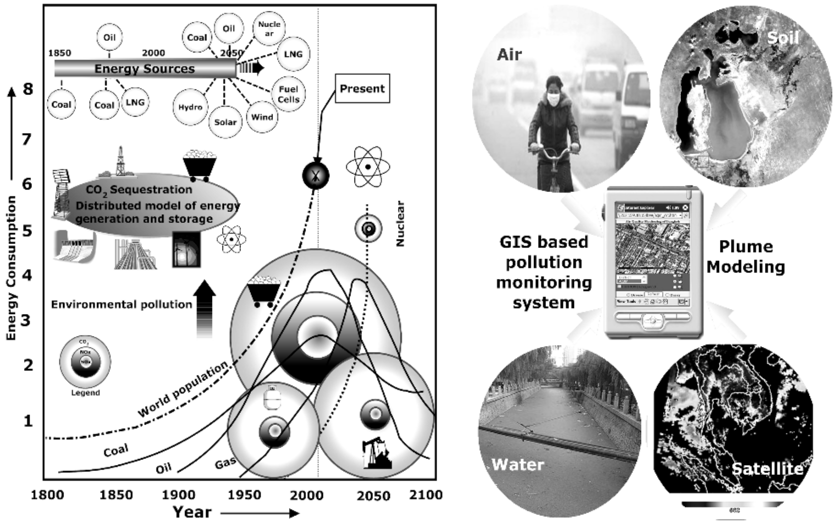


Figure 1. An overview of sources of energy, pollution level, and distributed model of energy in the future [1]. Right panel shows pollution pathways and monitoring system

Materials approaching nanoscale dimensions exhibit atypical characteristics with numerous unique applications. Advances in synthesis and characterization methods have provided the means to study, understand, control, or even manipulate the transitional characteristics between isolated atoms and molecules, and bulk materials. Due to rapid advances in nanotechnologies, the products and processes emerge more faster than policymakers can develop their safe handling practices. Hence, the use of such inter-disciplinary and transformational technologies has initiated a widespread perception-based public debate with scope ranging from favoring further research to its moratorium in advance of scientific risk assessment. This has resulted in perceived possible erosion of individual confidence and tipping of the playing field on the beneficial use of nanomaterials – encompassing risk, ethical, and legal considerations. Hence, it is imperative that a balanced, yet comprehensive perspective of this emerging technology be presented in terms of its potentials notwithstanding ethical, legal, and social consequences.

Given the above scenario, the objective of this investigation focuses on three interconnected underpinning aspects of sustainability: (a): responsible manufacturing of nanomaterials by employing principles of "green chemistry"; (b): production of nanomaterials using synthesis routes that are consistent with the principles of "green chemistry"; (c): use of nanomaterials to monitor, detect, and remediate environmental pollution; (d): drastically reduce waste and emission by-products with nanomaterials-based catalysts for enhanced efficiency; and (e): materials for underground CO_2 sequestration, efficient thin film photovoltaic devices, fuel cells, and biodegradable products.

An extension of the above study is to study the fate and transport of nanomaterials and to conduct a general risk-assessment to keep the public at-large informed. The interaction of a nanomaterial with its environment depends upon physicochemical properties, and is relevant to understand resulting toxicity and its environmental impact. To offset the possible risks associated with nanotechnology, recently, "voluntary codes of conduct" were introduced. It is argued that a well defined risk assessment modality is needed, as the "voluntary code of conduct" for using nanomaterials is somewhat trepidation based and not entirely on scientific methodology. An overview of general risk assessment practices and current research efforts for assessing nanotechnology risks is suggested by the authors and is discussed elsewhere [3].

2. Materials in Reduced Dimensions

Systems in reduced dimensional have one or more dimensions reduced such that material begins to display novel characteristics thus leading to tremendous potential. Solids in reduced dimensions are tantamount to reduction of the coordination number; hence the electrons have less opportunity to hop from site to site; thus reducing kinetic energy of electrons. A higher Coulomb interaction/bandwidth ratio at a site enhances electron correlation and Mott-transition leading to the appearance of magnetism. Furthermore, the symmetries of the system are lowered and the appearance of new boundary conditions leads to surface and interface states. A change of the quantization conditions alters the Eigen value spectrum and transport properties of the solid. A high surface area/volume ratio in nanoscale materials changes physical properties.

2.1. INTERACTIONS WITH MEDIUM

Size and surface collectively control characteristics of nanoscale materials due to the existence of large boundaries adjoining its surrounding medium in conjunction with interplay of physicochemical interactions. The surface free-energy is size-dependent and hence increases almost inversely with the decreasing feature sizes of the material. Response of a nanomaterial-medium system that is attributable to reduced dimensions is fundamental to developing a scientific model that predicts its response and pathways for toxicity, and is an exceedingly complex task due to a large matrix of parameters consisting of nanomaterials, the surrounding environment, and influencing mechanisms of interactions. Hence, as the production and diversity of nanoparticles increases, it is important to understand how engineered nanoparticles and biological systems interact in terms of bio-physico-chemical properties of engineered nanoparticles. An extensive investigation is underway in the context of specific functions ranging from bio-nanomaterials interface to toxic potential of industrial pollution. The characteristics that provide beneficial aspects are also believed to be responsible for toxicity of nanomaterials. Consequently, nanoparticle toxicity is studied in context of its ability to induce tissue damage through the generation of oxygen radicals, electron-hole pairs, and oxidant stress by abiotic and cellular responses [4]. Nanoparticles which are cationic are also believed to induce toxicity via acidifying endosomes that lead to cellular toxicity and apoptosis in epithelial lung through endosomal split through proton sponge mechanism (PSM), mitochondrial targeting, and cytosolic deposition. Nanomaterials composed of redox-active elements are particularly reactive and can possibly provoke potentially damaging chemical transformations. Even chemically benign nanoparticles may become active by light absorption. Hence, fundamental understanding of a nanomaterial-surrounding medium is vital to sustaining technological advances of nanoscale materials.

3. Sustainability – Environment, Economy, and Society

Sustainability in general, is the capacity to maintain a certain process or state indefinitely. According to the U.S. Environmental Protection Agency (EPA), sustainable development has been expressed as meeting the needs of the present without compromising the ability of future generations to meet their own needs [5]. The modern definition of sustainability refers to the capability of an ecosystem to maintain ecological processes, functions, biodiversity and productivity into the future. Growing scientific evidence indicates that the present generation is consuming the Earth's limited natural resources more rapidly than being replaced by the nature. To support a collective human effort to keep human use of natural resources within the sustainable development aspect of the Earth's finite resource limits, nanotechnology is proposed as one of the means to support the sustainable development by employing green nanotechnology[7] and using products that minimize energy consumption and reduce and mitigate environmental pollution.

3.1. RESPONSIBLE MANUFACTURING – GREEN NANOTECHNOLOGY

Green Chemistry refers to environmentally friendly chemicals and processes that result in reduced waste, safer products, and reduced use of energy and resources. Twelve principles of "Green Chemistry" were originally published by Anastas and Warner [6]. We have extrapolated the principles of green chemistry for the production and utilization of nanomaterials – commonly referred to "Green Nanotechnology" to include the production of nanomaterials employing principles of green chemistry, and responsible manufacturing which incorporate environmentally responsible production including the use of reusable and recyclable materials, and the restriction of chemicals or materials that can adversely impact the environment. Most manufacturers limit or ban use of certain chemicals from processes and packaging based on customer feedback, new legislation, guidance from non-governmental organizations (NGOs), recyclers, and internal assessments.

In this context, "green nanotechnology" thus refers to science and engineering at the molecular scale and green chemistry and engineering used collectively to minimize environmental impacts through resource-conserving and waste-eliminating improvements. Selected applications considered in our investigations include use of active and passive nanostructures and nanomaterials to reduce and isolate emission by-products with its use as catalysts with enhanced efficiency, materials for underground CO_2 sequestration, remediation of toxic metals in water streams, alternate sources of energy including efficient thin film photovoltaic devices and fuel cells. Further measures supporting responsible manufacturing include using recycled and recyclable materials, reducing water and energy consumptions, employing environmental friendly biodegradable and lightweight composites based consumable products for reduced power consumption, using lightweight and biodegradable materials to reduce landfill volume.

3.1.1. *Synthesis Routes*

Several methods to produce nanomaterials either by top-down (attrition) and bottom-up (self-assembly) approaches have evolved over a period of time. Attrition type processes are slow, and power intensive; but provide precise dimensional control while bottom-up approaches are desirable from a commercial manufacturing view-point. Following guidelines of responsible production and employing principles of green chemistry, our laboratories collectively focus on preparation of nanomaterials. The synthesis routes are selected in terms of energy demand, feedstock to materials conversion efficiency, emission byproducts, and scale-up cost metrics. Synthesis of nanomaterials employing electrospinning, laser ablation, plasma polymerization and solgel is employed and Table 1 provides a sustainability metrics of the fabrication processes to prepare nanomaterials. Experimental details of the fabrication processes are discussed elsewhere [7–9].

It is instructive to mention here that there are fabrication processes other than those mentioned in Table 1 that produce nanomaterials while employing principles of green chemistry. The processes described here are optimized in terms of metrics provided in Table 1 as well as the byproducts discharge and emission.

4. Nanomaterials Applications in Environment and Human Health

The perpetual increase in worldwide population has increased consumption of fossil fuels which in turn has increased pollution worldwide. Pollution poses major challenges worldwide and it is imperative to employ the latest tools that technology has to offer to minimize its impacts. Described below is a summary of collective efforts to monitor and mitigate pollution/contaminants from air, water and soil.

TABLE 1. Sustainability metrics of nanomaterials processes

Nanotechnology production process	Source material medium	Energy demand	Feedstock to materials conversion efficiency	By-products emission	Process to production cost
Electro-spinning	Polymers/dissolved	Very low	High	Minimum, under controlled environment	Simple process, easy to adopt, low scale-up cost
Sol-gel	Fluid/dissolved	Low	Medium	Minimum, under controlled environment	Simple process, easy to adopt, low scale-up cost
MAPLE	Gaseous	High	High	Minimum, under controlled environment	Complex process, vacuum facility, may require clean rooms
Plasma polymerization	Gaseous	Medium to high	Medium	Minimum, under controlled environment	Complex process, vacuum facility, may require clean rooms

4.1. ENVIRONMENTAL POLLUTION MONITORING AND MITIGATION

One of the objectives of our ongoing research is to develop a portable and real time air pollution monitoring system to be employed in densely populated cities worldwide. The system received input data from ground based sensors and its position coordinates. The data is superimposed using a map-server which gives pollution data vs. its coordinates. Image processed data from satellites such as ASTER, MODIS, and SCHIMACHY is also used in conjunction with this data for authentication. The prototype system developed is economical, almost maintenance-free and user-friendly [10] and is capable of monitoring gases such as NO, NO_2, CO_2, SO_2, CH_4, CO; aerosols, VOCs, and smog – viz. automobile emissions coupled with particulate matter (PM). It is intended to provide easy access to pollution data to public and policy-makers.

We have also investigated various ways in which nanomaterials can successfully be used to reduce/isolate atmospheric pollution. As an example, employing immobilized TiO_2 films, produced by sol-gel process, we explored removal of indoor odors under weak UV illumination. At 10 ppmv weak UV light of 1 $\mu W/cm^2$ was sufficient to decompose such compounds in the presence of TiO_2 photocatalysts. In an experiment, 150 μl of an *E. coli* suspension was placed under weak UV (1 mW/cm^2) illuminated TiO_2-coated glass plate. Under these conditions, there were no surviving cells after only 1 h of illumination, showing antibacterial effect [7].

Our efforts are also focused to investigate and mitigate water contaminants such as Arsenic (As), which is found in the natural environment and also from anthropogenic activities. As (III) is 4–10 times more soluble in water than As (V), and 10 times more toxic than As (V). We have described [2] a method based sorption on iron (III) oxides, such as amorphous hydrous ferric oxide (FeOOH), crystalline hydrous ferric oxide (ferrihydride) and goethite (α-FeOOH) which have been found to be effective in removing both As (V) and As (III) from aqueous solutions. Unfortunately, nanomaterials with small particle size (around 20–50 nm) are not suited well for sorption columns. However, with magnetite/maghemite, separation can be easily accomplished in a high gradient magnetic field. One of the methods under investigation is to incorporate selected nanomaterials into a well organized host. Nanoporous and microporous crystals, such as molecular sieves (zeolites) are ideal hosts for accommodation of organic and inorganic molecules and polymer chains due to their uniform pore size and ability to sorb molecular species. Incorporating iron oxides/oxyhydroxides based nanostructures in zeolites and nanoscale zero-valent iron (nZVI) technology would provide a necessary means for high capacity as removal. This method in conjunction with membrane and filtration technologies will eventually produce clean water for multitude of applications.

4.2. ENERGY GENERATION AND STORAGE

Energy consideration is an inevitable choice in implementing the scientific development concept, changing of the economic growth model, mitigating the strain on environmental protection and furthering economy and society forward to sustainable development. With diminishing fuel supply, a future energy scenario is likely to be a "distributed-source energy" generation and storage, and reduced dependence on fossil fuels leading to reduced pollution and GHG.

Several models for generating and on-demand delivery of energy have been proposed in the literature. Our focus is on hydrogen generation and storage, fuel cells, and means to enhance photovoltaic conversion efficiencies using nanomaterials. Hydrogen produces more energy/volume than any other known sources of fuels. The future of the "hydrogen economy" depends on developing safe and efficient methods for producing and storing hydrogen and on-demand delivery. Photo-electrolysis systems is an elegant and potentially inexpensive approach, however one of the critical components is semiconductor photo-electrodes requiring good visible-light absorption, high photochemical stability, and favorable energetic positions of the band-edges w.r.t. the water reduction and oxidation potentials. Virtually all photo-electrodes display a trade-off between photochemical stability and visible-light absorption. We studied feasibility of photo-electrolysis with a system in which n-TiO_2 semiconductor electrode was connected though an electrical load to a platinum back counter electrode placed under near-UV light and water splits into oxygen and hydrogen in the presence of UV light, without the application of an external voltage.

Fuel cells offer numerous possible applications and may actually be the main driver for hydrogen economy. Our efforts are focused on preparation of new materials for proton exchange membrane (PEM) fuel cells. A new series of polymers based on pyridine cycles originated from polyacrylonitrile (PAN) in a thermo-oxidative process were fabricated. The membranes were obtained by PAN–SiO_2 nanoparticles solution casting in thin films with simultaneous thermo-oxidation process [11].

One of the primary challenges in using hydrogen is its storage. Several efforts are in progress including use of metal hydride (MH) complexes. Recently, concept of hydrogen storage in MH to be integrated into the photo-electrolysis cell, thus leading to devices termed as photo-electro chemical conversion and storage (PECCS) cell in which the cathode is a MH allowing in-situ storage of the generated hydrogen. Activated carbons (AC), single-walled carbon nanotubes (SWNTs) and metal–organic frameworks (MOFs) are being investigated as hydrogen adsorption and storage materials [12]. The hydrogen storage capacity of nanofibers ranged from ≈ 15 > **Ç**> 1 wt% at moderate pressures and temperatures [13]. Experiments on SWNTs yielded adsorbed amounts <10 wt% due to narrow pore size distribution of SWNTs.

Using nanotechnology, we have investigated other creative routes for making inexpensive solar cells. Further research in our laboratories deals with developing 3D-nanostructured solar cells based on flexible substrates. To develop contacts, nanowires are grown directly onto contact pads to increase carrier collection efficiency. Experiments employing electro-active and conjugated poly-(3-hexylthiophene) polymers are in progress and will be reported elsewhere. Experiments are also in progress to use nanomaterials in betavoltaics as source of power for satellite sub-modules drawing energy from ionizing radiation in space to convert in electrical energy.

4.3. LIGHTWEIGHT MATERIALS IN RESOURCE CONSERVATION

New or improved high-performance lightweight materials that meet consumer expectations, military needs and regulatory mandates that could cause significant reduction in fuel-consumption without compromising cost, performance or safety are of particular interest for transport industries. Furthermore, there is a fast moving trend towards lightweight materials and structures for body armor and protection, building and construction, sports and leisure goods, and packaging. Unique characteristics of nanomaterials has led the research towards the development of lightweight materials and structures to withstand more arduous operating conditions; such as higher temperatures, dynamic loading, thermal and mechanical stresses, enhanced resistance to blast and shock, enhanced ballistic performance without structural degradation. Our research on nanomaterials explores how nanomaterials enhance reliability, efficiency and to reduce the impact of the harsh conditions on the structures, components, and the operating environments. The impact of lightweight components in transport and aviation industry will result in reduced fuel consumption and environmental pollution. Some of the materials that are under investigation include carbon fibers, protective coatings, and honeycomb, or bonded structures.

Using electrospinning, we have developed nanofibers using high performance polymers impregnated with CNTs [8]. Several research groups have reported CNT reinforced plastics for use in space shuttle due to their high elasticity, resilience, and thermal conductivity. To increase a soldier's survivability, sustainability, lethality and mobility while at the same time reducing his weight burden; military research involves equipping our soldiers with body armor made of nanocomposites due to their significant improvement in mechanical, thermal, and transport of water and air across the fabric. In a related aspect of our investigation, synthetic and regenerated polymers are studied for possible use in functional textiles and apparel. Composites of high performance polymers with metal oxides, glasses coated with rare earth metals, and carbon nanotubes are prepared and studied for electrical conductivity, optical response, and chemical and biological detection. The ability to develop polymer composites, ceramers, electro-ceramers, and bio-ceramers with varying characteristics and bio-compatibility offers tremendous potential for developing fibers with desired shapes and characteristics resulting in hybrid components. The functional components form integral parts of many functional wearable fibers leading to system on fiber (SoF). The resulting applications range from functional fibers embedded with data communications systems, protective armor, chemical–biological sensors, radio frequency identification devices (RFID), global positioning systems (GPS), to interactive geographical information systems (GIS).

4.4. BIODEGRADABLE AND BIOCOMPATIBLE MATERIALS

Significant advances have been made in the development of biocompatible and biodegradable materials for biomedical applications, where the goal is to develop and characterize artificial materials to measure, restore, and improve physiologic function, and enhance survival rate and quality of life. Typically, inorganic and polymeric materials have been used for such items as artificial heart-valves, synthetic blood-vessels, artificial hips, medical adhesives, sutures, dental composites, and polymers for controlled slow drug delivery. The development of new biocompatible materials includes considerations that go beyond non-toxicity to bioactivity as it relates to interacting with and, in time, being integrated into the biological environment as well as other tailored properties. One area of intense research activity has been in the use of biocompatible and biodegradable polymers for controlled drug delivery. To be used in medical devices and controlled-drug-release applications, the biodegradable polymer must be biocompatible and meet additional criteria to be qualified as a biomaterial, and be capable of sterilization and controlled stability in response to biological conditions. As an example, chitosan possesses a wide range of useful properties. Specifically, it is a biocompatible, antibacterial, and environmentally friendly poly-electrolyte; thus lending itself to a variety of applications including water treatment, additives for cosmetics, textile treatment for antimicrobial activity [14] novel fibers for textiles, and microcapsule implants for controlled release in drug delivery [15]. Hydrogels are materials consisting of a permanent, three-dimensional network of hydrophilic polymers and water filling the space between the polymer chains with applications in diverse fields ranging from bio-medical applications, viz., wound care products, dental and ophthalmic materials, drug delivery systems, implant materials, constituents of hybrid-type organs, and stimuli sensitive systems for agricultural, personal care, environmental, and industrial applications.

We have used all the synthesis methods mentioned earlier for preparation of bio-compatible and biodegradable materials. Using electrospinning, polymers investigated include copolymers with desirable hydrophilic/hydrophobic interactions, dendrimers for immobilization of enzymes, drugs, peptides, or other biological agents, and certain blends of hydrocolloids and carbohydrates. MAPLE was used by our group to deposit materials that mimic hydroxyapatite (HA), the natural mineral phase of bone and teeth. Despite good mechanical properties as metal material used in orthopedics and dentistry, Ti based alloys proved to cause inflammatory responses on long term tissue remodeling due to the unwanted leakage of toxic metal ions in the surrounding areas. This major drawback has been overcome nowadays by coating of the metallic surfaces with ceramic-like calcium-phosphate containing materials that mimic hydroxyapatite (HA), the natural mineral phase of bone and teeth [16]. The natural polymers most frequently mixed with HA due to their excellent biocompatibility and lack of toxicity are: gelatin, collagen, fibrin, chitosan, hyaluronic acid, glycosaminoglycans, and phosphorylated cellulose [17–20]. A general criterion for selecting a polymer for use as a degradable biomaterial is to match the mechanical properties and the degradation rate to specific parameters. The greatest advantage of biodegradable polymers is that they are broken down into biologically acceptable, metabolized and removable molecules. However, is should be noted that biodegradable materials do produce degradation by-products that must be tolerated with little or no adverse reactions within the biological environment.

4.5. GREENHOUSE GASES SEQUESTRATION

At present, approximately 82% of energy utilization is based on fossil fuels; nuclear power provides about 7%; and renewable energy sources account for the remaining 11%. Worldwide CO_2 emissions from human activity have increased to more than 33B Tons. The U.S. Energy Information Administration (EIA) predicts a 33% increase in CO_2 emission levels by 2030 unless appropriate sequestration and mitigation technologies are instituted. The CO_2 Sequestration Program contributes to the president's goal for developing technologies for substantially reducing GHG emissions. Program objectives require lowering the cost and energy requirements associated with CO_2 sequestration from large point sources and better understanding of factors affecting CO_2 storage durability, capacity, and safety in relation to geologic formations and ecosystems. Efforts are underway to adsorb and sequester CO_2 using nanoporous carbon as compared to absorption using relatively weak intermolecular forces. Liquid amine absorption is a mature technology for industrial CO_2 separation; however large scale CO_2 capture requires significant improvements to overcome drawbacks arising from the large amount of energy required for regeneration, corrosiveness, and solvent degradation. Solid sorbents include physical and chemical adsorbents such as zeolitic materials and activated carbons. Solid sorbents show promise either as standalone; or following dispersion, immobilization, and confinement of the amine group into porous solid support resulting in more stable, mass transfer efficient, less toxic, and less corrosive material. In advanced membrane reactors [21], fossil fuel conversion reactions such as the steam-reforming reaction and water–gas-shift reaction are combined with the in-situ separation of one of the reaction products. Efforts in our laboratories are in progress to sequester CO_2 using electrospun metal oxide nanofibers using a variety of Au/TiO_2 catalysts.

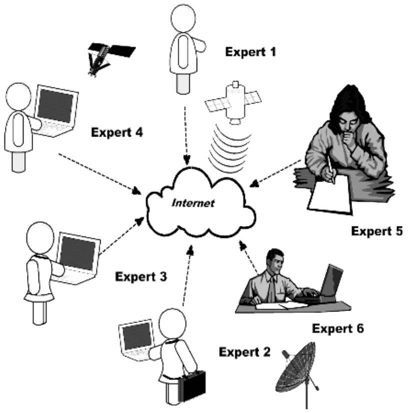
5. Life Cycle Analysis and Risk Assessment

Despite the beneficial effects and major developments in the field of nanomaterials, there is a significant gap in our knowledge of the environmental, health, and ecological impacts associated with nanostructured materials. Since innovations in the field of nanotechnology occur faster than the policymakers can develop safe handling practices; a comprehensive and fundamental investigation is necessary based on the dynamic transport of nanomaterials in the environment and its impact on human health and ecology. The complex nature of naturally occurring and engineered nanomaterials and transport either in the environment or via different exposure routes with human body necessitate a comprehensive and ontological modality. Studies relating to the thermodynamic properties and free surface energy of nanoparticles as a function of particle size, composition, phase and crystallinity effect particle dissolution in a biological environment, perceived to be leading to cytotoxicity through the release of toxic ions or chemicals, as described in earlier section of nanomaterials/environment interaction. Additionally, accumulation, dispersion, and functional surface groups play an important role in evaluating pathways of cellular uptake, subcellular localization and targeting of subcellular organelles.

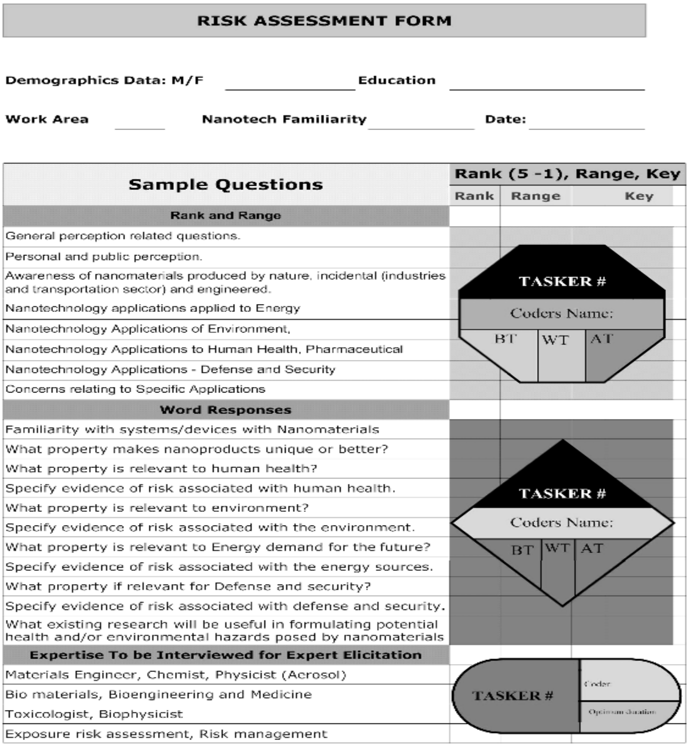
Life cycle analysis in conjunction with proactive risk assessment will ensure appropriate measures as reasonable scientific evidence is established. It also provides for technology to gain social acceptance based on its unambiguous assessment that the technology can be applied to a large scale production without harming the environment and the health of workers and general population. The general framework includes nomenclature and characterization; environmental fate and transport; and hazard identification – exposure and identification. Several methods and opinions have been evolved over a period of time, as an example, the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) has adopted an opinion on "the appropriateness of existing methods to assess the potential risks associated with engineered and adventitious products of nanotechnologies". As a result, several recommendations were made addressing various uncertainties with regard to potential health hazards and exposure, addressing gaps in knowledge; and further developing guidelines and methods.

One important aspect is risk assessment which is analysis based on a three prong approach viz. assess, manage, and communicate. Assessment is the process of identifying risk. Managing is the process of mitigating risks in an optimal manner. Communication ensures that policy and decision makers and the general public understand outcomes of risk assessment and risk management. Nanotechnology risk assessment occurs in a climate of uncertainty and change; therefore, effective decision making by participating experts is critical for a successful outcome.

The Delphi Technique is a structured interactive group communications technique effective for reaching consensus about judgments, forecasts, or decisions from expert panels [22]. The Delphi process occurs as follows: facilitator distributes survey to the expert panel; survey is answered anonymously and independently by an expert panel; facilitator summarizes and distributes results and rationale; expert panel anonymously and independently reviews summarized results and rationale; and panelists may revise individual responses (shown conceptually in Fig. 2a). The process of eliciting, summarizing, and distributing anonymous and independent responses continues until consensus, stable responses, or a given number of rounds is met. The Delphi Technique benefits decision making and forecasting processes involving expert panelists in many ways, viz.: the



(a)



RISK ASSESSMENT FORM

Demographics Data: M/F ______________ **Education** ______________________

Work Area ______ **Nanotech Familiarity** ____________ **Date:** ______________

Sample Questions	**Rank (5 -1), Range, Key**		
	Rank	**Range**	**Key**
Rank and Range			
General perception related questions.			
Personal and public perception.			
Awareness of nanomaterials produced by nature, incidental (industries and transportation sector) and engineered.			
Nanotechnology applications applied to Energy			
Nanotechnology Applications of Environment,			
Nanotechnology Applications to Human Health, Pharmaceutical			
Nanotechnology Applications - Defense and Security			
Concerns relating to Specific Applications			
Word Responses			
Familiarity with systems/devices with Nanomaterials			
What property makes nanoproducts unique or better?			
What property is relevant to human health?			
Specify evidence of risk associated with human health.			
What property is relevant to environment?			
Specify evidence of risk associated with the environment.			
What property is relevant to Energy demand for the future?			
Specify evidence of risk associated with the energy sources.			
What property if relevant for Defense and security?			
Specify evidence of risk associated with defense and security.			
What existing research will be useful in formulating potential health and/or environmental hazards posed by nanomaterials			
Expertise To be Interviewed for Expert Elicitation			
Materials Engineer, Chemist, Physicist (Aerosol)			
Bio materials, Bioengineering and Medicine			
Toxicologist, Biophysicist			
Exposure risk assessment, Risk management			

(b)

Figure 2. (a, b) DELPHI method and survey instrument [3]

technique supports expert panels ranging from a few participants to a few thousand participants; it effectively overcomes constraints in time, geographic location, cost, or anonymity needs; it proves effective when actuarial, technical, or economic data is unavailable thus mandating expert judgment; it has proven effective in the exploration and forecasting of novel, complex, or uncertain problems or events; and the technique overcomes social barriers related to diversity, hierarchy, personality, or hardened conflicts. Efforts are currently underway to prepare an initial comprehensive survey, which will be followed by a pilot study comprising of a small group of experts. The survey will be subsequently reviewed and revised accordingly. A large number of nanotechnology scientists, researchers, industry, and government experts are being contacted to participate in a formal Delphi Study for Assessing Nanotechnology Risks. A risk assessment survey instrument is developed and sample questions are displayed in Fig. 2b.

6. Conclusions and Way Forward

With wider use of nanoscale materials and devices in commercial goods, there is a growing concern, to responsibly leverage nanotechnology to mitigate environmental pollution, conserve resources and, ultimately, build a “green” economy. Nanotechnology spans crossroads of advancement and perceived technological concern, as unique applications continue to develop faster than policy makers can institute policies. Responsible manufacturing coupled with “voluntary code of conduct” in fabrication processes employing principles of “green chemistry” supports development of nanotechnology products that are not only environmentally benign themselves; but can be used to minimize potential environmental, health, and safety risks; to clean up discharge either as toxic waste or emission from stack and other legacy pollution problems; and to substitute for products that are less environmentally friendly. These applications coupled with other nanoenabled applications considered are energy generation and storage, materials which are lightweight yet provide strength and endurance for the transportation industry, and biodegradable materials to reduce landfill volume. A nexus of policies, processes and applications will likely render nanotechnology “green” and a path of sustainability.

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NANOTECHNOLOGY AND QUASICRYSTALS: FROM SELF-ASSEMBLY TO PHOTONIC APPLICATIONS

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Abstract. After providing a concise overview on quasicrystals and their discovery more than a quarter of a century ago, I consider the unexpected interplay between nanotechnology and quasiperiodic crystals. Of particular relevance are efforts to fabricate artificial functional micro- or nanostructures, as well as efforts to control the self-assembly of nanostructures, where current knowledge about the possibility of having long-range order without periodicity can provide significant advantages. I discuss examples of systems ranging from artificial metamaterials for photonic applications, through self-assembled soft matter, to surface waves and optically-induced nonlinear photonic quasicrystals.

Keywords: quasicrystals, quasiperiodic crystals, nanostructures, self-assembly, soft matter, metamaterials, nonlinear photonic crystals, surface waves, Faraday waves

1. Nanotechnology and Quasicrystals?

When organizers of the NATO Advanced Research Workshop on nanotechnology, held in St. Petersburg in June 2008, asked me to deliver a keynote lecture on quasicrystals I was certain that they had made a mistake. I have been studying quasicrystals for over 15 years and investigating nanomechanical systems for just about a decade, and although one always finds connections between different scientific fields, I had never expected such an invitation. Nevertheless, the organizers insisted and explained that they wanted to learn about the possibility of exploiting nontrivial symmetries – perhaps imitating what viruses do – and in general, learn the lesson of a scientific community that was forced by nature to keep an open mind and "think outside of the box".

This chapter is motivated by my presentation on quasicrystals at the NATO ARW on nanotechnology in St. Petersburg. I begin in Sec. 2 by describing the discovery of quasicrystals and the scientific revolution that followed. I argue that now that the surprise has long subsided, and we are well aware of the possibility for having long-range

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order without periodicity, we are equipped with much knowledge that can be adopted in other fields – possibly nanotechnology. Particularly relevant are efforts to fabricate artificial functional micro- or nanostructures, as well as efforts to control the self-assembly of nanostructures. I give an elementary introduction to quasicrystals in Sec. 3. I then continue in Sec. 4 with an overview on the use of quasicrystalline structures in artificial metamaterials for photonic applications, and proceed in Sec. 5 to give a description of our current studies of the self-assembly of soft matter, namely micelle-forming dendrimers and polymeric stars, into quasicrystals. I make an interlude in Sec. 6 to an even softer system – parametrically-excited surface waves in fluids – that spontaneously forms quasicrystalline patterns. I finish in Sec. 8 by mentioning some dynamical properties of quasicrystals that might be more easily investigated in soft-matter quasicrystals than in solid-state quasicrystals, introducing yet another physical system, that of optically-induced nonlinear photonic quasicrystals, which we have been using to study quasicrystals.

2. The Discovery of Quasicrystals as a Modern-Day

2.1. SCIENTIFIC REVOLUTION

For almost two millennia crystallography was predominantly concerned with the external morphology of crystals. Crystallographers studied the naturally-occurring facets of crystals, which always intersect at precise and characteristic angles. It was only in the 17th century that modern crystallography was born, thanks to the brilliant idea – attributed to such great scientists as Kepler and Hooke – that crystal shapes were the result of internal *order* of “atomic” units. In his study of tilings of the plane by polygons, Kepler [1] was quick to realize that very few regular polygons – namely the triangle, the square, and the hexagon – can tile the plane without introducing overlaps or leaving holes. Yet, this observation did not deter him from constructing a well-ordered tiling of the plane, consisting of pentagons and decagons that requires some of the decagons to overlap, and leaves holes in the form of 5-fold stars – a tiling that was to be rediscovered by Penrose more than 350 years later [2, 3]. Without realizing it, Kepler had discovered some of the basic properties of aperiodic order, commenting in his own words that “*The structure is very elaborate and intricate.*”

Unfortunately, by the end of the 18th century, when Haüy began formulating the mathematical theory of crystallography [4], Kepler’s insightful drawings of aperiodic tilings with decagonal symmetry were long forgotten. Consequently, mathematical crystallography was founded upon the premise that the internal order of crystals was necessarily achieved through a periodic filling of space. Thus, crystallography treated *order* and *periodicity* synonymously, using either property interchangeably to define the notion of a *crystal.* The periodic nature of crystals was “confirmed” with the discovery of x-ray crystallography and numerous other experimental techniques throughout the 20th century. As they are more “elaborate and intricate” and less commonly found in Nature, aperiodic crystals were completely overlooked. Periodicity became the underlying paradigm, not only for crystallography itself, but also for other disciplines such as materials science, solid state chemistry, and condensed matter physics, whose most basic experimental and theoretical tools rely on its existence.

This historical oversight was corrected with Shechtman's discovery of quasicrystals in 1982 – a discovery that sparked a *bona fide* Kuhnian scientific revolution [5], as described by Cahn [6], one of the co-authors of the announcement of the discovery, which appeared only 2 years later in 1984 [7]. In the famous Hargittai interviews [8] with all the scientists involved in the initial study of quasicrystals, Mackay is quoted as saying that

> It's a discovery of a material which breaks the laws that were artificially constructed. They were not laws of nature; they were laws of the human classificatory system.

Nature had found a way of achieving order without periodicity, and Shechtman was the first to pay attention to it, and not to dismiss it as an experimental artifact, as many must have done before him. He confronted a skeptical scientific community that was unwilling to relinquish its most basic paradigm that order stems from periodicity. His biggest challenger was Pauling, one of the greatest chemists of the 20th century and a leading crystallographer of that time. In a remarkable article, suggesting an alternative description of Shechtman's icosahedral quasicrystal as multiple twinning of periodic cubic crystals – a description that not much later was shown to be incorrect [9] – Pauling [10] concluded by saying that

> Crystallographers can now cease to worry that the validity of one of the accepted bases of their science has been questioned.

Today, thousands of diffraction diagrams later, compounded by high-quality experimental data – such as images from high-resolution transmission electron microscopes and atomic-resolution scanning tunneling microscopes – the existence of order without periodicity has been unequivocally established. Not only has the periodicity paradigm been questioned, as Pauling worried, it has been completely shattered. By 1992, only a decade after the discovery, the International Union of Crystallography, through its Commission on Aperiodic Crystals [11], was ready to publish a provisional definition of the term *crystal* that abolishes *periodicity,* and implies that *order* should be its replacement. The commission was not ready to give precise microscopic descriptions of all the ways in which order can be achieved. Clearly, periodicity is one way of achieving order, quasiperiodicity as in the Penrose–Kepler tiling is another, but the committee was uncertain whether there were other ways that were yet to be discovered. The Commission opted to shift the definition from a microscopic description of the crystal to a property of the data collected in a diffraction experiment. It decided on a temporary working-definition whereby a *crystal* is

> any solid having an essentially discrete diffraction diagram.

Thus, crystals that are periodic are now explicitly called *periodic crystals*, all others are called *aperiodic crystals.*

The 1992 definition is consistent with the notion of long-range order – one of the basic notions of condensed-matter physics [12, 13] – dating back to ideas of Landau in which the symmetry-breaking transition from a disordered (high-symmetry) phase to an ordered (low-symmetry) phase is quantified by the appearance of a non-zero *order parameter* – in this case, the appearance of Bragg peaks in the Fourier spectrum. Stated in plain words, long-range order – or in the context of our current discussion, long-range positional order – is a measure of the correlations between the positions of atoms in distant regions of the material.

The 1992 definition was left sufficiently vague so as not to impose unnecessary constraints on any further study of crystallinity. Indeed, the discovery inspired a renaissance in crystallography, and has made a great impact on mathematics [14], as can be seen by an ever increasing number of books [15–18]. Much effort has been invested in studying the characteristics of order, as well as in the development of diffraction theory [19–21], once it was realized that periodicity was not a necessary condition for order and for the appearance of Bragg peaks in a diffraction spectrum. In particular, Baake and several co-workers [22–26] have performed a systematic study whose purpose is to characterize which distributions of matter diffract to produce a pure point component in their spectrum, and thus can qualify as possessing long-range order. Sufficient progress has already been made, that we are now ready to complete the paradigm shift and adopt a permanent definition of crystal that is firmly based on the notion of *order* [27].

In October 2007 the quasicrystal community – consisting of mathematicians, physicists, chemists, materials scientists, surface scientists, and even photonics engineers – celebrated the 25th anniversary of the discovery in a “Silver Jubilee” conference [28]. Today, the science of quasicrystals, with its growing number of textbooks [15–18, 29–33], is a mature science. Old paradigms have been carefully transformed into new ones [34]; definitions have been changed [35]; space-group theory has been generalized to quasicrystals using two alternative approaches [36–39], and even extended to treat novel long-range order possessing color [40] or magnetic symmetry [41, 42]); and many fundamental problems – including Bak’s famous question: “Where are the atoms?” [43] – are finding their solutions [44, 45]. Nevertheless, other important questions have remained unanswered to this day. Many of these – such as the electronic and other physical properties of quasicrystals [46], the surface science of quasicrystals [47], and the importance of the phason degree of freedom [48] – were hotly debated at the “Silver Jubilee” conference [28], and continue to drive us forward. One particularly interesting set of questions, and the focus of this chapter, deals with metamaterials and soft-matter quasicrystals – the newly added members of the quasicrystal family.

We know today that quasicrystals are more common than one had originally expected. Scores, or even hundreds, of binary and ternary *metallic alloys* are known to form quasicrystalline phases [49] – mostly with icosahedral or decagonal point-group symmetry – and more are continuously being discovered. Nevertheless, it is only in the last few years that quasicrystals have been discovered (independently) in two different *soft-matter* systems: micelle-forming dendrimers [50–52] and three-armed star block copolymers [53–55]. These newly discovered *soft quasicrystals* not only provide exciting alternative experimental platforms for the basic study of quasiperiodic long-range order, but also hold the promise for new applications based on self-assembled nanomaterials [56–58], with unique electronic or photonic properties that take advantage of the quasiperiodicity, which is relevant to our focus here.

The current emphasis in the study of soft-matter quasicrystals is to find an explanation for their thermodynamic stability, and thus learn how to control their self-assembly. To this date, soft quasicrystals have been observed only with dodecagonal point-group symmetry. Their source of stability is therefore likely to be different from their solid-state siblings, yet a good understanding of the stability of one quasiperiodic system may help to understand the stability of the other. In what follows I shall review our initial understanding of what might be the source of stability of soft quasicrystals, while providing a concise background on the subject. I will try to emphasize the important relations between the variety of different physical and chemical systems that form quasicrystalline phases – atomic quasicrystals, soft quasicrystals, surface waves, and also artificially-produced structures and metamaterials.

3. Quasicrystals – Terminology and General Framework

Let us consider a scalar function $\rho(\mathbf{r})$ that describes the electronic density or the ionic potential of a material. The Fourier transform of a quasiperiodic density $\rho(\mathbf{r})$ has the form

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}\in L} \rho(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{1}$$

where the (reciprocal) lattice L is a finitely generated $\mathbb{Z}$ -module, i.e. it can be expressed as the set of all integral linear combinations of a finite number D of d-dimensional wave vectors, $\mathbf{b}^{(1)}, \ldots, \mathbf{b}^{(D)}$. In the special case where D, called the rank of the crystal, is equal to the physical dimension d, the crystal is periodic. We refer to all quasiperiodic crystals that are not periodic as "quasicrystals".[1] This term was first coined by Levine and Steinhardt [59, 60] in the first of a series of important theoretical papers that were published in the 1980s.

It is useful to introduce a physical setting based on the notion of symmetry breaking that was mentioned earlier [12, 13, 62]. Let us assume that the quasiperiodically-ordered state, described by $\rho(\mathbf{r})$, is a symmetry-broken stable ground state of some generic free energy F, invariant under all translations and rotations in $\mathbb{R}^d$. This is the same as saying that the physical interactions giving rise to the quasicrystal are themselves translationally and rotationally invariant, and that the ground state breaks this symmetry. The free energy F is a functional of $\rho(\mathbf{r})$, which in Fourier space takes the general form

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[1] Some older texts require crystals to possess so-called "forbidden symmetries" in order to be regarded as quasicrystals. It is now understood that such a requirement is inappropriate. See Ref. [35] for details, and Ref. [61] for examples of square and cubic quasicrystals.

$$F\{\rho\} = \sum_{n=2}^{\infty} \sum_{\mathbf{k}_1 \ldots \mathbf{k}_n} A(\mathbf{k}_1, \ldots \mathbf{k}_n)\rho(\mathbf{k}_1)\cdots\rho(\mathbf{k}_n). \tag{2}$$

Based on the idea of such a generic free energy, Rokhsar, Wright, and Mermin [36] introduced the notion of *indistinguishability*, namely that two functions $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$ are indistinguishable if a generic free energy cannot distinguish between them and assigns them both the same value. It then follows [36–38] that $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$ are indistinguishable if and only if

$$\forall \mathbf{k} \in L: \quad \rho'(\mathbf{k}) = e^{2\pi i \chi(\mathbf{k})}\rho(\mathbf{k}), \tag{3}$$

where $\chi(\mathbf{k})$, called a *gauge function,* has the property that $\chi(\mathbf{k}_1 + \mathbf{k}_2) \equiv \chi(\mathbf{k}_1) + \chi(\mathbf{k}_2)$ whenever $\mathbf{k}_1$ and $\mathbf{k}_2$ are in L, where '$\equiv$' denotes equality to within an additive integer.

Gauge functions are useful in describing the relations between the different symmetry-broken ground states of F. Dräger and Mermin [63] showed that gauge functions form a vector space V^* of all real-valued linear functions on the lattice L, and because L has rank D, V^* is a D-dimensional vector space over the real numbers. The space V^* contains, as a subspace, all the integral-valued linear functions on L. This subset, which has the algebraic structure of a rank-D $\mathbb{Z}$-module (just like L itself) is denoted by L^*. Gauge functions in L^* leave the ground-state density invariant. Gauge functions that belong to the quotient space V^*/L^* take the ground state described by ρ into a different, yet indistinguishable, ground state described by some other density function ρ'. Thus, one can parameterize all the related symmetry-broken ground states of F on a simple D-torus – the order parameter space c.

Different, yet indistinguishable, ground states may also be related by rotations $g \in O(d)$. In this case ρ' in (3) is simply a rotated version of ρ, and for each such rotation g there is a special gauge function φ_g, called a *phase function,* satisfying

$$\forall \mathbf{k} \in L: \quad \rho(g\mathbf{k}) = e^{2\pi i \varphi_g(\mathbf{k})}\rho(\mathbf{k}). \tag{4}$$

The set of all rotations satisfying (4) forms the point group of the crystal, and along with the corresponding phase functions completely characterizes its space group [36–38, 40–42]. Unlike periodic crystals, quasicrystals are not restricted in the order of their rotational symmetry. The point-group condition (4) is applicable to operations of any order (as long as the rank of the crystal is finite). Thus, in general, g may be an n-fold rotation of any order n.

4. Exploiting Quasicrystalline Order in Artificially Constructed Metamaterials

Interesting applications are starting to emerge lately that take advantage of quasiperiodic long-range order in metamaterials, or artificially constructed quasicrystals [64]. Two main features distinguish quasicrystals from periodic crystals in the practical sense of using them as metamaterials. The first and more obvious is the relaxation of any symmetry constraints. In dealing with quasicrystals for over a quarter of a century we have learned how to design structures with axes of symmetry of arbitrarily high order. Of course, as the order of symmetry increases, so does the rank of the crystal and therefore its complexity. Nevertheless, simple rank-4 2-dimensional structures already allow one to construct structures with axes of 5-fold, 8-fold, 10-fold, and 12-fold symmetry – a substantial improvement over the limited 2-fold, 3-fold, 4-fold, and 6-fold axes possible with periodic crystals. Most applications of quasicrysalline metamaterials to date are thus based on this notion. These are mostly *linear photonic crystals,* where quasiperiodic modulations of the index of refraction of different materials are used in order to engineer their optical response. These applications take advantage of the fact that there are no restrictions on the order of the rotational symmetry in order to obtain nearly-isotropic photonic band gaps [65, 66]. Dodecagonal (12-fold) quasicrystals are particularly useful as they are at the same time quite simple (the rank is only 4) yet the dodecagon is a far better approximation of a circle than the hexagon, which is the best one can achieve with periodic photonic crystals. Initial work is also carried out with *phononic quasicrystals* for controlling the propagation of sound waves [64].

The second feature of quasicrystals, useful for metamaterial applications, is the complete relaxation of any constraints on the positions of Bragg peaks in their diffraction diagrams. One may design quasiperiodic metamaterials in which the Bragg peaks are placed at predetermined positions in Fourier space. We have exploited this idea in the *nonlinear* optical domain [67–69], where recent technological progress has enabled to modulate the second-order nonlinear susceptibility with micron-scale resolution in various materials, such as ferroelectrics, semiconductors, and polymers. In these *nonlinear photonic crystals* the modulation can be achieved by planar techniques, thereby offering either one or two dimensions for modulation. Moreover, there are no photonic band gaps in these metamaterials, because the first-order susceptibility, and hence the refractive index, remain constant. We emphasize that the advantage of using quasicrystals in this case is not in their arbitrarily-high symmetry, but rather in the fact that there is no restriction on the combinations of wave vectors that may appear in their reciprocal lattices (provided that the symmetry of the quasicrystal is not of particular importance [38, 70]).

The novel optical devices that we have been developing are based on materials that facilitate the nonlinear interaction between light waves in the form of three-wave mixing. These are processes in which two incoming waves of frequencies ω_1 and ω_2 interact through the quadratic dielectric tensor $\chi^{(2)}$ of the material to produce a third wave of frequency $\omega_3 = \omega_1 \pm \omega_2$; or the opposite processes in which a single wave spontaneously breaks up into two. Three-wave mixing is severely constrained in dispersive materials, where ω ($\mathbf{k}$) is not a linear function, because the interacting photons must also conserve their total momentum. Even the slightest wave-vector mismatch $\Delta\mathbf{k} = \mathbf{k}_1 \pm \mathbf{k}_2 - \mathbf{k}_3$ appears as an oscillating phase that averages out the outgoing wave, giving rise to the so-called “phase-matching problem.” We have explained how one could fully solve the most general phase-matching problem using well-known ideas from the theory of quasicrystals [67]. The solution is based on the idea that in crystals, whether periodic or not, continuous translation symmetry is broken, as described above in Sec. 3. As a consequence, momentum conservation is replaced by the less-restrictive conservation law of crystal momentum whereby momentum need only be conserved to within a wave vector from the reciprocal lattice of the crystal. The fabrication of an efficient frequency-conversion device is therefore a matter of *reciprocal-lattice engineering* – designing an artificial crystal, from the quadratic dielectric field of the material $\chi^{(2)}(\mathbf{r})$, whose reciprocal lattice contains any desired set of mismatch wave vectors $\Delta\mathbf{k}^{(j)}$, $j = 1 \ldots N$, required for phase matching any arbitrary combination of N three-wave mixing processes.

The idea of using a 1-dimensional periodic modulation of the relevant component of the quadratic dielectric tensor, for the purpose of phase matching a single three-wave process, was suggested already in the early 1960s [71–73], and is termed "quasi-phase matching". Since then this approach has been generalized using more elaborate 1-dimensional [74–76] and 2-dimensional [77–80] designs, but only as *ad hoc* solutions for multiple processes. We have demonstrated that engineering the reciprocal lattice of a nonlinear photonic quasicrystal to contain any desired set of mismatch vectors – a task that 25 years of research in quasicrystals have taught us how to solve – provides the most general solution for the long-standing problem of multiple phase-matching [67]. We described elsewhere [68, 69] a number of novel optical devices that have actually been fabricated using these ideas, and tested experimentally. These devices attest to the general nature of the quasicrystal-based solution to the multiple phase-matching problem.

5. Towards Self-Assembly of Quasicrystalline Nanostructures – The Recent Discovery of Soft-Matter Quasicrystals

An important development accured recently with the experimental discovery that even soft matter can self-assemble into structures with quasiperiodic long-range order.[2] In one case, dendrimers that assume a conical shape assemble into micelles, which then pack to form a perfect dodecagonal (12-fold) quasicrystal [50–52]. In another case, *ABC* star-shaped block terpolymers – in which the length ratios of the three arms, *B*/*A* and *C*/*A*, can be chemically-controlled – assemble into a host of 2-dimensional columnar structures, one of which is, again, a dodecagonal quasicrystal [53–55]. This phase has also been reproduced numerically using lattice Monte Carlo simulations [87]. A similar square-triangle tiling has also been observed in a liquid crystal composed of T-shaped molecules [88], which forms yet a third soft system which may potentially self-assemble into a dodecagonal quasicrystal. The characteristic length of the basic building blocks

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[2] For the sake of historical accuracy, it should be noted that at some point the blue phase III of liquid crystals, also known as the "blue fog", was thought to have icosahedral quasicrystalline order [81, 82], but this eventually turned out not to be the case [83, 84]. Also, incommensurate helical twist-grain-boundary phases are known to exist in smectic liquid crystals [85, 86], but the quasiperiodic order in this case is essentially only along the 1-dimensional screw axis.

ranges in these systems from about 10 to about 100 nm – 2 to 3 orders of magnitude greater than the atomic length scales found in solid-state quasicrystals. This property of soft quasicrystals is what will potentially make them useful as functional self-assembled nanomaterials [56–58], and at the same time as a new experimental platform for detailed – real-space and real-time – study of quasiperiodic long-range order.

Investigations of these new soft members of the quasicrystal family of materials, are only at their infancy. For example, even the space groups of the observed phases have not been determined, although from the diffraction patterns of the dendrimer liquid crystals given by Zeng et al. [50, 51] it seems that they have a 12-fold screw axis, and therefore, most likely, the nonsymmorphic space group $P12_6/mcm$ [37]. More generally, the same questions [46–48] concerning the thermodynamic stability, the role of clusters in formation and dynamics, and the importance of phasons, apply to soft quasicrystals as they do to hard quasicrystals. Yet the answers may be more tractable (albeit possibly different as the systems are quite different). Thus, the study of soft quasicrystals will clearly have implications well beyond the limits of the specific soft systems that have been discovered so far, and is likely to promote the fundamental understanding of quasicrystals in general. Fortunately, the study of soft quasicrystals is happening at a point in time when the science of quasicrystals is ready and mature to tackle these newly discovered systems. We are no longer taken by surprise whenever a new chemical or physical system exhibits quasicrystalline structure. We are prepared with the appropriate tools to study and explore it, and hopefully also to exploit it for the control of the self-assembly of useful nanomaterials.

6. Insights from an Even Softer System – Quasicrystalline Surface Waves

Motivated by experiments with parametrically-excited surface waves (Faraday waves), exhibiting dodecagonal quasiperiodic order [89], Lifshitz and Petrich [90] developed some years ago a model for describing the pattern-forming dynamics of a 2-dimensional field in which two length scales undergo a simultaneous instability. This model is an extension of the Swift–Hohenberg equation [91], which is used for describing a variety of different pattern-forming systems [92]. Its dynamics is relaxational, $\partial_t \rho = -\delta F / \delta\rho$, driving a 2-dimensional field $\rho(x, y, t)$ towards the minimum of an "effective free energy" (2),

$$F_{LP}\{\rho\} = \int dx\,dy\,\{-\frac{1}{2}\varepsilon\rho^2 + \frac{1}{2}[(\nabla^2+1)(\nabla^2+q^2)\rho]^2 - \frac{1}{3}\alpha\rho^3 + \frac{1}{4}\rho^4\}\,, \tag{5}$$

yielding a dynamical equation of the form

$$\partial_t \rho = \varepsilon\rho - (\nabla^2+1)^2(\nabla^2+q^2)^2\rho + \alpha\rho^2 - \rho^3 \tag{6}$$

It essentially mimics the dynamics of a generic 2-dimensional material in search of its ground state, and therefore offers us important insight and a good starting point for our current investigation of soft quasicrystals. A Java simulation of the dynamical equation (6), starting from random initial conditions, and arriving at a quasicrystalline pattern can be found at http://www.its.caltech.edu/~mcc/Patterns/Demo4_6.html.

The Lifshitz–Petrich free energy F_{LP} is indeed generic, imposing only two requirements on a material, described by a 2-dimensional density $\rho(x, y, t)$: (a) The existence of two characteristic length scales, whose ratio is given by the parameter q; and (b) The existence of effective 3-body interactions, whose importance is given by the relative strength of the parameter α. In [90] we were able to show analytically (using standard methods [93, 94]), and demonstrate numerically, that if q is chosen around $2\cos(\pi/12) = \sqrt{2+\sqrt{3}} \cong 1.932$ one can obtain a ground state with quasiperiodic long-range order and dodecagonal symmetry, yet no choice of q yields globally-stable ground states with octagonal or decagonal symmetry. The latter two have insufficient triplets of wave vectors in the Fourier Lattice L [Eq. (1)] that add up to zero to overcome the cost of additional density modes, as compared with the hexagonal state. Thus, in 2-dimensions, the requirements of two length scales and 3-body interactions are sufficient to stabilize dodecagonal quasicrystals, but insufficient to stabilize octagonal or decagonal quasicrystals. This raises the possibility that the fact that the soft quasicrystals discovered to date are all dodecagonal, may be accounted for using a free energy similar to F_{LP}. Note that for hard quasicrystals the situation is different – decagonal quasicrystals are thermodynamically stable whereas octagonal and dodecagonal quasicrystals are believed to be metastable – indicating that the stabilization mechanism for soft quasicrystals might be quite different from that of hard quasicrystals.

7. Validity of Density-Wave Theories of Quasicrystals

At the outset, as we argue in more detail elsewhere [95], the experimental soft systems in which quasicrystalline order has been observed seem to satisfy the basic assumptions of the Lifshitz–Petrich theory described in Sec. 6. The asymmetric and heterogeneous structure of the star polymers and dendrimers will most likely require more than one length scale for an appropriate coarse-grained description.[3] Their ultra-soft repulsion and resulting strong inter-penetration [99–105] imply that 3-body interactions should be significant [106]. Thus, we expect that studies that we are currently undertaking will yield functionals similar in nature to F_{LP} of Eq. (5). Significant differences may emerge, nonetheless, as the systems considered here are 3-dimensional and differ in their microscopic structure. For instance, two order parameters rather than one might be required [55], which could potentially allow point-group symmetries other than dodecagonal to be observed.[4]

Another key insight can be drawn from a recent theoretical observation, according to which dispersions of soft, fuzzy, particles are essentially different in their thermodynamics

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[3] Indeed, coarse-grained free energies previously used for amphiphilic self-assembly [96] involve more than one characteristic length scale due to the asymmetry of the molecules and the resulting tendency to form curved interfaces.

[4] Models with two order parameters were suggested also for hard quasicrystals [97] and pattern-forming systems [98], yielding additional quasicrystalline ground-state symmetries.

from those of hard particles [107, 108]. The overlap of the soft "coronas" surrounding the particles leads to a driving force acting to minimize their interfacial area, in analogy with foams. Consequently, unusual liquid-crystalline structures can be stabilized in systems of soft spheres [107–110]. Both star polymers and flexible dendrimers fall into this fuzzy category [111, 112], yet they may be highly aspherical. Likos et al. [104] have also shown that stars and flexible dendrimers have the same kind of soft pair potentials. We thus expect such considerations of interfacial-area minimization to become highly relevant in the study of soft quasicrystals.

A 3-dimensional version of an LP-like free energy may remind the reader of the early attempts by Kalugin et al. [113, KKL], who extended the model of Alexander and McTague [114], using density-wave theories to establish that the icosahedral quasicrystal has lower free energy than the competing *bcc* phase. Narasimhan and Ho [115, NH] managed to show in their model that there are regions in parameter space in which a dodecagonal quasicrystal is favored and other regions in which a decagonal quasicrystal is favored. These attempts were eventually discontinued after it was shown by Gronlund and Mermin [94] that the addition of a quartic term to the cubic free energy of KKL reverses the outcome of the calculation, establishing the *bcc* phase as the favored one. For hard crystals it is unclear where to truncate the density-wave expansion of the free energy and whether such a truncation is fully justified. As we discussed in [95], for the soft systems considered here the truncation of the expansion should be more valid. We are therefore in a position now to reexamine some of the old conclusions, based on density-wave theories of quasicrystals, as they are likely to apply to *soft* quasicrystals. Roan and Shakhnovich [116] performed such a stability study for the case of icosahedral order in diblock copolymers and concluded that such order is only metastable. Nevertheless, we are encouraged by the old results of NH who established the stability of dodecagonal, as well as decagonal, quasicrystals within the same model.

8. Dislocation and Phason Dynamics – From Soft to Photonic Quasicrystals

Valuable knowledge about the nature of quasiperiodic order, important also for the control of its self-assembly, can be obtained by studying its topological defects [12, 13, 117], and its low-energy collective excitations – in particular those associated with the phason degrees of freedom. Much like phonons, phasons are low-energy excitations of the quasicrystal, only that instead of slightly shifting the atoms away from their equilibrium positions, the relative positions of atoms are interchanged. Their existence stems directly from the fact that the dimension D of the order parameter space V^* /L^* is greater than the physical dimension d. Thus, in addition to d independent (acoustic) phonon modes there are $D - d$ independent phason modes.

The existence of phasons as fundamental degrees of freedom, affecting the physical behavior of quasicrystals, has been clearly established over the years. Their role in a dynamical density-wave theory of quasicrystals was developed in a series of papers [9, 118–124] immediately following the announcement of the discovery of quasicrystals. Phasons have been observed in numerous experiments, whether directly or indirectly, throughout the past two decades [125–129], and are still a source of interesting analytical puzzles [130] and ongoing debate [48].

We have recently begun investigating the motion of dislocations and the dynamics of phasons in the dodecagonal ground state of the LP equation [131]. We are studying, both analytically and numerically, such questions as the climb velocity of dislocations under strain, the pinning of dislocations by the underlying quasiperiodic structure under conditions of weak diffusion, and the relaxation of phason strain as two dislocations of opposite topological sign merge and annihilate each other. These studies are impossible to conduct with either Faraday waves or hard atomic quasicrystals. Thus soft quasicrystals, with their 10 to 100 nm length scales, may become one of the first natural experimental system to provide real quantitative microscopic answers regarding the dynamics of the fundamental degrees of freedom in a quasicrystal – defects and low-energy excitations.

In the meantime we have embarked on the study of these unique dynamical degrees of freedom in a fascinating new artificial form of quasicrystalline medium – an optically-induced nonlinear photonic quasicrystal – which we have recently demonstrated [132]. In this systems beams of light interact nonlinearly by changing the index of refraction of a photorefractive material. Their dynamics is governed by a different type of equation – the so-called nonlinear Schrödinger equation. Nevertheless, it is capable of stabilizing structures with quasicrystalline order where the typical distance between crystal sites is 15 to 30 μm. This has allowed us to study the microscopic dynamics of dislocations [132] as well as phasons [133]. These artificial systems already provide useful information regarding the dynamics of fundamental degrees of freedom in quasicrystals. Similar investigations of soft quasicrystals, should provide valuable insight into their physical nature, as well as that of all quasicrystals, regardless of the physical or chemical system in which they are realized. This insight will be most valuable in trying to design and control the self assembly of quasiperiodic nanomaterials.

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OSCILLATIONS OF POLARIZED CHARGE IN SOLUTION OF SALT IN POLAR DIELECTRIC: POSSIBLE APPLICATION IN ELEMENT AND ISOTOPE SEPARATION IN BIOLOGY AND NANOTECHNOLOGY

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Abstract. In the work [1] is shown the possibility of the use the phenomena of the electrical-induced selective drift of cationic aquacomplexes in the water solution of the salts for creating of the new, non-electrode, power-saving technology of the solution enrichment by desired element. The development of the naturally-scientific basis of this technology has showed that inertial properties of formed in the solution over-molecular structural units – clusters depends from that's dimensions. Dimensions of these clusters are in limits from scores of angstrom to fractions of micron, at the same time liquid mediums are the base of functioning both biological and technological systems. Thus, water solution of salt contains nanoparticles and biological and many technological systems are functioning with the assistance of nanoparticles. For example, the ordinary blood circulatory system or many of chemical processing. The casual or intentional action of aperiodic electric field on systems containing salts solutions produces some positive or negative effects. This work shows new approach for theoretical describing of salts solution in dielectric liquids and contains some data on the realized experiments.

Keywords: electromagnetic field, solution, polar liquid dielectric, aqua complex, solvated ion, hydration shell, over-molecular cluster, polarization, directed drift, separation

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1. Condition of the Problem

At dissolution occurs complex formation therefore is formed supermolecular structure – in water solutions of hydrated aquacomplexes. Aquacomplex may be considered as nanoparticle, formed from central ion and molecules of water.

At action of the external periodic electric field the solvated ions–clusters are drifting [1]. The oriented drift of the polarized solvated ions allows organizing the technological process of element enrichment of water solutions of salts [2]. Experimental researches have shown, that it not the sole appendix of the found out phenomenon (effect). In particular, the solutions of salts of metals in the polar, liquid dielectrics (water, spirits, ketones) show interesting properties at action of the magnetic fields.

As show theoretical and experimental researches, the size of cluster is the quantity determining the majority of physical and technological properties of solutions. Nowadays, two approaches were developed for definition of properties of solutions. The opportunity of use of the plasma concept of a condition of solutions of electrolytes is noted in the works of M.M. Baldanov [3]. The second approach assumes the modeling of processes of solvation on the basis of the incorporated quantum-classical theory of the functional of density [4].

Both in that, and in other case, for the obvious reasons, properties of solutions are defined mainly by energy of multiparty interactions of ions in the dielectric medium. And it uniquely assumes attraction of such individual characteristics, experimental definition of which is impossible (a condition of an electroneutrality), are probable only theoretical estimations, or semiempirical processing of an experimental material on the basis of some plausible, but arbitrary assumptions.

The validity of the assumptions can be certain experimentally, for example, at comparison of observable and theoretical values of any parameter which value directly depends on the solution characteristic of the defined within the limits of this or that approach. Such works have been begun in 30th years of the last century [5].

In the works [3, 4] were received the radiuses values of the solvated ions, which compound units of angstroms. Use of such values at a theoretical explanation of the found out phenomenon (effect) of the selective drift of solvated cations under action of an asymmetric electric field [1] leads to estimated values of frequencies of the field (about 100 MHz) at which it is necessary to expect display of the effect. Nevertheless, the phenomenon takes place at the frequencies which are not exceeding units of kilohertz, and at the certain concentration of salt in water – tens of hertz. Besides there are the experimental data specifying that clusters represent submicron formations [6].

In the work the solution is shown as quasi-neutral system of polarized charges which interacting with external electric field and among themselves. Consideration is spent with the purpose of definition of the geometrical sizes solvated ions–clusters and general characteristics of process of influence on the solution of an external electromagnetic field. Results will allow defining opportunities of various appendices of the found out phenomenon (effect).

2. The Self-Consistent Field in the Water Solution of Salt

Let’s consider, that each cation (anion) causes the polarization of surrounded solvent (water): the “atmosphere” is forming around each cation (anion) with abundance of polarized molecules of the water. This “atmosphere” is shielding cation’s (anion’s) field. The generalized electronic shell of each polarized molecules of water is deformed concerning unperturbed configuration, when full spin of the molecule is a zero. The perturbation is caused by the action of the cation’s (anion’s) electric field. The deformation of the shell is cause that the part of nucleus’ charge or electrons in the water’s molecule will be uncompensated. This uncompensated part of a charge represents a polarizing charge of a molecule of water in a non-uniform electric field of the charged particle – cation (anion). According to representation about the self-coordinated field [7] there is such distribution of an electric field in system of the cooperating charged particles which creates the distribution of particles exciting a field. Salt solution is possible to consider as system of cooperating cations, anions, it is positive and negatively polarized molecules of water. For a finding of the self-coordinated field we shall use Poisson equation:

$$\Delta\varphi = -4\pi q \tag{1}$$

And Boltzman distribution:

$$n_k = \tilde{n}_k \exp(-\frac{Z_k e\varphi}{kT}), \tag{2}$$

where n_k – concentration of particles with charging number Z_k in a point with potential φ. For electrons, for example, $Z = -1$. But in a solution are not present free electrons. For cations $Z = m$, and for anions $Z = -m$, where m – valency of metal which salt is dissolved. $\tilde{n}_k$ in distribution (2) is a concentration of particles with charging number Z_k in a point with the zero potential, equal to average concentration of these particles on all volume of a solution.

Further an index i we shall designate cations, an index a– anions, $p+$ – polarized and being around of anions molecules of water, $p-$ – molecules of water around cations.

Average concentration $\tilde{n}_k$ satisfies to a condition of quasi-neutrality:

$$\sum_i \tilde{n}_i Z_i + \sum_a \tilde{n}_a Z_a + \sum_{p^+} \tilde{n}_{p^+} Z_{p^+} + \sum_{p^-} \tilde{n}_{p^-} Z_{p^-} = 0, \tag{3}$$

which show the fact, that the solution as a whole (from outside) is neutral.

Also following conditions take place:

$$\sum_i \tilde{n}_i Z_i = -\sum_a \tilde{n}_a Z_a ,$$

$$\sum_a \tilde{n}_a Z_a = \sum_{p^+} \tilde{n}_{p^+} Z_{p^+} , \tag{4}$$

$$\sum_i \tilde{n}_i Z_i = \sum_{p^-} \tilde{n}_{p^-} Z_{p^-} ,$$

In which it is considered, that charging numbers of cation and anion are equal on absolute value, but opposite, and charging numbers of the polarized molecules of water are determined by around of what they associated: around anions $Z_{p^+} > 0$, and around cations $Z_{p^-} < 0$.

Thus,

$$\sum_k \tilde{n}_k Z_k = 0 , k=i, a, p^+, p^- . \tag{5}$$

Also following connections take place:

$$\begin{gathered} Z_a = -Z_i = Z; \quad Z_{p^-} = \frac{1}{N_a} Z_a; \quad Z_{p^+} = \frac{1}{N_i} Z_i; \\ \tilde{n}_{p^-} = N_a \tilde{n}_a; \quad \tilde{n}_{p^+} = N_i \tilde{n}_i; \quad \tilde{n}_a = \tilde{n}_i = n_m; \end{gathered} \tag{6}$$

where N_a – number of molecules of water, associated around of one anion; N_i – number of molecules of water, associated around of one cation; Z – valency of metal, which salt is dissolved; n_m – concentration of molecules of salt in a solution, if to consider they are not dissociated.

Volume charge thus,

$$q = e \sum_k Z_k n_k , \tag{7}$$

where e – the module of a charge of electron (in system ***SI*** $1.6 \cdot 10^{-19}$C). The correlation (7) is very similar to expression (5) with that essential difference, which in it there is a value of concentration of particles in that point in which the potential of the self-coordinated field is determined.

Equation of Poisson will copy in the form of:

$$\Delta\varphi = -4\pi e \sum_k Z_k \tilde{n}_k \exp(\frac{Z_k e\varphi}{kT}) . \tag{8}$$

Using series expansion and considering connections (4) and (6), it is possible to receive function:

$$\sum_k Z_k \tilde{n}_k \exp(\frac{Z_k e\varphi}{kT}) \approx \frac{Z^2 e n_m \varphi}{kT}(2+\frac{1}{N_i}+\frac{1}{N_a}). \tag{9}$$

Even if takes place no more, than secondary hydration, in hydrate shell it will be concentrated more than 10 molecules of water. Therefore it is possible to consider, that 2>> $1/N_i$ and 2<< $1/N_a$. In view of this, equation of Poisson will become:

$$\Delta\varphi = -\frac{8\pi Z^2 e}{kT}\cdot\varphi . \tag{10}$$

The decision (10) for spherical symmetric distribution of potential (cation or anion) looks like:

$$\varphi = \frac{C}{r}\exp(-\chi r) , \tag{11}$$

where constant of insulation is:

$$\chi = \left(\frac{8\pi e^2}{kT} Z^2 n_m\right)^{0,5} . \tag{12}$$

The inverse value $l = 1/\chi$ refers to as length of insulation and it is possible to consider, that its value defines radius of solvation sphere within the limits of which the polarized molecules of water are built. They also insulate a field of cation (anion). Thus, value of cluster radius (solvated cation or anion) can be estimated, using:

$$r_{cl} \approx \left(\frac{8\pi e^2}{kT} Z^2 n_m\right)^{-0,5} \tag{13}$$

3. The Characteristic Values of Frequencies of Excitation of Effect of Oriented Drift of the Solvated Ions

The own frequency of solvated ion (cluster) can be expressed of following equation: $\nu = \nu_e + \nu_k + \nu_r$, where items correspond of frequencies of excitation of electron shells (e), oscillation an ion and solvated groups (*k*) and rotations solvated groups concerning an ion (*r*). It is supposed, that excitation of electronic shells or oscillation of ion and solvated groups can be initiated only after deformation solvated shell (screen), which inhibits influence of an electric field. Deformations (rotation solvated groups concerning an ion) correspond to item ν_r.

Frequencies of transition of oscillatory motions in rotary are defined by equation:

$$\nu_0 \cong h/(8\pi^2 I)\,, \tag{14}$$

where h – Planck's constant, I – the moment of inertia of system of the connected particles. The given equation is valid if cluster it is possible to consider as linear system of two rigidly connected particles (an ion and solvated shell), and oscillatory movement of any of particles causes rotation of cluster as the whole. These frequencies in conditions of the achievement of relative mobility of clusters, which is required for activation of process of the selective drift under influence of field, is possible to considered as the minimum frequencies of own free movements clusters. Broader range of frequencies of own motions of clusters, which is connected with free rotary-onward motions, can be presented in the form of set of the frequencies of the allowed quantum levels of free rotation by analogy to a spherical top (all of its three principal of the moment of inertia are equal):

$$\nu = J(J+1)h/(8\pi^2 I)\,, \tag{15}$$

And frequencies of onward moving:

$$\nu = (n_x^2 + n_y^2 + n_z^2)h/(8\mu d^2)\,, \tag{16}$$

where J – quantum number, $n_{x,y,z}$ – the projections of the vector of the rotation to coordinate axes, d – the size of cluster, μ – the brought weight of cluster. The frequency of onward moving is meant frequency of rotation of all clusters (an ion together with the solvated shell) as the whole when sets of all three main directions of the fluctuations will be transformed in each other.

If in formulas (15)–(16) the form of cluster take as spherical – "zero" approach, it is possible to consider, that $J = 1$, $(n_x^2 + n_y^2 + n_z^2) = 1$. The number of the molecules of water (the solvated groups) in the cluster, having radius r_{cl}, is g, $d = 2r_{cl}$, $r_{cl}=rg^{1/3}$, $r = (3V/(4))^{1/3}$, where r, V – radius and volume of the solvated groups, respectively. Thus $I = K_r \mu r_{cl}^2$, where K_r – the factor equal to the relation of the moment of inertia, corresponding rotation solvated shell around of an ion, to average of value of the projection of the oscillatory moment on the axis of rotation. This factor characterizes intensity of the Carioles interactions (the analogy to Carioles forces in the classical mechanics). It have value 0.4 for the rotation the solvated shell around cation (anion) and 1.4 – for the rotation around axis, passing regarding to surface cluster. As the weight of the solvated shell considerably surpasses weight of the ion, positions of the centre of gravity (the center of inertia) and the ion practically coincide. The values of the frequencies received in the formulas (14)–(16) for $J = 1$ (the minimal values), correspond to a case when only one aquacomplex is formed, and allow to estimate only values of the frequencies which should be expected in the experiments.

As follows from the ratio (13), the value of dimension of the cluster is inversely to a square root from value of concentration of salt in water. Values of the frequencies are inversely to the value of the moment of inertia of the cluster. The moment of inertia is proportional to the equivalent mass of the cluster, that is the quantity of molecules of water in the solvated shell $g = (r_{cl} / r)^3$, and the square of radius of cluster r_{cl}^2. It turns out, that the moment of inertia $I \sim r_{cl}^{\ 5}$ and values of the frequencies of excitation of various components of motions $\nu \sim r_{cl}^{-5}$. Thus, values of the frequencies $\nu \sim n_m^{2,5}$.

At present time there are several used approaches but only two forms that are checked in experiments. One of them was investigated for concentration of the salts in water solution, providing performing the condition $n_i << n_{\mathrm{H_2O}}$, where $n_{\mathrm{H_2O}}$ – an amount of the molecules of water in unit of the volume, n_i – for amount ion ditto, it is possible to expect that: *potential becomes too small on distances, smaller distances between most close located ions* [1]. Values of frequencies, corresponding to different components of the rotary-onward motion of cationic aquacomplexes, and values of the frequencies, corresponding to the turning of the oscillatory motion in rotary, are in limits from several hundreds hertz to several kilohertz. If the solution is considered as quasi-neutral system of polarized charges which interacting with external electric field and among them, frequencies of oscillations are much less (no more than 100 Hz).

4. The Fluctuations of the Polarized Charge in the Solution

In external electric field polarized due to deformation of the aquation shell of aquacomplexes are displaced. As a result there is a division of the aquacomplexes, displaced to a greater or lesser extent. Polarized charges of the divided aquacomplexes differ, at least, on absolute value. Thus, there is a division of charges and electrostatic forces in volume of a solution. Electrostatic forces should lead to excitation of own electrostatic fluctuations in volume on the average neutral (in an enough great volumes or for enough greater time intervals) a solution.

Let as a result of division of the polarized aquacomplexes in a solution there is a polarized charge $\boldsymbol{q}$. Thus

$$q = -\boldsymbol{divP}, \tag{17}$$

where $\boldsymbol{P} = \chi \cdot \varepsilon_0 \cdot \boldsymbol{E}$ – a vector of polarization; χ – a dielectric susceptibility of a solution; ε_0 – an electric constant of vacuum; $\boldsymbol{E}$ – a vector of intensity of the electric field acting on a solution. We shall remind that it is a question of solutions of salts of metals in polar dielectric liquids. Thus

$$\chi = \overline{n} \cdot \alpha, \tag{18}$$

where α – factor of polarizability of the solvated ion–cluster; $\overline{n}$ – average number of clusters in unit of volume of a solution, and $\overline{n} = 2n_m$, where n_m – number of dissociating molecules of salt in unit of volume of a solution.

The polarized charge of one cluster $\left(p = {}^{q}\!/_{\overline{n}}\right)$ will be defined, thus, by expression:

$$p = -\frac{\chi \cdot \varepsilon_0}{2 \cdot n_m} \boldsymbol{divE} = -\alpha \cdot \varepsilon_0 \cdot \boldsymbol{divE} \,. \tag{19}$$

The according to the law of preservation of a charge

$$\frac{\partial q}{\partial t} = -\boldsymbol{divj} \,, \tag{20}$$

where $\boldsymbol{j}$ – density of a current. Thus the current is carried by the polarized aquacomplexes. Then

$$\boldsymbol{j} = 2 \cdot n_m \cdot p \cdot \mathbf{v} \,, \tag{21}$$

where $\mathbf{v}$ – speed of the aquacomplexes, carrying a current. The equation of movement polarized aquacomplex, having weight m, will enter the name in the form of

$$m\frac{d\mathbf{v}}{dt} = p\boldsymbol{E} \,. \tag{22}$$

Differentiating the equations (20) and (21) and substituting (21) in (20), we shall receive

$$\frac{\partial^2 q}{\partial t^2} = -2n_m p\boldsymbol{div}\frac{\partial \mathbf{v}}{\partial t} \,. \tag{23}$$

Substituting in (23) expression for ${}^{\partial \mathbf{v}}\!/_{\partial t}$, received of (22), and considering, that $\boldsymbol{divE} = 4\pi q$, we shall receive

$$\frac{\partial^2 q}{\partial t^2} = -\frac{8\pi n_m p^2}{m} q \,. \tag{24}$$

The received equation describes simple harmonious fluctuation with circular frequency

$$\omega_0 = \sqrt{\frac{8\pi n_m p^2}{m}}\,. \tag{25}$$

If the solution is placed between two flat electrodes, the distance between which is not great, consideration of process can be spent in one-dimensional geometry. We shall designate through E_x absolute value of intensity of the electric field acting on a solution. Then

$$\omega_0 = \alpha \cdot \varepsilon_0 \cdot \boldsymbol{divE} \cdot \sqrt{\frac{8\pi n_m}{m}} \tag{26}$$

or

$$\omega_0 = \alpha \cdot \varepsilon_0 \cdot \frac{E_x}{\Delta} \cdot \sqrt{\frac{8\pi n_m}{m}}\,. \tag{27}$$

where Δ – thickness of a layer of a solution between the potential and earthed flat electrodes.

Thus, the density of a volumetric polarized charge in a solution will change with circular frequency ω_0 $\left(\nu_0 = {\omega_0}/{2\pi}\right)$ after action on a solution of an external electric field. Thus frequency of fluctuations is defined not by amplitude of intensity of this field, and divergence of intensity of a field in volume of a solution.

5. Influence of the Electromagnetic Wave on the Solution

As well as in plasma, any separation of charges in a solution of salt in liquid polar dielectric leads to fluctuations of density of a charge. On the average for many periods of fluctuations the solution behaves as quasi-neutral medium. Separation of polarizing charges is possible only on temporary intervals, smaller in comparison with temporary scale of separation of charges $t_0 \sim (\omega_0)^{-1}$. For spatial scale of separation of the charges d it is possible to accept distance which solvated the ion at the thermal movement migrate in time t_0, that is $d \sim {\langle \upsilon \rangle}/{\omega_0}$, where $\langle \upsilon \rangle$ – the average speed of thermal movement of solvated ions (clusters), having weight m. In spatial scales, greater in comparison with d, it is observed quasi-neutral the solution.

By definition the dielectric constant of the continuous environment ε is the relation of intensity of external electric field E to intensity of the weakened field inside of this medium E' (dielectric). Thus ε always is more than 1.

In a solution ${E}/{E'} > 1$. Hence for a solution $\varepsilon < 1$. Thus the smaller frequency of an external electric field ω, $\nu = {\omega}/{2\pi}$, the more “range” of fluctuations polarized solvated ions, that is amplitude of their displacement. It turns out, that with diminution of ω the dielectric constant of a solution ε decreases also.

Also behave also free electrons in plasma that is used in techniques of sounding of plasma by radiowaves. In case of plasma is critical value of frequency ω_k of radiowaves, at which dielectric constant of plasma $\varepsilon = 0$. Value of this frequency coincides with value the Longmuir frequencies of plasma.

In our case the analogue of Longmuir frequencies is frequency of fluctuations of the polarized charge in volume of a solution ω_0.

The dielectric constant of plasma is defined by the ratio:

$$\varepsilon = 1 - \left(\omega_k / \omega \right) \tag{28}$$

where ω – frequency of an external radio emission. If this frequency $\omega < \omega_k$, then $\varepsilon < 0$.

In Maxwell's works it is established, that factor of refraction of an electromagnetic wave in substance $\gamma = \sqrt{\varepsilon}$. At $\varepsilon < 0$ electromagnetic waves cannot extend in substance and should be reflected completely from it. Therefore in relation to waves with frequency $\omega < \omega_k$ plasma is an ideal reflector. By analogy it is possible to assume, that a solution salt in liquid, polar dielectric will be a reflector for waves with frequency

$$\omega_0 < \alpha \cdot \varepsilon_0 \cdot \boldsymbol{divE} \cdot \sqrt{\frac{8\pi n_m}{m}} \, , \tag{29}$$

where $\boldsymbol{E}$ – intensity of an electric field in a wave.

6. Conclusions

The solvation process of ions in solutions of salts in liquid, polar dielectrics provides an opportunity of development of essentially new technologies and techniques. The conditions providing use of process mass transfer for the decision of various applied problems, first of all are defined by the sizes of solvated ions (clusters).

In particular, action of periodic electric fields with various combinations of frequency, intensity and the attitude of amplitudes of intensity in half-cycles on solutions of salts in polar dielectrics causes excitation of rotary-forward motion solvated ions (clusters) and, hence, mass transfer.

On the figure is shown the scheme of experimental cell which was constructed for separation of solvated ions of cerium and lanthanum (Fig. 1).

At submission on the input of the separating element on the basis of a technological cell of the base mixture of two component (a water solution of the mix of salts $Ce(NO_3)_3$ and $Y(NO_3)_3$ with concentration 3.5 and 3 g/l, accordingly) the separation factor in an element without circulation of the solution after 4 h of influence of the field with intensity $E^+ = 14.3$ V/cm, factor of asymmetry $A^-/A^+ = 0.66$, with frequency 1.6 kHz have made: in the selection 1.00499; in the dump 1.00179; full 1.00679. In a solution there was an enrichment on the cations Ce^{3+}.

Checking of the condition of water in the solutions of sugars (α-methyl-D-glucopyranoside, α-methyl-D-mannopyranoside, α-methyl-D-glucopyranoside, lactose and saccharine) by means Spectrophotometer Perkin–Elmer Model 180 have showed, that a marked difference occurs between spectrums of light absorption by solution before and after asymmetrical electric field action. The received facts confirm that action of field on the solution causes either changes of certain conditions of water in the solution or changes of biological active compounds concentrations in the gap between potential and neutral electrodes.

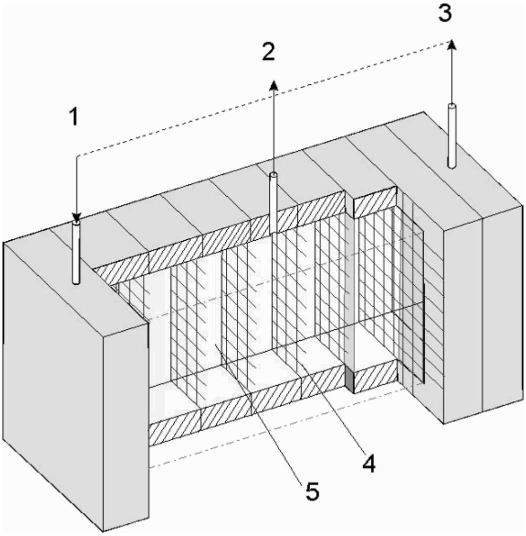

Figure 1. Technological cell: 1 – nipple for the solution inlet; 2 – nipple for the solution selection; 3 – nipple for the solution selection and circulation; 4 – insulated potential high-transparent nets; 5 – solution

Action of an electromagnetic wave on a solution salt in liquid, polar dielectric causes division of charges and leads to fluctuations of density of a charge. At the certain combinations of parameters of an electromagnetic wave and a solution it is possible to expect partial or its full reflection from the medium formed by a solution that allows considering the problem opportunities of use of electromagnetic waves for definition of parameters of solutions.

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ON THE POSSIBLE INFLUENCE OF RESONANCE CONVERSION ON FORMATION OF THE ORGANIC STRUCTURES

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Abstract. As known, an externally applied electromagnetic field can be drastically enhanced in the vicinity of the nuclei as a consequence of resonance properties of the electron shells. This interaction is due to resonance internal conversion. The reciprocal statement is also valid. Thus, the lifetime of the excited 3.5 eV ^{235m2}U nuclear isomeric state is shortened by orders of magnitude due to spin-flip interaction of the spin of the nucleus with the electron spin. We want to suggest that the analogous effect should take place also in complex nanosystems: organic molecules, carbon fullerens and nanotubes, atomic clusters. Similarly to the atomic nuclei, where electromagnetic, weak and other fields undergo strong renormalization in the bulk of the nuclear matter, the effect of resonance conversion gives rise to the effective electromagnetic field in the nano structures, which is responsible for their formation.

Keywords: atom, resonance, nucleus, valence, electromagnetic field

1. Introduction

As was demonstrated many times by Yu.B. Magarshak, there is an evident symmetry in all the great variety of organic nano structures which should be due to some basic field interaction. That might be founded on the electromagnetic, or even weak interaction, which acts between atoms (nuclei) in the molecules, and whose detailed structure remains to be not fairly well understood. We shall focus on the resonance interaction between the nuclei mediated by the electron shell, which is realised via bound (BIC), or resonance internal conversion [1–3]. The resonance conversion was observed in muonic atoms [4, 5] and 45-fold ions of ^{125}Te [6]. Internal conversion is a conventional mechanism of the electron–nucleus interaction which is approved by decades of practice of application to nuclear physics. It is applied to measuring spins and parities of the nuclear states. Being an alternative channel of nuclear deexcitation, internal conversion

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drastically affects the nuclear lifetimes, shortening them typically by seven to eight orders of magnitude and more [7]. Internal conversion is however a single-time mechanism, which is usually related with very short times. Moreover, it destroys the shell, and therefore bares a destructive tendency, able to break up molecular bonds. Mathematically, the conversion amplitude is calculated in the first order of the perturbation theory.

It was in the paper by Krutov [8] who proposed that due to high values of internal conversion coefficients (see next section), next orders of the interaction might be essential. He supposed that the converted electron may return back to its position, reemitting the nuclear quantum. This already sets a small bridge to a new sort of intranuclear interaction, as the photons can be absorbed by a neighbor nucleus in the molecule. It is fairly noticeable that the process was named by the authors "the electronic bridge". Discrete internal conversion was proposed in ref. [5], which is basically aimed at dealing with the discrete nuclear states. In the limit of zero energy of the nuclear photon, DC provides a mechanism of elastic intranuclear interaction which has an advantage of practically infinite time, which is only limited by the lifetime of the molecule. Due to this circumstance, this can provide remarkably noticeable effects even if the elementary single-time interaction itself may be small. Actually, discrete conversion is related with such fundamental processes in science as nuclear fission.

In 1939, Bohr and Wheeler proposed the version of nuclear theory, which since that time is applied for description of this wonderful process [9]. Ten years later, Wheeler told out an idea that fission of ^{238}U nucleus in the muonic atom can be induced by a radiationless muon transition $2s \to 1s$ [10]. Later investigation showed that the population of the $2s$ level is less probable, of a few percent of that for the $2p$ state, and additionally, the radiative $2s \to 2p$ transition makes a strong competition. However, it was shown that the radiationless transition probability for higher multipoles, $E1$ for the $2p$, $3p \to 1s$ transition [3], $E2$ for the $3d \to 1s$ [11, 12], and even $E3$ for the $3d \to 2p$ transition [13, 14] are all of approximately the same probability. Experiments fully confirmed the Wheeler's conjecture and the further predictions [15].

Calculations [13, 14] revealed the strong resonance coupling arising in muonnic atoms between the nucleus and bound muon. In refs. [6, 7] special attention was brought to the fact that the radiationless transition is a reverse conversion process. It was considered in terms of the radiative nuclear width and internal conversion coefficients (ICC). That explained the reason why higher multipole transitions turn out to be of about the same probability. In 1958, Morita proposed a similar process of Nuclear Excitation in Electron Transition, which is since known as NEET [16] between the nucleus and the shell, or the muon in the case of muonic atom. This coupling offers a real tool of mastering nuclear electromagnetic transitions through resonance with the electron shell, using laser or synchrotron radiation.

The present paper is built as follows. (i) We remind in main features general internal conversion theory. (ii) We present the theory of the resonance internal conversion and outline experiments where it was discovered. (iii) We make calculation of an unexpected mode of the spin–spin interaction of the protons in a sole or organic molecule and the related frequency of this kind of interaction.

2. Internal Conversion

As a result of prompt fission, the muon is entrained on one of the fragments, mostly on the heavy one. The fragment is excited, and emits γ's, neutrons, protons, alphas. Emitted γ's can be absorbed by the muon, which leaves the atom (Fig. 1).

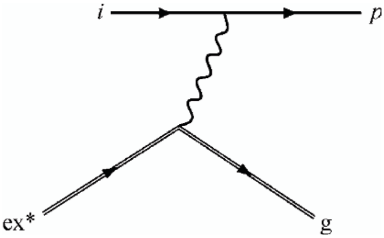

Figure 1. Feynman graph of internal conversion

Such a process is well known in electronic atoms. It is called *internal conversion*. The necessary condition is

$$\omega_n > I, \tag{1}$$

where ω_n is the nuclear transition energy and I is the ionization potential.

A very useful value is internal conversion coefficients (ICC), which is defined as the ratio of the conversion and radiative transition probabilities,

$$\alpha(\tau L) = \frac{\Gamma_c}{\Gamma_\gamma^{(n)}}, \tag{2}$$

τ, L being the type and multipole order of the transition. α is nearly independent of the nuclear model. This allows one to reverse Eq. (2) and put down

$$\Gamma_c = \alpha \Gamma_\gamma^{(n)} \tag{3}$$

Values of α are tabulated. Eq. (3) hence allows one to estimate the conversion transition probability, as soon as the radiative nuclear width is known. Internal conversion is one of the principal tools for nuclear spectroscopy.

3. Direct Evidence of Intra-Nuclear Interaction in UF_4 Molecule

Direct evidence of the resonance interaction of different atoms in a UF_4 molecule has been obtained in [17]. In that paper, decay of the 76.8 eV isomeric state of the ^{235}U was studied. This state mainly decays through internal conversion of the ^{235}U transition to the ground state in the upper shells. The energy of the converted electrons E_e is

$$E_e = E_n - I_k \quad , \tag{4}$$

where E_n is the nuclear transition energy, and I_k is the ionization potential of the *k*th shell. In accordance with (4), distinctive lines were observed in the spectrum of the conversion electrons which corresponded to ionization of different shells (Fig. 2). Surprisingly, among the lines, there was also one broadened peak at the energy of 42.6 eV, corresponding to the conversion in the 2*s* shell of the fluor atom.

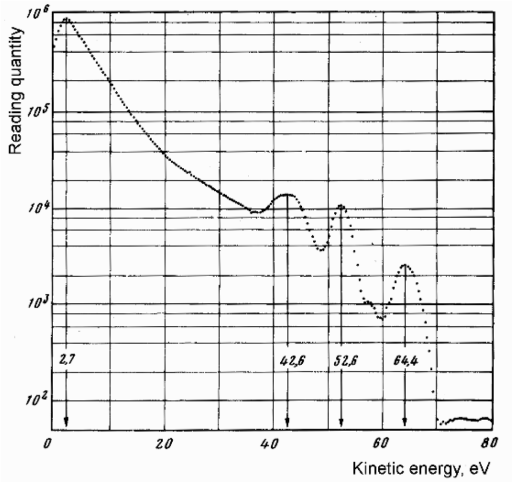

Figure 2. Spectrum of the conversion electrons of ^{235m}U introduced into the UF$_4$ matrix

This experimental result was explained in [18]. It was due to mixing of the 2*s* shell of the fluor atom with the 6$p_{1/2}$ shell of the uranium atom. Mixing occurs due to resonance interaction of the shells which have close binding energies. This mixing was also showed to lead to asymmetry in the angular distribution of the conversion electrons. The asymmetry has a quite general basis. The same reason causes the asymmetry of the muons converted from the fissile nucleus at the moment of separation of the two formed fragments [19]. A similar asymmetry arises in the angular distribution of the α particles within the frame of the surface cluster model, when α clusters formed on the nuclear surface escape the nucleus [20].

4. Resonance or Bound Internal Conversion (BIC)

If the condition (1) is broken, i.e. $\omega_n < I$, the conversion electron cannot leave the atom. It occupies an excited electron level, forming an unstable intermediate state (Fig. 3).

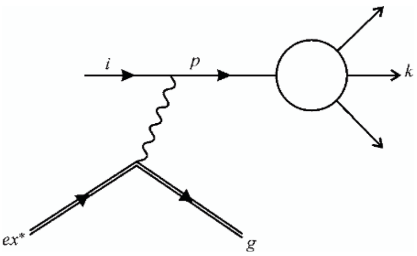

Figure 3. Feynman graph of the resonance internal conversion

This state then undergoes decay. This is mainly performed by the radiative electron transition, filling the hole formed in the place of the conversion electron. We still can formally calculate the α value by means of the formula, used for the traditional ICC calculations, inserting the wave function of the related discrete atomic state as the conversion electron function:

$$\alpha_d(\tau L) = \sum\nolimits_{\kappa} | M_{\kappa}^{(\tau L)} |^2, 0.1em M_{\kappa}^{(\tau L)} = Q_{\kappa}^{(L)} R_{\kappa}^{(\tau L)} \tag{5}$$

$$Q_{\kappa}^{(L)} = -\sqrt{\frac{\alpha\pi\omega}{L(L+1)}} C_{j_i - \frac{1}{2} L 0}^{j_f - \frac{1}{2}} ;$$

$$R_{\kappa}^{(ML)} = (\kappa_1 + \kappa)(R_1 + R_2)$$

$$R_{\kappa}^{(EL)} = L(R_3 + R_4) + (\kappa_i - \kappa_f - L)R_5 + (\kappa_i - \kappa_f + L)R_6$$

with R_i – the radial integrals

$$R_1 = \int_0^{\infty} G_i F_f X_L dr 0.1em \qquad R_2 = \int_0^{\infty} F_i G_f X_L dr$$

$$R_3 = \int_0^{\infty} F_i F_f X_L dr 0.1em \qquad R_4 = \int_0^{\infty} G_i G_f X_L dr$$

$$R_5 = \int_0^{\infty} G_i F_f X_{L-1} dr 0.1em \qquad R_6 = \int_0^{\infty} F_i G_f X_{L-1} dr.$$

Here $\alpha_d(\tau L)$ is the discrete ICC, τL is the type and multipole order of the transition, *EL* and *ML* stand for the electric and for the magnetic types, respectively. Subscripts *i* and *f* denote the initial and final states, respectively; $\kappa = (l - j)(2j + 1)$ is the relativistic quantum number, with l, j for the orbital and total angular moments; *G* and *F* are the big and small components of the radial wave function, normalized at

$$\int_0^\infty [G^2 + F^2(r)]dr = 1. \qquad (6)$$

Furthermore, $\alpha \approx 1/137$ is the fine structure constant, $M_\kappa^{(\tau L)}$ are the conversion matrix elements, ω is the nuclear transition energy. R_{1-6} are the radial integrals, with X_ν the interaction potential of the nuclear and electron transition current. With account of the finite nuclear size, the latter becomes

$$X_\nu = h_\nu(\omega r) \qquad (7)$$

for r ≥ R_0, with R_0 – the nuclear radius. For r ≤ R_0, nuclear model of the surface transition current provides an adequate description [21]:

$$X_\nu = \frac{h_\nu(\omega R_0)}{j_\nu(\omega R_0)} j_\nu(\omega r). \qquad (8)$$

In the case of discrete conversion, however, the α_d value acquires dimension of energy, due to another normalization of the wavefunction [5]. Therefore, it cannot serve as ICC (2) anymore. There is an evident way, to form a dimensionless factor R by multiplying α_d by the resonance Breit–Wigner factor. We add a subscript d to the sign of α_d, to distinguish it from a traditional ICC. Then the expression for R becomes as follows:

$$R = \frac{\alpha_d \Gamma / 2\pi}{\Delta^2 + (\Gamma/2)^2}, \qquad (9)$$

where Γ is the full width of the intermediate atomic state, and Δ is the defect of the resonance of the nuclear and electron transitions. With the account of BIC, resulting lifetime of the nuclear level will be

$$\lambda = \frac{\lambda_\gamma}{1 + \alpha_{tot} + R}$$

where λ_γ is the radiative lifetime, and α_{tot} is the total ICC.

5. Tuning BIC

It follows from Eq. (9) that the BIC probability can be enhanced in the case of resonance by the value of

$$\frac{R_{\text{res}}}{R} \simeq \left(\frac{\Delta}{\Gamma}\right)^2 \qquad (10)$$

For nuclei, typical values of $\Delta \simeq 1\,\mathrm{keV}$. Typical value of Γ is ~20 eV (which is a typical *K*-hole width), or $\sim 10^{-6}$–10^{-5} eV in the case of BIC in the outer electron shells. Therefore, expected effect can be around ten orders of magnitude and more [22, 6].

The idea is to arrange a two-photon resonance. Consider atom in an external field of a plane electromagnetic wave. Some atomic electron can go to an excited state by absorption of one or several photons from the field. The probability of multiphoton absorption increases drastically if the total energy of the absorbed photons approaches the difference of the electron levels. This effect is used by RIS – resonance ionization spectroscopy. Let us consider the two-photon resonance, and replace one photon of the field by the nuclear photon [3]. This is laser assisted nuclear BIC transition, as the electron makes a two-photon transition to an excited state, one photon being from the nucleus, and the other from the field. Necessary condition is then

$$\omega_n \pm \omega_l = \omega_a. \tag{11}$$

The two signs in (11) correspond to either an absorption, or induced emission of a photon of the field. The both probabilities are of the same value.

6. Resonance Conversion in Experiments

A bright example of resonance effect of BIC is provided by characteristic muonic X-rays from heavy prompt fission fragments. This radiation arises due to resonance excitation of the bound muon to the 2*p* state, with reemission in the succeeding back muon transition 2*p* → 1*s*. This resonance effect predicted in ref. [10] is shown in Fig. 3. The effect was experimentally studied in paper [4]. It was shown that taking this process into account leads to better value of χ^2 in filling the experimental spectrum of γ rays from prompt fission fragments.

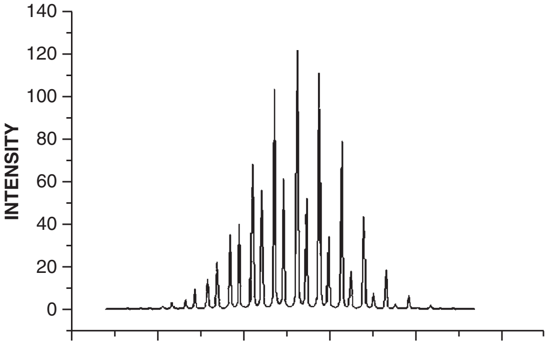

Figure 4. Spectrum of γ rays from prompt fission fragments, calculated with the account of the μ in the orbit

The other example was demonstrated by the 35 keV *M*1 transition in ^{125}Te [6]. In neutral atom, this level mainly deexcites via internal conversion in the *K* shell, with α (*M*1) = 11.5. But for 45- and 46-fold ions the condition (1) is broken. It was therefore expected that the lifetime will increase for these ions by an order of magnitude (Fig. 5).

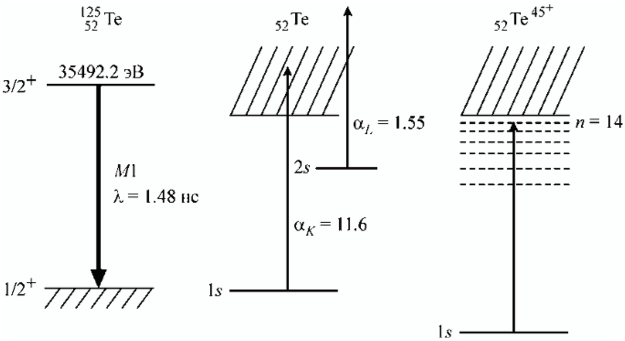

Figure 5. Scheme illustrating how traditional internal conversion transforms into the resonance one in ionized atoms of ^{125}Te

Experiments however showed that the lifetime holds [6]. The observed paradox was explained by the resonance conversion – BIC, which takes place of the ordinary one. In the succeeding papers, the fluorescence yield from the 1*s*-hole states caused by the resonance conversion was observed. *The observed numerical probability of BIC came to accordance with theory.*

A process of great importance for understanding possible consequences of the interaction through the bound electrons is mechanism of interaction of nuclear levels with different spins and even opposite parities. Such an interaction was assumed by Wigner yet. It was noted by Luboshitz [23]. That was discovered as we saw in the muonic atoms. A very strong effect of this kind is proposed in hydrogen-like ions of ^{229}Th.

The other component of our final theory is comprised by the hyperfine splitting. This is a classical effect of interaction of two magnetic moments in atom: that of the nucleus and an odd electron from the shell. In the next two sections, let us see what these look like in finer detail.

7. Hyperfine Splitting in ^{209}Bi^{82+}

The hyperfine shift (HFS) is given by the diagonal matrix element of the electron-nucleus interaction. The corresponding Feynman diagram is presented in Fig. 6.

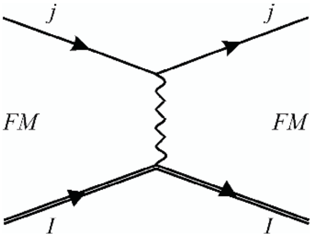

Figure 6. Feynman graph for the HFS

Comparison with Fig. 1 shows that this diagram is the same as that for the internal conversion amplitude. This means that if the QED amplitude is an analytical function of its kinematics variables, then this amplitude describes many processes along with the internal conversion: electron scattering on the nuclei, nonphotonic positron annihilation on bound electrons with nuclear excitation, pair and resonance internal conversion, and others [1, 2]. Specifically, the diagram in Fig. 6 is for a particular case of RC for the $M1$ interaction with the energy of the virtual photon $\omega = 0$. It was shown by Sliv [21] in the general case of internal conversion that the resulting matrix element depends on the nuclear model for the transition current. In the given case, that means that HFS depends on the space distribution of the magnetisation inside the nucleus. This is in contrast with the magnetic moment itself which can be measured with high precision using an independent model. We note that the $M1$ transitions are most sensitive to the nuclear model.

The diagram of Fig. 6 was calculated in a general form in [1, 2]. The shift is produced by the magnetic and quadrupole interaction with the nucleus. In Section 9 we consider a possible spin flip of two hydrogen nuclei in a molecule caused by the interaction of the magnetic moments of the protons. This arises in the second order of the perturbation theory on the hyperfine magnetic interaction of the protons with a common orbital electron. Analogously, quadrupole interaction can be also considered. Generally, that turns out to be of the same order of magnitude. Denote I, j the nuclear spin and the electron orbital moment. Then $L = 1$ for the magnetic, and $L = 2$ – for the quadrupole interaction. Let F be the full moment of the atom, and μ – the magnetic moment of the nucleus. For the hyperfine shift, the following expression through the ICC can be obtained.

$$\begin{gathered} E_{hfs}(M1) = (-1)^{j+I-F} - 3\frac{e\hbar}{2M_p c}\mu\sqrt{\frac{3}{\pi}}\frac{W(IIjj;LF)}{C(II10|II)}\frac{\sqrt{2I+1}}{(2L+1)!!}\times \\ \times\left(1+\frac{m}{M}\right)^{-3}\sqrt{\lim_{\omega\to 0}\omega^{2L+L_{\alpha\partial(\tau l)(2j+1)(2L+1)(L+1)/L}}} \end{gathered}, \qquad (12)$$

where m_e, M and M_p stand for the electron, nucleus and proton masses, respectively, C is Clebsh–Gordan coefficient, W is Racah coefficient.

This theory was compared to experiment in [1] for the hydrogen-like ions of ^{209}Bi. The results of the calculation of the magnetic hyperfine splitting in various nuclear models are presented in Table 1.

TABLE 1. Hyperfine splittings (h.s.) calculated for the hydrogen-like ions of ^{209}Bi in various nuclear models: surface (SC) and volume (VC) nuclear currents, uniform and Fermi (F) charge distribution, without penetration (NP), with polarization of a vacuum ruled out in comparison with experiment and other calculations

Model	Nuclear currents	SC	SC	SC	NP	VC	VC
	Charge distribution	U	F	U	–	U	F
	Vacuum polarization	VP	VP	No VP	VP	VP	VP
HFS		5.105	5.107	5.081	5.192	5.138	5.141
Experiment		5.0841(8)					
Calculation [11]		5.091					

The calculations are conducted by making use of the package of computer codes in RAINE [24]. Finite nuclear size, higher QED corrections for polarization of vacuum, and electron self-energy are included. We do not consider corrections for the nuclear recoil energy. That is of the order of (m/M), with m and M being the electron and nuclear masses, respectively, and hence contributing to the sixth decimal. As can be seen from the Table, the latter value is hardly distinguishable in experiment in view of the uncertainty brought about by the nuclear model [2] which is at the level of 1%. This result was expected from the internal conversion theory. Calculated values are in reasonable agreement with the experiment and other calculations. What we can know from comparison with the experiment is a characteristic radius of distribution of the magnetic current in the nuclear volume. The surface distribution looks most plausible, given that the magnetic moment is produced mainly by the last odd nucleon. In the case of s valence nucleons, or in the excited state of giant dipole resonance, a volume distribution can be expected which will be immediately reflected in the enlarged HFS.

8. Spin-Flip in Hydrogen-Like Ions of ^{229}Th^{89+}

A spectacular example of the spin-flip magnetic interaction with the orbital electron was presented in [25]. hydrogen-like ions of ^{229}Th have been considered. It was noted in ref. [26] that due to an extremely low energy, the hyperfine interaction arising in the hydrogen-like ions of ^{229}Th can mix nuclear states of the same parity, but differing by one unit of spin. This arises due to enormous magnetic field which is produced in the vicinity of the nucleus by the electron in the K shell [26]. Such mixing leads to a drastic effect of acceleration of the nuclear de-excitation from the isomeric state. This occurs via spin-flip of the orbital electron, just as transitions between normal components of hyperfine structure. To better realize the effect, one can imagine a neutral atom of ^{229m}Th with an excited nucleus. Its lifetime is hours, as mentioned before. If, however, all the electrons are stripped but one, or merely a hole is produced in the K shell, the nucleus gets deexcited promptly! This mechanism of acceleration may be compared to acceleration of interband transitions arising due to Coriolis mixing.

A relevant experiment could be conceived at GSI, in Darmstadt. Efforts should be made to detect the energies and lifetimes of the transitions. Then the four values: $B(M1)$,E_{isom}, magnetic moments μ_1 and μ_2 in the ground and excited states, are unambiguously determined by the experimentally observable lifetime of any of the transitions involving the $F = 2$ component, and three energies of the excited hyperfine components (with respect to the ground level with $F = 2$). Earlier, the hyperfine structure of ^{209}Bi has been measured there recently [27]. A quantity of atoms needed for the experiment can be taken from available artificial radioactive sources, or hydrogen-like ions can be produced directly in the experiment, e.g. in U–Be collisions. Then the components *II* to *IV* can be excited by irradiation with the field of a laser. Observation of the resonancely scattered photons would provide full information: separation energy and electromagnetic strength of the transition between these two states. That would also give an example how the probability of the electromagnetic transition in bare nuclei can be enhanced by orders of magnitude in comparison with neutral atoms. Such an experiment would also give a chance for discovering a new effect first predicted in paper [23], namely, spin mixing in nuclei arising due to hyperfine interaction.

Let us consider physics of this process in finer detail. In Fig. 7 we present a scheme of the components of the hyperfine structure of ^{229}Th^{89+}.

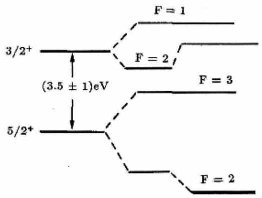

Figure 7. Hyperfine structure in the hydrogen-like atom of ^{229}Th^{89+}

The nuclear spin mixing arises in the ground and excited states with the total angular momentum $F = 2$, designated as *I* and *II*, respectively. The wave functions of the states can be given as follows:

$$\Psi_I\left(FM_2\right) = -\beta\left|\frac{3}{2}\frac{1}{2};2M_2\right\rangle + \left|\frac{5}{2}\frac{1}{2};2M_2\right\rangle \tag{13}$$

$$\Psi_{II}\left(FM_1\right) = \left|\frac{3}{2}\frac{1}{2};2M_1\right\rangle + \beta\left|\frac{5}{2}\frac{1}{2};2M_1\right\rangle \tag{14}$$

with $F = 2$. For the other two components,

$$\Psi_{III}\left(FM_1\right)=\left|\frac{5}{2}\frac{1}{2};3M_1\right\rangle \quad \left(F=3\right), \tag{15}$$

$$\Psi_{IV}\left(FM_1\right)=\left|\frac{3}{2}\frac{1}{2};1M_1\right\rangle \quad \left(F=1\right), \tag{16}$$

where

$$\left|jI;FM\right\rangle=\sum_{m,\mu}C\left(jmI\mu|FM\right)\chi_{jm}\phi_{I\mu} \tag{17}$$

is wavefunction of the atomic state with the total momentum F, j and I being the nuclear and electron momenta, respectively.

Consider first the transition $II \rightarrow I$. In the first order of the perturbation theory, a diagonal transition between the main components is possible, when the electron state is not changed. Single-particle estimate for the M_1 nuclear transition with the energy of 3.5 eV results in the lifetime of about 10 min (e.g., [28]), which value should be multiplied by a typical hindrance factor of about 300. The expected lifetime is, therefore, about 50 h.

Off-diagonal transitions between the admixed components with the same nuclear states also arise in the same order of the perturbation series. They can be considered as pure electron transitions between the states of hyperfine structure leaving the nucleus in the same state. They are much faster, and give the main contribution. Correspondingly, the amplitude of such $M1$ transition can be obtained by direct algebra as follows:

$$\begin{gathered}\left\langle F_2M_2;Ij\right|H_\gamma^{'}\left(M1;q\right)\left|F_1M_1;Ij\right\rangle=\left(-1\right)^{I-j-1+F_2}\sqrt{2F_2+1}\left\langle I\|1\|I\right\rangle\times\\ \times W\left(F_2IF_1I;j1\right)C\left(F_2M_21-q|F_1M_1\right)\end{gathered}, \tag{18}$$

where

$$\begin{gathered}\left\langle I\|1\|I\right\rangle=\sqrt{\frac{\alpha\omega\left(2l_i^{'}+1\right)\left(2l_f+1\right)}{\pi L\left(L+1\right)\left(2j+1\right)}}\left(2j_i+1\right)C\left(l_f0l_i^{'}0;L0\right)\times\\ \times W\left(l_fj_fl_i^{'}j_i;\frac{1}{2}L\right)\left(k_i+k_f\right)\int\left(G_iF_f+F_iG_f\right)j_L\left(\omega_nr\right)dr\end{gathered} \tag{19}$$

is the reduced matrix element of the electron $M1$ radiative transition. One may say that the nucleus remain a spectator in this transition. We made use of the fact that $H_\gamma^{'}\left(M1;q\right)$ is a tensor operator of rank 1, with q being the projection on the quantization axis. In Eq. (19), ω is the nuclear transition energy, j_i is the total moment of an initial state electron, l_i is the orbital moment of the initial electron, $l_i^{'}=2j_i-l_i$, l_f is the orbital moment of the final electron, L is the transition multipolarity,

$k = (l-j)(2j+1)$ is the relativistic quantum number, $j_L(\omega r)$ is the spherical Bessel function, G and F are the large and small components of the radial wave function, index i refers to the initial electron state, index f refers to the final electron state.

With account of the off-diagonal amplitudes, the expression for the radiative transition probability corresponding to the amplitude in Eqs. (13)–(16) acquires the following form:

$$\Gamma_\gamma(F_2 \to F_2) = 2(2F_2+1)W^2\left(l_f j_f l_i' j_i; \frac{1}{2} L\right)\beta^2\Gamma_e \tag{20}$$

where Γ_e may be considered as the electron widths, β^2 is the probability of the admixture, with the kinematic factors brought about by the hyperfine interaction with the nucleus. The calculated radiative widths Γ_γ for the $M1$ transitions have been calculated by means of the complex of computer codes RAINE [24]. Dirac electronic wave functions are calculated with account of the finite nuclear size. Transition energies between the components, as well as the value of the admixture probability $\beta^2 = 0.0206$, were used as calculated in ref. [26]. The results of the calculation are summarized in Table 2. One can see that account of the spin mixing leads to drastic acceleration of the radiative transitions, up to five orders of magnitude.

TABLE 2. The calculated radiative transition probabilities between various hyperfine components in the hydrogen-like ions of ^{229}Th

Transition	II → I	IV → I	III → I	IV → I
Energy, eV	3.02	4.17	1.04	0.09
Lifetime, s	0.037	0.027	0.11	8.6

9. Interaction of the Spins of Hydrogen Nuclei in a Molecule

Consider a sole H_2 molecule, or an ion of H_2^+, which is a part of a complex organic molecule. The two protons can interact through the electron. The Feynman graph is presented in Fig. 8.

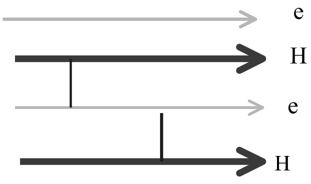

Figure 8. Feynman graph of the spin–spin interaction through an orbital electron in a hydrogen molecule

Like in the case of hydrogen-like Bi^{82+}, the interaction is mediated by a virtual photon, interaction with which can be accompanied by spin flip. Interacting with the photon, the protons can exchange with the direction of their spin, i.e., simultaneously change its spin projection. In the case of a sole molecule, this is possible if both the protons are in a singlet state, that is with the opposite spin direction. In the triplet case, the simultaneous change of the spin direction is possible, as the moment can be transferred to the rest of the molecule. Let us consider the singlet case.

In the case of H_2^+, the electron spin-flip occurs plainly. In the case of a neutral molecule, the spin-flip encounters with the Pauli exclusion principle, as the other 1*s* state, with the opposite spin direction, is occupied. Therefore, the electron must skip to the 2*p*, or 3*d* state. Virtually, such a process is possible for a time of $t \sim \hbar/\Delta E$, where ΔE is the violation of energy. Then, in the second interaction, the electron flips the spin again and comes back to the primary 1*s* state. Let us calculate the amplitude of this process.

This can be done in the resonance approximation [1]. According to the Feynman's superposition principle, amplitude of the graph in Fig. 8 can be represented as a product of the amplitudes of the two consecutive amplitudes of the discrete-conversion transition H_c, and the Green's function, or propagator $G_E(\mathbf{r},\mathbf{r}')$ of the electron propagating between the conversion vertices, E being the electron energy:

$$F_{s.-fl.} = H_c(\mathbf{r}')G_E(\mathbf{r},\mathbf{r}')H_c(\mathbf{r})\,. \tag{21}$$

The Green's function in the spectral representation reads as

$$G_E(\mathbf{r},\mathbf{r}') = \sum_n \frac{\phi_n(\mathbf{r}')\rangle\langle\bar{\phi}_n(\mathbf{r})}{E - E_n + i\frac{\Gamma_n}{2}}\,. \tag{22}$$

Here index n enumerates the states of the full set of the electron eigenstates in the intermediate state (Furry's representation). To assess the amplitude, one can restrict oneself by the nearest 2*s* state, in which case the denominator in (22) is minimal. Then we arrive at the following expression for the amplitude:

$$F_{s.-fl.} = H_c(\mathbf{r}')\frac{1}{E_{2s}}H_c(\mathbf{r})$$

As we saw, H_c is of the order of the hyperfine splitting. For a hydrogen like atom this is 5.9×10^{-6} eV (the famous 21-cm line). Substituting this value into (23), with $E_{2s} \approx 10$ eV, we get a numerical estimate $F_{s.-fl.} \sim 10^{-12}$ eV.

10. Conclusion

Resonance conversion is an instrument giving rise to interaction of the nuclei via the electron shell. In spite if that the magnetic interaction is very local, the probability of spin flip of the nuclei, turns out to be of a quite significant value. Typical frequency of oscillations of the system due to this circumstance is $\sim 5 \times 10^{-12}$ s^{-1}.

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FIELD DRIVEN CURRENT IN NONLINEAR LOW-DIMENSIONAL NANOSYSTEMS

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Abstract. We study the ratchet behaviour of polarons in diatomic molecular chains under the influence of an external electromagnetic field which is periodic in time. We show that in asymmetric chains a harmonic unbiased field causes a drift of polarons. This phenomenon has a threshold with respect to the intensity and the frequency of the field. In spatially symmetric chains a harmonic periodic electric field generates oscillations of polarons but does not result in their movement. Such a drift current can be induced in symmetric chains by a time periodic asymmetric external field. This complex dynamics of polarons is generated by the interplay between the Peierls–Nabarro barrier and dissipative effects in the system. The dependence of the amplitude of soliton oscillations and the velocity of the drift are calculated depending on the intensity of the field, its frequency and the coefficient of the energy dissipation.

Keywords: ratchet effect, polaron, Peierls–Nabarro potential, field driven current, low-dimensional nanosystems

1. Introduction

The ratchet phenomena have been attracting a great deal of attention due to their importance both for understanding of the functioning of biological motors and for promising technical applications in nanotechnologies, including molecular motors and ratchets. The ratchet phenomenon consists in the appearance of a directed current (drift) under the action of stochastic or deterministic unbiased (zero mean) ac forces [1]. As a result of many studies, the ratchet principles have been ascertained and now many interesting theoretical models of ratchets have been proposed and a large veriety of experimental realizations have become available (see, e.g., review [1] and references therein). In particular, semiconducting heterostructures, such as diode (n,p)-junctions,

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semiconductor superlattices, Josephson junction arrays, SQUID ratchets, quantum dot arrays with broken spatial symmetry have been engineered and shown to possess ratchet properties.

In this paper we show that the ratchet phenomenon can be realized in (quasi)one-dimensional molecular chains which support the existence of electron self-trapped states. Such states, generally called polarons and in one-dimensional systems known as solitons, are formed as localized states of electrons due to the electron–lattice interaction [2–5]. Their properties have been studied in great detail both theoretically and experimentally. The class of low-dimensional molecular systems in which polarons exist or are believed to exist, is quite large. It includes quasi-1D organic and inorganic compounds (like conducting platinum chain compounds), conducting polymers (e.g., polyacetylene [3], polypyrrole [6], polythiophene [7]), biological macromolecules (α -helical proteins [2], DNA [8]) etc.

In general, the necessary conditions for the ratchet effect under the action of stochastic or deterministic external forces, both in classical and quantum systems, involve the energy dissipation in the system and breaking of spatial and/or temporal symmetries [1, 9]. The mechanism for the appearance of the directed motion caused by the zero-mean force, has been established for particles moving in spatial periodic ratchet potential, and has been extended to soliton ratchets [10–13]. Some of the necessary requirements for the ratchet effect, are naturally intrinsic to solitons in molecular systems. Energy dissipation in molecular systems is always present due to the interaction of atoms with the many degrees of freedom of the surrounding medium which can be considered as a thermal bath. This is especially true for biological macromolecules which are surrounded by the cellular cytoplasm. In a molecular chain, due to its discreteness, solitons move in the Peierls–Nabarro potential which is periodic with the period equal to the lattice constant [14]. The presence of the Peierls–Nabarro potential plays essential role in the ratchet behaviour of solitons in discrete systems [12, 13]. Therefore, one can expect the ratchet phenomenon also for polarons in molecular chains. In molecular chains with a reflection symmetry the Peierls–Nabarro potential is symmetrical as it is in a simple molecular chain [14]. This symmetry can be broken in asymmetric chains with more complicated structure and one can expect that such chains would exhibit the ratchet effect under the influence of external harmonic forces. The temporal symmetry can be broken by applying an asymmetric periodic force, e.g. by apropriate biharmonic driver, which results in unidirectional (in average) soliton motion in discrete soliton ratchets [12, 13].

2. The Model and Dynamical Equations

To demonstrate the existence of the ratchet effect for polarons we have performed some numerical simulations of the polaron dynamics in asymmetric molecular chains in the presence of an external periodic unbiased electromagnetic field. We consider a diatomic molecular chain that contains two different atoms or groups of atoms in a unit cell, periodically arranged along the chain axis at their equilibrium positions, $z^0_{n,1} = na, z^0_{n,2} = na + b$, where a is a lattice constant and b is a distance between the two atoms in a unit cell. The total Hamiltonian of a molecular chain in an external field is represented by the following sum:

$$H = H_0 + H_{int}, \qquad H_0 = H_e + H_{ph} + H_{e-ph} \tag{1}$$

Here the Hamiltonian H_0 describes the states of electrons in a molecular chain taking into account the electron interaction with lattice vibrations, and in the approximation of the nearest-neighbour hopping interaction in the site representation H_e is given by the expression

$$H_e = \sum_n [E_1\, a^\dagger_{n,1} a_{n,1} + E_2\, a^\dagger_{n,2} a_{n,2} - J_s (a^\dagger_{n,1} a_{n,2} + a^\dagger_{n,2} a_{n,1}) - J_l (a^\dagger_{n,1} a_{n-1,2} + a^\dagger_{n-1,2} a_{n,1})], \tag{2}$$

where $a^\dagger_{n,j}$ ($a_{n,j}$) are creation (annihilation) operators of an electron on the site (n,j); E_j is the on-site electron energy accounting for the influence of the neighbouring atoms. Furthermore, J_s and J_l are the energies of the hopping interactions with the nearest neighbours from the same unit cell and from the neighbouring cell, respectively. In our work we have studied only one extra electron in the chain, and therefore, we can omit the electron spin index. The Hamiltonian of the lattice vibrations, H_{ph}, in the harmonic approximation and in the approximation of the nearest-neighbour interaction, is given by

$$H_{ph} = \frac{1}{2}\sum_n [\frac{p^2_{n,1}}{M_1} + \frac{p^2_{n,2}}{M_2} + w_s (u_{n,1} - u_{n,2})^2 + w_l (u_{n,1} - u_{n-1,2})^2], \tag{3}$$

where M_1 and M_2 are masses of atoms, and $u_{n,j}$ are the longitudinal displacements of atoms from their equilibrium positions. Also, $z_{n,j} = z^0_{n,j} + u_{n,j}$; $p_{n,j}$ are the momenta, canonically conjugate to $u_{n,j}$; w_s and w_l are the elasticity constants describing the strengths of the interactions between, respectively, the nearest-neighbour atoms belonging to one unit cell and to the neighbouring cells.

The electron–phonon interaction originates from the dependence of the hopping interactions J_s, J_l, of the site energy E_j on the interatomic separation. Taking into account such a dependence of the site energy only, we obtain the electron–phonon interaction Hamiltonian, H_{int}, which in the linear approximation with respect to the lattice displacements takes the form:

$$\begin{aligned} H_{e-ph} = \sum_n [\, & a^\dagger_{n,1} a_{n,1} \left[\chi_l (u_{n,1} - u_{n-1,2}) - \chi_s (u_{n,1} - u_{n,2})\right] + \\ & + a^\dagger_{n,2} a_{n,2} \left[\chi_l (u_{n+1,1} - u_{n,2}) - \chi_s (u_{n,1} - u_{n,2})\right]] \end{aligned} \tag{4}$$

Here χ_s and χ_l are the coefficients of the electron–phonon interaction between nearest neighbours.

Finally, the Hamiltonian of the interaction with the external electric field $E(t)$ is given by

$$H_{int} = -eE(t)\sum_{n}\left((na - z_0)a^{\dagger}_{n,1}a_{n,1} + (na + b - z_0)a^{\dagger}_{n,2}a_{n,2}\right) \tag{5}$$

After diagonalization of the electron and phonon Hamiltonians (2) and (3), the Hamiltonian of a chain, H_0, takes the form of the Fröhlich-type Hamiltonian

$$\begin{aligned} \mathrm{H}_0 = \sum_{\mathrm{k},\lambda} \mathrm{E}_{\lambda}(\mathrm{k})\,\mathrm{c}^{\dagger}_{\mathrm{k},\lambda}\mathrm{c}_{\mathrm{k},\lambda} + \sum_{\mathrm{q},\nu} \hbar\omega_{\nu}(\mathrm{q})\left(\mathrm{b}^{\dagger}_{\mathrm{q},\nu}\mathrm{b}_{\mathrm{q},\nu} + \frac{1}{2}\right) + \\ + \frac{1}{\sqrt{\mathrm{N}}}\sum_{\mathrm{k},\mathrm{q},\nu}\sum_{\lambda,\lambda'} \mathrm{F}^{(\nu)}_{\lambda,\lambda'}(\mathrm{k},\mathrm{q})\,\mathrm{c}^{\dagger}_{\mathrm{k},\lambda}\mathrm{c}_{\mathrm{k}-\mathrm{q},\lambda'}\,\mathrm{Q}_{\mathrm{q},\nu} \end{aligned} \tag{6}$$

where $F^{(\nu)}_{\lambda,\lambda'}(k,q)$ is the function of electron–phonon coupling. The electron and phonon spectrum of our chain has two electron bands and two phonon modes. The dispersion laws $E_{\lambda}(k)$ of the two electronic bands, labeled by the index $\lambda = U,L$ for the upper and lower ones, are:

$$E_{\lambda}(k) = E_0 \pm \frac{1}{2}\sqrt{\Delta_0^2 + 4J^2(k)} = E_0 \pm \frac{1}{2}\sqrt{\Delta_0^2 + 4J^2 - 16J_sJ_l\sin^2\frac{ka}{2}} \tag{7}$$

The frequencies of the two phonon modes, acoustical and optical, $\nu = ac, op$, are given by:

$$\omega^2_{ac,op}(k) = \frac{1}{2}\left(\frac{W}{\mu} \mp \sqrt{\frac{W^2}{\mu^2} - 16\frac{w_s w_l}{M_1M_2}\sin^2\frac{ka}{2}}\right) \tag{8}$$

Here $k = \frac{2\pi}{Na}\nu$ ($\nu = 0, \pm1, \ldots$) denotes the quasi-momentum, and we have introduced the following notation: $\mu = M_1M_2/M$, $M = M_1 + M_2$, $E_2 + E_1 = 2E_0$ and $E_2 - E_1 = \Delta_0$, $J = J_s + J_l$.

In the absence of an external field the Fröhlich Hamiltonian (6) describes the states of electrons interacting with lattice vibrations. Self-trapped states of electrons in such systems are usually described in the adiabatic approximation which is equivalent to the semiclassical consideration when the vibrational subsystem is treated as a classical one. In the adiabatic approximation the wave function of the system is represented in a multiplicative Born–Oppenheimer form which, for one extra electron in the chain, takes the form:

$$\left|\Psi\right\rangle = U\left|\psi_e\right\rangle,\ |\Psi\rangle = U|\psi_e\rangle, \quad |\psi_e\rangle = \sum_{n,j}\Psi_{n,j}a^{\dagger}_{n,j}\,|0\rangle = \sum_{k,\lambda}\psi_{k,\lambda}c^{\dagger}_{k,\lambda}\,|0\rangle, \tag{9}$$

where U is the unitary operator of the coherent atom displacements induced by the presence of a quasiparticle, whose state is described by $|\Psi_e\rangle$. Then, $|0\rangle$ is the corresponding vacuum state and $\Psi_{n,j}$ or $\Psi_{k,\lambda}$ are the quasiparticle wave function in the site or in the quasi-momentum represantation, respectivelly, and satisfy the normalization condition $\langle \Psi_e | \Psi_e \rangle = 1$.

Considering $\langle \Psi | H | \Psi \rangle$ as the Hamiltonian functional of the quasiparticle wave-function and of the lattice variables, we obtain a system of dynamic equations which describe the interaction between the quasiparticle and phonon subsystems. For numerical simulations it is convenient to write down the dynamic equations in the site representation. Below we will use dimensionless time measured in units of $\hbar/J$, energy measured in units of J, displacements measured in the length unit $l = \hbar\sqrt{2/JM}$, and to express all parameters in the dimensionless units using the following relations:

$$M_{1,2} = \frac{1}{2}M(1 \pm m), w_{s,l} = \frac{1}{2}W(1 \pm w), J_{s,l} = \frac{1}{2}J(1 \pm d), \chi_{s,l} = \frac{1}{2}X(1 \pm x)\,, \tag{10}$$

or, respectively:

$$m = \frac{M_1 - M_2}{M}, w = \frac{w_s - w_l}{W}, d = \frac{J_s - J_l}{J}, x = \frac{\chi_s - \chi_l}{X}, X = \chi_s + \chi_l \tag{11}$$

In these units the system of dynamic equations for a system, that is described by the total Hamiltonian (1) in the presence of an external electric field $E(t)$, has the form:

$$\begin{aligned}
i\frac{d\Psi_{n,1}}{dt} &= [-1 + \frac{D}{2} + (n - n_0)\,E(t)]\Psi_{n,1} + \frac{1}{2}(1+d)\Psi_{n,2} + \frac{1}{2}(1-d)\Psi_{n-1,2} + \\
&\quad + G[(1+x)(u_{n,1} - u_{n,2}) - (1-x)(u_{n,1} - u_{n-1,2})]\Psi_{n,1} \\
i\frac{d\Psi_{n,2}}{dt} &= [-1 - \frac{D}{2} + (n - n_0 + b)\,E(t)]\Psi_{n,2} + \frac{1}{2}(1+d)\Psi_{n,1} + \frac{1}{2}(1-d)\Psi_{n+1,1} + \\
&\quad + G[(1+x)(u_{n,1} - u_{n,2}) - (1-x)(u_{n+1,1} - u_{n,2})]\Psi_{n,2}, \\
\frac{d^2u_{n,1}}{dt^2} &= -\frac{C}{1-m}[(1+w)(u_{n,1} - u_{n,2}) + (1-w)(u_{n,1} - u_{n-1,2})] + \\
&\quad + \frac{G}{1-m}[2x\,|\Psi_{n,1}|^2 - (1-x)\,|\Psi_{n-1,2}|^2 + (1+x)\,|\Psi_{n,2}|^2] - \eta\frac{du_{n,1}}{dt}, \\
\frac{d^2u_{n,2}}{dt^2} &= \frac{C}{1+m}[(1+w)(u_{n,1} - u_{n,2}) + (1-w)(u_{n+1,1} - u_{n,2})] + \\
&\quad + \frac{G}{1+m}[-2x\,|\Psi_{n,2}|^2 + (1-x)\,|\Psi_{n+1,1}|^2 - (1+x)\,|\Psi_{n,1}|^2] - \eta\frac{du_{n,2}}{dt}
\end{aligned} \tag{12}$$

Here the intensity of the electric field $E(t)$ is measured in units ea/J and we have defined:

$$G=\frac{Xl}{2J},\quad C=\frac{\hbar^2 W}{MJ^2},\quad D=\frac{E_2-E_1}{J} \tag{13}$$

Here we have introduced into the equations for the atom displacements the damping force, which is described by the terms proportional to η in (12), to take into account the interaction between the atoms and the thermal bath that generates the dissipation of the energy. In all our simulations we have taken $\eta = 0.2$, unless indicated directly.

3. Ratchet Phenomenon in Asymmetric Chains

For our numerical simulations we have assumed free boundary conditions. To study the polaron dynamics, we have calculated first the stationary solutions of Eq. (12) in the absence of an external field, i.e., by setting $E(t) = 0$. We have chosen the numerical values of the parameters (13) so that the stationary solution (the stationary state of the Hamiltonian (6)) is self-trapped within few lattice sites, as is shown, for instance, in Fig. 1. For such properly chosen values of the system parameters, when the polaron size is not too small, Eq. (12) can be studied analytically in the continuum (long-wave) approximation (see, e.g., [2]). In this case one can show that Eqs. (12) can be reduced to the Schrödinger equation for the electron wave function in the self-consistent deformation potential. This potential is proportional to the electron probability at a given place and time so that the Schrödinger equation contains a cubic nonlinearity and is known as the nonlinear Schrödinger equation (NLSE). In the leading order approximation the NLSE has the soliton solution.

$$\Psi_{n,j}(t)=\sqrt{\frac{(1-P)\kappa a}{4}}\,\frac{\exp(-iEt/\hbar)}{\cosh\kappa(z_{n,j}-R)}, \tag{14}$$

where $z_{n,j}$ is the atom position along the chain and E and R are the eigenenergy and the c.m. coordinate of the soliton, respectively. The localization parameter of the soliton, κ, in the notation (10) is given by the relation:

$$K=\left(1-P\right)\frac{4G^2\left(1+x^2-2xw\right)\sqrt{1+D^2\!/4}}{aC\left(1-d^2\right)\left(1-w\ \right)}, \tag{15}$$

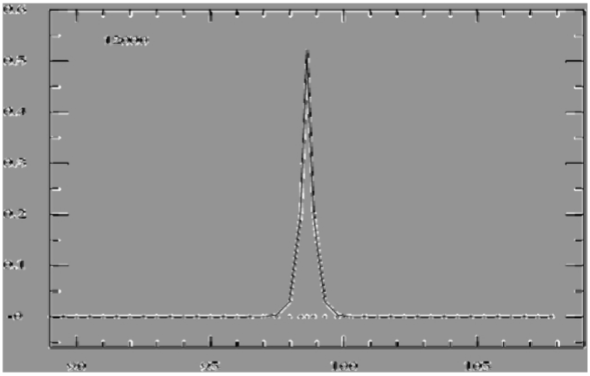


Figure 1. Stationary distribution of the electron probability as function of the lattice site for the parameter values: $G = 0.4$, $C = 0.22$, $d = D = 0.1$, $x = 0.05$, $w = 0.15$, $m = 0.3$

The soliton level is split from the bottom of the lower electron band

$$E = E_L(0) - \frac{\hbar^2 \kappa^2}{2m^*} \tag{16}$$

where m^* is the effective mass of an electron in the lower band. The energy sublevels near the bottom of this band give the main contribution to the formation of the soliton state (14). In (14) and (15) P is the weight coefficient determined by the contribution of the energy sublevels of the upper band to the formation of the soliton state, $P \ll 1$. For the values of the parameters used in our numerical calculations, the soliton profile, given by the analytical expression (14) in the stationary case agrees, to within a high accuracy, with the profile of the soliton, calculated numerically, Fig.1, at $P = 0.3$.

The obtained numerically stationary solutions of Eqs. (12) (at $E(t) = 0$) we then used as the initial conditions in the presence of the field at $E(t) \neq 0$. We have studied numerically the time evolution of such an excitation by calculating its profile, half-width and the position of the quasiparticle centre of mass (c.m.) coordinate for various forms of the external periodic unbiased electric field. The field, itself, does not significantly affect the profile of the soliton, though it causes oscillations of the c.m. of the soliton and of its width. In Fig. 2 we show the c.m. coordinate as a function of time for an asymmetric chain ($d = 0.1$, $D = 0.1$) in the presence of an unbiased harmonic field $E(t) = E_0 \sin(2\pi t/T)$ at $E_0 = 0.08$, $T = 2{,}000$ (note, all parameters are measured in dimensionless units, (d.u.)). This figure shows very clearly that the unbiased harmonic field causes a drift of the soliton, i.e., it generates a uni-directed current in the chain. The fine structur of the drift (the details of the oscillations) depends not only on the parameters of the field and dissipation coefficient, but on the asymmetry properties of the system as well, as it follows from the comparison of the two curves in Fig. 2. Moreover, a directed current of polarons under harmonic perturbation in molecular systems is also present if there is an asymmetry in the electronic subsystem only, as it is clear from the top curve in Fig. 2. Our results clearly show a ratchet behaviour of polarons.

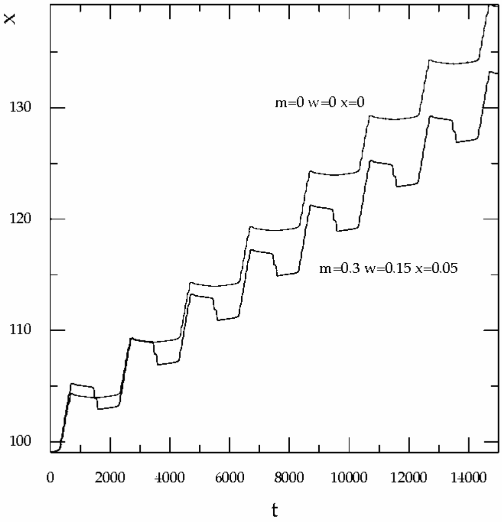


Figure 2. Position of the c.m. of the soliton as function of time in an external harmonic field at $G = 0.4$, $C = 0.22$, $E_0 = 0.08$, $T = 2{,}000$ d.u. in an asymmetric chain with: $d = D = 0.1$, $x = 0.05$, $w = 0.15$, $m = 0.3$ (bottom) and $d = D = 0.1$, $x = w = m = 0$ (top)

This effect has a threshold with respect to the intensity of the field and its period, i.e., the effect takes place provided that $E > E_{0,cr}$, $T > T_{cr}$. Thus, for instance, for $E_0 = 0.08$ and for the given chain parameters $T_{cr} = 400$ d.u. As one can see from Fig. 2, in the electric field periodic in time, the soliton trajectory is a sum of oscillations with a certain amplitude and a drift. Such behaviour is induced by the discreteness of a molecular chain accounted in the Peirls–Nabarro potential, which is periodic with the same period as the lattice [14, 15]. Notice that the presence of the Peirls–Nabarro potential is a characteristic of the discrete models and causes the uni-directional motion in various discrete soliton ratchets described by, e.g., the discrete sine-Gordon [10]) and the discrete nonlinear Schrödinger-type [13] equations.

For description of the soliton dynamics, both in homogeneous and in discrete cases, a collective coordinate approach is widely used [11, 16]. In the lower approximation, a discrete soliton of the form (14), can be viewed as a single particle and the c.m. coordinate of the soliton, $R(t)$, is one of such collective coordinates. In a molecular chain the dynamic equation for the c.m. coordinate of the soliton, $R(t)$, under the external force, $E(t)$, taking into account the lattice discreteness and the energy dissipation, takes the form:

$$M_s \ddot{R} = \gamma^* \dot{R} + f(R) + eE(t)\,, \tag{17}$$

where $M_s = m^* + \Delta m$ is the effective mass of the soliton, 'dressed' with phonons, $\gamma^* \propto \eta$ [17], and $f(R) = -dU_{PN}/dR$ with U_{PN} being the periodic Peierls–Nabarro potential,

$U_{PN}(R+a) = U_{PN}(R)$ (a is the lattice constant), [14]. Equation (17) is of the type well known to lead to the ratchet phenomenon [1] i.e. to a unidirectional (in average) motion of a particle which trajectory is a limit cycle phase locked to the external periodic drive $E(t)$.

In a chain with one atom in a unit cell, the Peierls–Nabarro potential is given by the expression $U_{PN}(R) = U_0\cos(2\pi R/b)$, where b is the lattice constant of the chain, and the height of the barrier depends on the electron–phonon coupling of the system [14]:

$$U_0 = \frac{4\pi^2 J}{\kappa b}\exp(-\frac{\pi^2}{2\kappa b}), \tag{18}$$

where k is given by Eq. (15) with $a = 2b$ at $d = w = m\ x\ 0$. A detailed study of the Peierls–Nabarro barrier in a diatomic chain will be reported elsewhere [18]; here we summarise these results by pointing out that this barrier is periodic:

$$U_{PN}(R) = U_1\cos(2\pi r) + U_2\cos(4\pi(r+\theta)), r = \frac{R}{a}, \tag{19}$$

and that its height depends on the square of the electron–phonon coupling, similarly to the case of a uni-atomic chain. The presence of the Peierls–Nabarro potential explains our numerical results and the existence of the threshold with respect to the intensity of the field and its period. For driving amplitudes below the threshold (depinning threshold) the soliton remains pinned to the lattice and its c.m. oscillates around the lattice site. The drift is possible when the intensity of the field exceeds the depinning threshold and the amplitude of the soliton oscillations exceeds the lattice constant (the period of the Peierls–Nabarro barrier). The oscillation amplitude depends on the intensity of the field and its period and, in rough estimation, is proportional to the square of the electric field period, $A \propto E_0T^2$. If the period of the external force is very small, this amplitude is less than one period of the ratchet potential and the soliton oscillates within the potential well of the Peierls–Nabarro barrier and, therefore, is trapped on a lattice site.

It is known that the broken spatial symmetry in the ratchet potential, which in our case is the periodic potential of the Peierls–Nabarro barrier, and/or of the time correlations in the driving force are crucial and lead to the ratchet effect [1, 9]. Numerical results shown in Fig. 2 clearly indicate a ratchet behaviour of polarons in asymmetric diatomic molecular chains under an unbiased harmonic (temporarly symmetric) field $E(t) = E_0\sin(2\pi t/T)$. This indicates that the Peierls–Nabarro potential (19) in asymmetric chains is asymmetric. To show this we have studied the dynamics of the soliton governed by the discrete equations (12) in a constant field, $E(t) = E_0 = const.$ $E_{th}(E) = E_{th}(-E)$ for symmetric chains, while $E_{th}(E) \neq E_{th}(-E)$ for asymmetric ones.

As is clear from Eq. (17), the soliton is pinned by the lattice and, in a static electric field, the soliton can move if the external field exceeds the pinning threshold value. In a symmetric chain this threshold is symmetric for fields E and $-E$, and is asymmetric for asymmetric chains. Results shown in Fig. 3 have prove that, indeed, as it is well known from the analysis of Eq. (17) [9, 19], the uni-directional motion of the soliton corresponds to the limit cycle which is phase-locked to the frequency of the external driver: $R(t + T_c) = R(t) + ka$, $\dot{R}(t+T_c) = \dot{R}(t)$ (a is the period of the ratchet potential, T_c is the period of the cycle). On this orbit, the average soliton velocity is expressed as

$$\langle V\rangle = \frac{1}{T_c}\int_0^{T_c} \dot{R}dt = \frac{ka}{lT} \tag{20}$$

with k and l being integer numbers. In this resonance regime, the soliton passes k sites during l periods of the external drive so that, except for a shift in space, its profile is completely reproduced after this time interval.

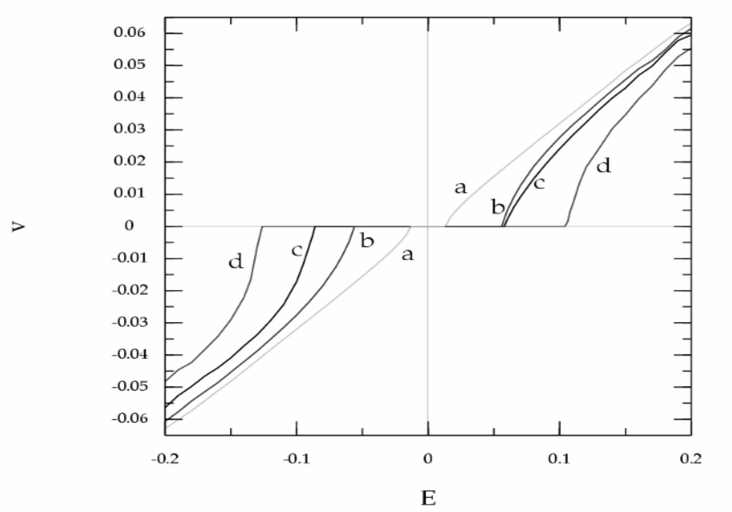


Figure 3. Dependence of the average soliton velocity on the constant electric E field for $G = 0.4$, $C = 0.22$, $b = 0.5$ and a – $d = D = 0$; b – $D = 0$, $d = 0.1$; c – $D = 0.1$, $d = 0.1$; d – $D = 0.2$, $d = 0.1$

The dependence of the velocity of the drift on the period of the applied field, obtained by numerical simulations of Eq. (12), is shown in Fig. 4. From here one can see that the soliton displacement is not a smooth monotonic function of T but a piecewise function with plateaus. The plateau values of the soliton velocity satisfy Eq. (20) and correspond to dynamic regimes, hich are limit cycles with rotation numbers ($\kappa = 1, 2, \ldots; l = 1$) phase-locked to the driver.

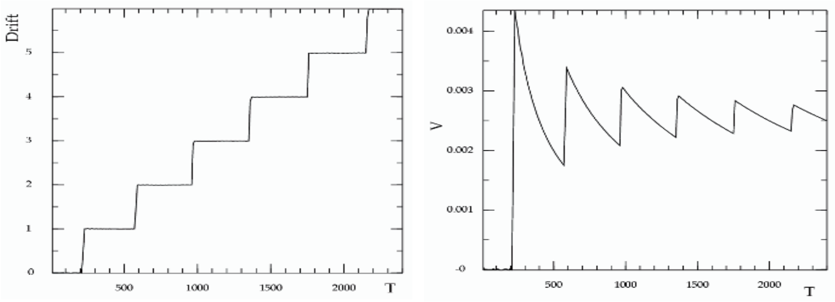


Figure 4. Displacement (in the lattice units) of the c.m. of the soliton (a) and velocity of the drift as functions of the period of an external harmonic field at $G = 0.4$, $C = 0.22$, $d = D = 0.1$, $x = w = m = 0$, $E_0 = 0.88$

Generally speaking, the possibility of a soliton to drift in the unbiased field and the properties of drift are many-parametric problems. To analize the corresponding space diagram, we show some of the two-dimensional crossections of the corresponding many-parametric space. First of all, it is worth to note, that one can expect the decrease of the soliton oscillation amplitude with the energy dissipation increasing, i.e., with the increase of the damping coefficient. This is indeed the case, as it is shown in figures below. The dependence of the amplitude of oscillations on the dissipation coefficient, η, is shown in Fig. 5 for the field of the same intensity, $E_0 = 0.88$, but of two different periods, $T = 1{,}000$ and $T = 500$; and at the same period $T = 500$ but for the different intensities $E = 0.08$ and $E = 0.06$, respectively. Here the value of the coupling is $G = 0.4$ except for the curve d for which $G = 0.38$. From this figure one can see that the soliton oscillation amplitude as a function of the absorption also has plateaus of different lengths due to the discreteness of the chain.

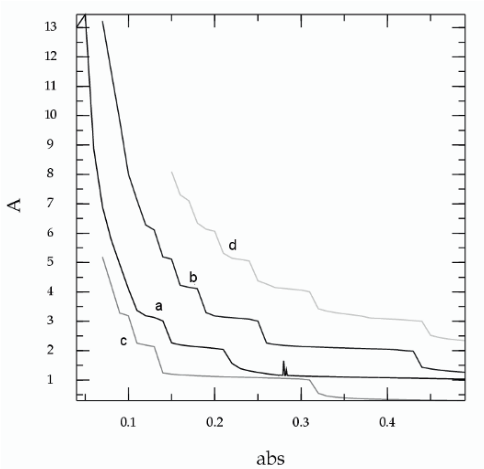
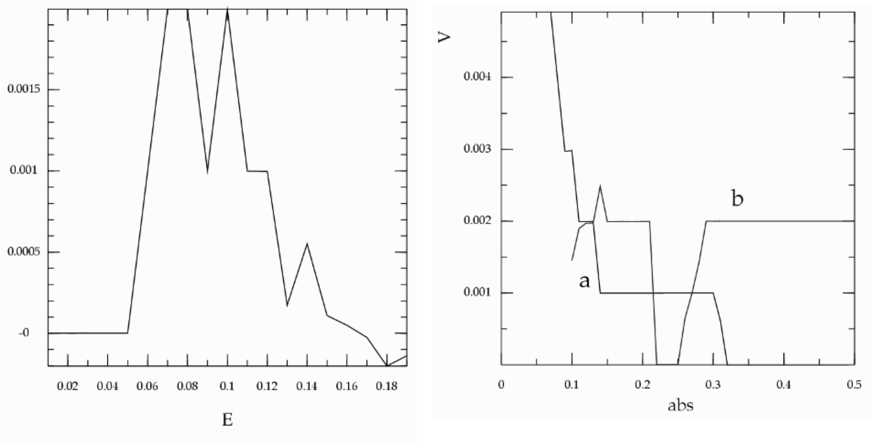


Figure 5. Dependence of the amplitude of oscillations on the absorption for the parameter values $C = 0.22$, $d = D = 0.1$, $x = 0.05$, $w = 0.15$, $m = 0.3$ with a – $G = 0.4$, $E = 0.08$ and $T = 500$; b – $G = 0.4$, $E = 0.08$ and $T = 1{,}000$; c – $G = 0.4$, $E = 0.06$ and $T = 500$; d – $G = 0.38$, $E = 0.08$ and $T = 1{,}000$

The dependence of the average soliton velocity on the damping coefficient and on the driver intensity is depicted in Fig. 6. As it is shown in Fig. 6a, the velocity of the drift of a soliton is nonmonotomic function of the field intensity, and increases above the critical value of *E*, provided *E* is not too big.



a b

Figure 6. Velocity of the soliton drift as function of the intensity of the field (a) and of the damping coefficient (b) for the chain $G = 0.4$, $C = 0.22$, $d = D = 0.1$, $x = 0.05$, $w = 0.15$, $m = 0.3$, $T = 1{,}000$, $\eta = 0.2$

Soliton drift results from the superposition of various oscillating processes with different periods. As a result, soliton dynamics is a higly nonlinear processes, and the dependence of the soliton velocity on the damping coefficient and on the field intensity is a nonmonotonous and the velocity can even change its sign, as it is the case in the very last part of the curve in Fig. 6a. When we choose properly the parameters of the chain and field, the drift velocity decreases with the absorption increasing (see Fig. 6b), and, as it was mentioned above, at too strong absorption there is no drift of the soliton at all. Neverteless, one can find such values of the parameters, that in a broad interval of the absorption the soliton does drift. One of such regimes with constant velocity is shown in Fig 6b for the field parameters $T = 500$, $E = 0.08$ except for the interval of absorption $\eta = 0.2$–0.29, for which a soliton is practically pinned by the lattice. Pinning of the soliton by the lattice is determined by the height of the Peierls–Nabarro barrier, which is bigger for the bigger values of the electron–phonon coupling, the latter is proportional to *G*. At a weaker coupling and at a bigger field period there are more intervals of the values of the absorption coefficient, at which the soliton is pinned. In the meantime in strong fields at too weak absorption the generation of phonons by the soliton accelerating in the field, is so strong, that the soliton becomes unstable and decays with time very fast.

The profile of the Peierls–Nabarro potential in a diatomic chain depends on the asymmetry parameters (11) and, depending on a ratio of coefficients and the phase relationship in (19) can have one- or two-minima structure. The Peierls–Nabarro relief is manifested in the oscillations of the soliton velocity in time. This relief is even more pronounced by the oscillations of the soliton wave function amplitude as it is shown in Fig. 7.

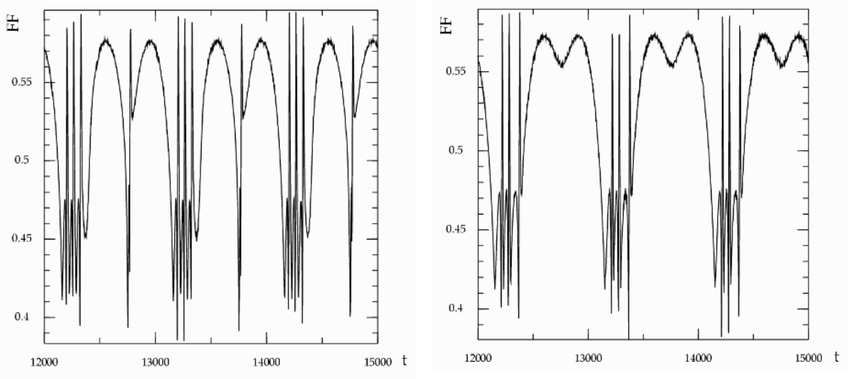


Figure 7. Time oscillations of the soliton amplitude $|\varphi|^2$ for $E = 0.08$, $T = 1{,}000$, $C = 0.22$, $G = 0.4$, $b = 0.5$, $d = 0.1$, $D = 0.1$, $\eta = 0.2$. (a) $m = 0.3$, $w = 0.15$, $x = 0.05$; (b) m, w, $x = 0$

In molecular chains, a soliton motion in the Peierls–Nabarro potential is accompanied not only by the oscillations of the soliton velocity in time, but also by oscillations of a soliton localization parameter κ [14] which determines also the soliton amplitude (14). Overcoming the Peierls–Nabarro barrier, the soliton gets broader and therefore, its amplitude decreases. From Fig. 7 one can see that a height of the barrier between the two inner minima of the Peierls–Nabarro relief in molecular systems with an asymmetry in the electronic subsystem only, Fig. 7b, becomes less than in the case when w, m x, $\neq 0$, Fig. 7a.

3.1. DRIFT OF POLARONS IN A SYMMETRIC CHAIN

Note that chains with only one nonzero anisotropy parameter, d or D, possess a reflection symmetry. In such cases a harmonic electric field does cause soliton oscillations around its initial position but it will not generate a soliton drift (this conclusion is confirmed by our numerical simulations). Instead, according to the symmetry consideration [9], one can expect the ratchet phenomenon to take place in a symmetric chain if an external unbiased periodic field is asymmetric in time. Indeed, this is the case, as is shown in this section below. In particular, Fig. 8 presents the trajectory with a unidirectional (in average) motion of a soliton in the unbiased biharmonic periodic field, $E(t) = E_0\sin(2\pi t/T) + \beta\sin(4\pi t/T - \varphi)$ ($E_0 = 0.08$, $\beta = 0.6$, $\varphi = \pi/2$). This figure shows that the unbiased biharmonic field causes a directed (in average) motion of solitons in the symmetrical chains.

Note that the case of $D = 0.1$, $d \neq 0$, applies to polyacetylene with alternating chemical bonds [3], while the case $d = D = 0$ corresponds to a simple chain with one atom in a unit cell with the lattice constant $a/2$. From Fig. 8 we see that, even in such simple systems, the ratchet effect takes place!

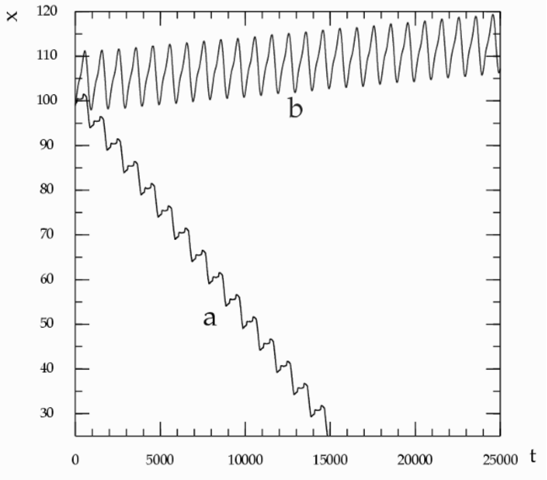


Figure 8. Position of c.m. of the soliton as function of time in an external biharmonic field at $G = 0.4$, $E_0 = 0.08$, $\beta = 0.6$, $\varphi = \pi/2$, $T = 1{,}000$ in a symmetric chain at: a – $C = 0.22$, $d = 0.1$, $D = x = w = m = 0$; b – $C = 0.25$, $D = x = w = m = 0$

The resulting average velocity of the soliton strongly depends on the chain parameters and parameters of the driving force $E(t)$. The important parameter is the parameter of the asymmetry of the biharmonic field, φ. In particular, Fig. 9 shows the amplitude of soliton oscillations and the velocity of the drift as functions of this asymmetry parameter. We see, that the direction of soliton drift and its velocity are determined by the asymmetry of the field and the dependence $V(\varphi)$ resembles a sinusoidal function which has been observed for soliton ratchets in other models (see, e.g., [13]).

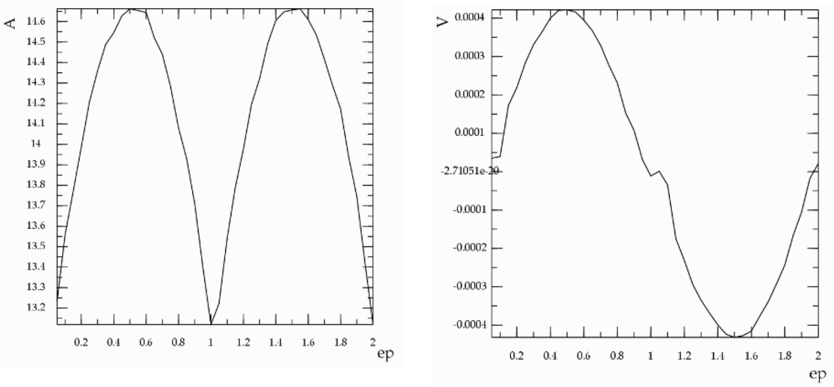
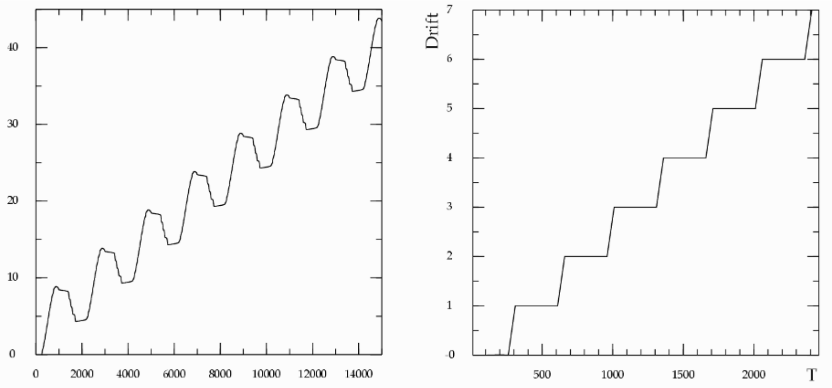


Figure 9. Dependence of the amplitude of soliton oscillations (a) and of the velocity of the drift (b) on the parameter of the asymmetry of the biharmonic field. The parameters are: $G = 0.35$, $C = 0.22$, $m = w = x = d = D = 0$, $E = 0.08$, $T = 1{,}000$, $\eta = 0.2$

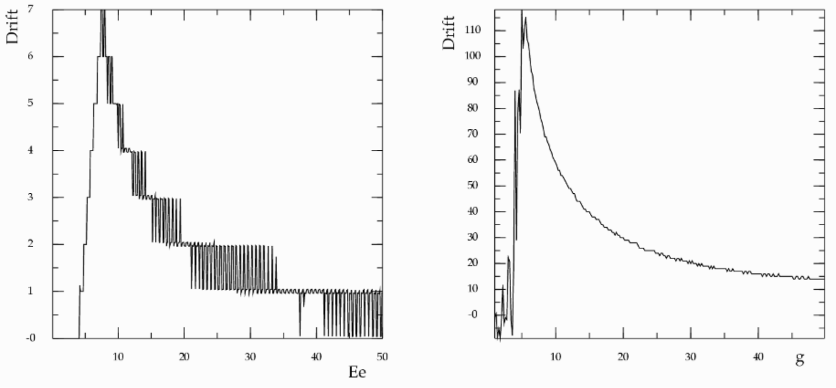
4. Discussion of the Numerical Results in Terms of the Collective Coordinate

As it is follows from Fig. 4, the main characteristics of the soliton dynamics, obtained by numerical simulations of Eq. (12), can be explained in terms of the collective coordinate, Eq. (17). To demonstrate this we have studied Eq. (17) numerically and show the results on Figs. 10 and 11.



a b

Figure 10. Position of the c.m.c. as function of time in the field $E_e = 8.7$, $T = 2{,}000$, $\gamma = 400$, (a) and the dependence of the velocity of the drift on the period of the field $E_e = 4.5$, $\gamma = 100$, (b) in the ratchet potential with the parameters $u_1 = 1$, $u_2 = 0.25$, $\theta = 1/8$



a b

Figure 11. Dependence of the velocity of the drift on the field intensity at $T = 2{,}000$, $\gamma = 400$, (a) and on the friction coefficient at $E_e = 8.7$, $T = 1{,}000$, (b) in the ratchet potential with the parameters $u_1 = 1$, $u_2 = 0.25$, $\theta = 1/8$

We have chosen the ratchet potential in the form (19) and found that Eq. (17) describes qualitatively and often quantitatively the dynamics of a soliton described by the discrete system of equations (12), as it follows from the comparison of Fig. 10a and b with Fig. 2 (lower curve) and Fig.4a, respectively. The best accordance corresponds to the ratchet potential parameters $U_2/U_1 = 0.25$, $\varphi = -1/8$ at which the profile of the potential (19) indeed has the two-minima structure.

Equation (17) describes only approximately the soliton dynamics. The soliton itself is a two-component entity, which includes the electron and lattice distortion components. Therefore, strictly speaking, the soliton dynamic equations in terms of the collective coordinate reads as

$$m^* \ddot{R}(t) + \int_0^t K(t-t')\ddot{R}(t')dt' = \gamma^* \dot{R} + f(R) + eE(t) \tag{21}$$

where the kernel $K(t)$ describes the retarded reaction of the chain deformation [20, 21]. The characteristic retardation time is $t_{ret} = \pi^2 / (\kappa V_{ac})$, where κ is the inverse width of the soliton (15), and V_{ac} is the sound velocity in the chain. In the adiabatic regime Eq. (21) reduces to Eq. (17). From the study of the influence of the alternating electromagnetic field on solitons [20, 21] we know, that there is a characteristic resonance frequency of the soliton, which defines three different regimes of soliton dynamics, namely, low-, high-frequency and resonant regimes. This resonance frequency is determined by the width of the soliton and by the phonon sub-system:

$$\omega_{res} = \frac{2\pi}{t_{ret}} = \frac{2\kappa V_{ac}}{\pi}, \tag{22}$$

The sound velocity can be calculated from the dispersion relation of the acoustic mode in the long-wave approximation (see Fig. 8)

$$\omega_{ac}(q) \approx V_{ac}^2 q^2 \tag{23}$$

where

$$V_{ac}^2 = \frac{w_s w_l}{MW} a^2 = \frac{a^2}{4} \Omega_0^2 C(1-w^2). \tag{24}$$

Therefore, the resonance frequency of a soliton in the dimensionless parameters reads as

$$\omega_{res} = (1-P)\frac{4G^2\Omega_0}{\pi C}\sqrt{C(1-w^2)}\zeta \tag{25}$$

where ζ depends on the asymmetry of the chain:

$$\zeta = \frac{(1+x^2-2xw)\sqrt{1+D^2/4}}{(1-d^2)(1-w^2)} \tag{26}$$

At the asymmetry parameters values used in our calculations, $\zeta \approx 1$.For the given values of the parameters we obtain that the resonance frequency of the soliton is much bigger than the frequencies of the ac field that result in the drift of the soliton: $T_{res} \approx 22.27 << T_{num}$. Therefore, such fields correspond to the low-frequency regime, $\omega << \omega_{res}$. In this regime the oscillations of the c.m. coordinate of the soliton are accompanied by the oscillations of the local deformation of the chain, the dynamical mass of the soliton is function of the frequency of the field and exceeds the dynamical mass of the free soliton. For instance, in a symmetric chain the dynamical mass of a soliton is given by the expression (see [20]):

$$m_{dyn}(\omega) = \sqrt{[m^* + \mu_1(\omega)]^2 + \mu_2^2(\omega)}, \tag{27}$$

where the expressions for values μ_i are given in [20, 21]. It follows from (27) that in the limit of very small frequencies the dynamic mass of a soliton is very close to the effective mass of the soliton in the absence of the field.

As we have discussed above, indeed, the Peierls–Nabarro relief plays essential role for the ratchet phenomenon in molecular chains, therefore, it is very important, that the frequency of the field is not too high as compared with the resonance frequency of the soliton so that the propagation of a soliton can be accompanied by the drift of the deformation field. According to the analytical study [20], during the oscillations the soliton emits sound waves in both directions. The amplitude of the deformational field, corresponding to this emission of sound waves, is proportional to the frequency and intensity of the field. Soliton drift takes place due to the absorption of energy from the external field. At low frequencies the amount of energy, absorbed by a soliton per field oscillation period, is proportional to the electromagnetic field frequency oscillations. We see, that our numerical results confirm these predictions.

5. Conclusion

In conclusion, our study has shown that the ratchet effect can take place in one-dimensional molecular systems which support the existence of large polarons (solitons). Such self-trapped electron states are formed at intermediate values of the electron interaction with lattice deformation. The coupling constant of this interaction has to be large enough as the Peierls–Nabarro barrier (18) is essential for the dynamics of the soliton; on the other hand, this coupling cannot be very large to prevent the formation of small polarons, whose transport properties are qualitatively different from those of the solitons. There is a large class of low-dimensional molecular systems, including biological macromolecules and some conducting polymers and inorganic compounds, which possess large polarons, as it has been proved by numerous experimental observations.

It is worth to point that in a certain sense, in spite of the different physical nature, molecular ratchets, considered here, are similar to the ratchet behaviour of the discrete cavity optical solitons [13], based on the discrete nonlinear Schrödinger-type equation (stationary molecular soliton can be described by the latter equation as well).

We note that similar to the deterministic fields considered here, symmetric white noise [22] also can cause uni-directed current of solitons in low-dimensional molecular systems, though the dynamics of solitons in such cases is less symmetric and more complicated than in the harmonic fields (we plan to report on this in the near future). The role of noise in inducing the ratchet effect is important for understanding biological motors functioning. Molecular solitons which are the charge and energy carriers during the metabolic processes in biological systems, according to Davydov's hypothesis [2], are formed in α -helical proteins. Such protein macromolecules possess highly asymmetric structure, and, therefore, their Peierls–Nabarro barrier is asymmetric. Moreover, these macromolecules are immersed in the cellular cytoplasm and are subject to thermal fluctuations. Therefore, in these systems the presence of a symmetric stochastic noise can result in the formation of a directed current of solitons, i.e., such systems can be good candidates for molecular motors.

On the other hand, there is a class of low-dimensional compounds, such as polyacetylene (PA), polydiacetylene (PDA), polytiophene (PT), etc., which provide experimental evidence for the existence of large polarons and bipolarons [6, 7, 23]. Based on our results we expect that, in these compounds, the unbiased alternating electric field can induce a directed current. In the compounds with an asymmetric unit cell, such as polyphenylene-venillene, polythienylene-venillene, this directed current can be induced by a harmonic periodic field, while in compounds with a symmetric unit cell, such as PA, PDA, PT, polyphenylene, polypyrrole, polyaniline, polyfurane, polysilans etc., this effect can be observed in periodic biharmonic, or, in the general case, in asymmetric periodic in time fields.

Moreover, the ratchet effect can take place also in compounds with the charge density waves (CDW) (see review [24]). Similar to the case of polarons, such CDWs are also described within the adiabatic approximation for the many-electron wavefunctions and in the limit of low concentration of electrons the CDW wavefunction reduces to the wavefunction of separated bisolitons [25], as was shown in [26]. In fact, the pinning of the CDW by the lattice in these systems does exist and it has been proved that the sliding mode of the CDW is possible in constant fields only above some threshold [24]. Indeed, the dc signal produced by biharmonic microwaves in TTF-TCNQ (tetrathiofulvalene-tetracyanoquinodimethane) has been experimentally observed [27]. Some features of experimental results were explained in [28] supposing that the charge transport in TTF-TCNQ occurs via rigidly sliding CDW (a CDW was modelled as a Brownian motion of a classical particle in the periodic potential within the collective coordinate approach, Eq.(17)). This agrees qualitatively with our results, though a further detailed study has still to be performed.

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BON-AQUA

THE IMPACT OF NOVEL TECHNOLOGIES ON THE ENVIRONMENT THROUGHOUT HISTORY

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Abstract. Several known historical processes or events, especially those with a manifest environmental impact will be assessed from a technological standpoint. Recent technological advances made results of technological intervention into the nature much more rapid than before and therefore the assessment of prior experiences is both helpful and necessary. Three types of consequences of technological intervention are discerned: (1) "slow progressors", i.e., such risks that accumulate throughout substantial time spans and are not instantaneously obvious, and those of (2) intermediate and (3) immediate impact. The capacity to reverse the negative consequences of each type of intervention inversely correlates with their manifestation speed. Specifically, the events of the third type often result from the "interaction with the absolutely unknown" often need to be remedied in an urgent manner. Each of these types of environmental impacts will be illustrated with a known historical event. It is likely that the same three types of negative consequences will be seen in the nearest future upon the development and utilization of novel bio-organical and biotechnological products. These risks will be also discussed in a historical perspective.

Keywords: technological risks, history of technology, environmental impact, manifestation speed, detection

1. Introduction

The aim of this essay is to attempt to look at several well-known historical processes or individual events from a technological standpoint. More specifically, I will focus on the impact of technological developments on mankind and the natural environment. It is telling that even upon a brief analysis, it becomes clear that the same technological risks, that are now rapidly catching the attention of the professional community as well as the general public, could be discerned in the earlier history of mankind. Apparently, there are some lessons we may either learn or ignore (humans usually swear to do the former and always resort to the latter, which is true for any historical lesson).

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Generally, the noticeable and oft-discussed examples of technological impact on nature are drawn from the last couple of centuries. The reason for this is the availability of verifiable data and our ability to make a reasonably stringent cause-and-effect analysis based on this data. While records from the earlier epochs are sometimes fragmentary, the distant past may still present valuable case studies or at least give us a sufficient "food for thought". It is also necessary to remember that the course of history has immensely accelerated over the last century and even during the last decades. Therefore, results of technological intervention, both positive and negative, that previously took centuries to shape, are now readily visible only after several years. The impact of even the more subtle advances is now often discernible within the life span of a single generation.

The largest part of the present essay will be dedicated to the negative/unforeseen consequences of the introduction of novel technologies, although many (in fact, most) had an immense positive influence on human wellbeing. It is not necessary to substantiate at length that it is much more important to remember one's failures or difficulties since this is the best medicine (albeit, not a "magic pill") against avoiding similar situations in the future.

Known examples of the negative consequences of various technologies can be broadly divided into several groups depending on the swiftness of their impact. I will start with the so-called "slow progressors", i.e., such risks that are not obvious immediately. They accumulate throughout substantial time spans and only then do they become apparent. Usually, this involves repeated and unmodified (or insufficiently modified) utilization of a particular technology. A single application of such a method presents negligible, or no risk. However, the situation changes substantially when the impact is multiplied many times over. Negative consequences caused by this type of technological intervention are rarely reversible since they take such a long time to accumulate. They include technological and hence societal stagnation (since support of the existing technological network often drains the resources from the development of a new one), dramatic environmental changes and also "an extreme technological dependency", i.e., over-reliance on a particular technological approach. The latter makes society vulnerable to the sudden unavailability of this technology due to natural or man-made catastrophic intervention. Such events cannot be "fixed" or remedied. They have already happened, no reversal is possible. Here we are talking about "historical lessons" in the strictest sense of the word.

Technological impacts of the second group also appear with time, albeit much smaller time spans are usually involved. Therefore, their consequences could be detected by a keen observer and therefore are at least partially known. Moreover, they could be remedied now or prevented in the future through better analysis and/or dissemination of available information. Thus, such risks are at least partially reversible. And lastly, I will talk about impacts of "immediate kind". In such a case, the unforeseen consequence of a novel technology arises and strikes instantly. Society originally either does not think about these consequences or is simply unaware about their existence. I will call these types of events as results of "interaction with the absolutely unknown". These consequences are usually acute and easily detectable. Therefore they need to be alleviated in an urgent manner, which is done either through abandonment of a particular technology or "the development of a technological antidote". Conversely, no action is taken if those that suffer the most from such an impact are viewed as unimportant or even expendable.

I will try to illustrate each one of these groups using well-known, oft-described and – discussed events from the annals of human history. It is my sincere opinion that future utilization of bioorganical and biotechnological products may lead to three types of negative consequences: (1) long-term impact on the environment or human population, (2) unforeseen adverse effects that will take some time to develop and (3) acute adverse effects that will become apparent immediately, especially if a broad group of people will be subjected to such a technological intervention. It is important that we are aware of these possibilities and try our best to prevent or alleviate them and also have a scheme allowing for their early detection.

2. "Slow" Effects – Agriculture in Ancient Egypt and Mesopotamia

It should be of no surprise that while talking about long-term and irreversible technological intervention we inevitably look at the history of agricultural cultivation. It is well-known that some civilizations degraded the land they had placed under cultivation, either through excessive irrigation, which caused soil sterilization via formation of a salt layer (likely, in the case of Mesopotamia between 2400 and 1700 BC), or through excessive harvesting of wood for construction and cooking, which resulted in soil erosion (in the case of the Indus Valley around 1800 BC, the loess plateaus of China in 3rd millennium BC, in Ethiopia around 1000 BC, in Greece around 600 BC, and later in Roman Italy, and yet later in the southwestern part of the North American continent, on the lands of the Anasazi and Hohokam societies, about AD 600–900 and AD 1100–1375, respectively) [1]. On the other hand, another majestic civilization, which also subjected the land to long-term cultivation efforts, was able to avoid environmental degradation of any kind. This is obviously the civilization of Ancient Egypt. Its agriculture was well adapted to the ecological conditions that prevailed along the Nile and is usually cited by ecologists as an example of not-so-hazardous human intervention. However, as I will try to show, Egyptian agricultural civilization also incurred technology-related consequences. But firstly, I will summarize the most basic features of two great agricultural civilizations of the Ancient Near East, these being Egypt and Mesopotamia and proceed to evaluate their environmental and historical impact.

Agriculture in ancient Egypt was completely dependent on Nile's silt. Herodotus described Egypt as "a rainless area but extremely fertile. Egypt is the gift of the Nile" [2]. Probably, by the 5th millennium BC, the Egyptians had already realized that the secret of the extraordinary fruitfulness of their fields lies in deposits of silt brought by Nile floods. Nile's mud contained all the important nutritious ingredients that would otherwise have to be added to the soil. Interestingly, it now looks like that no artificial irrigation was needed in ancient Egypt until the end of the Neolithic wet phase around 2350 BC (there are references to transport canal-digging processes from that time, but their role in the irrigation is uncertain [3]). This implies that the tremendous political power of the Old Kingdom (known for several impressive pyramid construction projects) was not connected to irrigation-related technological advances. It was only a series of low floods during the First Intermediate Period (XXII–XXI centuries BC), which lead to famine and to extensive irrigation development during the Middle Kingdom (end of XXI – start of XVIII centuries BC) including one major work under the royal patronage. Still, it facilitated the flow of the ordinary Nile flood into and out of the Faym depression and therefore extended the area of farmed land [3]. Only at this time do we first encounter irrigation-related terms: a canal, embankment, dyke, which were independently invented in different parts of Egypt [4]. Recent findings show that canal-building, maintenance and water allocation were managed by local consortia with no one higher than a regional prince at the head. Nor do any later documents suggest the existence of a central state institution dealing with these matters up to the time of Ptolemaic dynasty (IV–I centuries BC).

Collectively, under the Old Kingdom only natural irrigation had existed, and by the Middle Kingdom a distinction could be made between low-lying fields flooded by nature and higher land watered artificially. In the New Kingdom (starting from mid-II millennium BC) two further categories were recognized: “used” and “fresh” fields. At that time, the basin irrigation system consisted of a system of dikes necessary to retain the flood and encourage infiltration in the soil. Canals led the water to areas difficult to inundate. The flood waters ran through a series of regulated sluices into each basin. The water could be held for a month or more; the surplus was drained to a lower level and then returned to canals which emptied into the Nile [3].

The first mechanical device for guiding water to high-lying fields from the canals dates from a much later Persian Period, VI–V centuries BC. This was the Archimedes’ screw, a helix that could be revolved inside a sloping cylinder. It provided a much larger, faster and more continuous flow of water. By the New Kingdom, the shaduf, a balanced counterpoise, became the irrigating mechanism for gardens. Collectively, over a significant period of time we see a number of wide-ranging technological innovations that were aimed at better utilization of an existing and basically uncontrollable agricultural system, which was completely dependant on the level of the river Nile’s inundations. The river level, in turn, reflected the monsoonal rains in central Ethiopia and had no relationship to climatic fluctuations in Egypt [5]. It is then of no surprise that any major change in East African rainfall resulted in precipitous events in Egyptian history, e.g. abandonment of the floodplains in Lower Nubia ca. 1300 BC and probably played a significant role in serious geopolitical catastrophes, such as the disintegration of the Old and New Kingdoms after abrupt shifts of Nile regime in 2250 and 1200 BC, correspondingly [5].

Moreover, Egypt’s agricultural system had essentially not been changed up to the XIX century AD The growth of Egypt’s population from an estimated 3 million in 1800 to currently near 70 million necessitated dramatic changes, including, but not limited to switching from basin to perennial irrigation, mechanization, application of pesticides and chemical fertilizers, the consequences of which (such as soil salinization) are outside of the scope of this review.

Now we have to ask ourselves to what extent an Egyptian system, intricate, complex, but not intensive, was vulnerable to natural and man-made intervention? As we saw, natural events could have been disastrous. But even subtracting the catastrophes, how reliable was this system? Some scholars estimate that there would have been sufficient grain only every third year. However, at least in the later antiquity, Egypt seems to have had grain surpluses often enough that they could be stored in state granaries and even be exported. During Roman times, it was one of the bread baskets of Rome and it was forbidden for senators to visit Egypt on their own volition for fear of a grain-aided coup d'etat [6].

Still, low inundations in later times continued to be the main reason for bad harvests and they affected the whole of the country. Notably, the Egyptian system of irrigation prevented the salinization of the soil, but this was more a stroke of "natural" luck than the result of concerted effort. Moreover, complete reliance on a repetitious event such as a Nile flood resulted in technological, social and then civilizational stagnation. The potential for a cyclic event is not infinite. The Old Kingdom was an undisputed leader of the contemporary world, this was to a certain degree true for the Middle and even New Kingdom (save for the last century of its existence). However, by then Egypt's political power has drastically diminished.

Egyptian irrigation technology led to progress in other technological areas (the ax, the hoe, the plow all are independent Egyptian inventions). However, despite these technological advances, Egyptian culture became ever increasingly conservative and traditional, so that continued development was thwarted. Progress was hampered by the restraints of a rigid society clearly looking back in time and trying to reach the equilibrium that was lost forever. To what degree the technological inertia of a cyclic irrigation-dependent life-style translated into psycho-social inertia of the whole society, we cannot say. Yet it is clear that Egypt was never again as dominant a world force as in the III–II millenniums BC. The overall decline was already evident around 1000 BC and during the future centuries Egypt repeatedly succumbed to pressures from various brazen invaders, including the Assyrians, Persians, Macedonians, and Romans.

This brings us to the first set of conclusions. Dependence on a complex technological system results in two ever-persistent problems: necessity to maintain the infrastructure and vulnerability against major interference into this technological network. Still, there is a bright side in the former – continuous reuse of a technological innovation brings about its various modifications, improvements, etc. In the Egyptian case the general results were double-edged. On one hand, repeated dependence on a particular technology enabled continuous existence of the culture-in-question. On the other, it also precipitated the perilous circle of cyclical societal motion and stifled further innovation after a certain point in development was reached. Moreover, the repeated use of a single technology sometimes brings about the over-reliance on a particular technological feature. It is well-known that stagnant societies are especially vulnerable to external intervention or sudden internal instability. Ancient Egyptian history gives many examples of this observation.

Yet another, but different illustration of over-dependence on a complex and well-developed technological network is presented by the Mesopotamian civilization. Here the situation was rather different. It is well-known that the irrigation system used in ancient Mesopotamia was much more complex than the Egyptian system, which we identified as an example of technological stagnation caused by over-reliance on repeated "use of the same" structure/event/feature. Conversely, irrigation systems in Mesopotamia, as much as we know about them, were (and needed to be) continuously improved and were originally constructed as part of a collaborative social effort directed both from beneath and from above.

Mesopotamian rulers clearly regarded both flood control and irrigation as their responsibility [7]. Likewise, the same opinion was held by society as a whole and maintenance of irrigation canals was regarded as an important part of an individual's public and private life. Natural floods were disastrous (and much more violent than the Nile's) thus reinforced levees were needed. It should be noted that Mesopotamia's canal network was very intricate, and the slope of each canal was critical to its operation because the flow of water depended upon gravity [7]. This necessitated the digging of long channels, land surveying before construction, regular dredging, reed pulling and embankment fortifying [3, 5, 8]. Additionally, the independently invented system of bucket/counterweight (shaduf) was used to deliver the water from the river to the irrigation network if the water level in the former was lower than in the latter. I will not describe other technological inventions of the ancient Mesopotamians related to water delivery and transportation. Suffice is to say that they were capable of underground water transportation for long distances in Northern Mesopotamia (Assyria) and that a 50-km long underground conduit is still preserved near ancient Nineveh [7]. The obvious question that has to be posed: where is this system now? It is common knowledge for many centuries the vast parts of contemporary Iraq and neighboring areas could not be described as an agricultural haven.

There are two answers to this question. First is the outside man-made interference, which can also be called "damage from without". It is known that plundering invaders, first Parthians, and later Arabs and Mongols were responsible for considerable destruction of the irrigation systems. Moreover, upon completing the conquest of these areas, they did not concern themselves with sufficient investment into repairs, unlike early Mesopotamian rulers. Even more damage was done by the inability of the population to maintain the canal network through constant repair and innovation coupled with over-reliance on the waterways of the past. "Repeat of the old" haunted Mesopotamians as well as Egyptians. Alas, with time many old canals became unusable due to change of river courses.

Additionally and most importantly, repeated use of the same irrigation methods throughout Mesopotamia lead to an extensive salinization of the soil and, hence very low fertility. Basically, if surplus water was not drained from the land, the water table rose and brought up the salts, the accumulation of which over time made the soil infertile. It has been proposed that the effects of increased salinity were already felt in ancient times and in the beginning were dealt with successfully, i.e., by replacement of one type of agricultural produce by another – e.g., shift from wheat to barley over the second part of the 3rd millennium BC [8]. However, later effects were felt even stronger and it is possible, albeit not definitive, that increased soil salinization lead to complete abandonment of major urban centers of Southern Mesopotamia, i.e., the most ancient cities of Sumerian civilization. But again, the worst was still to come. The destruction of irrigation networks by invaders dealt an even stronger blow to the area where human civilization originated. What once was world's technological leader (should we say, not only in agriculture) is today a relatively backward country (and has been for centuries). Much of the prime land of ancient Mesopotamia was abandoned during the 2nd millennium AD [5]. Interestingly, the consequences of extreme salinity were already known to the Babylonians since one of the poetic images for describing a famine is the whiteness of the fields [8].

Here we clearly see a major and initially very successful technological intervention of the environment. The Mesopotamian civilization is a direct result of this intervention, with a much more ingenious effort and social organization than in Egypt. The same vulnerability against natural and man-made disasters is evident and, contrary to Egypt, a definite and rapid civilizational decline (not even stagnation) caused by irreversible environmental change. Still, one must say that Mesopotamian culture, Mesopotamian technological outlook and prowess were much more "active" or "extravert" than Egyptian, which can be called "re-active" and "insulated". It should be also noted that it was not per pure chance that many other technological (and not so technological) inventions that we currently use (measurement of time and establishment of calendars, writing, glassmaking, etc.) come to us from Mesopotamia rather then from Egypt (although Egyptians were also very capable of writing and calendar-drawing). "Active" cultures may bear more risks, but they are also much more fruitful. It is our task to try to reap fruits of our future activity while minimizing the risk of cultivation.

3. Effects of "Intermediate" Speed – Lead Utilization and Lead Poisoning: Then and Now

I will now turn to the second group of undesirable technological consequences. In this case, the introduction of novel technology leads to notable effects within a reasonably short time period. By definition, such consequences are almost immediately partially known to the public and thus, preventable, but sometimes continue to be underappreciated and thus non-remedied. One of the most well-known examples of such is the history of lead poisoning. The decades-old controversy over the use of lead as a fuel and paint additive is a mere footnote to centuries of torturous historic voyage of this useful but also deadly metal.

Lead was first mined in Asia Minor about 6500 BC. A 6000- to 8000-year-old lead necklace found in Anatolia was long cited as the earliest known lead object. However, it is made out of galena (PbS, lead sulfide or lead ore), and the earliest objects made of pure lead are bracelet from Yarim Tepe and small bead from Jarmo (Iraq), both probably dating to late 7th millennium [9]. The findings of lead are thus almost three millennia earlier than that of copper. Lead's easy workability, low melting point and corrosion resistance were among its obvious attractions and lead to its extensive technological use.

Acute lead toxicity was recognized by the II century BC Nicander of Colophon described the colic and paralysis that followed lead ingestion [10]. However, lead assumed a pre-eminent technological position when Romans devised projects for providing their towns with water [11]. The amount of lead consumed by the Romans was very high. It was estimated that 12,000 t of lead were used for the construction of just one of the siphon units of the Lyon aqueduct [11].

Other uses of lead were numerous. Lead was a key component in face powders, rouges, and mascaras; the pigment in many paints (hence "crazy as a painter" expression); a means of birth control; a sweet and sour condiment popular for seasoning and adulterating food; a wine preservative; the malleable and inexpensive ingredient in dinnerware; the basic component of lead coins; and a partial ingredient in debased bronze or brass coins as well as counterfeit silver and gold coins. The early victims of lead toxicity were mainly lead workers (interestingly, the patron god of smithies, Vulcan, exhibited several lead poisoning symptoms: lameness, pallor, and wizened expression) and, likely, wine drinkers.

Sugar of lead (lead acetate) was used to sweeten wine (to counteract the astringent flavor of tannic acid), and the gout that resulted from this was known as saturnine gout [12]. Now it is thought to be the result of lead, or leaded eating and drinking vessels. Other consequences of lead dinnerware utilization must have been multiple and prominent. It was calculated that lead-sweetened Roman wine contained up to 20 mg/l of lead and it was therefore hypothesized that decreased infertility and increased psychosis among the Roman aristocracy (many historical figures such as Caligula and Nero may serve as examples of the former and latter), and may have been an important factor in the fall of Rome [13, 14].

Notably, the negative effects of lead were known to the Romans themselves, and are mentioned by both Pliny and Vitruvius [11]. What they obviously did not realize was that their everyday low-level exposure to the metal rendered them vulnerable to chronic lead poisoning. The symptoms of acute lead intoxication appeared most vividly among miners who interacted with it on a daily basis and, not surprisingly, this work was done mostly by slaves. The unpleasantness of lead mining was neutralized late in the Empire when the practice was prohibited in Italy and consigned completely to the provinces [15].

Most importantly, readily abundant, easily malleable, lead (*plumbum*) was ideal for the production of water pipes, which were fabricated by *plumbarii* (plumbers) from fitted rolled sheets in a variety of diameters [16]. Hence its Latin name – *plumbum* and its connection to "plumbing" in English and other languages, e.g. Spanish "plomo (lead)/plomero (plumber)". Lead was the key component of inexpensive and reliable piping for the vast plumbing network that supplied Rome with water [15]. Such pipes were extensively used but also known to be a potential source of soluble lead. Still, it should be noted that Rome is situated on calcareous rocks, and the frequent cleaning of such limestone encrustation suggests that deposits of calcium carbonate in the pipes protected against corrosion and insulated against the introduction of lead into the water. The water also is likely to have flowed continuously and thus, not have been in prolonged contact with lead. And, as well as lead pipes, it also would have run through terracotta.

Therefore, many scholars tend to think that lead poisoning through the water was not as prevalent in ancient Rome as it would seem [17–19]. It is still unlikely, in my opinion, that these scholars, being acutely aware of the contemporary research of lead's effects on the human organism, would volunteer to use the water that passed through lead pipes or, moreover, allow their own children to do so. It is possible the hardness of Rome's water caused heavy deposits of calcium carbonate to form on pipes and in turn prevented the lead of the pipes from coming into contact with the water, thus reducing the chance of getting lead poisoning from drinking water. Leaded water might not have spread endemic dementia and psycosis in ancient Rome (although, chancely, *plumbeus* in Latin means both "made of lead" and "dull/not bright"), however, this debate is likely to be ongoing.

Still, another and more probable cause of chronic lead poisoning (plumbism or "saturnism" because its symptoms seemed indicative of the planet's characteristics) was not through the water but by consumption of *defrutum* or *sapa*. Several classical authors, notably Cato, Columella, and Pliny all describe how unfermented grape juice (*mustum*, must) was boiled to concentrate its sugar [17]. The question is whether the must was boiled in pots of lead or bronze. The former is explicitly invoked by Cato (in *De Agri Cultura*, ca. 160 BC), and also by Columella and Pliny (I century AD) [17]. Several researchers found that must reduced to one-third its volume contained lead approximately at the concentration of 1,000 mg/l, which upon mixing with wine will contain 21 mg/l of lead. Such concentration would definitely induce symptoms of lead poisoning [17, 20, 21].

Once again, the Romans knew that lead was toxic. Celsus (ca. 30 AD) listed white lead among poisons, but also recommended its use in a wide range of ointments applied to wounds to stop bleeding and reduce infection or inflammation [22]. Roman architect Vitruvius reported that "water is much more wholesome from earthenware pipes than from lead pipes. For it seems to be made injurious by lead, because white lead, a pigment base produced by soaking lead in vinegar… is said to be harmful to the human body" [16]. Furthermore, Vitruvius, who wrote during the time of Augustus, indicated that the Romans knew of the danger of lead pipes and, consequently, that terracotta was preferred [17]. "This may be verified by observing the workers in lead, who are of a pallid color; for in casting lead, the fumes from it fixing on the different members, and daily burning them, destroy the vigor of the blood; water should therefore on no account be conducted in leaden pipes if we are desirous that it should be wholesome. That the flavor of that conveyed in earthen pipes is better, is shown at our daily meals, for all those whose tables are furnished with silver vessels, nevertheless use those made of earth, from the purity of the flavor being preserved in them" [16].

However, both the Romans and Greeks continued to expose themselves to the effects of a metal they knew was harmful. More than wine (or water transported through lead pipes), the dainties and elaborate sauces prepared with *defrutum* are likely to have been the primary source of ingested lead by the Roman aristocracy. *Defrutum* was only one of several remedies to sweeten or preserve potentially sour wine [23]. Sea water and resin also were used, as was lead acetate (sugar of lead), which is formed by treating litharge with acetic acid [17]. Both Martial and Pliny complain about poisonous components that are put into wine by dishonest winemakers. Thus, one can draw one's own conclusions from this data that seems sufficiently consistent.

Many authors contend that contamination of the food and drink of ancients was very high. E.g., it was estimated that a liter of must contained 237 mg of lead or even more, up to 782 when it was manufactured according to the ancient sources [11, 24]. However, the first definitive description of lead poisoning epidemics comes only from the VII century AD [11]. Was it only for the lack of observation? Further reports followed promptly. Outbreaks of acute lead colic continued in Europe (Spain, France, England, Germany) up to the XVI century when German physician E. Gockel traced a colic epidemic to lead-adulterated wine, which in turn lead to banishment of lead from winemaking by the Duke of Würtemberg (with the death penalty as punishment for violators) [10, 20]. A new history of lead as a poison began in the late XIX century when it was demonstrated that even mininiscule amounts of it are harmful, especially in children [10, 25].

Granted, it will be a gross oversimplification to blame lead poisoning for "the fall of the Roman Empire". Still, one must not forget that XX century evidence of lead poisoning through the use of tetraethyl leaded-gasoline (first attested in 1920s) and childhood lead poisoning via lead paint (first attested in 1890s and definitely identified in 1904) [10, 25] shows that it could significantly affect the afflicted populations. Recently, there were a number of studies (operating with the data unavailable in ancient times) demonstrating various degrees of correlation between lead utilization and defects in children's development or even violent crime rate in several countries. Moreover, we now know that even picomolar concentrations of lead are toxic and the manifestations of acute symptoms are not necessary for the development of lead-related effects [10].

And yet, lead paint was effectively outlawed in the U.S. in 1978 despite the accumulation of a large body of knowledge regarding the effects of lead poisoning in children by the 1940s [25]. Also, starting with the 1975 model year, American automakers began to equip new cars with pollution-reducing catalytic converters designed to run only on unleaded fuel after five decades of continuous utilization of leaded fuel.

It is clear that the Romans knew lead to be dangerous, although they did not associate it with their lead cooking vessels. However, there is a noticeable difference between the "pure knowledge" and its application even in the case of medical necessity. It is obvious that ancient society was simply not capable of effective "de-leading" through communication of information and societal feedback. Furthermore, it cannot be blamed for such a "backward" behavior since it took nearly a century for much more potent and well-informed modern societies such as British and American to put a barrier to human lead poisoning in the XX century. Could the Romans have been more efficient than near-contemporary Americans?

Interestingly, in a report to the U.S. Surgeon General on the effects of leaded gasoline submitted in 1926 we can read a prophecy that in my opinion summarizes many technological risks of present, past and future: "It remains possible that, if the use of leaded gasoline becomes widespread, conditions may arise very different from those studied by us which would render its use more of a hazard than would appear to be the case from this investigation. Longer experience may show that even such slight storage of lead as was observed… may lead eventually to recognizable lead poisoning or to chronic degenerative diseases of a less obvious character".

4. Immediate (High-Speed) Negative Technological Impact – Novel Infectious Diseases and Drugs

A typical and often-cited prototypic event of "interaction with the unknown" is the development of or confrontation with a novel toxic (poison) or infectious substance (bacteria or virus). The obvious example is the discovery of radioactive elements, which lead to incurable diseases in many scientists that worked in this field in the early XX century or the development and introduction of new drugs with unforeseen side effects. The history of thalidomide is probably the best known, but current drug developers are not immune from similar disasters, although to a lesser degree. Recently, a new immunological drug led to a phenotypically unique fatal and near-fatal reaction in test subjects within minutes of administration. The six trial volunteers suffered multiple organ failure which almost killed them, after receiving injections of TGN1412, a monoclonal antibody designed to calm the immune system, but which resulted in a so-called "cytokine storm" or acute immune malfunction [26, 27].

These and similar events have affected relatively small groups of individuals and were effectively remedied as they needed to be. We know very well that contemporary biologists, chemists and physicists are wearing protective gear and are unlikely to touch novel chemicals with their bare hands (or, even less so, to taste them as their predecessors were doing until the XIX century). Similarly, extensive drug testing in animals is now prerequisite before their first assessment in humans. Thus, we can either easily discontinue the use of acutely dangerous technology or prevent its negative impact with an antidote. However, this applies only if a small group of individuals is affected. It is much more difficult to draw the same lessons if a technology instantly affects larger social groups or the society as a whole. Immunization of thousands of people with polio vaccine containing potentially carcinogenic virus SV40 (in 1960s) could not have been reversed, but luckily it did not result in a medical disaster.

Yet another contemporary example of immediate harm after "interaction with the unknown" is the introduction of HIV into the worldwide population from within Sub-Saharan Africa, which occurred during our lifewatch. The persistent dangers of avian influenza and West Nile disease epidemics that luckily have not materialized thus far are another two examples in the same vein. It is apparent that the possibility of rapid spread of these and other infectious diseases is directly linked with modern transportation technologies, which are capable of carrying large number of humans from and to virtually every corner of the world. This example has many similarities with the well-described event that took place upon human migrations of the relatively recent past, which interestingly have not attracted much attention until the XX century. Although, it is not always helpful to pronounce judgments, there is no doubt that this lack of attention was caused by the fact that the industrial (or "Western") world did not suffer from this interaction as much as those areas, which encountered new infectious agents brought by the European migrants. Over the course of history they have brought many different “HIV”s to various parts of the world.

However, it might be helpful to start with the only infectious disease that may have preceded HIV as being acquired by Europeans from overseas. This often-quoted example of introduction of New World disease into the Old World is syphilis, which may have occurred in Europe immediately after Columbus’ expedition although this question has been hotly debated and is unlikely to be settled [28, 29]. We may as well accept this theory just to remind ourselves that infectious agents may travel both ways and that no society is now immune to the rapid introduction of unknown and dangerous disease. Therefore, modification of living objects envisioned by many biotechnological projects should be performed with the utmost precautions.

It is imperative to remember that humans are extremely vulnerable to hence non-encountered infectious agents. May I remind as an example that the Columbian exchange brought many deadly diseases to the New World. This was a single event of catastrophic consequences. It lead to severe population losses in American Indian populations (new diseases against which those communities had no immunity, included bubonic plague, cholera, influenza, malaria, measles, scarlet fever, smallpox, tuberculosis and typhoid). It is now accepted that within a few decades of European arrival the native population dropped 90–95 % mostly due to disease [29]. One study gives that from 1519 to 1597, population of central Mexico decreased from 11 to 2.5 million [30]. The example of a South American tribe that in the beginning of the XX century numbered nearly 7,000 individuals and was virtually extinguished in less than 50 years despite significant societal efforts to the contrary [30] makes those estimates very believable.

The main underlying reason for this catastrophe being unidirectional (affecting American Indians and not Europeans) is clearly the absence of immunity in an unexposed population. Similar dramatic events have occurred in other parts of the colonized world, notably in Africa and Australia (Darwin wrote that “wherever the European has trod, death seems to pursue the aboriginal”). The first example of bacteria-driven genocide is probably that of the Canary Islands’ natives Guanches, which were effectively wiped out by two major epidemics that helped the Spanish to conquer the islands in the late XV century. By the end of the XVI century there were only few a Guanches left, all of them of mixed blood [31]. “Very few experiences are as dangerous to a people’s survival as the passage from isolation to membership in the worldwide community” [31]. A similar fate struck Tasmanians as well as many South American Indians.

However, one must also appreciate the historically small influx of migrants from these countries into Europe. This situation has been completely reversed in the latter decades of the XX century and has lead to major changes in world epidemiologic prognosis. In fact, any mass migration or even individual travel will bring new diseases to hence uninfected parts of the world (numerous examples can be given). Since humanity is unlikely to abandon or even limit its mobility, this is a risk that must be constantly managed. The reverse epidemiological trend may be underway. Contemporary European and North American populations are unevenly vaccinated artificially or naturally against diseases that are currently non-prevalent in these areas of the world and are therefore very vulnerable to the sudden occurrence of known and unknown diseases, which might be introduced (or re-introduced) from overseas.

It is also well-known that a major population center, especially one that is intimately linked to the international exchange of goods and people will be an especially soft target for an epidemic. It should not surprise us that Athens, Rome and Constantinople were all severely decimated by repeated epidemics and it is not per chance that the Black Death entered Europe via Italian ships. One can easily define the existence of such big trading cities as a result of complex technological breakthrough, be it in the past or in the present, which could not be attained without a highly developed means of transportation (e.g., maritime or aviation skills), production, commerce, social management, etc. Such heavily populated "technological" centers are always at risk for epidemics even without a precipitating event such as mass migration, war, etc. Rapid advancement of new diseases is intimately connected to the potential danger from newly developed drugs as discussed above. Epidemics of novel diseases will necessitate rapid intervention with such novel, possibly insufficiently tested medicines. Thus, a full circle is made, encountering the risk of introducing of a "novel poison" into the general population.

I will conclude by noting that all historical examples (these and dozens of others) are most certainly unable to prevent future technology-driven disasters or, stating it mildly, the negative consequences of novel technologies. There is only one remedy. All technologies should be extensively tested, both the short- and long-term consequences of their application must be studied in detail and the results of these studies need to be effectively communicated both to cognoscenti-of-the-art and society as a whole, which should be both well-informed and sufficiently empowered in order to make a correct decision in every particular case.

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NANOTECHNOSCIENCE AS A CLUSTER OF THE DIFFERENT NATURAL AND ENGINEERING THEORIES AND NANOETHICS

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Abstract. In the modern scientific landscape we can see as yet more a special type of scientific discipline – a scientific-technological discipline. Nanotechnology is not only a new type of scientific-engineering discipline, it also evolves in a "non-classical" way. Nanotechnology is at the same time a field of scientific knowledge and a sphere of engineering activity, in other words – NanoTechnoScience – similar with Systems Engineering as the analysis and design of large-scale, complex, man/machine systems but now as micro- and nanosystems. Nanoethics is an important and inalienable part of the NanoTechnoScience.

Keywords: scientific-technological disciplines, techno-science, engineering theories, nano-ontology, NanoTechnoScience, nanosystems engineering

1. Introduction

The world in which we live in the 21st century is certainly shaped by globalisation, electronic worldwide information distribution, dissemination, and resonance as well as a planetary almost ubiquitous presence of the media and network interlockings rendering it ever more difficult to orient oneself in the overflow of information and to select the necessary relevant orientation. Knowledge and results in any scientific discipline or technical development are not fixed for decades or centuries as they used to be, but they are changing all the time at an unbelievable rate of innovation and expansion. At the

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same time, there is almost limitless storage (and storing capacity) and extremely massive addition and "overflow" of information elements in the ever growing networks mediated and realised on a global scale through the so-called new technologies and scientific-technological disciplines.

The sphere of scientific-technological disciplines, which are intensively elaborated today, along with the natural-scientific, mathematical, social disciplines and humanities, incorporates a great number of the most varied fields of research, engineering, and design. They have at present or are founding disciplinary organizations (a specific range of publications and a limited research community), and now have a stable position in science. In addition, as shown above, by the second half of the 20th century, a majority of the scientific-technological disciplines had begun their own theoretical studies, which have received the status of a technical theory. We have today in the scientific community more connection between science and technology (also in the basic research sphere). We are saying already about "technoscience". In the modern scientific landscape we can see as yet more a special type of scientific discipline – a scientific-technological discipline. New scientific-technological disciplines are unique in that they emerge at the interface between the scientific and engineering activities and are supposed to ensure an effective interaction of the two aforementioned types of activity. Characteristic of the scientific-technological disciplines is a more close relationship with the engineering practice.

2. Nanotheory as a Cluster of the Different Natural and Engineering Theories

There are many different definitions of nanotechnology.

Nanotechnology is:

(1) *The sphere of the scientific and engineering activity* that connected with

- Organization of the process of creation, fabrication, implementation, use and development of nano-scale systems, that is, cooperation of the various design tasks and coordination of the different specialists who solved these tasks
- Support to assemble and to integrate of the heterogeneous parts of the designed nanosystem in the organic whole

(2) *The sphere of knowledge*, the complex scientific and engineering discipline that would integrate

- Means, methods, operations and procedures of design and research of the nano-scale systems
- Methods and principles of the organization of the scientific and engineering activity
- Knowledge and methods of the modern mathematical, technological, natural and another sciences that used for analysis and design of the nano-scale systems and for organization of the scientific and engineering activity

(3) *A concrete-methodological position* that is connected with holistic investigation of the nano-scale systems and of the process of their research, generation, implementation and fabrication from the cybernetics (algorithmic) and systems approach point of view.

One of these definitions, a so-called ‘real’ definition, which is specialized to different already existent fields and intended applications, refers to a list of particular cases of current research topics. “Such lists typically include scanning probe microscopy, nanoparticle research, nanostructured materials, polymers and composites, ultra-thin coatings, heterogeneous catalysis, supramolecular chemistry, molecular electronics, molecular modeling, lithography for the production of integrated circuits, semiconductor research and quantum dots, quantum computing, MEMS (micro-electromechanical systems), liquid crystals, small LEDs, solar cells, hydrogen storage systems, biochemical sensors, targeted drug delivery, molecular biotechnology, genetic engineering, neurophysiology, tissue engineering, and so on” [1].

So nanotechnology comprises the emerging applications of nanosciences. Some applications of nanotechnology can be more or less defined. “The unusual properties of carbon nanotubes make possible many applications from battery electrodes, to electronic devices, to reinforcing fibers, which make stronger composites. … we describe some of the potential a ins that researchers are now working on. However, for the application potential be realized, methods for large-scale production of single-walled carbon nanotubes will have to be developed. The present synthesis methods provide only small yields, and make the cost of the tubes about $1,500/g ($680,000/£). On the other hand, large-scale production methods based on chemical deposition have been developed for multiwalled tubes, which are presently available for $60/£, and as demand increases, this price is expected to drop significantly. The methods used to scale up the multiwalled tubes should provide the basis for scaling up synthesis of single-walled nanotubes. Because of the enormous application potential, it might be reasonable to hope that large-scale synthesis methods will be developed, resulting in a decrease in the cost to the order of $10/£” [3].

Molecular electronics, early recognition of the carcinoma on the molecular level and paint coating that change colour in response to change in temperature or chemical environment from the experts’ assessment refer to the more long-term perspective. “… it is important to recognize that the use of nanostructuring or nanostructures to generate, fabricate or assemble high surface area materials is at an embryonic stage. The effect of the nanostructure and our ability to measure it will be increasingly important for future progress and development of materials for the marketplace” [4].

But the hydrogen accumulation in the nanostructures is estimated as existing in the stage of the technological realization [5]. “Current applications of nanoscale materials include very thin coatings used, for example, in electronics and active surfaces (for example, self-cleaning windows). … nanoscale electronic devices currently being developed are sensors to detect chemicals in the environment, to check the edibility of foodstuffs, or to monitor the state of mechanical stresses within buildings. Much interest is also focused on quantum dots, semiconductor nanoparticles that can be ‘tuned’ to emit or absorb particular light colours for use in solar energy cells or fluorescent biological labels. … Applications of nanoscience and nanotechnologies are also leading to the production of materials and devices such as scaffolds for cell and tissue engineering, and sensors that can be used for monitoring aspects of human health. Many of the applications may not be realised for ten years or more (owing partly to the rigorous testing and validation regimes that will be required). In the much longer term, the development of nanoelectronic systems that can detect and process information could lead to the development of an artificial retina or cochlea. … So far, the relatively small number of applications of nanotechnologies that have made it through to industrial application represent evolutionary rather than revolutionary advances. Current applications are mainly in the areas of determining the properties of materials, the production of chemicals, precision manufacturing and computing. In mobile phones for instance, materials involving nanotechnologies are being developed for use in advanced batteries, electronic packaging and in displays. The total weight of these materials will constitute a very small fraction of the whole product but be responsible for most of the functions that the devices offer. In the longer term, many more areas may be influenced by nanotechnologies but there will be significant challenges in scaling up production from the research laboratory to mass manufacturing" [6].

The divided development of physics (electrical engineering – electronics – microelectronics – material design – quantum effects), biology (cell biology – molecular biology – functional molecule design) and chemistry (complex chemistry – supramolecular chemistry) in perspective must be integrated in the nano level [5] (Fig. 1).

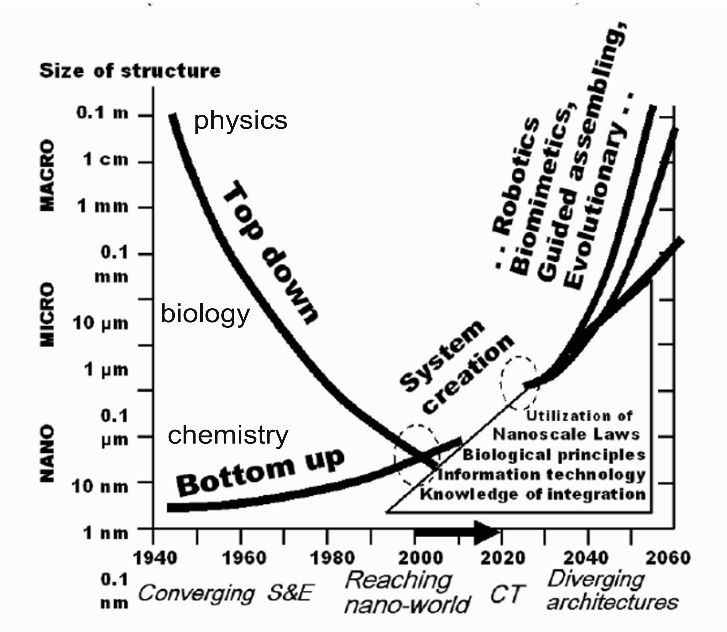

Figure 1. Reaching the Nanoworld (~2000) and NBIC methods for systems creation from the nanoscale (2000–2020) [7]

Exactly such cluster of the different theories is nanotechnology which at present seems to be the most typical representative of the modern technoscience. And indeed it integrates all these heterogeneous theories from large number of different disciplines including physics, chemistry, biology, medicine and engineering sciences? “As a simple example we can take a Biosensor which allows the detection of DNA sequences by turning the surface Plasmon resonance of nanosized gold particles in a suspension. It can be easily seen that in such a problem *quantum physics*, *chemistry*, *biology and finally microtechnology* are involved” [2]. “Although we were able to develop non-viral gene transfer systems that were efficient enough to gain commercial success *in vitro,* the use of this material *in vivo* did not pan out because of the lack of efficiency and untoward effects found in some biological systems. To improve this work and to expand the application of synthetic materials to other applications, became convinced that *a multidisciplinary approach involving chemists, engineers, and biologists was necessary*” [7].

This is only the orientation on the general or may be even “universal” world of view – nano-ontology. “The most common of these define nanotechnology as the investingation and manipulation of material objects in the 1–100 nanometre range, in order to explore novel properties and to develop new devices and functionalities that essentially depend on that 1–100 nanometre range. Whether intentionally or not, this definition covers all classical natural science and engineering disciplines that investigate and manipulate material objects, including chemistry, materials science, solid state physics, pharmacology, molecular biology and chemical, mechanical and electrical engineering” [1]. So nano-objects are identified only with ultimate general ontological properties – with appropriate dimensions which are determined without respect to their nature.

Nanotechnology is not only a new type of scientific-technological discipline; it also evolves in a “non-classical” way.

There are two basic methods for the development of ‘classical’ technical sciences: first, from the new applied research directions of any natural-scientific theory; and second, they may ‘bud out’ from a corresponding, basic technical theory within the framework of a ‘family’ of homogeneous scientific-technological disciplines which have recently emerged, and which are oriented on use in the engineering practice and design not only of natural sciences, but for social sciences and the humanities as well. The range of design tasks has also been enlarged, and now includes the problems of social and economic, engineering and psychological, systems and other aspects. Finally, there appeared such scientific-technological disciplines, which are the result of complicated interdisciplinary processes taking place in the technical sciences. Such scientific-technological disciplines may be referred to as the modern complex of (‘non-classical’) scientific-technological disciplines. Among them are, for example, systems engineering, ergonomics, systems design, informatics, operations research, and so on. The present complex scientific-technological disciplines represent a reality of contemporary science. However, they do not fit into the traditional forms of organization or methodological standards. It is precisely the sphere of these investigations and disciplines where an ‘internal’ interaction of social, natural, and technical sciences is being realized today. These sciences also summarize research and design (R&D) orientations and form a single R&D-establishment (for complex research and system designing) in the process of solving complex scientific and technical problems and tasks. The corresponding investigations, for example, in the field of artificial intelligence, require a special management support and search for new forms of scientific organization (for instance, in temporary scientific teams and problem groups). To this type of the modern scientific-technological discipline also nanoscience & nanotechnology belong.

I. Hacking [8] and R. Giere [9] combine structural view (see Fig. 2) with technological approach to the understanding of the scientific theory, which more corresponded with nano-scientific research.

Mathematical structure - CORE „K“
(Newton’s laws, Maxwell’s equations, hyperbolic geometry, etc.)

***K* = < *M*p, *M*pp, *M, C* >**

M*pp** is set of ***partial potential Models

M*p** is set of ***potential Models

M is set of ***Models** and*

C is set of ***Constraints*** (restrictions which essentially binds together
some of applications of a theory)

I is set of ***intended applications of theory***, which conditions
I ***M*pp** must be meet

Basic element of theory (“theory-element”) *„T“ is* ***T* = < *K, I* >**

Hierarchical structure of such elements is the **Network *„N“***
of the different elements of this theory.

Figure 2. Structural concept of the scientific theory [11–13]

The so called non-statement view of theories as set-theoretical predicates or model sets was mainly developed by Sneed and Stegmüller – after ideas by Suppes. This approach which is also called a structuralist view of theories understands a “theory” as a totality or net of theory elements which are partially ordered by specialising relations or constraints, i.e. edition of special laws. (Occasionally and originally the ordered pair of the mathematical structural core K and the set of partial potential models being the intended possible applications – the ordered pair {K, I} – is called a theory – or nowadays “theory-element” a partial potential models of a theory comprise all the applications conceived of which are not yet described by theoretical functions and observables, namely the models of intended applications.) By definition the structural core (defined only by mathematical relations) comprises the potential and partial models as well as constraints (i.e. theoretically acquired interconnections between the partially overlapping partial potential models) and the models themselves (i.e. the factual systems are really successfully described by the theory). Empirical statements and hypothesis of a theory are now met in the statement that the respective intended applications of the theory belong to the applications of the net (or the structural core) fulfilling the constraints. The set of partial potential models (i.e. the real systems which are intended for application of the theory without theoretical functions) are supplemented by the respective theoretical functions leading to this set of potential models. To be sure the adding of theoretical functions and specialisation (by added special laws) has to lead to a partial set of “fulfilled” models (M) such that the whole sequence of theoretical functions has to satisfy the constraints. According to the structuralist non-statement approach a theory consists simply of an ordered pair of a mathematical framework of formulae (structural core) and a set of possible attended applications and constraints. The possible applications are object systems of real systems which are up for application of the theory and which are usually given by certain paradigmatic initial models usually proposed by the founder of the theory. The theory then is an ordered set theoretical predicate (after Sneed and Stegmüller). “Formally, a core K may be represented either as a quadrupel K = [M_p, M_{pp}, M, C] or as a quintupel K = [M_p, M_{pp}, r, M, C]. Here, M_p, M_{pp}, and M are the sets mentioned ... C is a set of constraints, i.e., a subset *of the power set of M*; and the *restriction function* r: M_p – > M_{pp} transforms an element of M_p, i.e. the potential model, into an element of M_{pp}, i. e., into a partial potential model by “lopping off” all theoretical functions” [10]. The total theory might be an extended core leading to a theory net by adding specialised laws and respective new constraints, restriction functions and new intended models to be inserted in to the set of potential models and fulfilled models. In short, a theory is therefore a relation predicate defined over the set of potential models of applications. The predicate “... is a theory” states the existence of a relation between the mathematical structural core and the set of at the time specified set of intended applications of a theory, the set of potential models being extendable: further potential, previously not intended applications can be integrated (e.g. extension of Newtonian classical dynamics to include gravitational systems by adding a law of gravitation or the extension by adding Hook’s law of linear restoring force to include harmonic motion). A series of interesting results can be derived from this new conception: it is possible to speak of one *and the same* theory, even if the set of special laws of the theory and the set of intended models is expended, as long as the structural core (the mathematical basic laws) of the theory are maintained. E.g. Newtonian mechanics of the Newton’s first three axioms is specialised by adding special laws like Hook’s law or the law of gravitation remaining still the same theory, but differentiated and specified.

Ronald Giere understands theory as a population (family) of models or still better “a family of families of models”, which can be related to the reality only indirect. “A real system is identified as being similar to one of the models” [9]. In the relation of the theoretical models with the real systems technology plays a decisive role.

Giere [9] understands “theory as comprising two elements: (1) a population of models, and (2) various hypothesis linking those models with systems in the real world. Thus, what one finds in the text books is not literally the theory itself, but statements defining the models that are part of the theory.” Important is the relation of similarity between the models and their real systems to which the models apply as cases of application: “the links between models and the real world ... are nothing like correspondence rules linking terms with things or terms with other terms. Rather, they are again relations of similarity between the whole model and some real system. A real system is *identified* as being similar to one of the models.” (eb., p. 86) Theories in that sense are no linguistic entities or just frameworks of formulae but heterogeneous sets consisting of abstract constructs, the theoretical models, and linguistic entities hypothesis about the fitting character of these models and their similarity with reality susceptible to grading and perspectives. With respect to relating and combining theoretical models with real systems to be covered *technology* now plays a decisive role.

Like Hacking's also Giere's constructive realism sees a proof of reality in the successfully managed technologies in handling entities (e.g. electrons) which earlier had the status of a theoretical entity, i.e. they are applied to cover and characterize new models or other theoretical entities. (If we routinely use nowadays electron rays in accelerators or in electronic microscopes successfully to resolve other scientific tasks, we understand in this technological sense the theoretically postulated electrons which were earlier mere theoretical entities now as scientific-technological *real entities.)* Insofar as electrons and protons are manipulated and applied in big technology measurement instruments and appliances to probe and prove the structure of other elementary particles like gluons, quarks etc., these electrons and protons now are "real" indeed. So "some of what we learned today becomes embodied in the research tools of tomorrow" [9].

For example such theoretical entities as quantum dots have found applications among biologists in fluorescent biological labels to trace a biological molecule. "Nanocrystals, also called quantum dots (QD), are artificial nanostructures that can possess many varied properties, depending on their material and shape. For instance, due to their particular electronic properties they can be used as active materials in single-electron transistors. Because certain biological molecules are capable of molecular recognition and self-assembly, nanocrystals could also become an important building block for self-assembled functional nanodevices. The atom-like energy states of QDs furthermore contribute to special optical properties, such as a particle-size dependent wavelength of fluorescence; an effect which is used in fabricating optical probes for biological and medical imaging. So far, the use in bioanalytics and biolabeling has found the widest range of applications for colloidal QDs. Though the first generation of quantum dots already pointed out their potential, it took a lot of effort to improve basic properties, in particular colloidal stability in salt-containing solution. Initially, quantum dots have been used in very artificial environments, and these particles would have simply precipitated in 'real' samples, such as blood. These problems have been solved and QDs are ready for their first real applications" [14].

This application of the quantum dots as marks and contrast agents in the other experiments is a technological verification and an indirect demonstration of the reality of the quantum dots. "Nanotechnologies already afford the possibility of intracellular imaging through attachment of quantum dots or synthetic chromophores to selected molecules, for example proteins, or by the incorporation of naturally occurring fluorescent proteins which, with optical techniques such as confocal microscopy and correlation imaging, allow intracellular biochemical processes to be investigated directly" (Fig. 3) [6].

The objects of the nanosciences exist first of all only as computer models that simulates in the definite form the operation of the oncoming system, that is to say, the designer's plan. Scientific investigation is always connected with the computer simulation und all, what we see in the display, is already determined from the some theory and their mathematical representations that are defined in the software of the simulation modeling.

Nano-ontology or nano-scientific world of view has a function of the methodological orientation for the choice the theoretical means and methods to a solution of the scientific and engineering problems. This is allows to change from one explanation and scientific world view to another without any problems. For example, electron in one place is considered as spherical or point electron charge, could be rolled spherically symmetric over the nucleus or as "the freed electrons travel through an external circuit wire to the cathode" or in "various electron trajectories", secondly – as "one can view the electron charge between the two atoms of a bond as the glue that holds the atoms together", thirdly – "the electrons in a nanotube are not strongly localized, but rather are spatially extended over a large distance along the tube", and in forth electrons as in the quantum theory can be viewed as waves: "If the electron wavelength is not a multiple of the circumference of the tube, it will destructively interfere with itself, and therefore only electron wavelengths that are integer multiples of the circumference of the tubes are allowed" [2].

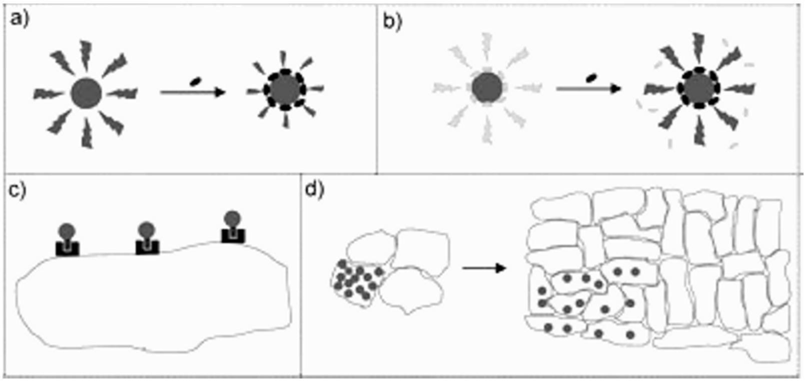

Figure 3. (a) Analytic detection by quenching of the quantum dot fluorescence (red) upon binding of the analyte (black) to the quantum dot surface. (b) By binding an appropriate organic fluorophore (green) as acceptor to the surface of the donor quantum dot fluorescence resonance energy transfer (FRET) occurs. FRET is stopped upon displacement of the acceptor dye from the quantum dots surface by the analyte. (c) Specific cellular receptors (black) can be labeled with quantum dots that have been modified with appropriate ligand molecules. (d) If a cell (grey) within a cell colony is labeled with quantum dots this cells passes the quantum dots to all its daughter cells and the fate of this cell can be observed [15]

In the so called 'teleological' definition nanotechnology is defined "in terms of future goals. To be specific, one needs to provide more than just generic values, such as health, wealth, security and so on, and more than just relative attributes like smaller, faster, harder, cheaper" [1].

So nanotechnology is at the same time a field of scientific knowledge and a sphere of engineering activity, in other words – NanoTechnoScience [16] – similar with Systems Engineering as the analysis and design of large-scale, complex, man/machine systems but now as micro- and nanosystems. "Nanoscience is dealing with functional systems either based on the use of sub-units with specific size-dependent properties or of individual or combined functionalized subunits” [2]. Nano systems engineering is the aggregate of methods of the modeling and design of the different artifacts (fabrication of nanomaterials, assembling technology for construction of comprehensive micro and nano systems, micro processing technology for realizing micromachines etc.). “Microsystems engineering and nanotechnology are two disciplines of miniaturization in science and engineering, which complement each other. Nanotechnology provides access to so far unused, completely novel effects. Microsystems engineering allows for the development of complete systems solutions due to its highly systemic potentials” [41]. Nano systems engineering as well as Macro systems engineering includes not only systems design but also complex research. Design orientation has an influence on the change of the priorities in the complex research and of the relation to the knowledge not only to “the knowledge about something”, but also to the knowledge as the means of activity: from the beginning *control and restructuring of matter* at the nanoscale is a necessary element of nanoscience (Fig. 4) [5]. Theories and generally speaking, methodical and methodological concepts as well as normative structures of actions and procedures in the nanotechnoscience would guide us in the form of interpretations and schematisations.

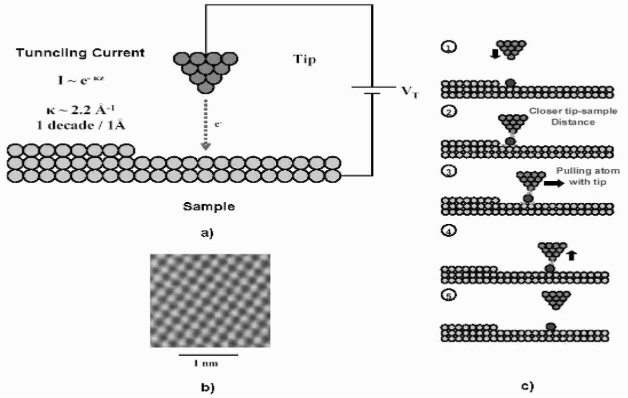

Figure 4. (a) Basic schematic of an scanning tunneling microscope (STM). (b) STM image of the Ag(001) surface. (c) Schematic diagram of molecular manipulation with the STM

The philosophy of this sometimes so-called new experimentalism, of a pragmatic technology oriented provenance and the action theoretic perspective may avoid these over-simplifications and at the same time refine the structural interconnection between idealized cognitive models or indented partial potential models of theories by stressing technological realisations and materialisations and action theoretical as well as operational sequences (as to be found in the design of operations and experiments etc.). It is in such a way that also the design theorist may relate his methodology or metamethodical conception of operative principles of design to the fulfillment of functional requirements and the optimisation or satisfycing of plurifunctional conditions – somehow independent of absolute truth claims (in the sense of substantive empirical true or truth-like theories). It seems to be typical for design tasks. “Nanotechnology is the engineering of functional systems at the molecular scale K.E. Drexler was talking about building machines on the scale of molecules" [17]. "Manufactured products are made from atoms, and their properties depend on how those atoms are arranged. This volume summarizes 15 years of research in *molecular manufacturing*, the use of nanoscale mechanical systems to guide the placement of reactive molecules, building complex structures with atom-by-atom control. This degree of control is a natural goal for technology: Microtechnology strives to build smaller devices; materials science strives to make more useful solids; chemistry strives to synthesize more complex molecules; manufacturing strives to make better products. Each of these fields requires precise, molecular control of complex structures to reach its natural limit, a goal that has been termed *molecular nanotechnology*. … Our ability to model molecular machines – of specific kinds, designed in part for ease of modeling – has far outrun our ability to make them" [18].

Micro-Nano Systems Engineering is a quite new direction in Systems Engineering (Fig. 5).

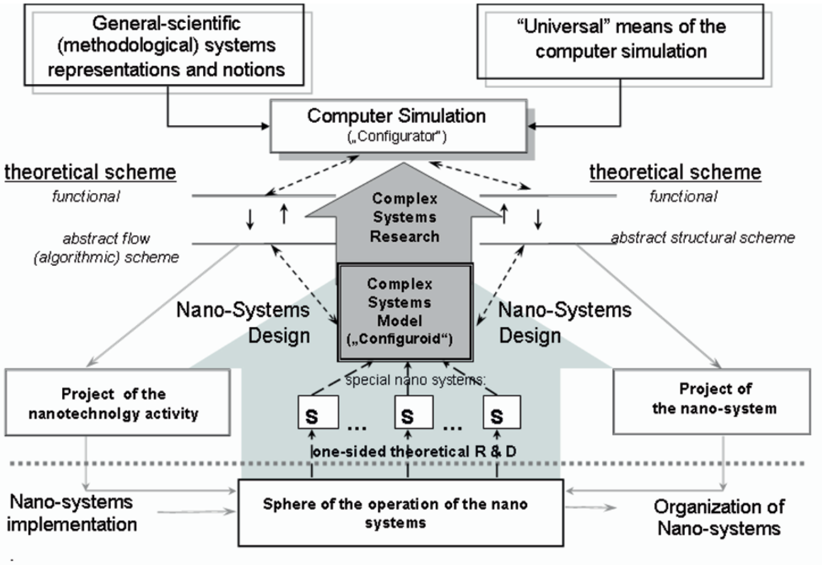

Figure 5. Nanoscience and Nanotechnology as technoscience

Micro/Nano Systems Engineering or systems engineering for micro and nanotechnologies is assembling technology for construction of comprehensive micro/nano systems, micro processing technology for realizing micromachines, microelectromechanical systems (MEMS), and microsystems. "The microsystems field has expanded to embrace a host of technologies, and microelectronics has now been joined by micro-mechanics, micro-fluidics and micro-optics to allow the fabrication of complex, multi-functional integrated microsystems". Micro Systems Engineering is the technologies and capabilities available in this highly interdisciplinary and dynamically-growing engineering field: "including, design and materials, fabrication and packaging, optical systems, chemical and biological systems, physical sensors, actuation, electronics for MEMS and industrial applications”.[1]

Generalized structural schemes came into being by way of generalizing different structural schemes: automatic control theory, network theory, switching circuit network theory, computer logics, and those used in socio-economic case studies – are combined in the so-called structural analysis of complex systems. Such unified abstract structural schemes make it possible to study an object in the most general form. For example, in the course of structural studies of automatic control systems, nothing remains but relations, their number, differential order, sign, and configuration. In the nanotechnology there are quantum circuits [3] or the schematic structure of the single-electron box: “Schematic structure of a single-electron box, consisting of a quantum dot (island), an electron connected to the dot through a tunneling junction, and an electrode coupled to the dot through an ideal, infinite-resistance, capacitor (left). Equivalent circuit of the single-electron box (right)” [2].

Generalized algorithmic schemes were applied in cybernetics and in the transformation of matter, energy and information. Actually, they are idealized representations of any system’s functioning, and they are the starting point for computer programming (they are related to the respective functional schemes in the theory of programming). Further manipulation of the model can be done in the simulation languages adequate to the problem. A respective algorithmic scheme of model (system) functioning is then developed on the basis of the structure given. It is automatically translated into a/the machine code and, in its turn, corresponds to a functional (mathematical) scheme. In nanotechnology such generalized algorithmic schemes can be for example the algorithm of lithography (“Steps in the formation of a quantum wire or quantum dot by electron-be lithography: (a) initial quantum well on a substrate, and covered by a resist; (b) radiation with sample shielded by template; (c) configuration after dissolving irradiated portion of resist by developer; (d) disposition after addition of etching mask; (e) arrangement after removal of remainder of resist; (f) configuration after etching away the unwanted quantum-well material; (g) the final nanostructure on substrate after removal of etching mask”) and the algorithm of the microscope image processing. “Transmission electron microscope image processing for a Ni particle on a Si0 substrate, showing (a) original bright-field image, (b) fast Fourier transform diffraction-pattern- type image, (c) processed image with aperture filter shown in inset, (d) image after further processing with aperture filter in the inset, (e) final processed image, (f) image of SiO substrate obtained by subtracting out the particle image, and (g) model of nanoparticle constructed from the processed data” [3].

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[1] Gianchandani, Y., Tabata, O., Zappe, H. (eds.) Comprehensive Microsystems. Vol. 1–3. Hardbound (2007). http://www.elsevier.com. See: http://www.me.kyoto-u.ac.jp/micro/english/laboratory/micromachine/micromachine.htm.

3. Nanoethics as an Important and Inalienable Part of the NanoTechnoScience

Although the human being is not the creator of nature but the latter's creature (s)he seems to be able to imitate and continue processes of creating: In a sense, humans create new materials, even new elements, artificial environments and imposing and very potent technical appliances, procedures and operations as well as systems. Is man nevertheless "the dominator and processor of nature" ("maître et possesseur de la nature") as the mathematician and philosopher Descartes had noted at the beginning of the era of enlightenment?

On the other hand, man being a very tiny grain of dust in the cosmos extending billions of light years cannot really feel elated as "the crown of creation" any longer: He had to experience in the history of Western science "several sorts of basic weaknesses and traumata" ("*Kränkungen*" after Freud) restricting the position of centrality and the respective conviction and complacency: loss of the astronomical centrality within the world (whether in our own planet system or galaxy or the cosmos at large), loss of the property of being "the objective and aim of creation" and the special position compared to other animals. Even the traditional opinion that he would be the being exclusively determined by reason had to be given up in the last century. Nevertheless, the human being enjoys even today still a special position in the order of nature – in so far as only humans can theoretically know and explain "nature", develop successful predictions and powerful explanations by using its theories, by manipulating according to their knowledge great parts and objects of nature and materials rather successfully. Humans would use all this for the aims to "exploit" nature for reaching man-made goals etc. This "power" – which might lastly even figure as a negative destructive technological encroachment on parts of natural systems – would be an expression of her or his special position. *Power and knowledge engender responsibility* – a special responsibility of the knowing and powerful being. This responsibility of the human being does not only pertain to human fellows as well as to the future but also to whole life-worlds including natural systems (ecosystems) of the so-called "spaceship earth".

This will also show up in the newly discovered and developed capability of being able to systematically and genetically change hereditary dispositions, or genetically to engender new biological kinds or even, e.g. so called chimaeras, mixtures out of different biological kinds. The biotechnical engendering of clones is nowadays already possible, however not yet without mistakes and risks.

Will humans now indeed become the technical "masters and dominators" over life and kinds amounting to being a sort of dominator of living nature? Will they play up as some sort of almighty beings in small proportions including potential fantasies of almightiness towards greater scales? Are humans allowed to change their hereditary stock or even "clone" human beings?

Technical and gentechnological successes should not induce a new complacency or self-overestimation, a new technological hubris in a world and period evidencing evermore delimitations, side effects and impairments of natural systems connections, in particular those ones induced by human encroachments on nature. Without doubt the sentence of the bible “Subdue earth!” was essentially involved, did lead to switch some directions. It is true that there was also the biblical imperative to cultivate, heed and preserve the Garden of Eden; yet the idea and imperative of *dominium terrae* is still very powerful, even practically almost dominating our relationship with nature. Instead of stewardship for nature we have domination and manipulation as a strategy. Did we take too literally this imperative of domination over the earth, did we exaggerate it until the limits of the possible or even bearable or even go beyond these limits? In fact it is true, even today humans are subdued by natural laws, they remain – in spite of all their technological power – a tiny part or a powerless particle within the cosmos at large. Elated and especially required is this being at most by its knowledge and indeed also in the moral sense: regarding its responsibility for the future of humankind and lately even of the biosphere and the ecosystems of the planet. Relative power – and indeed destructive power in the first place – would engender a special responsibility for those beings and systems which are dependent on the technological encroachments, or notably on non-interfering. Nature itself will thus become an objective of human responsibility.

Scientists believe that if nanotechnology makes it possible to model some process, the technologist ought to apply “everything he has understood”, ought to implement this process in reality. Edward Teller, the so-called father of the hydrogen bomb, stated in an interview that “the scientist or technologist ought to apply everything he has understood and should not put limits on that: whatever you understand, you should also apply. This statement constitutes … an overstated ideology of technocratic feasibility. It would turn, so to speak, Immanuel Kant’s old dictum “out implies can” into a reverse technological imperative “can implies out”. Whether or not man is allowed to, or ought to make, apply, produce, initiate, carry though everything he has able to make, or he can make and do certainly comprises a specific and precarious ethical problem, indeed. This is also acceptable for nanoethics and nanotechnology.

What real conditions are needed for the realization of the any professional ethics?

Our civilization would be inconceivable without the many things brought about by engineering. Engineers and designers have brought to life what once seemed incredible and fantastic (manned space flight, television, and so on), but they have also developed sophisticated means of mass destruction. Although technology is *per se* ethically neutral, the engineer cannot be indifferent regarding its application. However, a humanistic or anti-humanistic orientation of an engineer does not only find expression under extreme circumstances, it also has its implications in the engineer’s attitude towards the users of the products or with respect to the environment. The primary aim of technology and technical activity is to be useful to man, and this principle must be followed both in general and in detail. You can hardly consider it good if an engineer has not done his best to ensure ease of use, safety, absence of noise and pollution, and other requirements placed on the installation, building, or machine that he had designed. Even if those have been engineered through the effort of a large team of professionals, the moral responsibility of each member of the team for the product as a whole should not be diluted. There is another important facet of the problem. Many current manufacturing processes in the mass production of food, drugs, agricultural products and the like are known to be harmful to man and to nature. Today, the social responsibility of engineers and designers to society as a whole and to their clients is particularly topical. While philosophers and scientists argue about the best way to transform the world, engineers and designers are actually transforming it, not always to the best advantage, and often to the detriment, of people, society, and even mankind as a whole. That is why the problems of scientific, technological and business ethics, social responsibility scientists and engineers play a more and more important role in modern technocience and society [19]. But what are the conditions for the realization professional ethics in social praxis?

This is first of all the existence of the developed scientific and engineering community and then the development of the self-consciousness of scientists and engineers through scientific and engineering education systems. It is also important to have in society the social structures and social institutions that support of the relevant and moral orientation of scientists and engineers.[2] But these conditions do not else exist for the time being in nanoscience and nanotechnology. There is as yet no sustainable scientific and engineering community in the nanotechnoscience because of its principal interdisciplinarity. There are no special nanoethics courses in the system of nanoeducation and there is a lack of the necessary institutional support in the Russia. In Germany different aspects of scientific and engineering ethics are discussed and investigated already many years ago. See for instance, the short description of their activity in [21].

That is why nano-scale implantants are already implemented in the human organism and even in the human brain without satisfactory scientific explanation and technological development [22, 23]. In the last time there is an exponential growth of new firms which manufacture and sale different nanoproducts. “Currently, special attention in the public risk debate is being paid to synthetic nanoparticles. A vast potential market for nano-based products is seen in this field. New products, based on new properties of nanomaterials can be brought about in admixtures or specific applications of nanoparticles, for instance, e.g. in surface treatment, in cosmetics, or in sunscreens” [24]. “The Food and Drug Administration (FDA) says the rising number of cosmetics, drugs and other products made using nanotechnology do not require special regulations or labelling. In the US, at least 300 consumer products, including sunscreen, toothpaste and shampoo are now made using nanotechnology, according to a Woodrow Wilson International Center for Scholars report. The FDA treats products made with nanotechnology in the same way as other products – requiring companies to prove their safety and efficacy before allowing them to come to market. However, some product categories, including cosmetics, foods and dietary supplements are not subject to FDA oversight before they are sold, which already worries some advocates. Producing them with nanotechnology adds another layer of concern. … The group cites studies showing that certain nanoscale particles can cause inflammatory and immune system responses in animals” [25].[3]

In the 17th–19th centuries human society outlined the understanding of scientific and technological progress as continuous improvement of society and nature on the basis of the growing capacity of scientific knowledge of the world. Up to the middle of the 20th century this illusion and relating to it cosmic, natural scientific and technological Utopias led to blurring up limits of human cognition and technological activity, to

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[2] Institutional support is required [20].

[3] See also [26, 27].

development of scientific and technological optimism concerning the chance to make human society happy with the help of more and more advanced achievements of science and technology. This belief in continuous scientific and technological progress, absolutisation of a value-free scientific research, illusion of actual "creatability" of the world on the basis of the obtained knowledge resulted in the emergence of a scientific religion, based mostly on the belief in the power of scientific knowledge and the progressive character of technological activity, grounded on this knowledge. There appeared an illusion that if technology has made the Man of an animal, then, combined with science, it could make a God out of Man, the Creator of not only artefacts but of matter, nature and life as well. Scientific and technological progress is subconsciously taken as a way beyond the limits of the possible. Such notions come back to philosophy of science and philosophy of technology of the late 19th – early 20th centuries, but it was Francis Bacon who had already first mentioned this in his works in the 17th century.

Since that time science was regarded as a means to multiply human knowledge aimed at creating man-made conditions and equipment to facilitate human life. Bacon's confidence in the fact that scientific and technological progress is a humanistic or humanitarian one was also supported by the idea of cultivating ethically neutral knowledge and moral responsibility for its application that could possibly harm people. The task of Bacon's programme of scientific development was to convince the great men of the world that financial and organisational support of science was necessary and useful for society and the state. This programme aimed at "arranging science as an intensive enterprise and institutionalising it socially so that its inventions could serve the man's well-being" [28]. This is the very main goal of *New Organon* and social Utopia *New Atlantis* by Francis Bacon. Multiplication of the man's power, establishment of the man's domination over nature, all useful kinds of art, manufacture, mechanisms and machines with the help of experiments, paying no attention to theology, ethics, politics, metaphysics, grammar, rhetoric and logic – that was the motto of the London Royal Society. This separation of natural science research from all ethical and religious matters that had a progressive character at that time is coming now to antagonism with modern social development because it blurs the limits of the possible for an individual and humanity in general, placing the former alongside of God the Creator as he produces Heaven on the Earth with the help of industry, technology and science. In 1812 Sergey Bulgakov in *Philosophy of Economy* exclaimed with bitterness and suspense: Our generation seized up with this passion to a greater extend is loosing its loosing all limits to define the possible. "The world is plastic, it can be reconstructed and even reconstructed in various ways. We live under the impression of the more and more increasing might of our economy that opens boundless vistas for cultural creativity" [29].

It is only through the connection between science, technology and economy that the slogan *Knowledge is Power* can be realised. This connection, on the one hand, leads to an instrumentalisation of knowledge, and on the other hand, to a growing dependence of even "pure" science on technology and economy. Man is placed in the centre of the world, his economic activity being interpreted as "a new force of nature, a new world-transforming factor that fundamentally differs from the other forces of Nature". Technology, according to Bulgakov, is "a combination of possible methods of man's impact on nature for definite purposes set in advance". The very possibility of technology comes from the actual accessibility of nature for man's impact. Nature is treated as a passive source while man is an active, conscious source and in this sense he becomes the centre of the universe, subordinating the rest of nature to himself. "His potential world domain gets partly and gradually realised through the economic process" [29]. But the Man does not equal God, he "does not have omnipotence, ability to create everything he wants out of nothing". Man can act freely and originally only when he deals with the methods to use his own nature, his own nature as well as environment being given to him. But in the USA, we already find as an objective in the foreground a task in "bionanotechnology" to make an ideal soldier ("Soldier Nanotechnologies") with extension of human sensory abilities and expanding brain functions through technical aids [30]. "Nanotechnology, in combination with biotechnology and medicine, opens perspectives for fundamentally altering and rebuilding the human body. At present, research is being done on tissue and organ substitution, which could be realized with the help of the nano- and stem cell technologies. Nanoimplants would be able to restore human sensory functions or to complement them, but they would also be able to influence the central nervous system. While the examples of medical applications of nanotechnology cited remain within a certain traditional framework – because the purpose consists of "healing" and "repairing" deviations from an ideal condition of health, which is a classical medical goal, – chances (or risks) of a remodelling and "improvement" of the human body are opened up. This could mean extending human physical capabilities, e.g., to new sensory functions (for example, broadening the electromagnetic spectrum the eye is able to perceive). It could, however, also – by means of the direct connection of mechanical systems with the human brain – give rise to completely new interfaces between man and machine, with completely unforeseeable consequences. Even completely technical organs and parts of the body (or even entire bodies) are being discussed, which, in comparison with biological organisms, are supposed to have advantages such as – perhaps – increased stability against external influences" [31].

We mentioned ethical problems which originate today even more in connection with the extended power of humans to encroach in non-human environments, on "nature". This would be valid especially as regards the possibility of new manipulations and encroachments on the genetic basis of life, the hereditary structures figuring in the genes. There is also a problem of the neurosensory men–machine interface that is a question of the compatibility of the damaged bio(natural) system and introduced implant (artificial system). A problem of sensoric–neuroelectronic interfaces would occur, if implants are inserted in an injured or partially damaged biological system. An injury within the central nervous system may hardly be healed or regenerate in a natural way. On the contrary, generally additional parts of the injured biological system will also degenerate or deteriorate. For instance, the spinal ganglion as a second station of the hearing nerve tract or conduit may loose up to 75% of its cells, if the auditory nerve is destructed. The same is true for peripheral sensorial and motoric elements after destruction of peripheral nerves. This secondary degeneration may be procrastinated or even stopped in the future, by electrical stimulation and neuroprotective substances to be applied in time. There are also attempts to insert active implants in higher centers of the central nervous system, since here the degree of degeneration after peripheral damages is notably smaller. … At this moment, technical implant systems are a sort of on–off switch for complex biological networks. The inserting of microelectrodes in the brain associated with integrated wirings and circuits enabling preprocessing of signals including adaptive feedbacks would open up future opportunities for healing and enhancement… Yet the problem remains that the technological stimulation is but relatively "coarse". The central nerve system has still to process these stimulations in a manner that would engender a meaningful simulation pattern. The limitations are not to be overlocked: Even a well functioning implant in the retina will not make colour vision possible, since all visual information by the implants are transposed in a scale of grey tinge. Also auditory implants within the scope of second or third neurons of the auditory nerve tract do not go beyond very rudimentary linguistic understanding or experience of music.

Nevertheless, due to the extreme manipulative capabilities of human encroachments there develops a rather or even totally a new ethical situation of the orientation towards humanitarianism. This requires new behaviour rules and possibly even a new ethics in a stricter sense. "One of the important restrictions of research in the area of sensoric implants would probably result from the fact that effective tests of functioning would only be possible in human themselves. This would result – especially if the technology is of commercial interest – in a tendency towards quick, sometimes too little prepared clinical experiments. This would refer particularly to the development of neuro-electronic interfaces which do not only replace destructed functions, but also those enhancing human performance capacity in healthy subjects being an example for the so-called neuroenhancement".

The future of "nature" and of human life seems to be in danger or at risk. "The prometheic spirit of man does not seem to be able to control or be a master of the technologies originated by him, to dominate the energies of nature unleashed by him… The organic-irrational is displaced by technology and the mechanical–rational. This switch does however unleash new irrational forces beyond any additional rationalization. Man has however not yet adapted to the "new nature" engendered by technology and the machine; he does also not know whether he will be able to breathe and exist in the new electrical and radioactive atmosphere, in the new metallic reality without animal warmth. We cannot yet survey the destructive consequences being engendered by the technological discoveries and developments endangering man in his natural existence".

"When part of the population will be equipped with implants in the central nervous system for therapeutic aims, scenarios of misuse with respect to the psychic manipulation of individuals up to larger human groups by other-directed telemetric manipulations are conceivable. By electrostimulation one could induce an impact on the subjects with implants or actively encroach on actions by inducing pains or motoric blockages. Under some conditions not even a direct contact with the subject is necessary, telemetric connections by remote impact are conceivable. It was, e.g., demonstrated already that you can switch off the human sense of balance or equilibrium by remote manipulation via a weak electric current (so-called Galvanic Vestibular Stimulation, GVS). The current was transmitted in the similar way like by a hearing aid. The subjects started staggering and swaying and finally dropped… The psychic manipulation by electrostimulation may not only be used for the treatment of depressions but similarly also like party drugs and pep-pills to brighten up one's own mood. A direct connection towards the "center of reward" in the depth of the brain could make possible ecstatic experiences by pushing a button."

The human power of intervening in and changing nature by using nanomachines, but also the mentioned new possibilities of manipulation and encroachment on life, even on human life itself, would lead towards new challenges for an *ethics for the future* ("Zukunftsethik", after H. Jonas) to be developed.

Trying to channel this rather "wild" expansion and growth of the rampant *technoscience super-structure* and its technological development and *systems technocracies* would indeed require a sort of revival or resuscitation of apparently old-fashioned virtues of *reason* in such domains as philosophy, humanitarianism, social responsibility and technology assessment. To note, the instigating effect of military developments and research for and in technology and the applied sciences is still going strong: R&D lead the way – mostly, indeed, in the form of military research and development, even frequently in so-called "pure basic research". The problem of the technology assessment in the nanotechnology become complicated because there is no developed scientific community and therefore are no any experts in nanoscience and technology. " … we need to distinguish the loose everyday sense of 'an expert' – which can mean no more than an individual who knows a lot about a topic – from a more specific sense of the term, which is used when we are discussing the social role that experts should play. There are four features of expertise important to this social role that should be made explicit: (1) The expert has specialized training and knowledge not easily available to a layperson; (2) this knowledge is usually technical (this means at least the knowledge which is of specific methods for knowing or doing things); (3) the expert is recognized as such by his/her own professional community; (4) the professional community is recognized as legitimate within the larger society. While the first and second features apply unproblematically to nanoscitech, the third and fourth are more complicated" [32]. In this case one of the key role in nanotechnoscience play the philosophical reflexions from the interdisciplinary and transdisciplinary point of view. We have to *reinstall philosophy*, in a rather modern and *up-to-date*, primarily future-bound form and fashion and *cross-disciplinary* combination. We have to develop, if not reinvent, a *practice-oriented* philosophy of technology, planning, risk assessments, responsible decision making, globalisation, etc. combined with notable perspectives for a human and humane future orientation, the creative designing of new ways and strategies to confront the mentioned overriding problems of social over-flooding and to develop a kind of rather optimistic activism, achievement-orientation and socially responsible normative stance in all our institutions of education and, beyond that, in our social and political as well as all-too-human lives.

Bulgakov emphasises that the theory of technological progress was transformed in the 20th century into a kind of progress theology that foretold the achievable with the help of modern technology future of the happy, proud and free man. To bring happiness to as many people as possible was put forward as a goal of that super modern religion where human society equipped with technological knowledge played the role of God [29]. That interpretation of progress comes close to philosophy of technology by Fred Bon, according to which the question ‘What should I do to be happy?’ is the most important question of technology [33]. The first Russian philosopher of technology, P.K. Engelmeyer,[4] who also came from the initial premise of Bon, deemed the significance of technology in modern culture to have an eudemonical approach: “Man is a hammer-man of his happiness”. These words express so called technological optimism of the first philosophers of technology. “Technological optimism is more evident in the statements that treated technological process as the cause of cultural progress in general or just identified with the progress itself… The extreme form of technological optimism was characterised by specific euphoric expectations of the future when Humanity will be able to reach material but not cultural Heaven on the Earth and even obtain cosmic power” [35]. However, Fred Bon as well as Engelmeyer consider this goal of achieving Happiness to be subordinated under a higher idea of achieving virtue. “Technology is an application of our life knowledge to life itself, i.e. on the one hand, to maintaining of life (protection), on the other hand – to expanding of life (aggression). All that hinders life is vice and harm, all that promotes life is virtue and use. Technology is a means to fight against Harm and its conversion into Use”. Ethics deals with the matter of virtue whereas technology deals with the matter of use. “As the goals of Virtue and Use interrelate, or as they sometimes differ, ethics and technology may interrelate or differ”, respectively [33]. Speaking about the eudemonical ideal S. Bulgakov mentions that this ideal, if taken as a scale for the assessment of historical development, inevitably leads to immoral consequences. Technology begins to dominate over Man, not to serve him, and makes him not happy (as, for example, Engelmeyer thought) but miserable.

According to Bulgakov, first, the eudemonical ideal leads to an idealisation of human requirements, second, this idea treats the sufferings of one generation of people as a bridge to the happiness of the next generations. It makes no difference among to the concept if these are of the sufferings of the present generation to achieve happiness of their children and grandchildren (according to Dostoyevsky, to manure future harmony by personal sufferings), as the communist ideas promised, or, on the contrary, happiness of the present generation is achieved at the expense of the destroyed life space for all generations to come, if we speak about squandering of natural resources and contamination of environment. It is well-timed to remember Dostoyevsky saying that to build your own happiness upon unhappiness of the others is an immoral thing. “The first and the main task that theory of progress sets itself is to show that History has sense and the historical process is not only evolution but progress as well. This task is too heavy for empirical science as it has a metaphysical character. The absolute law of Virtue that should become the law of our life when applied to historical development tells us to

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[4] About F. Bon see [34].

mean well in history and do our best to promote the realisation of Virtue, tells us, in other words, to mean progress. Progress is, from this point of view, a moral task, not existence, but the absolute imperative." [29]. The energy transmitted by huge machines rendering amounts of energy not available before and multiplied by the technological power of man regarding interference and change executed by humans over nonhuman environment, over nature and especially the availability of interventions and even nanomachines will lead to extraordinary challenges for the mentioned "future ethics". From the immensely grown capabilities of technological impacts totally new situations for ethical orientation will occur not only regarding behaviour rules but also pertaining to responsibility and provision as well as providence and caring for the future. This would require new norms, in part changed values and frames of reference: this is beyond any doubt a totally new situation in the history of humankind: humans had never before had such power to destroy or decisively harm all or some life in a specific ecological system or even on a global scale by using their technological interventions and interferences as well as encroachments on these natural entities. Ethics would gain a new humanistic relevance not only ecologically speaking but also as a new future-oriented ethics of responsibility.

As we can see, the situation in the 20th century has changed. "We cannot hope for omnipotence of Nature any longer. The natural mechanisms are not sufficient at present to preserve the biosphere. New methods for regulations, based on the understanding of natural processes and to some degree of the managing such processes, are required. The anthropogenic regulation is the forecast of natural cataclysms and punctual decrease in speed of the process. It is the choice between the immediate profit and long-term revenues in the usage of natural resources" [37] and mankind.

Making reference to Renan, Berdiayev warns that technology can provide man, even a small group of people with a great destructive power. "*Soon peaceful scientists will be able to produce upheavals of historic and cosmic character*". This leads to the concentration of power in the hands of those who possess technological secrets. The future of all humanity depends on this. In Berdiayev's opinion, "the technological epoch", the epoch when technology dominates over the human soul, will inevitably end in victory of the human spirit, not in negation of technology, but in its subordination to the human spirit and spiritual values of life. Technological civilisation, society of technology and machines want man to be their part, deprived of personality. "Technology would perpetrate a deadly punch to the humanistic ideal of Man and culture. The machine is essentially anti-humanistic." Technology is always merciless to the living stock, but it is mercy to all the living and existing stock that should restrict the power of technology in our life [38]. "Mighty strides in physics have been characteristic of our era. Within physics there is occurring a genuine revolution. But the discoveries, which the physics of our era is uncovering, are characteristic of the decline of a culture. Entropy, connected with the Second Law of Thermodynamics, radioactivity and *the decaying apart of atoms of matter*, the Law of Relativity – all this tends to shake the solidity and stability of the physico-mathematical world-perception, and it undermines faith in the lasting existence of our world. I might say, that all this – represents a *physical apocalypsis*, a teaching about the inevitability of the physical end of the world, the death of the world" [39]. In the relation to nanotechnology we may today speak about Nano-Armageddon or apocalyptic(al) nanoethics. "The recent excitement about nanotechnology is only the latest offspring that comes in the bizarre form of apocalyptic ethics, propagated particularly by influential transhumanists" [40].

Indeed, overriding multi-disciplinary knowledge and information are and have to be used almost everywhere (any large-scale practical problem whatsoever is multidisciplinary!) on the one hand, and we are, on the other, bound to a human, humane, humanitarian, and ecological perspective, i.e. as regards the latter one of sustainability and sustainable development, that have to be taken into account in all essential social and political realms leading beyond the mere addition of information, extension and scope of networks as well as the ever faster breaking waves of innovations in technologies and applied sciences to be implemented for economic, military and industrial practice. Many people even talked about "the military–industrial complex" having undergone a mutation towards an "economic–industrial–technological–scientific complex" of technoscience bearing the characteristics of a real "super-structure" (after Gehlen's terminology) impregnating all areas and walks of life. That is to say nanoethics has to combined scientific, technological or engineering and economy ethics.

It would distinguish the human being most specifically that it should bear responsibilities and duties not only for his own actions but also for and as regards other living entities of nature and natural systems. As such a distinguished part of the totality of nature, as a specifically powerful agent (s)he has to take over a representative responsibility for "the total" in relationship and proportion of his technological power. This is true also morally speaking. It is indeed specifically human and a characteristic of part of their special position and dignity that humans may and have to attribute to other beings and kinds some "right" of existence and preservation, quasi-rights so to speak. That means that they have to take over duties of protection towards them *without reciprocity*. This applies to the total system as well as the larger systems of nature, since the human being is the knowing being who is able to go beyond its anthropocentric purview lending a (quasi) right of existence to other living beings. This overall ethics of *stewardship* seems to be more dignified and humane than the traditional self-limitation on human interests and comprehensive domination. This should be an insight not only in ecological ethics but also for nanoethics.

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RISK IN DECISION-ORIENTED AND SELF-CHANGING SOCIETY

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Abstract. Western industrial societies are characterised (historically) by a high measure of social security, which is underpinned by highly diverse safety nets. In addition, the life expectancy of the population is rising steadily because a comprehensive healthcare system either prevents plagues, epidemics and many other illnesses or sharply reduces their impact. In a society which has not faced a serious threat of war for decades it is remarkable that fear of the future has become a public issue and a reason for protests against new technologies. We might well ask how the future has come to be essentially interpreted in terms of risk rather than progress. But risk itself is a form of communication which is rich in preconditions. Risk is a challenge to calculate in the present an unknown future. Since the things that can happen depend on decisions to be taken in the present, there is a "multiple stage arrangement of contingency" (Luhmann): the possibility of damage is created incidentally, thus avoidably. Decisions under risk are paradox to the extent that they attempt to include the unknown in considerations. Decisions are to be made on matters, which, in principle, cannot be decided. We always speak of communication of risks whenever this construction is used to mark out the future and missing knowledge in situations requiring decisions. Decisions with regard to uncertainty can only be made as a part of social of processes or hypothetical situations. Processing uncertainty, ambiguity and impossibility is the most distinctive characteristic of future-oriented decision making and risk communication. We should distinguish risk from danger, but we must also make a distinction between who decides about risk and those who are affected by this decision. The emergence of risk society is embedded into three general transformations in modern societies which are affecting our lives today. Each is connected to the increasing influence of science and technology, although not wholly determined by them. The first transformation can be called the *end of nature;* and the second *the end of tradition* and the third *facing the unknown.*

Keywords: complexity of society, multiple stage contingency, functional differentiation, temporal horizon of modern society, reflexive modernization, self-reference of risk

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1. The Return of Uncertainty in Society

Western societies are characterised by a historically unique level of private wealth and social security that is supported by a highly effective social safety net. The life expectancy of the population is rising steadily. A comprehensive healthcare system either prevents plagues, epidemics and many other illnesses or sharply reduces their impact. Not only the danger of economic poverty and illness but many other common hazards have been curtailed. In a society which has not faced a serious threat of war for decades it is remarkable that fear of the future has become a major public issue and a reason for protests against new technologies.

The interesting question that therefore arises is how the contentious language of risk has been able to gain so much ground in the public arena in modern society. We need to ask why the future has come an essentially contested matter interpreted in terms of risk rather than progress [1]. In response, there are at least three ongoing debates in society that deal with the issue of society's danger to itself and that may shed some light on the renewed public role of uncertainty [2]:

1. There is the question of the consequences of using complex advanced technologies. Whether rooted in physics, chemistry or biology, these technologies have a high potential for devastating catastrophes. In the event of accidents or total failures the damage is out of all proportion to the purposes of the technologies. What is more, existing facilities for compensation based on operator liability also fail, because the scale of damage is so huge that it is uninsurable. A characteristic of advanced technologies is that total control is not possible. Accidents can only be made more improbable, not ruled out altogether. If the vulnerability to catastrophe can only be contained but not eliminated, the technical problem of safety measures becomes a social problem of acceptance of possible man-made catastrophes [3].

2. In the course of the risk debate it has emerged that a further dimension of uncertainty is generated socially. The discussion involves the growing discrepancy between the intentions and the consequences of technological actions. Through and with the help of genetic engineering, humanity can now try and manipulate the conditions of its own evolution. Precisely because it gives humanity access to the self-replicating mechanisms of the biological foundation of human life, genetic engineering sharply impacts humanity's cultural understanding of itself and its identity. It is impossible from our present vantage point to forecast the scale of the associated social and cultural changes and shifts in humanity's view of itself. In other words, we are seeing an intervention in evolution whose effects cannot be even remotely predicted [4].

3. A third type of uncertainty appears in the non-spectacular consequences of daily actions, i.e. the long-term ecological changes due to everyday acts and decisions. Whether these involve road transport, CO_2 production, clearing the tropical rain forests and the massive use of detergents, the consequences of our behaviour are the destruction of forests, possible climatic change or the pollution of our ground water. Typical for dangers that result from everyday conduct in modern life is the long interval and complex relationship between cause and effect. Moreover, the effects of this type of uncertainty can only be made evident by science and that the gap between action,

consequences and causative agents is so great that it is impossible to establish a clear relationship between them [5].

The very ambiguity of ecological damage and the globality of the consequences make prevention difficult.

What is common to all there areas of man made generated hazards is that no one can predict with certainty how great the danger really is. The modern issue of risk involves an "irresolvable ambivalence" [6]. Not only is uncertainty produced on a previously unknown scale, but all attempts to solve the possible problems make us even more aware how fragile modern societies happen to be. This can be briefly illustrated in terms of the three cases cited above (advanced technology, genetic engineering and ecological consequences).

The development of advanced technologies has led to complex and hard-to-control industrial structures where there is a risk that their actual purpose of producing energy, materials etc. will be increasingly overshadowed by their side effects (impact on humanity and nature). Not only are increasing safety measures failing to make technology safer – empirical studies are showing that adding safety installations increases the complexity of the system as a whole and so makes it more vulnerable to accidents. Society is aware that technically created risks are not being solved but at best transformed into a different kind of uncertainty. This is the situation which results in widespread awareness of contingencies which combines the knowledge that other decisions could have been taken and the knowledge that nobody can rule out a disaster, however small the probability of its occurrence is calculated to be.

The example of genetic engineering shows that risk includes the opportunity to shape. Transforming the dangers of denaturing humanity into risks – in other words, starting to calculate the potential and drawbacks of intervening in evolution without regard to metasocial rules (religion, tradition) – is a prerequisite for scientific and experimental exploration of the biological mechanisms creating life. The more human action is involved in the shaping process, the faster social structures will change, i.e. they become more dependent on decisions; at the same time, the unforeseen consequences of action increase and, perhaps of decisive importance, the future becomes less predictable, as it is based on decisions which could have been different. Absence of knowledge becomes central in its importance for decisions relating to the future.

The most difficult problem, however, is probably the problem of ecological consequences. Changes in nature and in manmade second and third "nature" can be fast or slow, sudden or gradual. They are the results of virtually invisible causes or actions by vast masses of people. Changes in the ecosystem are not amenable to linear or causative interpretation, and so lie outside all present classical models of analysis and notions of reality and action tied to ideas of causality. They make us aware to a great extent of the complexity and interdependence of the world, as the synergetic effects are caused by the acts of many individuals. Here, uncertainty is a matter of attribution: first, there is uncertainty about whether the causality yielded by research for the emerging problem is really valid (destruction of forests) or entirely different factors are playing a role. Second, more and more consequences and effects are attributed to humanity (climatic catastrophe) without knowing precisely whether conditions of natural evolution not yet amenable to our influence are responsible for the changes. This situation could be described as one of enhanced responsibility with growing uncertainty.

The language of risk reflects a new uncertainty in society which takes the form of conscious perception of the future as contingent on the present [7]. Seen in these sociological terms risk means that possible damage is already attributed to decision-making attitudes and although it is impossible to know the scale of the damage, the emergence of the damage. This ignorance (unpredictability of the consequences of a decision) becomes part of the decision. The only thing that is certain is that a decision must be made, as there is no social entity which future damage can be attributed to, leaving only decision-making under conditions of uncertainty. The expansion of the potential for decision and the disappearance of any metasocial rules with the resulting pressure to choose options has resulted in society increasingly viewing its future today in terms of risk [8, 9].

2. New and Old Risks

The concept of risk was not invented in the twentieth century. It comes from the Latin and may be traced to seafaring.

Risks have thus always been known and ways of treating them have been developed. It is possible to distinguish traditional risks from those of the industrial welfare state. Traditional risks are mainly due to individual decision making. They can be attributed individually since their effect is temporary. They are entered voluntarily and usually conceived as an opportunity to gain something.

The risks of the industrial welfare state are collective risks due to production and social life situations. Systems of insurance and state welfare programmes have been developed to counteract them. Here again, damage and gains are weighed against each other. Their point of reference is collective precaution for existence. Social security is a problem of society as a whole and at the same time a high cultural value. A societal awareness of risk for social issues emerges, forcing the state to develop appropriate legal measures to combat or minimise social uncertainty [10].

The latter part of the twentieth century saw the rise of societal risk awareness due to the most advanced products of scientific and technological progress. Nuclear power facilities, chemical plants, genetic engineering and other products of scientific technology are today at the centre of the public debate on risk. I can here only point to a few selected aspects of the newly created risks, with which they may be distinguished from all previously known risks.

The new risk situations are characterised as follows [11]:

- Harmful impacts which are no longer limited in time and space – following a nuclear accident, large areas of the earth remain contaminated for centuries and the radioactive cloud from Chernobyl did not stop at any borders.
- The causes and responsibilities for damage cannot be blamed on individual decision makers or organisations. Acid rain or climate change are collectively caused problems or damage. Too many variables and their mutual interrelationships are effective to be able to form simple causal chains and to identify the cause directly.

- New risks are abstract. This means that they cannot be experienced directly. It is only through scientific measurements that we can learn anything about harmful radiation or the poisons in our food. We mainly learn about the dangers from the media and must rely on reports. These in turn have to rely on science and its methods. We are concerned with communicated risks which we can either believe or disbelieve, only we cannot check them ourselves.
- Technological and scientific risks cannot be calculated economically since they possess specific dynamics of their own. They always require additional security measures which lead to further costs. It is precisely on account of their enormous potential for damage and their possible cumulative effects that the costs for avoiding damage can by far exceed the costs for production.
- The openness of modern technology makes it possible to recognise its risks and possible dangers only once it has been introduced. They cannot be anticipated. Society itself is transformed into a laboratory. In contrast to previous technological developments it is no longer possible to distinguish between experiment and application.

Summarising, one might say that new risks depend mainly on social definition, can only be experienced through social communication, and that they create political conflicts.

3. Risk and Danger

All of these thoughts can be summarised under the ultimate formula of *risk*. Modern society is experiencing its future in the shape of the risk of decisions [12]. In order to be able to put it this way, one has to tailor the concept of risks, endowing it with a sense of precision which is seldom, if ever, achieved in the widely sprawling area of current risk research.

It is foremost necessary to underline the relationship with decisions and thus with the present. A risk is an aspect of decisions, and decisions can only be made in the present. One can, of course, speak of past decisions and their risks and also of future decisions. In these cases, one is however, referring to past or future presents and not to the present past or the present future, which are no longer or yet topical. Thus risk is a form for current descriptions of the future from the angle that one can only make a decision for one or the other alternative with respect to risks.

Risks concern possible, but not yet certain, and largely improbable damage which can result from a decision, and thus be caused by it, while not taking place if another decision is made. One thus only speaks of risks if and to the extent that impacts can be attributed to decisions. This has led to the idea that one could avoid risks and bank on security if one made different decisions, for example not to install nuclear power plants. This is however an error. Any decision can trigger unwelcome impacts. It is only that advantages and disadvantages and probabilities and improbabilities are distributed differently according to which decision is made [13].

If one at all discusses situations from the angles of decisions and risks, there is no escape. The logic of the definition of the situation is transferred to all alternatives. To this extent there is a universal principle of making an issue of time and the future which only permits weighing the extent of damage and probability – which is precisely the conventional calculation of risk [14].

To the extent that society expects decisions and the appropriate mobility, there are no longer any dangers which can be attributed only externally. One might be affected by natural catastrophes – but one could have moved away from the endangered area or have insured one's property. To subject oneself to danger is again a risk. We do not need to fly, even if there is much to be said for it. We are after all mammals which can live without flying.

The concept of risk further operates with a difference in time, namely with the difference between the assessment before and after the occurrence of the accident. Only such decisions are risky, that one would regret if the damage took place. In management science this is called post-decisional regret. It is not only the simple increases in costs which lead to one not regretting the decision itself. Instead the term focuses exactly on the paradox of contradictory judgements before and after the event. However one may view this paradox of synchronously opposite attitudes, the paradox unfolds, as logicians would say, through time itself. Thus it is dissolved by the difference in time so that there is only a *single* plausible judgement at each point in time. The concept of risk however neutralises this life technique of chronological succession. It collects the contradiction in the present, creates the paradox anew and solves it in a different way, namely by means of rational risk management. If the improbable happens, one can defend oneself against accusations by saying that one had decided correctly, namely according to the rationality of risk [13].

We thus recognise that the concept of risk embodies a multidimensional problem that is already complex in the logical sense and cannot be adequately handled with the relatively simple means of classical two-value logic, requiring instead logic richer in structure. The practical consequence is that risk can be observed very differently depending on how which differences are weighted in which way. The problem thus returns to the social dimensions, to society and thus ultimately to politics [15]. And in contrast to Einstein's flying observer in the universe, there are no mathematics to enable conversion from one perspective into the other.

There are numerous indications that modern society really perceives its future in the shape of a currently existing risk. One need only think of the possibility of *insuring* oneself against numerous accidents. Insurance does not create certainty that the accident will not take place. It merely guarantees that the property situation of the person affected does not change. Industry provides the possibility to insure oneself. One has to take a decision on this, however. In this way, *dangers* against which one could insure oneself are changed into *risks*. The risk lies in the decision between insuring or not insuring oneself.

Other problems of risk are the result of general participation in the economy. There are distances of time between receiving and spending money which do not exist for immediate exchange of goods – be it, that one can only spend money after it has been received, be it that one invests money in the hope of making gains. In modern society a part of these risks is taken over by the banks, but in everyday life there is also economic risk – which is only obscured by the fact that it is fairly uncertain, which needs and desires one wishes to satisfy with the money one has received [16].

We take a final example from politics. In older societies the difference between rulers and the ruled was regarded as *natural* order, and it was assumed that nature does not allow arbitrariness, that it excludes pure despotism. Or there was the belief that the ruler had been installed by God and then in situations of grief one could raise one's eyes to heaven in prayer. Today, appointment to all offices, including the very highest, is the subject of decisions. And this makes the danger of misuse of power or wrong political decisions a risk.

The switch from danger to risks is, as these examples have shown, the contra-intuitive, unintended purpose of numerous institutions of modern society, which were originally conceived for completely different purposes [17].

The form of making an issue of risk encompasses very different situations. In their logical complexity and the ultimately paradox uniformity of risk is mirrored, or so one might assume, the complexity of modern society, which can only describe its future in its present – and on the other hand cannot describe it?

We have seen that risk itself is a form of communication which is rich in preconditions. Risk is a challenge to calculate in the present an unknown future. Since the things that can happen depend on decisions to be taken in the present, there is a "multiple stage arrangement of contingency" (Luhmann): the possibility of damage is created incidentally, thus avoidably. Decisions under risk are paradox to the extent that they attempt to include the unknown in considerations. Decisions are to be made on matters, which, in principle, cannot be decided. We always speak of communication of risks whenever this construction is used to mark out the future and missing knowledge in situations requiring decisions. Decisions with regard to uncertainty can only be made as a part of social processes or hypothetical situations. Processing uncertainty, ambiguity and impossibility is the most distinctive characteristic of future-oriented decision making and risk communication [18].

4. On the Difference Between Decision-Makers and Those Affected by Risks of Decisions

The transformation of risk elements into formal calculations, as is attempted in every form of risk calculation, carries within it the potential for social and political conflict. This quickly emerged in public debate on the assessment of the consequences and the potential impact of new technologies. Specifically with respect to risks that do not involve individual options for action but entail impacts on third parties, decisions on risks cannot separate the acceptability of damage to others from the actual formal calculation. This is particularly the case when no clear statement can be made regarding the likely scale of damage. The question of social and environmental compatibility, a normative criterion, is inevitably involved. As pollution limits, it is not possible to establish any objective limit below which it is possible to determine whether something is harmful or not. Instead risk assessment and limits represent the result of a dynamic process of debate and disputes in which conflicting interests have to be accommodated. This, however, merely shows the complexity of risk calculation, and behind this façade a fundamental social change appears to be taking place [12].

With the development and implementation of new technologies and the recognition of an increasing number of irreversible impacts on the environment, a new element of conflict has emerged separating decision-makers from those affected by these decisions. As explicated by Niklas Luhmann, the difference amounts to the distinction between risk and danger [7].

Risks are situations where possible future damage can be attributed to an individual's own decision, while dangers relate to damage and hazards from external sources over which the affected individual has no control whatsoever. Although today all dangers of a technical or ecological nature are caused by deliberate actions and decisions by knowledgeable agents – this is the essence of the thesis that modern society poses a danger for itself – the technological and ecological dangers are perceived by some as risks and by others as dangers – and people behave accordingly. There are several reasons for this.

1. The costs and benefits attributed and associated with technical and ecological risks in fact may not correlate and do not simultaneously affect the same set of actors. As a result, a cost-benefit calculation no longer supplies relevant information for a decision. Individuals at risk from new technologies, e.g. neighbours of nuclear power stations, inhabitants of certain industrialised regions or nearby residents of major chemical plants, bear disproportionately great burdens while the benefits may be generally distributed or profit an entirely different segment of the population [19].

2. There is a basic disjunction between those causing risks by decisions and those affected by the risks. This is due to the extensive functional differentiation within modern society. As the chains of action and impact have become longer, decisions and the consequences of decisions no longer coincide geographically, temporally or socially [20].

3. Technical and ecological hazards are societal or collective risks. For the individual actor, dangers constitute not unlike social norms external constraints that are imposed rather than voluntarily accepted. Whether ecological risks are caused by the acts of many (such as the destruction of forests) or whether technical risks arise as the result of decisions of a few decision-makers, one thing is quite evident: individuals neither desired nor are able to share in the decision-making process under which risks are accepted. Risks are events that occur without the individual's knowledge, assent or direct involvement. Faced by this situation the individual agent only has the choice between moving away from the danger, coming to terms with it – or protesting.

As soon as risky decisions in the fields of ecology or technology are taken, the distinction between decision-maker and affected individual invariably emerges. The decisive difference is that the stratification involved does not discriminate between specific classes and does not create social differences. The distinction between decision-makers and those affected is based on the division of societal function and power. The distinction is institutionalised, in part through the functions of the various subsystems in modern society. This is one of the main reasons why ecological protest movements tend to be poorly organised in the long run: they become enmeshed in the web of functional differentiation in society [21].

The points of view of the two sets of agents are correspondingly distinct: from the point of view of the decision maker, the threat presents itself as a risk, from that of the affected individual as a danger. The decision maker tries to rationalise the decision with the help of calculations, estimates, scenarios etc. The decision-making agents even try to take the view of the affected individual into account by factoring the question of acceptance and by instituting educational campaigns on the risk. However complex and constrained by situation specific conditions of the decision on possible risks may be the decision can never involve seeing the risk as a danger and hence switching to the position of an affected individual.

Conversely, those affected by the decision taken, the bystanders see the consequences of the risky decision invariably as dangers. They see themselves faced by a danger which they cannot control, to which they have to adapt in some way and which they only know is regarded as a risk by the individual responsible for causing it – leaving uncertainty and fear to them as agents.

Technological and ecological hazards generate dissension with respect to a future constituted by different agents as either a risk or as a danger. The fact that uncertainty emerges as a hidden but common denominator and those future states of affair become the shared point of reference for agents on both sides of the divide means that there are no general, rational criteria that can be mobilised resolving this conflict [22, 23].

The emergence of risk society is embedded into three general transformations in modern societies which are affecting our lives today. Each is connected to the increasing influence of science and technology, although not wholly determined by them. The first transformation can be called the *end of nature*; and the second *the end of tradition;* and the third *facing by the unknown.*

5. The End of Nature

The end of nature does not mean a world in which the natural environment disappears. It means that there are now few if any aspects of the physical world untouched by human intervention. The end of nature is relatively recent; it has come largely as a result of intensification of technological change [24].

This seems to have something to do with the cleft between the past and the future. If the future is highly likely to differ from the past (why otherwise so dramatise this distinction?), and if there is no time in the present, how do we turn the page from the past to the future – blindly? We will see that – and how – the attempt is made to avoid at least this consequence, or to denounce it as ‘decisionism’. However, what remains – as the irreducible residue after every counteractive effort at orderly execution – is precisely what we refer to as risk.

Be that as it may, in the transitional period heralding the modern era, dependence on decision making and thus the value of paying attention to the future increases. Much that had used to happen more or less of its own accord in the course of life now requires the making of decisions – and against a background of a greater range of choice, thus with higher information values. In this connection it is inevitable to think in the first place of technological developments and hence of the increase in production options. But this is true only for part of what has happened, and moreover for a part that took effect only relatively late. In contrast to what one might expect, the development of production technologies has depended less on scientific progress than on the development of the relevant markets and capital reserves. But there are many other cases. We could mention, for example, the incursion of state-planned statutory law (or similarly common law as transformed by judges for the purpose of modifying society) into unwritten local customary law – a process that began in Europe as long ago as the sixteenth century. Or, as medical knowledge of chemistry and biology develops (and if we consider the case of cancer, we see that this does not necessarily hold for therapeutic techniques), disease is transformed from an ever-present danger into a risk relating to one's way of life.

These changes mentioned here only in excerpt show the societal range of a new type of phenomenon. The novelty, however, lies not in the feasibility, in the capacity of systematically shaping societal conditions. We need only recall the accounts of the foundation of cities in antiquity to realise that, given the greater complexity and broader range of possibilities, we can do not more but less in this respect than could the ancients. The novelty lies uniquely in the expansion of the decision-making potential, in its more complex ramifications, in its greater wealth of alternatives [25]. Translated into the conceptual language we are proposing, this leads to a transformation of dangers into risks. More and more states – whether existing or aspired to – are seen as being consequent to decisions, i.e. are attributed to decisions [26]. Much is due to the dual intervention of the more pervasive technological development and more pronounced individualisation of entities and processes formerly regarded as constituting Nature. We should, however, also remember the institution of insurance, which can be understood as an agent for transforming dangers and risks – into the risk of not having taken out insurance coverage.

6. The End of Tradition

If we date the beginning of modernity back to the middle of the eighteenth century, modern societies are infinitely more complex than previous societies. The increase in complexity does not only affect the increase in alternatives for action for human beings, but the overall structure of society has also totally changed. This will be explained for a few selected points.

Modern society is developing from a differentiation primarily by strata to differentiation into functional sub-systems. This means the differentiation and constitution of such component systems as science, politics, industry etc., each of which becomes in a sense autonomous. They do this by reproducing their own orientation patterns and are longer governed by a development logic of society as a whole.

Some decisive impacts are linked with the switch to functional differentiation. The integration of society is no longer achieved by successful living together of humans, but is created by the interplay of the self-perspectives of the component functional systems [27].

Functional differentiation leads to an a-centric society. Modern societies no longer have a central instance for self-reflection and self-control. Neither the state, nor capital and even less the proletariat are the location in which the general interest of society is anchored, since there no longer is any such general interest.

The temporal horizon of modern society has shifted from the past to the future. It is not simply that the space of possibilities for society has expanded immensely. It is probably of similar importance to modernity that the past is no longer the yardstick for action, but an uncertain future. An increasing number of decisions in the life of each individual are taking the shape of a risk calculus – decisions for which only the future will tell whether they were right or wrong. Social contingency is becoming the dominant experience in the life of any modern person. Any action could have been taken in another way. Any social fact reveals itself as the result of a decision and thus as conceivable completely differently. The pressure on decisions in modern society has thus increased enormously. Even to live conservatively is on the basis of decision, and conservation (conservare) thus on the quiet develops into a process of selection [28].

If one today speaks of risk society (Ulrich Beck and others), this means a twofold experience of the industrial society: the increased possibility of catastrophic damage, whose likelihood of happening is however much lower, and risky decisions as phenomena accompanying action in daily life. The first is an immediate result of the mechanisation of society. Nuclear power facilities, large-scale chemical plants, biotechnology and computers are examples for this entire development.

The other experience is the result of functional differentiation. A growing number of areas of human action are no longer subject to generally acknowledged and binding rules. Customs, traditions and values – as Max Weber has emphatically described – have changed during the course of the occidental rationalisation process into problems of decision-making.

Both developments have had the effect that uncertainty has become a dominant public issue [29].

The emergence of individualism and the foundation of scientific and technological progress are the decisive factors of modernity. The detachment of the human being from traditional ties, the formalisation and rationalisation of his life world and the maturing of modern natural science, which has its target in the experiment and practical control of nature, determine our constitutive experience.

7. Facing the Unknown

There is a third characteristic of knowledge modern society. We could it name facing the unknown. Certainly, knowledge would not have become a predominant resource if it could not become transformed in marketable goods and services. It is not less true; however, that every state of knowledge opens up even more notions of what is not known. The more society relies on knowledge, the more it understand, describe, predict, construct, and control this change becomes illusory – simply because of lack of knowledge.

This is exactly the reason why knowledge experts and symbolic analysts are needed and expected to create islands of certainty to allow orientation and planning. Demand for knowledge expertise may differ in several respects: by its purposes, ranging from understanding to predicting and constructing; its form of communication, which may be more propositional or more practically embedded; and its scope of application. It may be a rather general theoretical belief system, a generalized rule, a simulation model, a special case experience, or just the solution of an urgent problem. Wherever such expertise is invested, the expectation is to obtain some certainty. But certainty does not exist only in degrees of quality ranging from absolutely valid, to reliable under conditions, to better than nothing. It is also exposed to a second order knowledge about knowledge, or expertise on expertise. Every form of expertise depends on choices with respect to heuristics, methods, or data bases and could have been formulated differently. Where there are choices there are risks. But if, in turn, risks can only be reduced by additional expertise, then the net result may be a steady loss of certainty in society. Even if infinite amounts of information were accessible and could be processed by advanced knowledge technologies, the well known problem of acting under bounded rationality would not be solved but enhanced. The constant examination and reformulation of social practices in the light of incoming information about those very practices is also conceived in Giddens' model of reflexive modernization".

Information is a deeply ambivalent matter. It is at the same time an event and a difference. It is a double-sided concept: it helps at it disturbs. In a sense, it contains its own counterpart. From one minute to the next it continues to reproduce knowledge and non-knowledge. As information it produces continuance opportunities, but on the other side it renews the background knowledge that there are other possibilities. Information must not be correct, just plausible. It must enable the crystallisation of sense and thus permit the continuation of operations and the transfer of the ambivalence of knowing and not knowing to the next situation. To this extent, the information society is chronically uninformed.

The debate on the risk society and also the disturbing ecological discourse current in advanced industrial states during the past 20 years has made it obvious that the lack of knowledge is a source of societal dissense. Like these, the issue of risk forces a revision of the basic terms of societal theory. Risk makes aware of the contingency of societal life – everything could also be possible differently and points at the same time into the past and the future. Any decision can have both good and bad impacts. Awareness of these facts increases the importance of approaches in science which use uncertainty as their point of departure. The aim is not to eliminate uncertainty, but operating with uncertainty must become a societal learning process. It is only when one takes on risk than one can avoid failing on its account.

The latter part of the twentieth century saw the rise of societal risk awareness due to the most advanced products of scientific and technological progress. Nuclear power facilities, chemical plants, genetic engineering and other products of scientific technology are today at the centre of the public debate on risk. Technological and scientific risks cannot be calculated economically since they possess specific dynamics of their own. They always require additional security measures which lead to further costs. It is precisely on account of their enormous potential for damage and their possible cumulative effects that the costs for avoiding damage can by far exceed the costs for production.

8. Conclusion

The thesis that risks are social constructions is rooted too deeply in the psychological approach to perception to be able to capture the full meaning of the term “risk”. It is true that there is no such thing as “objective risks”. However, there are always perceived, interpreted facts which depend on the specific context and are determined by a specific culture. Correspondingly there is variation of perception, description and assessment of risks throughout the population. This does still not explain why the issue of risk is now a secular problem for all industrialised countries. It is no longer the issue of class which occupies the public. Instead, overcoming the ecological crisis and its associated risks now divides society into conflicting parties. In contrast, it will be argued here that the significance of the risk issue is to be understood in connection with processes of societal transformation. These have led to a new paradoxical type of actions and to a new societal conflict. With the conquest of society by a new functional differentiation, the uniform meta-social order is getting lost. Neither religion nor science are able to provide people with a uniform view of the world, in which the most important signposts are anchored. Instead, system-specific views are increasing asserting themselves, each having its own rationality. These can no longer be reconciled or even generalised. At the same time, or possibly linked with this, the temporal structure of society is changing. The past no longer has any value for orientation, the future is transformed into the goal of actions. This can be seen most clearly for the acceleration of scientific work. Scientific work is per se future work.

With the loss of a common culture and the opening of the present towards an uncertain future, enormous pressure on decision making and a high degree of social contingency are created. This is what can be said to be new in the risk society [29]. During the course of progressing functional differentiation, possibilities to take decisions have increased enormously, at the same time increasing the richness of social alternatives. This process has also had the impact of transforming former dangers into risks, so that there are no longer any dangers, only risks. The difference between risks and dangers now emerges as a social difference. For the decision maker control of an uncertain future is changed into a risk, which can be calculated one way or the other. For a person affected by a decision which he or she cannot influence, there is a danger. However this danger has been created socially and this is what gives the issue of risk its explosive power.

If one regards risk as “a calculated uncertainty dependent on decisions”, then a paradox quickly becomes apparent [30]. Any decision referring to an uncertain future is subjected to a double problem. It has to operate with costs and benefits – and at the same time determine which risk exists if a decision is not taken. Decisions not taken can also have their negative and positive impacts, and are in no event neutral with respect to the future. The “two-faced character of risk” points to the self-reference of risk. If decision making and refraining from decisions are both equally uncertain with respect to the future, any kind of striving for security, which does not wish to take any risks, falls into the black holes of the rationality of risk [31].

If one regards the paradox of risks and its societal roots within the evolutionary development pattern of functional differentiation, one may recognise that many ways proposed to lead the way out of risk society lead straight back into it.

In a society which produces new risks each day, Ulrich Beck's proposal [26] to rely on the self-destructive powers of large-scale technology remind one of the recipes in the arsenal of objective philosophy of history, which still believed in a teleological sense of history. Even an extension of the selection criteria to include ethics, democratic co-determination and institution with veto rights while breaking the "access of industry" to ways of using technology does not lead the way out of the principle dilemma of risk policy. This would only lead to an increase in the size of what has to be decided, but not to the possibility of being able to discriminate clearly between good and bad impacts. This disregards that conjuring up the dangers and radical measures designed to combat them ignores the fact that the very production system mentioned as the source for all these dangers produces the basis for all life which is the target of rescue actions.

If one considers the new situation created by the risks of modernity, the first thing would be not to support hurried solutions whose lack of usefulness is already apparent through their terminology, which is like the mark of Cain. The aim of this lecture is to draw attention to the *social dimension of risk* [32]. With the advance of science and technology in society, and also with the increasing differentiation of social aspects, the issue of risk is achieving the same rank as the issue of poverty had in the nineteenth century and the issue of insurance had in the twentieth century.

Like these, the issue of risk forces a revision of the basic terms of societal theory. Risk makes aware of the contingency of societal life – everything could also be possible differently and points at the same time into the past and the future. Any decision can have both good and bad impacts.

Awareness of these facts increases the importance of approaches in science which use uncertainty as their point of departure. A case in point is when Richard Rorty makes contingency the starting point for a new philosophy of freedom by writing "It is not any great, necessary truths about human nature and their relationships with truth and justice that will determine what our future leaders will be like, but a multitude of small, contingent facts" Rorty 1992). The aim is not to eliminate uncertainty, but operating with uncertainty must become a societal learning process. It is only when one takes on risk than one can avoid failing on its account.

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TECHNOLOGY-INDUCED RISKS IN HISTORY

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Abstract. Our perception of risk contains three main aspects: (1) probability of the risk occurring; (2) the extent of possible damage; (3) the degree of voluntary or involuntary exposure to risk. History of risk assessment has been traced in several areas, such as transportation, and has largely focused on insurance. Construction projects constitute one of the oldest areas of technology where accidents continue to occur, while health has always been a fragile commodity. Urbanization has multiplied the risks of illness and death, while natural catastrophes, though still frightening, have ceded their central place to technology-based disasters in the Western perceptions of risk. The human has become the main source of danger to the very survival of the planet. The Enlightenment utopia of scientific progress resulting in social and moral progress of humanity has collided with the awareness of new technology induced risks. Life on Earth began without humans, and it may end without them. Our civilization is the first that faces an end to be brought about by our own technological ingenuity.

Keywords: risk, survival, progress, technological threats

1. Introduction

New technologies pose new risks. However, how new is this problem? Since when and how have humans learned to assess such risks? How often has it led them to abandon innovative technologies or to abstain from developing them? Are risks involving food and drugs, i.e. substances directly introduced into human body, perceived differently from risks stemming from technologies that remain on the outside of the body? Has the progress of medicine diminished or amplified societal aversion to health risks? Are risks presented by military technologies assessed differently from those linked with peacetime technological innovation? How has the concept of risk itself evolved in the last two centuries since the onset of the industrial revolution? How have the regulatory measures reflected this evolution? What has been the interaction among government agencies, professional associations and civil society with respect to management of

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technological risk? While all of these questions are important, this paper attempts to answer some of them using the history of technology and the history of ethics.

Our perception of risk contains three main aspects: (1) probability of the risk occurring; (2) the extent of possible damage; (3) the degree of voluntary or involuntary exposure to risk. Risk management, i.e. attempts to reduce the uncertainty implicit in the use of new technologies, can be expected to vary not only in time but also between cultures. However, the present paper will focus mostly on Western cultures, leaving aside many fascinating issues involved in perception of new technologies in non-Western civilizations.

The concept of risk is etymologically linked with navigation. It stems from a classic Greek word ριζα, used by Homer in *The Odyssey* which would mean “reef” or “cliff”. This is how the early Italian word “risico” migrated to several European languages, including English. It is an ambiguous term connoting both a danger and an opportunity. The principle of “the hiding hand” introduced by the American economist Albert Hirschman postulates that a company may succeed not because it is aware of all the risks involved but because it underestimates them [1]. The risk is also present in the biblical narrative of Adam and Eve whose curiosity overcame the fear of being expelled from the Garden of Eden.

2. Transportation

Indeed, the oldest trace of humans dealing with risk is probably related to the perils of transportation in Ancient Shumer. Later, in Babylonian culture, an entire category of trader-lenders emerged who would insure long-term expeditions against material loss. While camels can hardly be considered a technological artefact, ships certainly can: the kind of ship that seafarers use determines the degree of risk. Maritime transportation remains perilous, and is perhaps the oldest continuous area of risk assessment but hardly the only one.

Imperial expansion also involves risks. Thus the Roman authorities assessed the risk of a shipwreck (as well as that of an armed attack) when supplying their troops around the Mediterranean basin. The decline of the Roman Empire brought to a halt the development of risk assessment, an activity that regains importance almost a millennium later, in the context of the Hanseatic League in the North of Europe. Risk assessment becomes a common activity in the 13th century as transportation technologies evolve and become more reliable. The globalization of trade and finance make risk assessment indispensable and begins to depend on experts in maritime and fluvial transportation.

In the fateful year 1789, a few months before the fall of Bastille, made its appearance the first report of a traffic accident. Ground transportation technology was still relying on horse power but the idea of risk to pedestrians was born, and will become important a century later when the automobile will conquer the road and make the life of the pedestrian so much riskier. The introduction of the steam locomotive was an important intermediate stage in this development.

The most emblematic danger of modernity is the risk posed by debris of space vehicles. While routine space travel remains firmly in the domain of science fiction, several thousands of tons of space debris circulate around the Earth with varying degrees of risk of causing a major disaster. Progress in transportation technologies has thus brought about an unprecedented kind of risk.

3. Habitation

Construction projects constitute one of the oldest areas of technology where accidents continue to occur. Mutual aid societies were reportedly organized during the building of the pyramids in Egypt and of the Temple of Solomon in Jerusalem to protect families from the loss of a breadwinner. Medieval building fraternities (that would later inspire the Masonic lodges) served also as effective instruments of technology transfer with the purpose of risk prevention. New building methods would become known in the framework of intricate networks of exchanges among the fraternities' members.

A major fire in London in 1666 renews the interest in risks involved in construction. Within a week, 13,200 houses and 87 churches are reduced to ashes. This time, the risk relates not only to the builders, who can suffer from technological artefacts, but also to the users of completed buildings. Similar tragedies in other parts of the world lead to the formulation of building codes and municipal or royal regulations that attempt to reduce the risk of fire. Closely related to this phenomenon is the expansion of insurance companies to life and domestic property insurance.

It is also in the 17th century that risk becomes an object of scientific inquiry. In 1653 the French mathematicians Blaise Pascal and Pierre de Fermat exchange ideas about probabilities with respect to interrupted games and the eventual sharing of the proceeds. Thus begins the mathematics of probabilities. Shortly before his death, Pascal meets his Dutch confrere Huygens who continues the study of probabilities trying, according to Pascal, "to subjugate the uncertainty of chance to the Laws of geometry". Risk becomes a respectable field of research, even though some of its applications, such as life insurance, experience difficulties. The same Colbert who encourages the development of the French maritime fleet – and therefore encourages maritime insurance – prohibits life insurance as an activity resembling games.

4. Human Life: Individual and Collective

However, risk assessment as applied to human life gains popularity in England. Edmond Halley, better known for his observation of the hitherto eponymous comet in 1681, presents the first mortality tables to the Royal Society of London in 1693. He had done his research in Breslau (today Wroclaw) and applied to life insurance calculations. A few years later, in 1714, the Swiss mathematician Jacques Bernoulli argues in his work *Ars Conjectandi* that "it is rather improbable that in a great number of experiments the frequency of a given event deviates significantly from its probability. Thus is formulated the Law of large numbers. Bernoulli's compatriot and colleague, Euler, also contributes to the mathematics of risk during the same period. Curiously, both of them would eventually link their lives with St Petersburg by joining the fledgling Imperial Academy of Sciences.

Finally, in 1762, the foundation of the Equitable Society for the Assurance of Lives and Survivorships in London marks the transformation of risk assessment into a commercial, and therefore routine, operation. France follows suit and by a special Order in Council of the King, the illustrious statesman Jean-Baptiste Colbert introduces fire insurance. Assessments of eventual risks of fire further affect the development of building technologies. One of the more spectacular consequences of this trend is the razing of 120,000 lodgings in Paris under Napoleon III and the building of 200,000 new ones. This major urban renewal is associated with the contribution of George-Eugène Haussman, whose name is immortalized in one of the wide boulevards that he traced in the French capital. Many of the new buildings constitute investments on the part of insurance companies who are naturally inclined to reduce risks of fire and make sure that the safest technologies are used in the project. In fact, the frequency of fires in Paris is reduced by one quarter between 1877 and 1904.

Attempts to prevent criminal behaviour in order to reduce the risk to society intensified with the progress of medicine and physical anthropology in the late 19th century. It is also intricately linked with the emergence of urban proletariat that frightened the bourgeoisie that had in fact caused this development through their enterprise and thrift. The proletarians, the *misérables*, had to be controlled. This fear is known in a wide range of variants: from the fear of the descendents of Algerian immigrants in France to the fear of the Black that is common to many countries. In the late 19th century, Cesare Lombroso in Italy developed a sophisticated system of early diagnostic of criminality through analysis of facial and cranial features. Others looked into genetic factors. A new source of optimism was found in eugenics, a new science promising to improve the human race. When eugenic measures, such as sterilization, were widely applied to criminals and mental patients in the 1920s and 1930s, few voices of protest were heard, mostly from the usual "enemies of progress" such as religious leaders. It took another world war and the industrialized mass murder rationalized by medical doctors and physical anthropologists to bring the eugenic enthusiasm to a halt. The risks of such technological progress appeared truly frightening.

These were the times of the Universal Declaration of Human Rights and decolonization of Africa and Asia. As struggle against institutionalized racism took off in the United States, European countries became racially mixed. The balance between nature and nurture tilted seemingly irrevocably towards the latter. Any scientific discussion of hereditary factors of social behaviour remained beyond the pale up to the end of the millennium. Progress of genetic engineering, work on the human genome and, at the same time, growing social and racial tensions in most Western societies experiencing significant economic and social polarization, restored to life century-old hopes of early diagnosis of criminal behaviour. Not only scientists but political leaders such as Tony Blair and Nicolas Sarkozy publicly supported such measures. While risks associated with the use of such technologies are yet to be assessed, there are scholars warning about a new onset of science-based racism and social control.

Risk assessment is developing another important link with genetics. Insurance companies begin to resort to genetic profiling in assessing risks of malady and death. The family's medical history has long played an important role in such assessments.

The use of genetic information may further reduce the risk for the insurance companies in insuring patients but is certain to make the latter's welfare less assured.

The Industrial Revolution further popularizes the perception of technology-related risks. Such risks concern industrial property but also life and health of the workers. While Saint-Simon sees in the industrial and scientific progress a source of social advancement, joint efforts of mathematicians, demographers and statisticians bring about mechanisms of multifarious risk assessment in industry.

The involvement of insurance companies affects not only technology but also labour relations. Thus a French insurance company instructs its inspectors to pay attention to the mood among the workers since "workers are usually devoted when the boss is just and kind. Otherwise, the risk of fire increases as a result of foul play or indifference". It would be germane to recall that the very term "sabotage" stems from the French "sabot", a wooden shoe, that disgruntled workers used to throw into the machine to subvert the industrial operation.

Applications of risk assessment to insurance inspire laudatory articles from major social thinkers of the 19th century. They see the fate of man improve as the chance is tamed with the help of science. The French Civil Code promulgated in 1804 and copied in many countries around the world makes an individual "responsible for the damages he causes". Insurance companies oblige the entrepreneurs to improve lighting and other aspects of working conditions in factories since such improvements reduce the risk of accidents. New technologies create new kinds of risk, which are mainly assessed by insurance industry that becomes indirectly involved in running factories.

5. Health

Health has always been a fragile commodity. Urbanization has multiplied the risks of illness and death. Infectious diseases spread rapidly even though the progress of hygiene and medicine caused optimism of reducing risks to human life. However, when the number of deaths attributed to Spanish Influenza in 1918 surpassed the combined fatalities of World War I, this kind of optimism began to fade. Moreover, it was progress in transportation technologies – easy and accessible air travel – that brought about the current plague of AIDS and the so far marginal danger of avian flu. The risk to health correlates closely with access to wealth: Western societies have been more successful in combating diseases not only because of their technological proficiency but also because of the availability of economic resources put to the cause of prevention and treatment. The fare of an AIDS patient in Paris or Montreal cannot compare to that of a similar patient in Lagos or Bangkok. Access to clean water is another factor that divides mankind in terms of risk to health. While fatalism prevails in many countries in the world, Western attitudes appear overly optimistic. Some advertisements of medical devices makes one wonder whether what is sold promises immortality rather than a cure against a specific disease.

At the same time, genetically modified food has become a major concern in industrialized countries with developed civil society. Caution characterizes some countries, such as Germany or France, where compulsory labelling and outright ban on such food have been enforced. North America represents the other pole: the customary optimism about new technologies has practically given a free hand to industrial companies promoting applications of genetic engineering to victuals. This example shows important limitations to globalization that may be less global that some would make it appear.

And yet, it is the “low tech” tobacco and cars that seem to pose the highest risks to human health. The risk related to smoking can be seen in an accounting perspective: the accumulated cost of health care caused by smoking, of anti-tobacco advertisement and of loss of revenue due the premature death related to tobacco is well below the taxes paid on the sale of tobacco products [2]. Moreover, pension funds, both public and private, gain from the premature death of smokers, usually leaving this world six years earlier than the non-smokers.

6. Two Kinds of Disaster

Natural catastrophes, while still frightening, have ceded their central place to technology-based disasters in the Western perceptions of risk. The human has become the main source of danger to the very survival of the planet. Whereas natural disasters remain a major source of risk in our civilization, forecast and prevention technologies have made it possible to assess such risks. The calculated risk of industrial catastrophes has replaced the fatalism in the face of natural disasters.

The invention of the lightening rod in the second half of the 18th century was the opening salvo in the emergence of modernity that promised to prevent natural disasters. Seismology, among other sciences, has tried to minimize the risk to life associated with earthquakes. What is germane to the topic of this paper is that as early as the 18th century philosophers debated whether the Lisbon earthquake in 1755 was due to “nature” or, as Jean-Jacques Rousseau caustically remarked, nature had not concentrated thousands of tall building in one place. The human element appears to take the centre stage even in risk of natural disasters.

Indeed, natural disasters continue to affect the poor more than the wealthy. This applies to individual countries – the experience of Katrina is quite telling in this respect – and particularly to the world at large. Citizens of Bangladesh are more likely to be affected by natural disasters than those of more developed countries where technology is more readily available to foresee, prevent and palliate natural disasters. The growing scarcity of water represents a serious risk of warfare to control access to water reserves and to prevent chaotic migrations of millions of desperate people in search of remaining drinking water. Current wars for control of oil may appear benign in comparison.

The Bulletin of the Atomic Scientists, founded in the United States soon after the end of World War II, monitored the risk of a nuclear confrontation between the superpowers and relayed its assessment by means of a clock that was approaching midnight. The closer the minute hand was positioned on the clock the more imminent the nuclear war. The cold war and the arms race between the Soviet Union and the United States engendered a massive fear of a nuclear holocaust, particularly in the United States. The apocalyptic pictures of the end of life on Earth spread from science fiction to films and, eventually, to government publications. This prepared the ground for the spread of environmental doom scenarios that would similarly affect the entire world without regard to the political ideology or the colour of the skin.

The risk of planetary warming and subsequent changes in the sea level and other major parameters that affect life on Earth must be seen as a qualitatively new phenomenon. While natural disasters, however tragic, are localized in time and space (the Titanic or Katrina), the effects of warming are not. A flood, the fall of an immense meteorite or a major earthquake cannot destabilize life of this planet the way even a minor change in climate can. Thus according to Jin Hansen of NASA, an increase of three degrees Centigrade may bring about the rising of the sea level by 2.5 m, which would in turn wipe out such cities as Boston, New York, Philadelphia, Washington and Miami.

Concerns about the technological suicide of humanity date back several decades. One of the first to question the effect of technological progress on the survival of humans was John von Neumann, a pioneer in mathematics of risk assessment and, more generally, in game theory. He warned against the growing incompatibility between decentralization of decision-making with respect to the use of technologies and the growing globalization of their long-term effects. The recent withdrawal of Canada and the United States from the Kyoto is an example of such fundamental incompatibility. Moreover, contrary to optimistic scenarios of globalization (often confused with Americanization), public understanding of science and technology related risks broadly varies among countries. An international study conducted by Harvard's Sheila Jasanoff shows that public attitudes to genetically modified food products and to stem-cell research remain incompatible even among major Western countries. This makes it unrealistic to develop universal regulations with respect to risks stemming from new technologies.

At the same time, industrial interests emerge as potent actors in counteracting public concern about environmental risks by means of publicity, lobbying and even attempts at censoring undesirable scientific data and producing appropriately oriented research papers. Such pressure has led to shelving important reports on technology assessment and, as in the case of France's College for the Prevention of Technological Risks (CPRT according to the French acronym), to the abolition of entire agencies initially created to produce independent expertise of risks of new technologies.

New forms of warfare such as guerrilla and other non-governmental agencies (e.g., Al Qaeda or private security firms) tend blur the border between criminal acts and legitimate warfare. Unlike the field of natural disasters, new technologies of warfare augment, rather than reduce, the risk. The ongoing proliferation of nuclear and other mass destruction weapons has gone beyond legitimate states, however "rogue" they may appear from certain perspectives, and may be soon within the reach of non-governmental agents. The broad-minded sharing of Pakistani nuclear technology by Dr Abdul Qadeer Khan, the father of the Pakistani nuclear bomb, may be just the first known case of such clandestine technology transfer. In other words, new technologies constitute a risk not only in cases of negligence such as Bhopal or Chernobyl but in cases of potential terrorist acts.

Countries, if they are strong, wage wars on foreign territory. The cold war and the sign of an ongoing climate change have brought this rule to an end. However advanced, no missile defence can protect a country against a rising sea level. But the human casualties of such developments are likely to be proportionate to the level of technological sophistication – and wealth – of the countries affected. On the other hand, less technologically developed countries may be spared large-scale disasters due to malfunctioning of complex systems on which industrialized societies depend so much.

7. Mastery of Technology

Contemporary perceptions of risk are more often than not associated with technology, i.e. with humans' inability to manage, control and master all elements of the systems they create and make work. Another important aspect is the rush many of them experience to apply innovations on a large scale.

When failures occur, these – unlike those of natural disasters – are attributed to "the functioning of the system". While technologies may be infallible (this is what used to be said about the Titanic), human control of such technologies is not. Hindsight studies of technological disasters point in the same direction: the inability or reluctance of humans to take warning signs in earnest. This may be caused by individual negligence, political considerations (such as the need to launch a space vehicle before a politically significant date) or institutional cultures. When whistle blowers go public they are often shunned and denounced. This was the case of Roger Boisjoly who had warned about the faulty design of the solid rocket boosters that, if left unaddressed, could lead to a catastrophic event during launch of the space shuttle Challenger. Soviet Academician Valeriy Legasov who denounced the laxity at nuclear power stations after investigating the causes of the Chernobyl disaster presents a similar case. He committed suicide a few months later, ignored and unrecognized. It was only eight years after his death that he was posthumously awarded the title of the Hero of the Russian Federation. This is precisely what happened on January 28, 1986.

All this makes the prospect of total human mastery of technology rather distant. Moreover, technology also remains the source of another kind of risk: a willful use to harm other humans, which includes wars, terrorism and insanity. This kind of risk is no longer limited to actual soldiers on the front and has cost millions of lives since the emergence of the technology-based total war in the 20th century. The invention of gas warfare by Fritz Haber may be considered an important landmark in this development. What technological innovation has made possible is to attack the vital functions, such as breathing or drinking. But even without a hostile intent, some technologies may produce disastrous effects on vast regions and even on the entire planet, the risk of which resembles the dread of medieval epidemics.

8. Conclusions

The Enlightenment utopia of scientific progress resulting in social and moral progress of humanity has collided with the awareness of new technology induced risks. To quote the French philosopher of technology Jean-Jacques Salomon, “however proud of their scientific and technological successes they may be, knowledge-based societies bear within themselves, thanks to these very successes, ferments and germs of their own destruction” [3]. He identifies three kinds of technology related risks: insidious (e.g., air pollution or asbestos), direct (Chernobyl or Bhopal) and potential (human cloning or global warming). A telling example of how current technologies may affect future generations is the uncertain fate of nuclear waste.

The American Frances Fukuyama, who had somewhat prematurely foreseen “the end of history” after the dissolution of the USSR, forecasts the end of *human* history and the onset of *post-human* history, which he attributes to future successes of genetic engineering. It may well be that post-humans will be no longer concerned about risk assessment: humans will have become easily replaceable. The computer expert and the inventor of Java language Bill Joy, whom President Clinton asked to assess the risks of information technologies, believes that genetics, robotics and nanotechnologies are capable of replacing humans, or at least of changing the human nature [4].

As the French anthropologist Claude Lévi-Strauss remarked in his *Sad Tropics*, life on Earth began without humans, and it may end without them. Our civilization is the first that faces an end to be brought about by our own technological ingenuity. The Spanish artist Francisco Goya, upon witnessing and illustrating the horrors of Napoleonic wars in his country, concluded “the sleep of reason produces monsters “(*el sueño de la razón produce monstruos*). It may well be that reason also produces monsters when fully awake.

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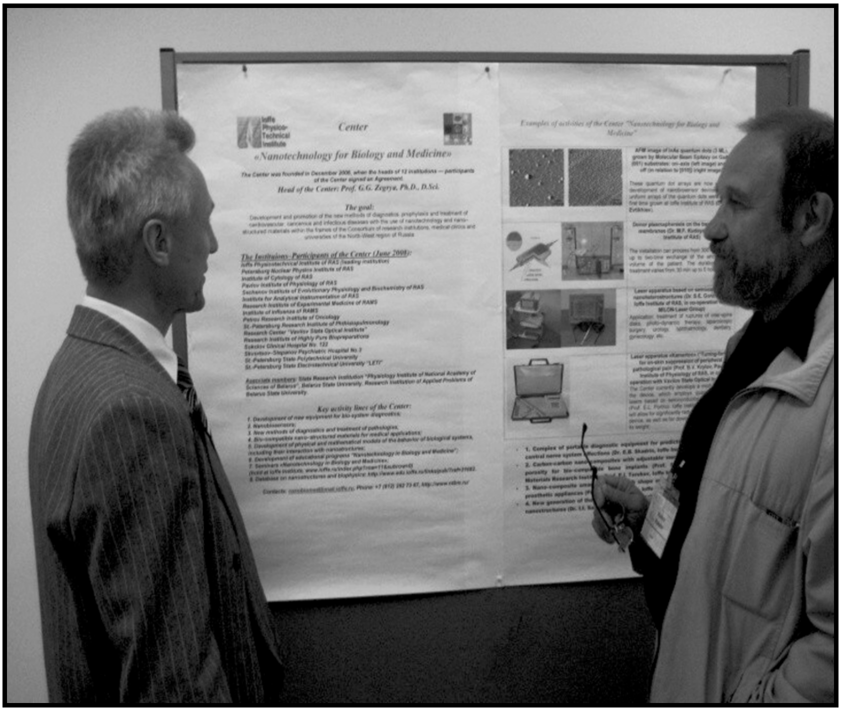
Ioffe Physico-Technical Institute
Center
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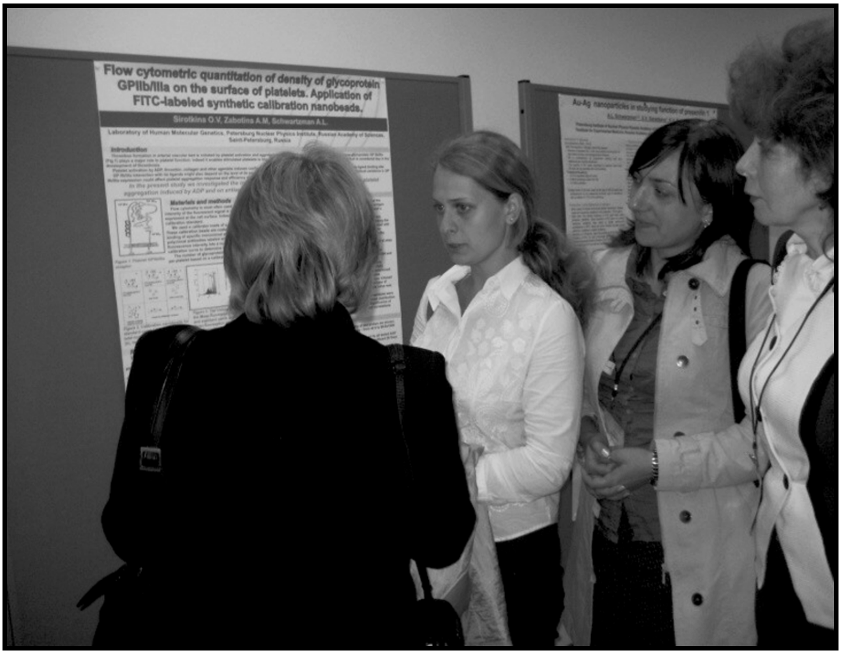
Head of the Center: Prof. G.G. Zegrya, Ph.D., D.Sci.
The goal:
The Institutions-Participants of the Center (June 2008):
Key activity lines of the Center:
Examples of activities of the Center "Nanotechnology for Biology and Medicine"


Flow cytometric quantitation of density of glycoprotein GPIIb/IIIa on the surface of platelets. Application of FITC-labeled synthetic calibration nanobeads.
Sirotkina O.V, Zabotina A.M, Schwartzman A.L.
Laboratory of Human Molecular Genetics, Petersburg Nuclear Physics Institute, Russian Academy of Sciences, Saint-Petersburg, Russia
Introduction
Materials and methods
Au-Ag nanoparticles in studying function of

NANOTECHNOLOGY: PERSPECTIVE FOR FUTURE AND NANORISKS

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Abstract. The technogenic type of development tends to standardize public life to a much greater extent than the traditionalist one. Science, education, technological progress and an expanding market generate a new way of thinking and a new lifestyle while transforming the traditional cultures. A radical change of values means a transition from the technogenic civilization to a new type of civilizational development, a third type in relation to both its traditionalist and technogenic predecessors. Nanoscience and nanotechnology accumulate all changes in the modern science and technology. In this case we can not describe of nanosystems as a pure analogy with the mechanical systems. There are hybrid nanobiomachines. Nanotechnology is considered today as the beginning of the nanotechnological revolution and the future technological means fort the survival of the mankind. But these expectations are darkened from reasonable assumptions of the unforeseen assumptions negative consequences and risks from the implementation of these new technologies.

Keywords: technogenic civilization, civilizations development, scientific rationality, nanorisk, nanomachine, nanosystem, nanoethics

1. Introduction

Today we are speaking about a new scientific and technological revolution, which have positive and also negative consequences for our civilization and create may be a new type of the civilizations development at all.

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2. Nanotechnology and Future of the Modern Civilization

To start with, the notion of civilization should be specified, and a view on types of civilizations development be introduced. The concept of "civilization" is used in many meanings. In my view, it is important to identify three main ones. The first of these denotes a totality of mankind's achievements which characterize man's separation from the animal kingdom and his ascension up the ladder of social development. In this meaning, civilizational achievements are primarily understood as an evolution, systemic complication and expansion of the "second nature", to wit, the world of man-made objects and processes, which directly surrounds man and secures his survival in nature. In this sense, civilizational achievements are described as technical and technological innovations such as the invention of the wheel, steam engine, automobile, and aircraft, or the taming of electricity and atomic energy. Apart from these, there are civilizational achievements that provide for the regulation of social ties and human relations. The invention of the written language, the coming into being of law, market and money, democracy and human rights also represent civilizational achievements.

The second meaning of "civilization" characterizes a specific type of society that arises at a definite stage in historical development, where a transition occurs from the primitive state to the first rural and urban civilizations of antiquity. This understanding is based on an integral, systemic vision of society complete with the peculiarities of its culture, its basic cultural values, its social relations and institutions, its method of interaction with nature, its types of human personalities and way of life, which are reproduced in the process of the civilization's existence. This was the sense in which Arnold Toynbee used the term "civilization", while identifying different types of civilizations in the history of mankind. Within this second meaning civilization is perceived as a specific social organism that is characterized by specific interaction with nature and peculiarities of its social ties and cultural tradition. Let me emphasize that this approach by no means implies that civilization and culture are opposed to each other. Each civilization implies a specific type of culture. And it is solely due to this type of culture that it is reproduced.

And, finally, there is a third meaning of the word "civilization". Oswald Spengler, for one, believed that civilization and culture were contraries. In this case, civilization is understood as technological and technical inventions, while culture, as the basic values and states of man's spiritual world. Consequently, it is put on record that progress in equipment and technology does not automatically lead to moral progress. On the contrary, it occasionally is even linked to moral regress. In this sense, it is often claimed that civilization and culture are not quite one and the same thing, representing as they do different aspects of social history. This opposition, as I believe, is appropriate only within a very narrow framework such as the one for discussing problems like the crisis of modern civilization and, accordingly, that of modern culture. Here we can say that a civilization, based on technical and technological progress, and culture as man's spiritual development do not concur or may even be opposites.

Later in this article, when we discuss civilizations and types of civilizations development, I will use the term "civilization" in its second meaning. This means I will consider it as a certain integral social organism implying a definite type of culture.

Current research into the general systems theory shows that any complex developing system must contain information that secures its own stability. A system exchanges matter and energy with the outside environment and is reproduced in accordance with information that is fixed and represented in the appropriate codes. These information codes contain a record of the system's preceding interaction with the environment and define methods of its subsequent interaction. But then it is necessary, from the point of view of the theory of developing systems, that information structures be identified in social organisms as well, structures that have a function identical to the role genes play in forming and developing biological species.

The basic values of culture are such structures. These are represented by categories of culture – worldview universals underlying the functioning and development of a vast number of suprabiological programs of human activities, behavior and communion, which exist as different code systems and constitute the "body of culture". The worldview universals are the same thing for a society as genes are for a living organism. They organize a very sophisticated array of different cultural phenomena as an integral system and come out as the basic structures of the social code, acting as DNA of sorts in social life. While forming an integral picture of man's vital world and expressing a scale of value priorities of an appropriate type of culture, the meanings of worldview universals (the categories of "nature", "cosmos", "space", "time", "man", "freedom", "justice", etc.) determine which fragments of the continuously renewed social experience should join the stream of translation and which should remain outside that stream. (The latter means they will not be passed on to the next generation and will not play any important role as it comes into its own). Thereby they determine what knowledge, beliefs, value orientations, targets, models of activities and behavior will predominantly regulate people's behavior, communion and activities, or, in short, shape their social life. In this respect, the functioning of culture's universals is indeed very much reminiscent of what DNA does as a specific matrix synthesizing proteins and other substances that build cells and multicell organisms, matrix that determines the principal structure and functions of them. The system of worldview universals is a cultural-genetic code of sorts, which reproduces social organisms. No radical changes in social organisms are possible without changes in the cultural genetic code. No new types of society can arise without that.

We may identify two types of civilizations development in the history of mankind after its transition from the epoch of barbarianism to civilization. Historically, the earliest one is the *traditionalist type;* the other type is often called the *Western* type after the region where it sprang up. Currently it is represented not only by the countries of the West. I call this civilization *technogenic civilisation* because its constant yen for and use of new technologies – not only industrial ones that underpin economic growth but also social governance and social communication technologies – play the decisive role in its development. The majority of civilizations identified and described by Arnold Toynbee belonged to the traditionalist type.

In recent years I have analyzed in detail and written about the difference of these two types of civilizations development. For this reason, I will limit myself to only a schematic exposition of my concept. Let me stress once again that the standard "civilizational approach" emphasizes differences between civilizations. Of course, each of the traditional cultures of China, India, Antiquity, and European Middle Ages has a clearly pronounced specificity of its own. And yet they possess certain invariant traits characterizing the traditionalist type of development. By the same token we can identify general characteristics of this type of civilization – technogenic civilizations, which are fused with the historically specific traits of this type of development.

The technogenic civilization began forming in the European region approximately in the 14th to 16th centuries. The Renaissance, the Reformation and the Enlightenment were the epochs when the nucleus of its value system took shape. It included a specific concept of man and his place in the world. It is in the first place the view on man as a proactive creature that opposes nature and is destined to transform the latter and bend it to his will. Organically linked with this understanding of man is the understanding of activity as a process directed at a transformation of objects and their submission to man. And again we may state that the value of transforming, creative activities is characteristic solely of the technogenic civilization and that it was lacking in the traditional cultures. Inherent in them was a different understanding best expressed by *wu-wei,* the famous principle of old Chinese culture, which proclaimed the ideal of minimal action based on the feeling of resonance of world rhythms. This principle was alternative to the ideal of transforming action based on an active interference in natural and social processes. Traditional cultures never aimed at transforming the world and making man the lord of nature. But this understanding predominates in the technogenic cultures, applying there not only to natural but also to social objects which become exposed to social technologies.

In further characterizing the basic values of technogenic cultures, we may single out the understanding of nature as an inorganic world, which is a specific, logically organized field of objects constituting the material and resource for human activities. It was assumed that this resource was unlimited and that man could draw them from nature without restriction. The opposite view was current in the traditionalist cultures, which saw nature as a living organism with man as a small particle thereof.

Next we must speak about the value of an active, sovereign human personality. While the traditionalist cultures defined personality primarily through its inclusion in strictly determined (and often ordained from birth) family-and-clan, caste and class relations, the technogenic civilization asserts, as the value priority, the ideal of a free individuality, an autonomous personality that may join different social communities and has equal rights with others. This understanding is linked with the priorities of individual freedoms and human rights that the traditionalist cultures ignored.

The value of innovations and progress, things equally lacking in traditional societies, holds a special place in the system of dominant vital meanings of the technogenic civilization. It is appropriate to remind the reader of an old Chinese saying whose approximate modern version is this: “The hardest fate that may befall one is to live in an epoch of change”. But for our civilization change and progress is a value unto itself. It is like a two-wheeled bicycle which is only upright while it is on the move and falls the moment it stands still. Here innovation is the main value that was lacking in the traditionalist cultures where innovations were always restricted by tradition and were disguised as one.

The technogenic culture views successful human transforming activities leading to positive results for man and to social progress as determined by the knowledge of laws governing the change of objects. This understanding is organically linked with the priority value of science which furnishes knowledge of these laws. In this type of culture, scientific rationality is a dominant in the system of human knowledge and actively impacts on all other forms of it.

Finally, a specific understanding of power and force can be singled out among the technogenic culture's value priorities. It considers power not only as man’s power over man (this is present in traditional societies as well) but also, and above all, as power over objects, moreover, objects which may serve as targets of dominance-asserting power impacts: they are not only natural but also social phenomena. They too become objects of technological manipulation.

Many other specific features of the technogenic civilization’s culture stem from this system of values. These values are a genome of sorts of the technogenic civilization; they are its cultural-genetic code underpinning its reproduction and development.

Immediately upon their inception, technogenic societies start bringing influences to bear on traditional civilizations, forcing them to alter. Occasionally these modifications result from a military occupation or colonization but more often than not they are consequences of catching-up modernization which traditional societies have to implement in the face of the technogenic civilization. Japan, for example, took the path of technogenic development after the Meiji reforms. Russia, which experienced several modernization epochs based on the implantation of Western experience, went the same way. The largest in scale were the reforms put into practice by Peter I and Alexander II. Transformations this country saw after the October revolution of 1917 can also be seen as a specific type of catching-up modernization. It was a response to a historic challenge that dictated the necessity of an accelerated industrialization. Soviet socialism and Western capitalism competed as two different options and two development strategies within the technogenic civilization.

Upon entering the phase of postindustrial development, the technogenic civilization started a cycle of expansion to different countries and regions of the world. The technogenic type of development tends to standardize public life to a much greater extent than the traditionalist one. Science, education, technological progress and an expanding market generate a new way of thinking and a new lifestyle while transforming the traditional cultures. What we currently call the process of globalization is a product of expansion of precisely the technogenic civilization. It is being instilled into different regions of the world primarily through technical–technological expansion, giving rise to entire epochs of modernization in traditional societies and shunting these to the truck of technogenic development. Modernization is assuming the scale of modem globalization processes.

The technogenic civilization has bestowed numerous achievements on mankind. Scientific and technological progress and economic growth have led to a new quality of life, secured a growing level of consumption and medical care, and increased average life expectancy. The majority of people linked their hopes for a better future to the progress of this civilization. A mere 50 years ago, few could believe that precisely the technogenic civilization would lead mankind to global crises and put it literally on the verge of self-destruction.

The ecological crisis, anthropological crisis, accelerating alienation processes, invention of ever new mass destruction weapons threatening the whole of mankind with extinction are all by-products of the technogenic advance.

Much has been said about the ecological crisis. There is a growing realization that it will only build up as different countries seek to put the ideals of the consumer society into practice. Sustaining Western way-of-life standards leads to a progressively increasing anthropogenic pressure on the biosphere. Five percent of the world population inhabiting the USA accounts for nearly 45% of energy expenditures and over two-thirds of emissions polluting the environment (these calculations take into account the activities of US-controlled transnational companies).

Considering a tendency towards increased energy consumption in a growing number of countries and an exponentially rising environmental pollution, the forecasted doubling of the world population within the next 15 to 20 years will inevitably bring about an unprecedented environmental disaster.

Some no less menacing prospects are facing mankind in connection with the anthropological crisis. It has numerous manifestations and tendencies, of which the main one is the danger of changes in the human gene pool. Dangerous modifications occur in the human genetic core as it is exposed to a build-up of mutagenic factors resulting from environmental pollution impacts, both direct (chemical and radioactive pollution) and indirect (emergence of ever new types of pathogenic microbes and viruses). Biologists are writing about the growing damage being done to genotype structures that have evolved over millions of years. The operation of natural factors serving to preserve the gene pool (natural selection) is dramatically restricted in human society, while social processes – like wars – that might be interpreted as performing the selection function operate in the opposite direction. A large number of healthy young men have perished in wars without an issue. Moreover, current genetic studies revealed facts that certain injuries tended to bring an unfavorable mutagenic influence to bear on the genetic structures in the human organism.

People's growing exposure to stressful pressures is a second significant indicator in the context of the anthropogenic crisis. Modern life with its fast-changing social situations, instability, and enhanced rivalry in all spheres of activity plunge people in an alternating sequence of stressful states. Overexertion leads to a growing incidence of not only cardiovascular and oncological but also mental diseases. Such a grave mental illness as depression is emerging among the most widespread diseases of the late 20th and early 21st centuries. To escape depressed states, people are increasingly resorting to various psychotropic drugs. Francis Fukuyama says in his book *Our Posthuman Future: Consequences of the Biotech-nological Revolution* that 10% of the entire US population is on an antidepressant, Prozac®, or its analogues (but the percentage doubles if only the adult, able-bodied population is considered). However, this drug, while enhancing self-estimate and blocking uncontrolled aggression, has certain side effects, including memory weakening and amnesia, sexual dysfunction, and brain damage.

The current tendencies towards redesigning man's biological basis are a third group of factors aggravating the anthropological crisis. They have sprung up within the framework of progress in genetics and development of new biotechnologies.

In principle, deciphering the human genome opens opportunities not only for curing hereditary diseases but also for enhancing some human capabilities (mental and physical). Already today some studies aim at achieving, for example, a higher blood hemoglobin level as a hereditary characteristic. Blood doping, a punishable offense in the world of sports today, is likely to become a genetically designed property of the human organism (manufacture of would-be Olympic champions). Simultaneously, a microchip implantation method is being developed enabling a better functioning of the human nervous system. Silicon chips are surgically implanted in the brain to restore functions obliterated by Parkinson's disease.

All those ongoing experiments with man's biological component have some far-reaching consequences. A new notion, "posthuman", is already in use, and though it is not always clearly defined, one of its component meanings implies the idea of change in the human biological core. The technogenic civilization opens a new zone of risks. The systemic wholeness of genetic factors in human existence is no guarantee that a restructured gene programming certain properties of a future organism wouldn't distort some other properties. But on top of that there is also the social component of human life. We must not overlook the fact that, deep down, human culture is linked with human corporeality and the primary emotional pattern it dictates. Let us assume that the well-known personage from Orwell's anti-Utopia, *1984,* managed to implement his grim plan of genetically modifying the sexual love feeling. People lacking this emotional sphere would be totally indifferent to Byron, Shakespeare and Pushkin, to name just a few, or for that matter to entire chapters in human culture. Biological prerequisites are not simply a neutral background of social existence; they are the soil that sprouted human culture and made possible the states of human spirituality.

The aggravation of global crises generated by the technogenic civilization brings up this question: Is it possible to overcome these crises without changing the basic system of values underlying the technogenic culture?

I proceed from the assumption that this system of values will have to be changed and that the effort to surmount the global crises will require modifying the aims of human activities and their ethical regulators. A radical change of values means a transition from the technogenic civilization *to a new type of civilizational development, a third type in relation to both its traditionalist and technogenic predecessors.*

There are different interpretations of postindustrial society. Usually it is regarded as a simple continuation and a specific stage of technogenic development. In this instance, there is no question of changing the basic values. The case in point is just shifts that new technologies introduce in the way of life, social communication and interstate relations. This approach has engendered an interpretation of sustained development as a prolongation of the current technological progress coupled with certain environmental restrictions. Given present-day globalization tendencies, this interpretation leads to the implementation of the notorious Golden Billion concept.

But a different point of view is possible as is a different strategy of global civilizational change. From this point of view, postindustrial development is not a simple extension of the technogenic civilization. Rather, it should be interpreted as a transition to a new type of civilizational development.

This is where the following question arises: Does modern culture form prerequisites for that transition?

Current philosophical and social studies have repeatedly expressed the idea that we should change our nature strategy. These ideas were first developed in the Club of Rome's research. We also know works on ecological ethics whose most radical currents proclaim a renunciation of the ideal of human dominance over nature. An alternative ideal is being put forward, which says that we must not feel superior to animals and plants or only see them as a means securing our livelihood. These ideas on a new ethics have numerous supporters. Among Western writers I would single out Baird Callicott, Leslie White and Robin Attfield. And, of course, it would be only fair to mention their first source, Albert Schweitzer's ideas about reverence for life. Attempts are being made to expand the understanding of the categorical imperative, applying it not only to the sphere of moral relations between people but also to the man – living nature relationship. A majority of scientists and intellectuals upholding the new ethics ideas accompany their speculations about the new attitude to nature with references to the caring attitude to nature characteristic of traditional societies.

But what are the chances that this system of new worldview images and ethical regulators will strike root in the mass consciousness? After all, they are largely orientated to a contemplative attitude to nature that is sooner inherent in traditional than technogenic cultures. But a return to the traditionalist type of development is impossible. It was able to provide essential benefits only to a small portion of the world population. During the Renaissance epoch, when the technogenic civilization was preparing to take off to a start, the entire world population amounted to 500 million people. In our day and age there are six billion people living on the Earth, and meeting their needs even at a minimal level is out of the question unless modern technologies are employed. Besides, it must not be forgotten that the caring attitude to nature and reverence for it in traditional cultures was linked with a certain contempt for human beings whose life came second on the scale of value priorities. Therefore, while speaking about the potential residing in Eastern cultures, we ought to practice a discerning attitude. As for the priority value of man, his spirit and his activities characterizing the Western civilization, it, judging by postindustrial development tendencies, will stay, albeit in a new dimension.

The ideas of a new ethics and new value orientations connected with modern tendencies in scientific-technological development are prerequisites of new strategies in activities and a new concept of nature. It is a problem that should be analyzed separately with account taken of changes introduced by the economy of knowledge, information consumption growth, and opportunities deriving from new energy-saving technologies.

Intensive application of scientific knowledge in practically all spheres of social life, revolution in means of storage and getting knowledge (computerization of science, appearance of complicated and expensive technical aggregates, which attend to investigation crews and function like means of industrial production etc.) change the character of scientific activity. Along with disciplinary investigations, interdisciplinary and problem oriented forms of investigation activity are more and more advancing to the forefront. While classical science aimed at comprehension of more and more narrowing, isolated fragment of reality, presenting object of such and such scientific discipline, specificity of modern science of the late 20th century is determined by complex investigations, where specialists of various spheres of knowledge take part. Organization of such investigation in many respects depends on determination of priority directions, their financing, manpower training etc. In the very process of determination of science research priorities, along with purely cognitive aims, economical and social problems are playing the more and more important role.

Realization of complex programs engenders a special situation of joining, in a whole activity system, of activity of theoretical and experimental, fundamental and applied knowledge, intensification of direct and reverse connections between them.

In interdisciplinary investigations, science usually faces complicated system objects, which are studied in separate disciplines only in fragments, so effects of their system structure can be not discovered at all in narrow disciplinary approach, but only in synthesis of fundamental and applied problems in problem oriented search.

Unique systems, characterized by openness and self-development, more and more often become objects of modern interdisciplinary investigations. Objects of such type gradually start determining also character of object spheres of the main fundamental sciences.

Dealing with such systems requires fundamentally new strategies. Self-regulating systems are characterized by cooperative effects, fundamental irreversibility of processes. People's interaction with them takes place in such a way that the man's action itself is not something from outside, but as if is included into the system, every time transforming the field of its possible states. Entering the interaction, man now deals with not hard things and properties, but with certain "possibility constellations". Every time, in the course of his activity, man faces the problem of choice of a certain line of development from a number of possible ways of the system's evolution. Moreover, this choice is irreversible and, in most cases, cannot be simply calculated.

Among objects of modern science a specific place belongs to natural complexes, which include man as a component. Examples of such "man-measured" complexes can be medical–biological objects, including biosphere as a whole (global ecology), objects of biotechnology (first of all, genetic engineering), "man–machine" systems (including complicated information complexes and artificial intellect systems) etc.

In the process of their investigation and practical assimilation, a special role comes to knowledge of prohibitions on certain strategies of interaction, potentially containing catastrophic consequences.

In this respect, the ideal of value neutral investigation is transformed. Objectively true explanation and description conformably to "man-measured" objects not only assumes, but also prescribes including axiological factors into the explaining statements. It becomes necessary to explicate connections of fundamental intrascience values (search for the truth, growth of knowledge) and extrascience values of social character. In modern program-oriented investigations this explication is realized in social examination of programs. At the same time, in the course of the investigation activities with "man-measured" objects, the investigator has to solve certain ethical problems, determining limits of possible intrusion into the object. The inner ethics of science, stimulating search for the truth and aiming at augment of new knowledge, constantly correlates, in these circumstances, with general humanist principles and values. Development of all these new methodological directions and notions of the studied objects leads to considerable modernization of philosophical foundations of science.

Scientific cognition is now considered in the context of the social conditions of its existence and its social consequences as a specific part of the life of society, determined at each stage of its development by general state of culture of the corresponding historical epoch, its value orientation and worldview attitudes.

Nanoscience and nanotechnology accumulate all above mentioned changes in the modern science and technology. In this case we can not describe of nanosystems as a pure analogy with the mechanical systems.

3. Nanosystems as Hybrid Nanobiomachines

The standard definition of nanomachine – a *mechanical* or *electromechanical* device whose dimensions are measured in nanometers – more correspond with the notion of machine as mechanical mechanism (see in the Fig. 1 – the mechanical model of such nanomachine).

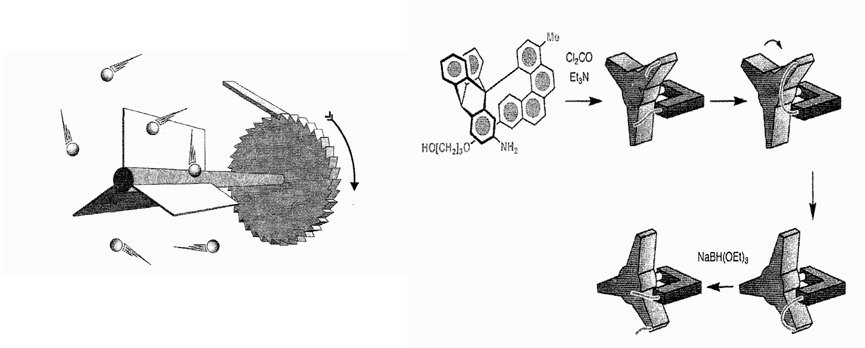

Figure 1. The Pawl machine, consisting of a vane and a wheel that can only turn in one sense of rotation. The vane is in a thermal bath of gas molecules at equilibrium. The whole device is considered to be reduced to microscopic size, so gas molecules can randomly bombard the vane to produce motion. … A molecular model of a Pawl machine allowing for unidirectional rotation ... The rotation is assisted by the formation of a covalent chemical bond that occurs only in one direction [1]

So nanotechnology is at the same time a field of scientific knowledge and a sphere of engineering activity, in other words – NanoTechnoScience [2] – similar with Systems Engineering as the analysis and design of large-scale, complex, man/machine systems but micro- and nanosystems. "Nanoscience is dealing with functional systems either based on the use of sub-units with specific size-dependent properties or of individual or combined functionalized subunits" [1]. Nano systems engineering is the aggregate of methods of the modeling and design of the different artifacts (fabrication of nanomaterials, assembling technology for construction of comprehensive micro and nano systems, micro processing technology for realizing micromachines etc.). Nano systems engineering as well as Macro systems engineering includes not only systems design but also complex research. Design orientation has influence on the change of the priorities in the complex research and of the relation to the knowledge not only to "the knowledge about something", but also to the knowledge as the means of activity: from the beginning *control and restructuring of matter* at the nanoscale is a necessary element of nanoscience [3].

Drexler rigid machines as nanoscale devices are also fabricated from hard moving parts, cogs, bearings, pistons and camshafts: "the combination of a bearing and shaft suggests the possibility of extended systems of power-driven machinery. The outer surface of the bearing suggests the possibility of a *molecular-scale gear*. The controlled rotary motion of the shaft within the ring, together with the concept of extended systems of machinery, suggests the possibility of *controlled molecular transport and positioning*, which is necessary for advanced *mechanosynthesis*" (see Fig. 2) [4]. "Drexler started with a conventional definition of machine: "Just as ordinary tools can build ordinary machines from parts, so molecular tools will bond molecules together to make tiny gears, motors, levers [...] and assemble them to make complex machines". … The functions performed by the various parts of molecular machinery are also essentially mechanical" [5].

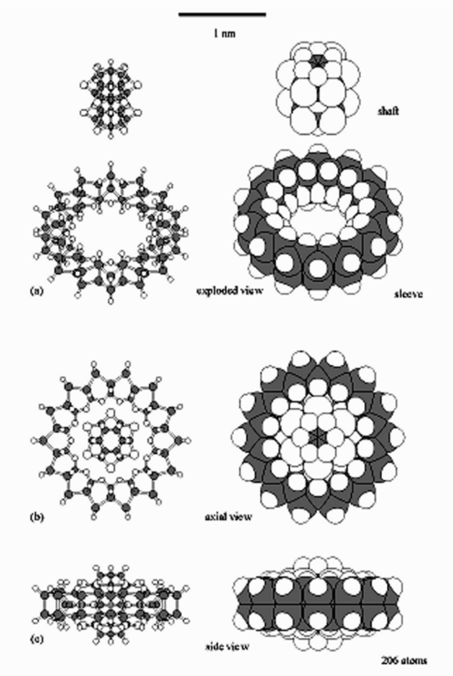

Figure 2. Molecular-scale gear

But in nano systems engineering are produced also an artificial systems for example to transport anything in the natural environment. This is already *hybrid nanomachine* which can not describe from the mechanical or electronic point of views but only as cybernetic “machine”. But cybernetic “machine” is isomorphic feedback models in mechanical, hydrodynamic, electrical, biological and other systems. But this model can not adequate describe living organisms as open systems. In contradistinction to cybernetics concerned with feedback arrangements, – said Lüdwig von Bertalanffy, – General Systems Theory is From the systems approach point of view are all living organisms the open systems and all machines the closed systems. The model of open system is applicable to living phenomena such as those of metabolism, growth, metabolic aspects of excitation, etc. [6].

Nanotechnological objects are mostly hybrids of nature and art. There are nanotechnological systems (*hybrid nanomachines*) in which objects of biotic origin are used. “DNA-molecules, for example, are utilized in electronic components. Other nano-products are to have new kinds of biocompatible (e.g. coatings of artificial joints) or bioanalogue (e.g. hydrophobe) features. … Nanotechnological constructions are to reproduce traditional electronic components (switches, diodes, transistors, etc.) on a nanoscale. One main goal of this effort is to open up new dimensions of data processing, namely through the storage of large amounts of data in the smallest possible space …” [7] Nanomachine can be also a symbiosis of the natural bio self-replicating object and artificial device. “DNA nanomachine (a) A simple device composed of three short single strands of DNA can be made to operate as a tweezer that opens and closes on the addition of another strand. The base sequences are chosen to make parts of A and B and parts of A and C complementary with each other so that double strands form; this produces the tweezer that is initially in the open state. (b) The addition of a strand F that is complementary to the unpaired sections of B and C causes the tweezer to close when pairing occurs. The tweezer opens again when a strand Fbar is added that is complementary to F: Fbar pairs with F to form a doubled stranded DNA by-product. The energy source for the machine is the hybridisation energy of the FFbar by-product” (Fig. 3) [8].

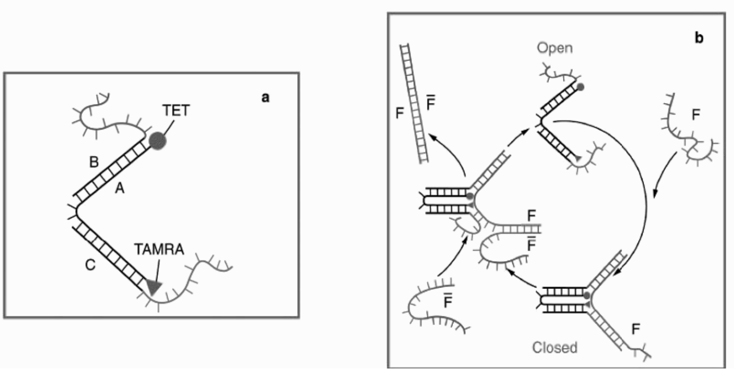

Figure 3. “Cells, natural self-replicating machines, make a variety of minerals including magnetite and silica – and they do this under water, using chemical techniques four billion years old. Mechanically guided covalent chemistry has already been accomplished with a scanning probe microscope” [8]

The cybernetic model as flow diagram of the transforming inputs into outputs was transferred on the people as parts or human elements of systems (with the sense organ, the brain, and the output transducer) and on the biosystem at all. Flowing through systems (flow systems) are “streams of some “working fluid” (which may be matter, energy, or information) … Whatever the nature of the throughput, it may pass through the system in a number of different forms. Thus energy might be electrical or hydraulic. If electrical, it might in the form of either a direct or an alternating supply at a range of possible voltages, frequencies, and so on. This *form* of the throughput is often termed *language*. There is no objection to this so far as information systems are concerned, but it seems a little unnatural to refer, for example to the “language” of a reagent in a chemical system as “aqueous” solution” [9].

This transference has as a consequence the description of the properties of the engineering systems similar with living organisms:

(1) Living systems are self-regulating systems and systems with adaptation, that correspond with the phenomenon of homeostasis in the complex technological systems. The prototype of the homeostasis is the heat regulation of the warm-blooded animals: “Homeostasis … is the ensemble of organic regulations which act to main lain the steady state of the organism and are effectuated by regulating mechanisms in such a way that they do not occur necessarily in the same, and often in opposite, direction to what a corresponding external change would cause according to physical laws. The simplest example is homeothermy” [6].

(2) Self-organization is the major characteristics of complex technological systems and living organisms as well – systems evolve out of lower order to higher order or level of complexity: “Complex automata are autonomous, self-organized totalities made up of several integrated levels with a hierarchy of structures” [5].

(3) Design of artificial systems (learning automaton) that are capable of evolving and learning as living organisms.

(4) Modeling of the behaviour of the living systems became a basis for the development of the prototypes of the new technological systems, for example in bionic or as biomimetism. “*Bionics* (literally, ‘units of life’) was an attempt to evaluate the efficiency of an organism or a machine, to measure the structures and processes by which the ‘purposes’ or ends of the system were fulfilled …‘bionics’ was defined “as an attempt to understand sufficiently well the tricks that nature actually uses to solve her problems, this enabling us to turn them into hardware” … The term ‘*biomimesis*’ was introduced in 1961 at the second symposium on bionics by Warren S. McCulloch, a neuroscientist member of the Research Laboratory of Electronic at MIT, as a generic concept. Taking the term in its most extensive sense, “the imitation of one form of life by another”, MeCulloch … included the mimetic strategies to avoid enemies or catching preys that are predetermined in the genes of insects. McCulloch divided biomimesis into two distinct fields, cybernetics and bionics” [10].

Cybernetic “machine” is isomorphic feedback models in mechanical, hydrodynamic, electrical, biological and other systems. “Modern servomechanisms and automation, as well as many phenomena in the organism, are based upon feedback arrangements far more complicated than the simple scheme … but the latter is the elementary prototype. In application to the living organism, the feedback scheme is represented by the concept of homeostasis." But this model can not adequate describe living organisms as open systems. "Ashby asks about the "fundamental concept of machine" and answer, the question by stating "that its internal state, and the state of its surroundings, defines uniquely the next state it will go to." However, such representation … is too restricted for a theory to include biological systems … A "self-organizing" system, according to Ashby, can have two meanings, namely: (1) The system starts with its parts separate, and these parts then change toward forming connections (example: cells of the embryo, first having little or no effect on one another, join by formation of dendrites and synapses to form the highly interdependent nervous system). This first meaning is "changing from unorganized to organized." (2) The second meaning is "changing from a bad organization to a good one" (examples: a child whose brain organization makes it fire-seeking at first, while a new brain organization makes him fire-avoiding; an automatic pilot and plane coupled first by deleterious positive feed back and then improved). … However, in overcoming this limitation, Ashby introduced another one. His "modern definition" of system as a "machine with input" as reproduced above, supplants the general system model by an other rather special one: the *cybernetic model*, i.e., a system open to information but closed with respect to entropy transfer. This becomes apparent when the definition is applied to "self-organizing systems." Characteristically, the most important kind of those has no place in Ashby's model, namely, systems organizing themselves by way of progressive differentiation, evolving from state of lower to states of higher complexity. … the living organism … is not an Ashby machine because it evolves toward increasing differentiation and inhomogeneity … we cannot replace the concept of "system" by the generalized "machine" concept of Ashby. Even though the latter is more liberal compared to the classic one (*machines defined as systems with fixed arrangement of parts and processes*), the objections against a "machine theory" of life … remain valid" [6].

4. Environmental and Biological Nanorisks

Nanotechnology is considered today as the beginning of the nanotechnological revolution and the future technological means fort the survival of the mankind. But these expectations are darkened from reasonable assumptions of the unforeseen assumptions negative consequences and risks from the implementation of these new technologies. "On the one hand, there are far-reaching expectations with respect to potential contributions of nanotechnologies to welfare, health, sustainable development and to new information and communication technologies. Often, nanotechnology is even regarded as key technology of the new century, sometimes even as the kernel of a third Industrial Revolution. On the other, however, people are aware that there might be a "dark side" of the accelerating technological progress. Concerns about possible risks and side-effects of nanotechnologies have been expressed in public debate and in the media for some years. A lot of ELSA (ethical, legal and social aspects) activities have been undertaken …, and many expert groups worldwide are still debating about risk analysis, risk assessment, public perception and regulation of nanotechnologies" [11]. Frequently more and more critics of nanotechnology tell about elaboration of special nanoethics [12–19]. More and more often today's complex research programmes and technological projects pass the social expertise that includes some ethic components. This is a important speciality of the modern technosciene that is the part of the new post-non-classical type of scientific rationality. "Classical science assumes that true knowledge of an object is conditioned by the elimination, in the process of theoretical explication and description, of all that which has to do with the subject, its goals and values as well as the means and procedures of its activity. Non-classical science (its example being a relativist quantum physics) takes into account the relation between the knowledge of an object and the nature of the means and procedures of the activity in which the object is discovered and cognised. Nevertheless, relations between intrascientific and social goals and values are still outside scientific reflection, though defining implicitly the nature of knowledge (defining what it is that we isolate and conceive in the world as well as the way we do it). The post-non-classical type of scientific rationality extends the field of reflection on activity. It is aware of the relation not only between the knowledge of an object and the specific nature of the means and procedures of activity, but between this very knowledge and the structure of the goals and values of such activity as well. At the same time the relation between intrascientific and extrascientific goals is brought to light. In overall investigations of complex self-developing systems more frequently than ever becoming dominating objects in natural science and technology (including the objects of ecology, genetics and genetic engineering, "man – machine – environment" technical complexes, modern information systems, etc.) the elucidation of the ties between intrascientific and social values is performed through social expertise of respective investigation programs" [20].

"Nanotechnology comprises not only the manipulation of natural molecules, but also the creation of molecules not found in nature. … some nanotechnological objects are clearly distinct from comparable natural objects, while others are identical to natural objects. Nanotechnology, however, does not only create an artificial world that is distinct from nature. It also relates to natural processes and materials in a new way. In this respect it is difficult to separate it from nature. … Nature as that which is not produced by human action. This understanding gives rise to a distinction between natural and synthetic objects. … an object is to be defined as artificial if it can be scientifically demonstrated that it was produced by human action. This criterion makes the distinction between natural and artificial objects an empirical matter, subject to experimental methods of assessing the naturalness of technological products … An artificially produced object would therefore belong to nature if all scientific methods available at a given time could not succeed in distinguishing it from an identical natural object. Processes of self-organization in the production of quantum points are a good example of this form of influence. Each component of self-organizational processes that are used in the production of nano products and each property of completed nano products can be assessed to determine whether it is natural or artificial" [21].

Nanotechnology creates new possibilities for the modification of the molecular and atomic structures, implantation in the human organism of the new micro- and nanoequipment to enhance and to extend of the human perception and sense organs. "Beispielsweise ist der Versuch, die menschlichen Sinne um die Bereiche des Ultraschallhörens zu erweitern oder Infrarotsehen für bestimmte Berufsgruppen über Retina-Implantate zu ermöglichen, nicht mehr abwegig, da Cochlea-Prothesen bereits klinisch etabliert sind und der Einsatz von Sehprothesen zukünftig möglich erscheint. Unklar ist allerdings, wie das menschliche Gehirn die Informationen über neuartige Sinne verarbeitet und wie sich diese Sinneserweiterung auf die Menschen auswirkt" [22]. Nanotechnology creates not only new technologies and artificial systems in nano scale but also new biological and hybrid organisms. The objects of the nano manufacturing are also even molecules. The situation has dramatically changed and the changed situation requires new ethics – nanoethics. "Ethical reflection on nanotechnology has, in fact, already coined new terms such as "nano-ethics", but has, to date, hardly accomplished more than to proclaim a need for ethics in and for nanotechnology" [12].

One of the first known German philosophers of technology Friedrich Dessauer, specialised in radiology, devoted one of his books *Nuclear Power Engineering and the Atom Bomb* (1948) to this subject-matter. At the end of his book he writes: "*Reliability* and *Safety* in the space of natural scientific research and technological design are the factor which moulds the present generation and a new stratum of society that has been brought up in the space of natural scientific research and technology and that will seize social power… Natural scientific research and technology make world's history". (He mentions, however, that natural scientific researchers and engineers are often not interested in preserving and historical or humanitarian traditions.) "The social problems which deal with discovery and technological utilisation of energy of fission are no longer national, they have become the problems of the whole world's community" [23]. This fact leaves a special impression on discussion of nuclear power safety and responsibility of scientists, engineers and politicians for this safety. No assertion of national, economic, or technical expediency or higher scientific interests can justify the moral and material damage that can be inflicted on people. This all are applied also to the nanotechnology in which is very difficult to separate scientific research not only from the technological development and design but also from nanomanufacturing. Nikolay *Berdiayev* shared this opinion stating in his article *The Man and the Machine* [24] that the domination of technology destroys personality. Which is why he believed that fighting against the hegemony of technology was necessary to save the human image and that technologization of culture would inevitably lead to dehumanization of the man. Expediency is brought into the mechanism from outside by man the designer, and it depends on the organization. This is where, according to Berdiayev, the *mechanism* differs for the *organism* that carries expediency within. The culture of "making" wins in the contest with Nature in the 20th century that can be hailed the triumph of technology. But this Pyrrhic victory shakes people's belief in the irreversible natural order of things. Everything can be made, recut, remoulded, even human psyche. This very illusion dominated in the minds of many in the 1930s and got personified into the unprecedented programme of remoulding of the people from the capitalist past in the camp forge of socialist reconstruction in the first five-year-plan periods. This idea of the correction of the mistakes of the nature is quite similar with the nano-biotechnological program of the improvement of human beings.

Backed by modern technology, the man begins to consider himself the cosmourge, the designer of the world that he can recut in different ways according to his requirements. This fundamental illusion of modern technocracy-oriented society was bitterly stated by Sergey *Bulgakov* in *Philosophy of Economy* published in 1912. But the man is not God, he is a part of nature and he cannot replace it with a totally man-made environment, though he tries to do it but all in vain. As a result, nature revenge itself with more frequent disasters, global change of the climate and other irreversible changes that put at stake the very basis of the man's existence as a species. Bulgakov believes that to overcome this misunderstanding of the world, we have to transform the machine into the organism, gradually and carefully transplanting the artificial into the natural, but not replacing the natural by the artificial. According to Bulgakov, technology is also a system of all possible means to influence Nature. The very possibility of its existence lies in significant accessibility of nature for human activity. Which is why the man, being an active and conscious part of the world's organism, becomes its centre, and potential domination of the man over the world is realised through economic mechanisms. But the man is not God: he cannot create everything he wishes out of nothing. The man can act freely and genuinely if he finds method to use his own nature. But he receives his own nature as well as his environment as given facts [25–27].

Foresaids is pertinent to the nanotechnology where is important to investigate not only intended positive but also possible unintended consequences of such intervention in the thin-layer natural nanostructures (for instance, in the neuronal brain processes) [26, 27]. You can see in the Fig. 4 the possible exposure routes for nanoparticles and nanomaterials based on current and potential future applications of the nanotechnoscience.

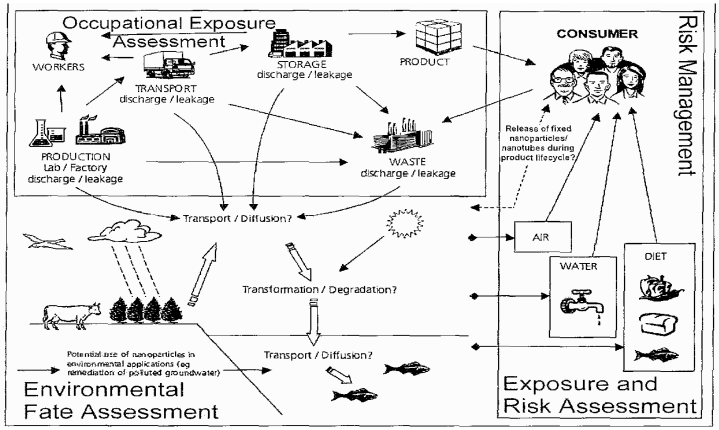

Figure 4. The possible exposure routes for nanoparticles and nanomaterials in the environment

These fine nanoparticles, that is difficult to detect, can penetrate for example in lungs or even through cell membrane and the modern science has no answer what they bring us [1, 3, 28]. Therefore nanoethics became the first place in the different scientific discussions about nanotechnology but not else in the Russia.

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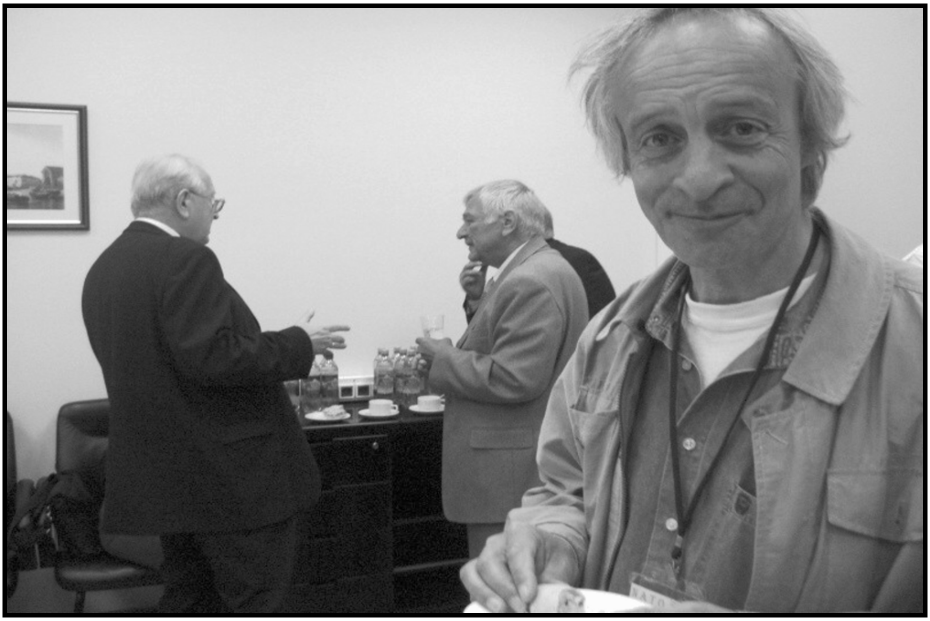

EVALUATION OF SUSTAINABILITY OF THE CARBON AND SILICON ECOSYSTEM: FROM NANOPARTICLES TO MACROWORLD

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Abstract. Rapid development of nanotechnologies has led to a complicated problem of utilization, storage and treatment of waste nanodevices of silicon and carbon origin. The processes of physico-chemical and biogeochemical destruction of carbon–silicon–uranium nanoparticles of Chernobyl origin has been studied. The period of half-destruction assessed by leaching of different radionuclide from particles is between 5 and 25 years. Natural ecosystems are generally of carbon and silicon origin. The behavior of radionuclide in natural media is observed over a period of 20 years. For the balance calculations we have utilized the *Geochemical Transition Factor (GTF)* that represents the quantity of substance, which is accumulated by living matter from the area unit. The main part of total carbon is involved in biogeochemical cycles in the forest ecosystem. Anthropogenic activity leads to a considerable imbalance of carbon isotopes. The distribution of carbon isotopes between different biotic levels demonstrates that radiocarbon of artificial emission is substantially less bio-available than those from natural sources. The environmental ability to recovery, lies in decontamination of carbon trophic circuits, is an order of magnitude greater than the rate of natural attenuation and corresponds to the removal of artificial matter from natural silicon media. The modern sustainability of the silicon and carbon ecosystem is determined by an insignificant quantity of artificial matter involved in biogeochemical cycles.

Keywords: Nanodevices, silicon, carbon, nanoparticles, Geochemical Transition Factor, recovery, sustainability, biogeochemical cycles

1. Introduction

Nanomaterial is a material with a size of less than 1 μm, and a typical example thereof is a carbon nanotube (CNT) (Fig. 1). The nanomaterial includes a zero-dimensional

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structure such as nanoparticles and quantum dots, one-dimensional structure such as carbon nanotubes and nanowires, and two-dimensional structure such as nanodiscs.

CNT related nanostructures possess remarkable electrical, mechanical, and thermal properties. To produce these nanostructures for real world applications, a large-scale controlled growth of carbon nanotubes is crucial for the integration and fabrication of nanodevices and nanosensors.

The research of CSC scientists working at NASA's Ames Research Center in Moffet Field, California, has helped pave the way to building transistors from carbon nanotubes, tiny structures created from a single layer of carbon atoms whose size is measured in nanometers. Scientists had theorized that transistors could be made from nanotubes. CSC researchers Manjeri Anantram, Cun-Zheng Ning, Deepak Srivastava and Toshishige Yamada, joined by researchers at NASA and academic institutions, took a closer look at how to actually create such transistors. Their discoveries include algorithms to model such applications, new techniques of information transmission, carbon structures that operate like transistor switch terminals and methods for harnessing nanotube chains for electronic systems [1].

A nanomaterial such as a carbon nanotube generally shows semi-conductive or metallic properties during its manufacturing process, and these properties may be used for application to various sensors and electrical devices such as a field effect transistor (FET) and a single electron transistor (SET). Because of the feature that the nanomaterial emits electrons and x-rays by an electric current applied thereto, the nanomaterial is used for developing field emission displays and lamps.

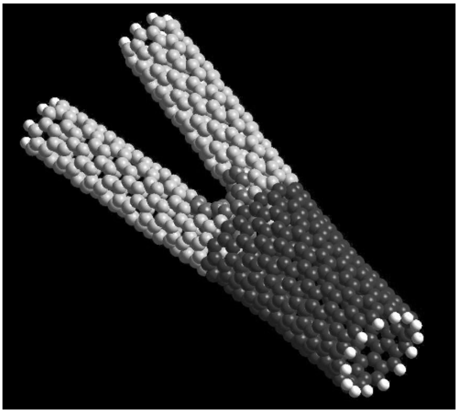


Figure 1. Model of a carbon nanotube switch [1]

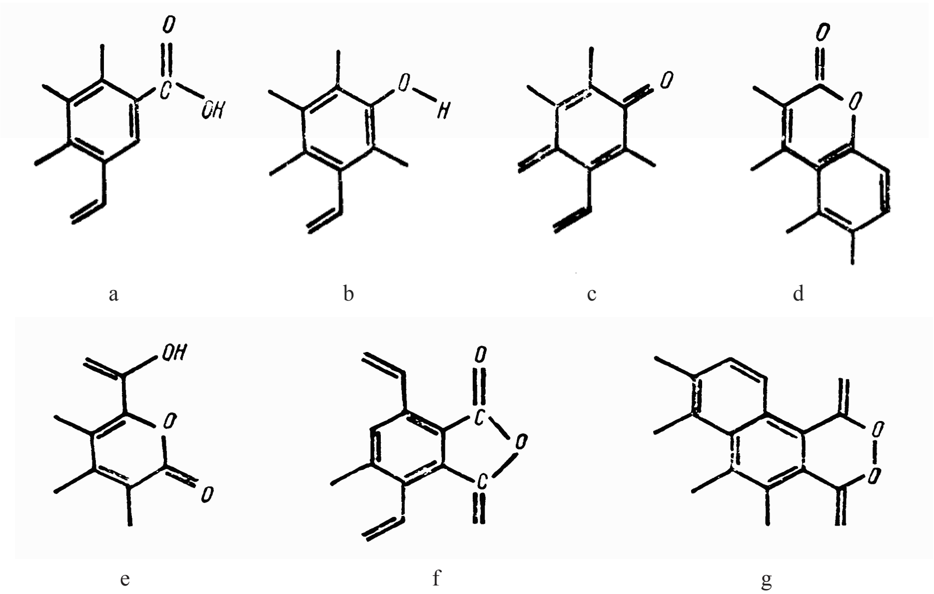
Various methods can be used for depositing the nanomaterial to a substrate. To name a few: a method of bonding the nanomaterial one by one by using an electron microscope; a method of growing the nanomaterial between electrodes; a method of patterning a thin layer by photolithography after shaping the nanomaterial into a thin layer; a method of using an atomic microscope or a dip pen; and a method of moving the nanomaterial contained in a solution by using an electrical or magnetic field can be used [2].

Rapid development of nanotechnologies led to a complicated problem of utilization, storage and treatment of waste nanodevices of silicon and carbon origin.

Carbon (together with hydrogen) is the main structure element of organic molecule and living organisms. The bioavailability of carbon is considerably higher than that of silicon. Therefore the carbon based particles are subjected to biogeochemical destruction more extensively than particles of silicon origin. We have studied the processes of biogeochemical destruction of graphite particles subjected to a high temperature (up to 3,000°C) and neutron irradiation in the damaged Chernobyl reactor.

2. The Structure and Composition of Particles

Graphite has a hexagonal structure. Carbon atoms are situated at vertexes of regular closely arranged hexagons similarly to benzene rings. Binding energy is 170 large calories per g-atom. Basal planes are parallel and interconnected by Van der Waals forces. Binding energy in perpendicular direction to basal planes is between 1 and 4.36 large calories per g-atom. For this reason graphite has full-blown anisotropy of physical properties and propensity to formation of intercalation substances, i.e. inclusions of atoms, ions or molecules of foreign matter into flat interstices of the lamination. Graphite is stable against hostile environment and oxidation. At the same time alkali and earth metals are able to intercalate in graphite.



a b c d

e f g

Figure 2. Surface functional clusters of graphitized carbon materials: a – carboxyl, b – phenol, c – carboxyl of quinone type, d – normal lacton, e – lacton of fluorescent type, f – acid carboxyl, g – cyclic peroxide

The graphite powdering results in destruction of crystals in all directions and is accompanied by a considerable increase of the surface with a high concentration of broken π- and σ-links. These unsaturated radicals are centers of chemical absorption of oxygen. The saturation of graphite surface with oxygen is passed under the atmospheric pressure. Absorbed oxygen is irreversibly bonded with the graphite surface. In the presence of water steam oxygen clusters are partially hydratized.

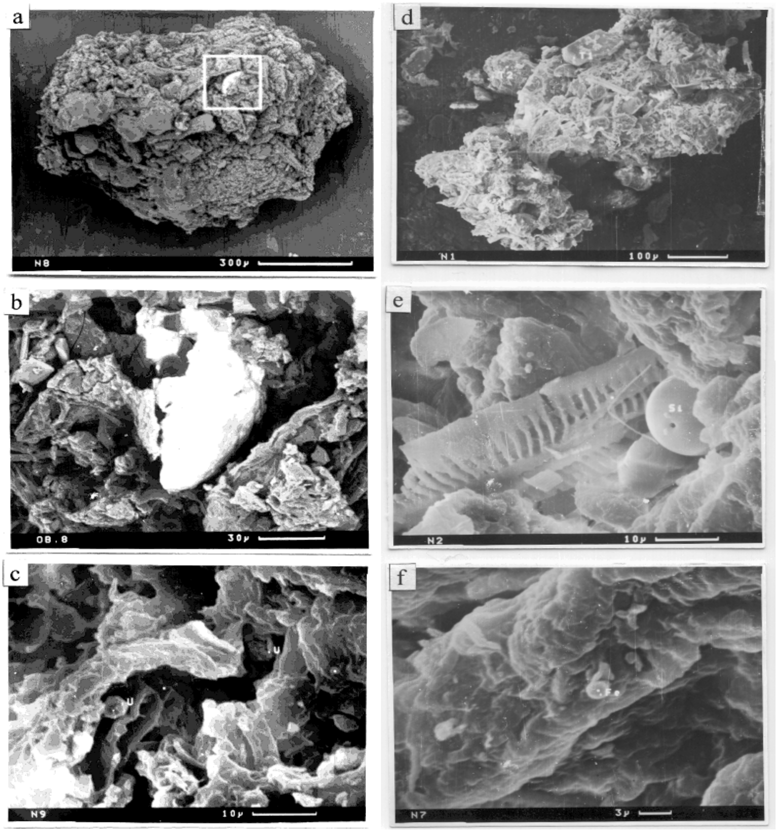


Figure 3. Fuel and condensation hot particles of Chernobyl origin: (a) General view of conglomeration particle of graphite–silicate composition. Bitmap electronic snapshot. Section with U fragment is accentuated. (b) Blowup snapshot of contour in reflected electrons. A construction of U inclusion of 80 μm in size can be seen. (c) Particle of substantially graphite composition, scanned under the translucent electronic microscope-microanalyzer. Confused-stringy graphite aggregates. Isomeric (octahedral) U inclusions are situated in the center of picture. (d) Bitmap electronic snapshot of micro-conglomeration particle of fuel disseminated in the engineering material matrix array. Composition: Si, Al, K, Cu, Zn, Fe. (e) Bitmap electronic snapshot of silicate condensation particle. Near the spherule the fragment of diatom skeleton is situated. (f) Bitmap electronic snapshot of Fe condensation spherule

Graphite surface contains also carboxyl, carbonyl, and ether functional clusters (Fig. 2). Oxygen-containing clusters are mainly presented by graphite acid (graphite oxide $C_x(OH)_y$). This substance is chemically stable and protects the graphite surface from future oxidization. Graphite is non-oxidizable in the air up to 400°C. In nature graphite does not change over thousands of years.

Graphite was used for deceleration of heat neutrons in the damaged nuclear reactor in Chernobyl. During the operation fission products are accumulated in graphite. Subjected to the neutron flux of high energy stable isotopes of carbon and nitrogen are transformed to radiocarbon [3]:

$$^{13}C(n,\gamma)\rightarrow {}^{14}C \tag{1}$$

$$^{14}N(n,p)\rightarrow {}^{14}C \tag{2}$$

During the active release about $(0.8–2.3)\cdot 10^{12}$ of ^{14}C in solid phase was removed from the damaged reactor to the environment. The size of the graphite particles was between decimal fractions to 1 mm.

They have a complicated structure: micro-conglomerates of fragmental grains of quartz, feldspar, stratiform silicates, condensation hollow spherules of SiO_2, spherules of Fe, natural organic fragments etc. (Fig. 3). Actual radioactive bearers are presented by essence graphite and uranium particles of 1–80 μm in size (in most cases of 1–3 μm). In the fine mixture with the U oxide presence of metallic phase of fine U or probably of Zr and Zn has been observed. The size of coherent distance blocks is assessed in $L < 10$ nm by the widening of lines at the selected area diffraction pattern. When a particle is included in the stratiform silicates a faint signal of U apparently corresponding to immobile form has been presented in the spectrum of discriminating X-radiation.

3. Physico-Chemical Destruction of the Graphite–Silicate Particles

The intercalation of fission products in graphite allowed us to assess the rate of graphite-silicate particles destruction in a series of experiments on radionuclide water leaching. We have leached the particles every 2 months with the distilled water in Soxhlet's extraction apparatus (Table 1).

Between the leachings particles were dried and exposed to the atmosphere in normal conditions. The direction of the leaching process is specified in the experiment. The general approach to description of irreversible processes of destruction presumes using the kinetic equation of the first order:

$$N = N_0(1-e^{-k_D t}) \,, \tag{3}$$

TABLE 1. Kinetics of fission products leaching from graphite–silicate particles

Time between leaching, days	Leaching, %	
	^{137}Cs	^{90}Sr
50	0.20—0.26	2.1—3.1
	0.24	2.63
116	0.86—1.1	3.7—5.2
	1.0	4.3
174	0.96—2.3	4.4—7.0
	1.7	5.5
220	1.3—2.8	5.9—8.9
	2.1	7.6
330	1.5—3.6	9.1—14.5
	2.5	11
382	1.7—3.7	10—16
	2.7	13
k_D, s^{-1}	$(0.63—1.2)\cdot10^{-9}$	$(3.3—5.3)\cdot10^{-9}$
	$9.3\cdot10^{-10}$	$4.2\cdot10^{-9}$
$D_{1/2}$, years	18—35	4.1—6.7
	25	5.4
$\frac{k_{D(^{90}Sr)}}{k_{D(^{137}Cs)}}$	4.1—5.2	
	4.6	

where N_0 corresponded to the quantity of intercalated radionuclides originally contained in solid phase of the particles, N is quantity of radionuclides removed from particles in statu of time t, k_D is the rate constant of the particle destruction conjugated with the time of half-destruction ($D_{1/2}$) by the equation:

$$k_D = \ln 2 / D_{1/2} \tag{4}$$

The difference between the rate constants of particle destruction assessed by leaching of different radionuclides is about 4.6 times (Table 1, Fig. 4). This fact could be explained by difference in chemical properties of appropriative elements. Particles are of a complicated graphite and silicon structure. Cs has a strong property to substitute K in the structural positions of minerals. So ^{137}Cs intercalated in reactor graphite may transform to silicon mineral structure during the exposition between leachings. Therefore the assessment by ^{90}Sr is more acceptable. Summarizing we can assess the limits of half-destruction of graphite–silicon particles owing to physico-chemical processes in 5 and 25 years.

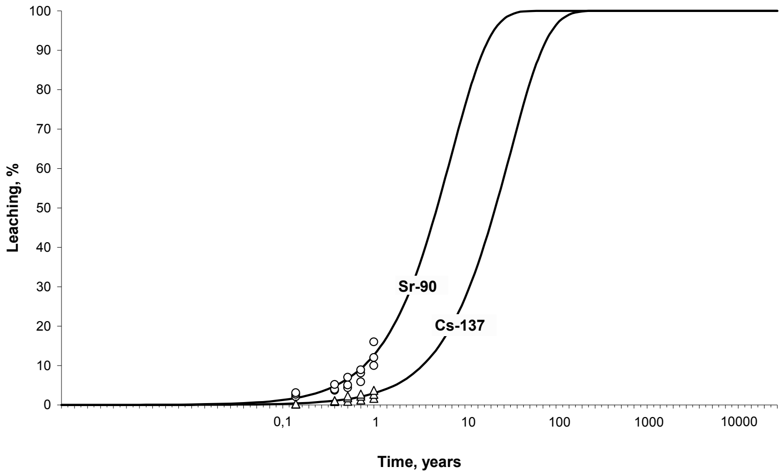


Figure 4. Time-dependent leaching of radionuclides from graphite-silicon particles of Chernobyl origin

4. Biogeochemical Destruction of the Graphite–Silicate Particles

Physico-chemical destruction of the particles promotes the transformation of chemically inert graphite to bioavailable forms. Graphite particles, when exposed to distilled water over a period of 6 months, are substantially disintegrated by mycelium clumps (Fig. 5).

The biogeochemical destruction of particles was studied jointly in the Institute for Environmental Geochemistry and Institute of Microbiology and Virology of NAS of Ukraine in a series of experiments [4].

Assimilation of radioactive graphite by *Acremonium*, *Arthrinium*, *Aurebasidium*, *Cladosporium*, *Paecilomyces*, *Phialophora*, *Scopulariopsis* secured from soils was studied in Czapek's medium with the addition of a mixture of irradiated and inert graphite as the only source of carbon. A check experiment was worked out with the addition of sucrose and inert (non-irradiated) graphite to the Czapek's medium. In the experiment with inert graphite a considerable increase of mycelium biomass was not observed. An addition of irradiated graphite to the substrate resulted in growth of mycelium biomass. During 60 days mycelium biomass increased up to 30 times and ^{14}C concentration in substrate and biomass arrived to equilibrium (Table 2).

The accumulation factor (A_f) of ^{14}C is considerably more in the check experiment owing to a high bioavailability of carbon source in the utilized substrate. The accumulation of ^{14}C in mycelium biomass from the substrate based on irradiated graphite was not exceeding factor 2. The accumulation of radiocarbon is slightly decreasing in high radiation fields probably due to the depression of the microorganism's activity.

Thus graphite particles of artificial origin are strongly subjected to physico-chemical and biogeochemical destruction that determines the threat of utilization, storage and treatment of waste nanodevices.

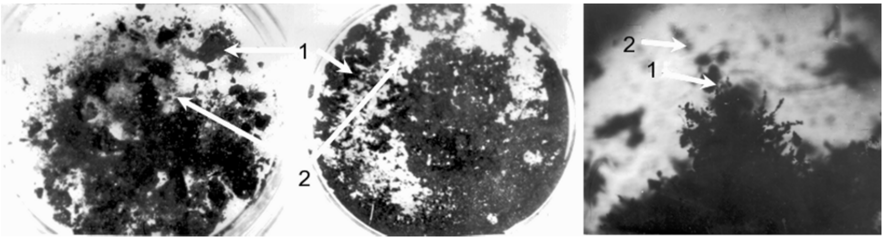


Figure 5. Biogeochemical destruction of graphite [5, 6]: ^{14}C concentration: a, c – 20,000; b – 4,000 Bq·g^{-1}; a, b: 1 – graphite, 2 – mycelium clumps; c – photomicrography: 1 – floccus covered with graphite, 2 – mycelium clumps

TABLE 2. Accumulation of ^{14}C by *Cladosporium cladosporioides* (Fres.) de Vries (according to [4])

Source of carbon	^{14}C, Bq·g^{-1}		A_f
	Substrate	Mycelium dry biomass	
Sucrose 20 g·dm^{-3} (check experiment)	0.22	24.1	110
Mixture of irradiated and inert graphite	2.100	3.700	1.76
Irradiated graphite	32.000	36.000	1.13

5. From the Nanoparticle to the Macroworld

From the premises one can suggest the strong bioavalability of nanoparticles of carbon origin. Similarly to nanodevices the natural environment is of carbon and silicon origin. Carbon (and hydrogen) is main structure component of organic molecules and living organisms (0.48% of Earth crust), and silicon (27.6%) is corresponded to non-living matter. Silicon–oxygen compounds represent the media of the living organism's nutzrition.

The biosphere is a unique realm of the earth's crust, which is occupied by life. Life is concentrated only in this external thin layer of our planet. All organisms are always divorced by the acute, impassable bound from inert matter. The main forms of biogenic migration concerned with the substance of living matter are determined by four factors: genetic properties of living organisms, intensity of biogenic flux of atoms, technique of activity of living organisms, and changes in order of atoms induced by the insertion of new substances in the biosphere [7]. The last of these is the most effective and strong factor of biogenic migration that was based on the theory of biogenesis and technogenesis [8].

The modern period of the evolution of biosphere is determined by an intensive development of the technosphere. Technogenesis leads to the degradation of living conditions of the ecosystem; it is accompanied with the development of power-consuming production, and conjugation between the concentration of some chemical elements, and dissipation of others. Owing to anthropogenesis a number of substances (artificial isotopes and organic matter) were produced. This matter does not exist in nature and/or not proper to geochemical media. Anthropogenic factors have led to specific changes in the biosphere: global (e.g. climatic), and local (appearance of new or mutation of existed species). The behavior of man-caused elements substantially differs from their nature analogues – this is determined by the form of their entry into the environment and leads to the formation of artificial anomalies. Therefore anthropogenic activity leads to the technogenical evolution of the biosphere and the infraction of the main geochemical principle of invariability of biosphere and geochemical cycles of chemical elements.

The technogenic evolution of the biosphere leads to a number of global problems [9]:

- Poisoning of air, water and soil with industrial and agricultural sub-products, that leads to a deficiency of clean freshwater, and, probably, oxygen of air
- Lack of pollution-free areas over the Earth
- Deficit of food caused by demographic problems and soil erosion
- Depletion of mineral resources and an energy shortage
- Geological, geochemical, and climatic imbalance in nature
- Thermal pollution of the planet

E. Le Roy and P. Chardin predicted the transformation of the biosphere to a new evolutional state, when the intellectual activity of mankind becomes the determining factor of development. This state was named the “noosphere”. Now we can consider that the technosphere is the intermediate modern stage between the biosphere and the noosphere. The evolution of biosphere follows the following scheme:

$$biosphere \xrightarrow{technogenesis} technosphere \xrightarrow{noogenesis} noosphere$$

The modern process of transformation of the technosphere to the noosphere has been named as *noogenesis*. Global problems of technogenesis have led to a reconsideration of the usual approach to biogeochemical investigation and unfold biogeochemical research on a considerably broader scale. The new scientific branch, which studies interferences of living and non-living matter on the formation of chemical and cenotic composition of biosphere in the conditions when man is becoming the main geological force, has been named *biogeochemistry of the noosphere*.

The strategic task in this field is the determination of the criteria for transformation of quantitative parameters to qualitative ones, i.e. reflection of changes in chemical composition of living and non-living matter peculiar to the unsaturated zone on the cenotic composition of biogeocenose under the anthropogenic impact. The modern global task is the determination of limits of biosphere capacity to artificial by-products and environmental capability to self-clearing taking into account synergetic effects. The solution of this problem will determine future possibility of human life on Earth.

The technosphere is characterized by catastrophic development. The exclusion zone created after the Chernobyl catastrophe combined with a local artificial area is an example of the most characteristic features of the technosphere. The explosions at the Reactor No. 4 of the nuclear power station of Chernobyl in Ukraine provided a point source for the distribution of artificial transuranium elements and fission products and a unique opportunity to trace the mechanisms by which they are distributed. The possibility to distinguish artificial contaminants and natural analogues provided an opportunity for the determination of their balance distribution and temporal redistribution as well as a quantity of matter involved in biogeochemical cycles.

6. Biogeochemical Flux of Artificial Matter in Semi-Natural Carbon and Silicon Ecosystem

For the balance calculations we have utilized the *Geochemical Transition Factor (GTF)* that represents the quantity of substance, which is accumulated by plants from the area unit:

$$GTF = \frac{\Psi_p\left[Bq/m^2\right]}{\Psi_s\left[Bq/m^2\right]}, \tag{4}$$

where Ψ_p corresponds to radionuclide content in biomass, gathered from 1 m^2, and Ψ_s is density of soil contamination (20 cm in depth) of this area.

This factor indirectly make allovance to ground biomass reproduction. The research of radionuclide distribution in meadow ecosystems show that only an insignificant part of artificial pollution is involved in biogeochemical cycles. In the meadow ecosystem from n·10^{-4} to n·10^{-2} part of ^{137}Cs and ^{90}Sr is cycling between soils and plant (Table 3).

TABLE 3. GTF of radionuclides for meadow biogeocenoses within Chernobyl's contaminated area, n·10^{-3}

Radionuclide	Soddy-weakly-podzolic sandy and loamy	Soddy-weakly- and medio-podzolic gleyish	Peaty-gley	Turf-gley	Peaty-meadow
^{137}Cs	0.07–0.32 0.21 (40)	0.49–1.39 0.81 (5)	0.47–1.81 0.95 (4)	1.53–7.58 3.74 (3)	0.61–13.0 6.41 (4)
^{90}Sr	1.0–8.5 2.9 (37)	9.2–34.7 19.7 (5)	0.9–1.0 0.95 (4)	0.48–0.71 0.60 (3)	0.02–0.48 0.26 (4)

Intensity of biogeochemical flux

⇐ ^{90}Sr • ^{137}Cs ⇒

Note: for this table and tables below: limits of values are over the line, simple mean values are underlined, number of test points is in parentheses

TABLE 4. GTF of ^{137}Cs in the system "Soil-Milk", n·10^{-5}

Soil	1991	1993	1994	1996
Soddy-weakly- and medio-podzolic	4.0–30 13.6 (7)	1.3–64 12.4 (7)	2.6–5.9 3.6 (7)	1.5–4.3 2.9 (7)
Turf-gley and peaty-gley	32–89 49 (6)	8.9–46 20 (6)	8.0–46 19 (6)	4.5–26 16 (6)
Peaty-meadow	113 (1)	52 (1)	23 (1)	21 (1)

The terrestrial biomass productivity increases in flood plain meadows in comparison with soddy-podzolic soils. At the same time, GTF for ^{90}Sr decreases by one order of magnitude in flood plain meadows. The correspondence of the increasing of GTF with the biomass growth shows the conjugated effect of ^{137}Cs accumulation observed in the flood plain plants. Between $n \cdot 10^{-5}$ and $n \cdot 10^{-4}$ part of ^{137}Cs is included in higher trophic chains (Table 4).

We have considered the *biogeochemical flux* of matter as quantity of substance, which is transferring during the time unit through the area unit of conditioned interface between biotic and abiotic constituents of landscape.

Observation of 15-year dynamics of GTF on more than 50 test sites within the 60-km zone bordering the Chernobyl NPP allows us to determine the integral rate constant for radionuclide biogeochemical flux (k_P):

$$GTF_{plant} = L_P \cdot e^{-k_P t} \cdot M \, , \tag{5}$$

where L_P is landscape factor defining the part of radionuclide mobile species, which are able to include in biogeochemical migration, M corresponds to the part of radionuclide mobile species in soil at the time t.

TABLE 5. Parameters of radionuclide biogeochemical flux in meadow ecosystem

Radionuclide and system	Biogeochemical parameter	Soil type		
		Soddy-podzolic	Turf-gley and Peaty-gley	Peaty-meadow
^{137}Cs "Soil-Plants"	k_P	0.28–0.45 0.32	0.12–0.26 0.21	0.03–0.125 0.07
	L_P	0.15–0.42 0.25	0.16–0.21 0.20	1.0
	k_P/λ	13.9	8.7	3.0
^{137}Cs	k_m	0.32	0.15	0.07
"Soil-Cow Milk"	L_m	0.012	0.022	0.058
	k_m/λ	13.9	6.5	3.0
^{90}Sr "Soil-Plants"	k_P	0.20–0.37 0.29	0.26–0.40 0.35	0.30–0.40 0.38
	L_P	0.55–0.73 0.62	0.12–0.22 0.15	0.0037–0.08 0.04
	k_P/λ	12.5	15.2	16.5

The ratio between integral rate constant of biogeochemical flux (k_P) and the constant of radioactive decay (λ) characterizes the ability of ecosystem to self-clearing (plants decontamination). Comparing with the decay rate self-clearing occurs from 3 to 14 times faster for ^{137}Cs, and about 15 times faster for ^{90}Sr in dependence of landscape-geochemical conditions (Table 5). The intensity of biogeochemical fluxes of ^{137}Cs and ^{90}Sr is growth in opposite directions.

The same approach is applicable for assessment of the rate of radionuclide flux in the "Soil-Milk" system. Parameters for this system were calculated taking into account cow ration and average milk yield. The landscape factor for “milk” is considerably lower than for “plants”. No more than 6% of mobile caesium is able to involve in higher chains of trophic circuit. But integral rate constants of intensity of biogeochemical flux are in good accordance for these two chains of trophic circuit (Table 5). The intensity of biogeochemical flux to cow milk raises accordingly the biomass productivity.

The bioproductivity of the forest ecosystem is substantially higher. About 23% of ^{137}Cs is distributed between living layers, 30% corresponded to litter layer, and about 50% contains in mineral layers of soil (Fig. 6). The main part of radionuclide containing in organic matter is corresponded to primary fallouts. Probably decomposed litter contains a great part of primary fallouts, which were presented by hot particles of fuel and condensative origin. No more than 15% of Cs-137 was found in the tree canopy. On the whole we can conclude that about 90% of caesium-137 is contained in non-living organic and inorganic matter of pine-tree forest. And only 13% is included now in active biological cycling.

Am-241 is the only isotope which is accumulated in the natural environment. Its half-decay is 433 years against of parent isotope Pu-241 with half-life about 14 years. Therefore we pay special attention to this radionuclide, because in the nearest century it will become significant dose-formative after the decay of comparatively short living isotopes. Compared with other transuranic elements Am has the highest mobility and bioavailability in natural ecosystems.

About 3% of Am-241 is included in active biogeochemical cycling. The main reserve of this isotope is related to primary fallouts, which is now contained in decomposed litter and mineral soil layers (Fig. 7).

Carbon is the principal structural component of organic molecules. Therefore environmental distribution of carbon isotopes is of great significance. The main part of total carbon is involved in biogeochemical cycles in forest ecosystem (Fig. 8). The part corresponded to non-living matter is about 10%.

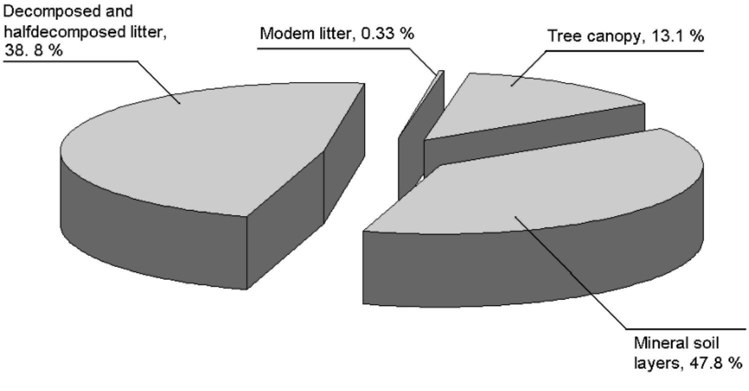


Figure 6. Balance of ^{137}Cs in forest ecosystem

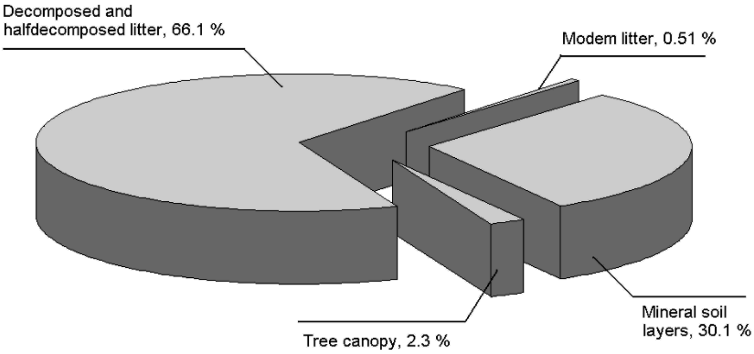


Figure 7. Balance of ^{241}Am in the forest ecosystem

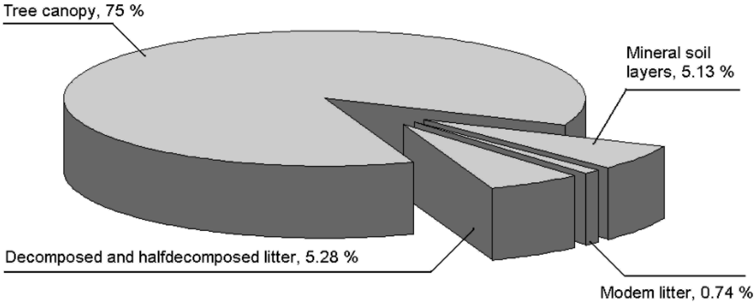


Figure 8. Carbon balance in the forest ecosystem

Anthropogenic activity leads to a considerable imbalance of carbon isotopes in the pine-tree ecosystem that primarily depends on the properties of anthropogenic fallout. Radiocarbon of artificial origin (arising from the accident) is equally distributed now between living and non-living constituents of the forest ecosystem. The distribution of carbon between different biotic levels of the forest ecosystem (Fig. 9) demonstrates that accidental emission is substantially less bioavailable than emissions from natural and global sources. It is evident that a sizable part of ^{14}C was released during the accident as uranium–carbon–silicon hot particles. These particles have been relatively stable during the 20 years since the accident and are contained in soil and decomposed litter. The latter is the nearest source for secondary emission of ^{14}C, especially in the case of forest fire. In natural conditions secondary ^{14}C emission from soil and decomposed litter is absorbed by higher layers of litter and moss. Present-day secondary cycling of $^{14}CO_2$ of accidental origin in the forest is limited by the soil-litter-moss layer.

The limitation of anthropogenic activity within the contaminated area led to a recovery of natural peaty landscapes. The modern auto-rehabilitation processes are more rapid and deep than man-caused conversion of the environment in the past. The biodiversity in the evacuated zone, which covers more than 4,000 km^2 in Ukraine, Belarus and

Russia, is higher there than before the accident. Some 100 species on the IUCN Red List of threatened species are now found within the abandoned area. Around 40 of these, including some species of bear and wolf, were not seen there before the accident [10].

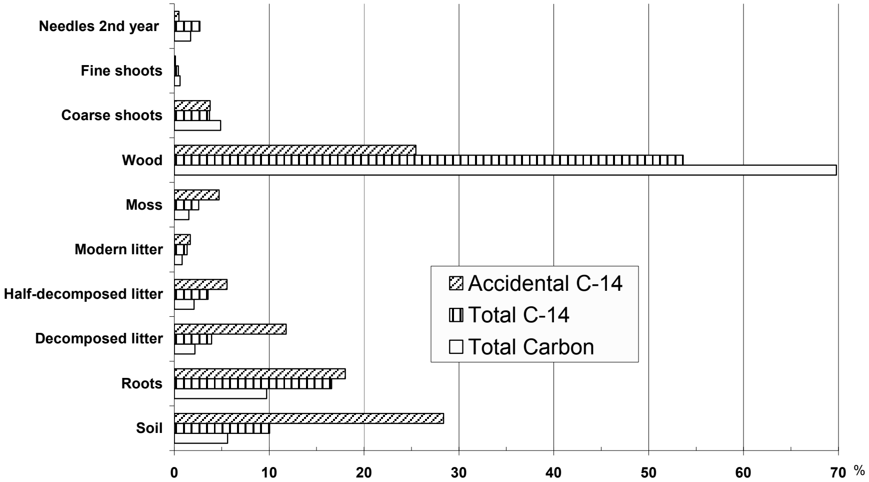


Figure 9. The distribution of carbon isotopes in the forest ecosystem

7. Conclusions

Nanoparticles of Chernobyl release are considered as an analogue of carbon and silicon nanodevices. Intercalated long-life radionuclides are a marker for the evaluation of particle destruction. Completely physico-chemical destruction of carbon and silicon nanoparticles of Chernobyl origin assessed by leaching of different isotopes is approximately 100 years that corresponded to 10 periods of half-destruction. Microbiological destruction of particles occurs substantially rapidly.

Artificial radionuclides intercalated into graphite–silicate particles are substantially less bioavaliable than the matter of natural origin.

Experience of geoecological investigations gives rise to a conclusion about the comparative sustainability of the modern state of biosphere in spite of the catastrophic development of the technosphere. The recovery of natural ecosystems is more rapid and deep than man-caused conversion of the environment in the past. Certain catastrophic processes are not leading to global changes in the biosphere that are determined by the sustainability of biogeochemical fluxes and an insignificant quantity of artificial matter involved in biogeochemical cycles.

We know at least two examples during the Earth's history when the biosphere was partially annihilated: in the Jurassic and Glacial epochs. Now man has become the main geological force. The exceeding of limits of biosphere capacity to anthropogenic loading may result in the annihilation of mankind. We are able to destroy ourselves during the artificial transformation of the biosphere. However, even if mankind were to be annihilated, the biosphere would remain and would soon recover to a sustainable state.

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CARBON DISCS AND CARBON CONES – NEW HIGH RISK MATERIALS FOR NANO-SENSORS WITH LOW DETECTION LIMIT AND FAST KINETICS

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Abstract. Carbon cones (CCs) are the fifth form of carbon discovered in the so-called Kværner Carbon Black & H_2 Process (CB&H). Under well-defined conditions, CB&H produces a carbon material composed of microstructures, which are flat carbon nano discs (CND) (80%) and carbon nano cones (CNC) (20%). The carbon cones consist of curved graphite sheets: in ordinary periodic graphite, each layer consists of hexagonally arranged carbon atoms, and the five different angles observed are consistent with the incurrence of one to five pentagons at the cone. CNDs consist of stacked graphite sheets, with average radii between 0.4 and 1.5 μm and thickness between 20 and 50 nm. According to the quantum theory of nanographite, the characteristic geometry of the CNDs implies high mechanical and chemical stability in addition to the sensitive electrical properties required by transducers for nano-sensors with low detection limit and fast kinetics. This new material is expected to open new and high risk perspectives in nano-sensor technology by overcoming the major limitations of currently available nanostructures which consist of wires or tubes (including carbon nano-tubes) by improving their kinetics and sensitivity.

Keywords: carbon cones, carbon discs, nano-sensors

1. Introduction

Prior to 1985 carbon was only known in two crystalline forms, i.e. graphite and diamond. The third carbon form, namely fullerenes or buckyballs, was then discovered. In 1991 elongated fullerene analogues, the carbon nanotubes (CNT) which are the fourth form, appeared [1]. Carbon cones (CC) are the fifth form of carbon, fundamentally different from all the so far known carbon structures, and were accidentally discovered [2] in 1997 in the so-called Kvaerner Carbon Black & Hydrogen Process (CB&H) [3].

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This emission-free process decomposes hydrocarbons directly into carbon and H_2, based on a specially designed plasma torch. Under well-defined conditions, CB&H produces a carbon material composed of microstructures, which are flat carbon discs (70%) and cones (20%) as shown in Fig. 1. However, minute quantities of fullerene cones were first produced in 1994 [4]. At the same time, the first theoretical studies of such structures were reported [5, 6]. These cones are distinctly different from the naturally occurring helically wound graphitic cones [7] and from carbon nanohorns [8]. A review of the current knowledge of carbon cones and related conical carbon particles can be found in [9].

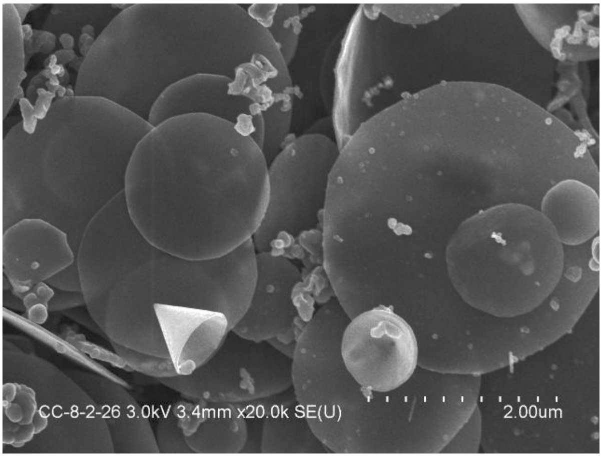

Figure 1. Scanning electron microscopy (SEM) picture of CNDs and CNCs of varying sizes and thickness (grains are carbon black particles)

The carbon cones consist of curved graphite sheets formed as open cones with one to five carbon pentagons at the tip with successively smaller and discrete cone angles, respectively. The physics of carbon cones has been relatively little explored until now. These carbon cones may be imagined formed from graphene sheets by cutting out

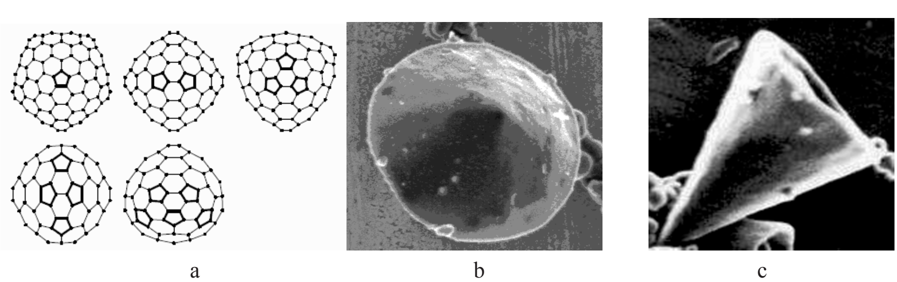

Figure 2. (a) Predicted tip structure of the five stable carbon cones; (b) SEM image of a carbon cone with two pentagons at the tip; (c) cone with four pentagons. The widths of the images in (b) and (c) are about 1 μm

sectors of $n \times 60°$ from the flat sheet and then connecting the cuts. The strain at the cone tip will give rise to the formation of $(6 - n)$ pentagons near the tip and cone angles of 112.9°, 83.6°, 60.0°, 38.9°, and 19.2° for one, two, three, four, and five pentagons, respectively. Carbon discs are special case of cones with the cone angle 180°.

The carbon cone particles formed in the Kvaerner Carbon Black & Hydrogen Process [3] are not single walled but have thicknesses of typically 20–50 nm with 50–150 layers. The expected atomic configurations at the tip of the cones [10] are shown in Fig. 2a. Figure 2b and c show scanning electron microscope (SEM) images of cones with two and four pentagons, respectively.

Extensive *ab initio* simulations have been performed in order to determine the exact geometry and electronic properties of "small" CCs (up to 300 atoms). It is found that the localization of the valence orbitals of carbon nanocones is determined by the topology alone. What appears to be a connection between curvature and gross electronic properties is instead a consequence of topology; it determines *both* the localization of the valence orbitals and the geometry [10–13]. This allows graph-theoretical deduction of electronic properties. As an example, a class of cones with invariant symmetries of the valence orbitals has been found [12]. It can also be deduced that the presence of non-even circuits, like the pentagonal rings, promotes a non-uniform distribution of charge. This makes cones more reactive than flat graphite and open-ended nanotubes. Car-Parrinello simulations of heated, hydrogenated cones, indicate that the hydrogen released at normal temperatures has preserved its molecular form during capture and storage. The positive quadrupole moment of H_2 is attracted by the dipoles of the cones and the stable conic anions [13] with one or five pentagons at the tip.

2. Experiments

We have performed experiments to characterize the structure and properties of these carbon nanoparticles. Scanning electron microscopy and atomic force microscopy (AFM) have shown that the cones actually have the theoretically predicted cone angles (Figs. 2 and 3). However, the cones consist of multiple carbon layers and show typically faceting along the edges. Extensive TEM studies of the disk-shaped particles have shown that the thickness distribution for the disks is peaked around 10–20 nm thickness with a few thicknesses up to about 60 nm [14]. We believe that the thicknesses of the conical particles are similar. The surfaces of both cones and disks appear slightly corrugated with structural details in the ~10°nm range.

Work on purification of the samples, separating cones from disks and soot have been going on for some time, but have not been successful so far and giving amounts insufficient for x-ray or neutron diffraction. We have performed structural studies using neutron powder diffraction and synchrotron x-ray diffraction of the as-produced raw material. The x-ray diffraction data for the raw material show only relatively broad peaks, but with improved crystalline quality after heat treatment to 2,700°C, as shown in Fig. 4. However, since the raw material consists of only about 20% cones, the scattering origins mainly from the disks that become more graphite-like with larger crystalline domains after heating.

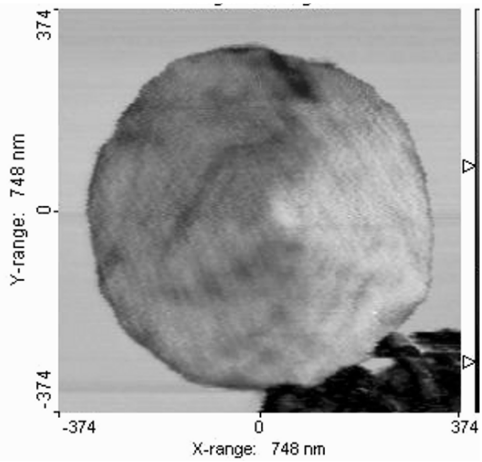

Figure 3. AFM image of a conical carbon nanoparticle, top view

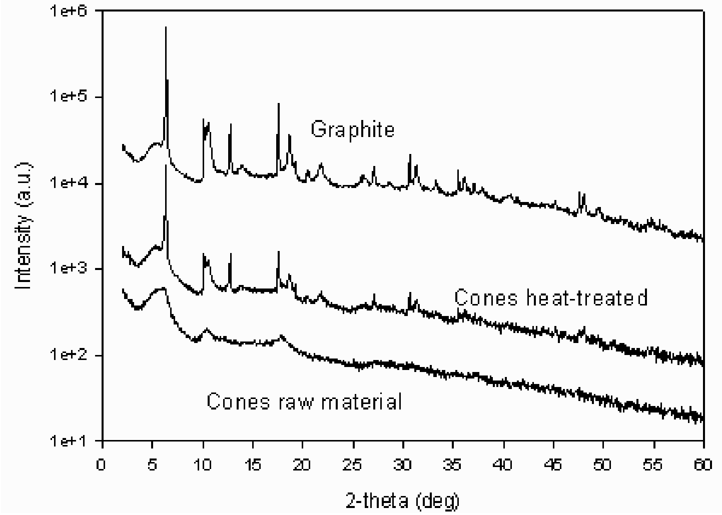

Figure 4. High-resolution x-ray powder diffraction data (» = 0.375 Å) of the carbon cones raw material, the heat-treated (2,700°C) raw material, and commercial graphite powder. The curves have been shifted vertically for clarity

Earlier experiments have indicated that this form of carbon may be capable of releasing H_2 near room temperature [15]. This work is currently under progress with new experimental results [16].

The mechanism behind the enhanced hydrogen absorption is still not understood. However, it is likely that the enhanced affinity is related to the very particular geometrical arrangements of the cones. Ideas along the same lines have recently been put forward in relation with carbon nanohorns [17], where there are indications that there are unusually strong substrate–hydrogen interactions close to the tip of the nanohorns. However, it is important to understand that the carbon cones that we study are very different from the nanohorns. The former are unusually regular structures with exceptionally well-defined tip geometry. Also the nanohorns show promising hydrogen storage capabilities, but they are currently expensive to produce. Current work on up-scaling of the carbon cones production process may make cones relatively cheap to obtain in large amounts.

The CC particles have also been suspended in various organic solvents and exposed to external electric fields. Optical microscope images of the carbon cones/disks suspended in silicon oil between two closely spaced electrodes at moderate AC electric field strengths showed clearly motion of the particles and aggregation into chain-like structures [18]. The electrorheological properties of such suspensions are now under investigation [19]. In addition, the particle powders show interesting electrical properties that will be further explored.

3. Application in Sensor Technology

Recent developments in sensor technology have shown that the use of silicon nanowires or carbon nanotubes in electronic detection methods may be the next great leap in monitoring minute quantities of chemical and biological species. Current nanowire/nanotube-based sensors use antibodies, enzymes or receptors to recognise the target to be detected, that is, the respective antigen, substrate or ligand. The main advantages of such sensing methods (biomolecules as recognition elements and nanowires/nanotubes as electrical transducers) are the high specificity of biomolecular interactions and the remarkable sensitivity of the transducers. In this respect nanowire/nanotube-based diagnostic technology requires much less biological sample than existing detection methods, rendering analyses feasible with just one drop of blood.

Silicon nanowires (SiNWs), with a diameter in the range of 2–100 nm and a length ranging from hundreds of micrometer to a few millimeter, exhibit conductivity properties and extremely high sensitivity to outside electric fields. For their application in biosensors, SiNWs are connected to a constant voltage source and coupled covalently to a bioreceptor specific for a target biomolecule. The binding of the charged target analyte to the receptor brings its charge close to the SiNW nanowire, which induces a change in resistance of the latter. As a result, there is a variation in the current that flows through the system. The small diameter of SiNWs allows minute charges (even of a single biomolecule) to impart significant changes in the sensor current flow.

Carbon nanotubes (CNTs), with diameters in the range of 0.5–50 nm have also been found to exhibit excellent performance in promoting electron transfer when used as electrodes in electrochemical reactions. Similarly to SiNWs, CNTs exhibit charge-sensitive conductance. For this reason, CNTs have recently attracted a great deal of attention for their potential use as nanotransducers in electrical sensing devices for biomolecules and gases. The electronic properties of CNTs combined with their nanometre size and graphitic surface chemistry make them ideal candidates for chemical or biochemical sensing. CNTs can be non-destructively oxidized along their graphitic sidewalls or ends and subsequently covalently functionalized with species having molecular recognition properties.

Driven by the need for a breakthrough solution in nano-bio-sensing, we propose to investigate Carbon Nano Discs (CNDs) as a new transducer for bio sensors. CNTs represent a well studied model system, however their geometry imposes certain diffusion/accessibility issues (e.g. target molecules will interact mainly with the external surface). On the other hand, CNDs consist of stacked graphite sheets, with average radii between 0.4 and 1.5 μm and thickness between 20 and 50 nm. According to the quantum theory of nanographite, the characteristic geometry of the CNDs implies high mechanical and chemical stability in addition to the sensitive electrical properties required by nanosensors with low detection limit and fast kinetics. This new high risk approach is expected to open new perspectives in biosensing by overcoming the major limitations (i.e. slow kinetics, insufficient sensitivity) of currently available nanostructures (wires, tubes).

4. Conclusion

Carbon cones and carbon discs are a unique new type of carbon nanoparticles with very interesting properties both from a theoretical point of view and for potential applications. They occur with only five distinct cone angles which all have been found in material produced by the Kvaerner CB&H process. Although it has proved difficult to separate pure samples with the various cone angles so far, extensive experiments have been done on the raw material, and computer simulations have indicated unusual electronic properties which may be utilized for, e.g., hydrogen storage applications. We propose that this unique carbon material could expected open new and high risk perspectives in nanosensor technology by overcoming the major limitations of currently available nanostructures which consist of wires or tubes (including carbon nano-tubes) by improving their kinetics and sensitivity.

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BIODYNSENSING: SENSING THROUGH DYNAMICS OF HYBRID AFFINITY/CELLULAR PLATFORMS; TOWARDS APPRAISAL OF ENVIRONMENTAL AND BIOLOGICAL RISKS OF NANOBIOTECHNOLOGY

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Abstract. Chemical cues and nano-topographies present on the surface or in the extracellular medium strongly influence the fate and adhesion of biological cells. Careful tuning of cell–matrix interaction via engineered surfaces, either attractive or repulsive, require non-invasive, long time monitoring capabilities and lay the foundation of sensing platforms for risk assessment. Aiming to assess changes underwent by biointerfaces due to cell–environment interaction (in particular nanotechnology products), we have developed hybrid cellular platforms allowing for time based dual assays, i.e., impedance/dielectric spectroscopy (IS) and Surface Plasmon Resonance (SPR). Such platforms comprising Flow Injection Analysis (FIA) have been advanced to assess the interaction between selected (normal and malignant) cells and nano-patterned and/or chemically modified surfaces, as well as the impact of engineered nanoparticles, revealed by the related changes exhibited by cell membrane, morphology, adhesion and monolayer integrity. Besides experimental aspects dealing with measurement set-up, we will emphasize theoretical aspects related to: dielectric modeling. Aiming for a quantitative approach, microscopic models on dielectric behavior of ensembles of interconnected cells have been developed and their capabilities will be outlined within the presentation. Assessment of affinity reactions as revealed by dielectric/impedance assays of biointerfaces. Modeling the dynamics of the impedance in relation to the "quality" of cell layer and sensor's active surface, this study presents further developments of our approach described in Analytical Chemistry, 2002. Data analysis. This issue is related to the following basic question: Are there "simple" Biosensing Platforms? When coping with cellular platforms, either in suspension or immobilized (on filters, adhered on surfaces or entrapped, e.g., on using set-ups) there is an intrinsic nonlinear behavior of biological systems related to cellular mechanisms involved in sensing, i.e., adaptation to stimuli. This should not mean that when coping with living cells, stray effects might not also corrupt the measurement itself, introducing distinct dynamics. Besides targeted/

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specific process, analytical platforms might exhibit additional ones due to “stray influences” that could include the effect of, e.g.: supporting matrix, nonspecific binding and temperature variation. Stray processes interfere with the desired ones and the measured data could display a non-monotonous behavior.

Keywords: differential impedance spectroscopy, microscopic models, red blood cells, interconnected cells, Surface Plasmon Resonance, affinity sensors, cellular platforms, Flow Injection Analysis

1. Introduction

Assessment of environmental and biological risks of nanobiotechnology, as well as of gentle (i.e., non lethal) bio-effects of various (noxious) agents is still an open and demanding interdisciplinary issue. The concept of sensing and detection has to be readdressed in view of the huge number of analytes to be assayed to comply with REACH[1] requirements for analysis, labeling and most of all, toxicological assessment. Tremendous progress has been made in the ability to measure particular compounds at very low concentrations. However, evaluation of rare or previously unknown compounds, metabolites and mixtures is still presenting considerable analytical challenges, while being particularly relevant in terms of possible health effects. Nanobiotechnology provides the accurate tools for nanoanalytics (from recognition, labeling, histochemical application and signal enhancement to surface modifications to mimic the in vivo environment) [1]. In the same time, it raises concerns regarding the “noninvasiveness” of the developed tools.

With the advent of concerns regarding hazardous effects of engineered (nano) particles and the documented “cocktail effect”, novel analytical and predictive tools based on the interaction with bio-macromolecules or living cells are highly required.

Real-time monitoring of biomolecular recognition processes in living cells is a significant challenge for the next phase of genomics and proteomic technologies [2] leading to improved understanding of cell–environment interactions and to powerful tools for fundamental research and applications.

We are addressing this challenge by coping with both theoretical and instrumental aspects fostering development of hybrid sensing platforms able to integrate both recognition elements (affine compounds and/or cells immobilized on top of chips) and electro-optical analytic systems suitable for time based assays.

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[1] REACH dictates new rules on the Registration, Evaluation and Authorisation of CHemicals. It requires manufacturers and downstream users of chemicals to register their substances and to list possible adverse effects on human health or the environment. REACH is the first law to require such information on about 30,000 substances currently produced and used in the EU. Less than one percent of these have been thoroughly tested for adverse effects to date [*EMBO reports* **7**, 10, 968–971 (2006)]. These tests must look at various effects, including toxicity, carcinogenicity, mutagenicity hence most must be conducted on animals since the battery of in vitro tests is reduced. Ironically, the EC is also updating its directive on the use of animals in research with the overall aim of reducing the number of animals used.

To this end, significant advancements have been achieved in terms of:

- New measurement concepts suitable for multiplexing (with capabilities for multiple analyses)
- Label free, real time monitoring, based on combined assays (e.g., electro-optical), in differential arrangements
- Development of realistic models for sensitive detection provided by sensing platform (either bioaffinity or cellular)
- Nonlinear data analysis to reveal the dynamics of superposed processes

Usually, the impact of a specific stimulus is related to the magnitude of the variation of a signal between an initial (reference) level and a plateau, eventually occurring when a "stationary" regime is reached. However, the response of an analytical platform (bioaffinity or cellular) to a specific stimulus (e.g., target analyte) may not always exhibit a monotonous evolution. This could be related with superposition of (several) processes with different dynamics, rendering difficulty in analysis. When coping with *cellular platforms*, either in suspension or immobilized (on filters, adhered on surfaces or entrapped, e.g., on using type set-ups) there is an intrinsic nonlinear behavior of biological systems related to cellular mechanisms involved in sensing, i.e., adaptation to stimuli while stray effects might also corrupt the measurement itself, introducing distinct dynamics.

Since non monotonous behavior is not necessarily exhibited merely by living systems, each process should be carefully addressed. Depending on the method of investigation, the measurements comprise information solely provided by the "active" spot, (e.g., interface: bioaffinity chip/sample) or may also include additional ones that could involve other interfaces, bulk or/and (external) noise. Besides the targeted/specific process, analytical platforms might exhibit additional ones due to "stray influences" that could include the effect of, for e.g.: alteration of supporting matrix, nonspecific binding and temperature variation. Combined assays (e.g., electro-optical), in differential arrangements, are effective avenues to provide real time, "unbiased" information on the targeted biosensing process, offering new measurement concepts with multiplexing capabilities and widened analytical range to be used for appraisal of Environmental and Biological Risks of Nanobiotechnology.

2. Assessment of Interfacial Processes Using Combined Electro-Optical Assays

Why interfacial processes? When generating functional nanostructured and mesoscopic architectures, the interaction, self organization and dynamics of constituent bricks of nanobiotechnology are highly dependent on the nature, quality and structure of the surface. Cell fate and development depends on a plethora of signals coming from cell environment. New evidence is accumulated pinpointing surface topographies and structures as equally relevant beacons as chemical cues and gradients in controlling the state and development of cellular systems. Seen in the context of cell relevant (nano) scales, the ability to manipulate surfaces and tailor their properties poses not only technological challenges but also conceptual ones, opening exciting biological/non biological interaction avenues.

2.1. SURFACE PLASMON RESONANCE

Surface plasmon resonance (SPR) sensing has been demonstrated [3] to be a powerful and quantitative probe of the interactions of a variety of biopolymers with various ligands, biopolymers, and membranes, including protein:ligand, protein:protein, protein: DNA and protein: membrane binding. It provides a means not only for identifying these interactions and quantifying their equilibrium constants, kinetic constants and underlying energetics, but also for employing them in very sensitive, label-free biochemical assays.

Surface plasmon resonance (SPR) is a physical process that occurs when p-polarized light hits a metal film under total internal reflection conditions and the evanescent wave produced at the interface resonantly interacts with the free electrons cloud in the metal. Methods based on SPR enable real-time monitoring of changes in the refractive index of a thin film close to a surface. They are used for real-time, label free measurement of biomolecular interactions.

In a prism based configuration, the active surface (the reflection site) is coated with a thin film of gold (~50 nm) so that under resonant conditions, the incident light photons are absorbed by the surface plasmons determining a shadow in the intensity of reflected light. The resonant conditions are dependent on the refractive index of the medium in close proximity to the sensing surface rendering applicability for biointeraction analysis (BIA) with bioaffinity surfaces. The most common SPR measurement techniques imply constant wavelength and variable angle. SPR assays usually cope with detection of the angle corresponding to the minimum intensity of reflected light.

The limited spatial sensitivity (only a thin layer of around 300 nm is addressed by the evanescent wave) becomes a major drawback when trying to analyze larger analytes and particularly cells.

It is inherently a nonspecific technique that depends for selectivity on the quality of the modified sensing surface.

According to the basic theory of SPR measurements, the relationship between the maximum resonance signal and the molecular weight of the analytes is:

$$R_{\max} = (\mathrm{mw}_{\mathrm{analyte}}) / (\mathrm{mw}_{\mathrm{ligand}}) \cdot n(A) \cdot R_{\mathrm{immobilized}}, \tag{1}$$

where $R_{\max}$ is the theoretical response, $\mathrm{mw}_{\mathrm{analyte}}$ and $\mathrm{mw}_{\mathrm{ligand}}$ are the molecular weights of the analyte and the ligand respectively, n is the number of active sites on the ligand and A is the fraction of active sites on the immobilized ligand, while $R_{\mathrm{immobilized}}$ represents the signal related to the amount of bound protein on the surface (in RU-resonance or relative units).

Despite SPR sensitivity, the direct detection of small molecules is difficult to be achieved, since due to their low molecular weight binding events might not cause large enough measurable changes of the interfacial properties. In the same time, the detection of whole cells poses some conceptual and technological challenges.

Differential impedance spectroscopy for fast biosensor applications

On the other hand, differential impedance spectroscopy is an electric measurement method allowing for impedance/dielectric data, related to the behavior of a sample versus a reference channel, to be collected and analyzed using proper software routines [4]. The electrical properties of the sensitive surface of the modified electrode are analyzed using a differential arrangement in which the undesired background contributions of the bulk conductivity, nonspecific coupling and temperature are eliminated.

The measurement principle is based on applying a sinusoidal electrical signal and acquiring the response signal of the electrode system. From this response the amplitude and phase of the electrode impedance is calculated and then further used to derive other parameters based on the equivalent circuit of the electrode sample system, by analyzing time and frequency dependent variations of impedance.

The impedance is calculated as the ratio of the voltage across the probe, $\mathrm{U}(\mathrm{i}\omega)$, and the current $\mathrm{I}(\mathrm{i}\omega)$, generated and respectively measured by the impedance analyzer during the experiment: $\mathrm{Z}(\mathrm{i}\omega) = {}^{\mathrm{U}(\mathrm{i}\omega)}\!/_{\mathrm{I}(\mathrm{i}\omega)} = |\mathrm{Z}| \cdot \mathrm{e}^{\mathrm{i}\varphi} = \mathrm{Z}_{\mathrm{Re}}(\omega) + \mathrm{i}\mathrm{Z}_{\mathrm{Im}}(\omega)$ where i equals $\sqrt{-1}$, |Z| is impedance modulus, φ is the phase angle between current and voltage, $\omega = 2\pi \mathrm{f}$ (with ω units in rad s^{-1}) and *f* is the excitation frequency (Hz).

In the following, it is not intended to derive a microscopic model of the interface electrode–electrolyte but to tailor a phenomenological one, suitable to depict the complex phenomena taking place at the surface of the sensor.

Biorecognition processes involved in labeling require the functionalization with affinity compounds (e.g. antibody) specific to the target analyte.

We are interested in monitoring the dynamics of bioaffinity processes (e.g. Ab–Ag interaction) using impedance measurements of the modified electrodes in a differential arrangement; this study extends the frequency range below and above the frequency of 10 kHz considered in [1]. The differential set-up offers the main advantage in comparison with the single channel, of high amplification (of the signal containing the desired information eliminating influences of the background – temperature and electrolyte composition, or nonspecific coupling) and compensation of electrode/bulk impedance effects.

Despite the potential advantages of using impedance (dielectric) spectroscopy to study biomolecular reactions, very few of such practical biosensing systems are currently available. Major fundamental issues still exist due to possible ambiguities associated with data interpretation. In addition, compared to other biosensors that are based on optical or microgravimetric principles, the sensitivity of direct impedimetric biosensor is relatively low. This may be attributed to the slow rate of data collection when using the existing device. Unlike simple chemical systems, ideal electrical circuits may be inadequate to describe the surface distribution, the microscopic properties, and the electronic behavior of the biomolecular reactions. Consequently, the application of Electrical Impedance Spectroscopy has been severely limited to corrosion and interfacial processes at simple chemical interfaces.

The differential admittance (the real and the imaginary components) between a reference and an active sensor (where the Ab–Ag reaction takes place) is revealed by measuring the related differential signal amplified by a factor of thousand, thus resulting in a dramatic change in sensitivity. It is worth to emphasize that the reference electrode is similar with the active one with the difference that on its surface is entrapped an antibody either inactivated or specific to an antigen not susceptible to be contained by the probe. Since both sensors have nearby impedances, the differential signal (carrying the information on specific binding) can be amplified at a factor much larger than the signal across the individual sensor(s) increasing the sensitivity of detection.

We describe the virtues of differential impedance spectroscopy to monitor the interfacial biomolecular reaction between immobilized antibody and the antigen-binding partner. The function of most macromolecules changes once immobilization has occurred. We show that affinity reaction, e.g., antibody–antigen (Ab–Ag) can be directly monitored using a dual-channel, low frequency impedance analyzer using covalent immobilization chemistry in the absence of a redox probe. The evidence of affinity binding is revealed by the evolution of differential admittance. The proposed approach may be applicable to monitoring other surface interfacial reactions such as DNA–DNA interactions, DNA–protein interactions and DNA–small molecule interactions.

From a basic electrical scheme, with impedance elements within the interface in parallel, the equivalent impedance of a probe, Z_{probe} is given by:

$$Z_{\text{probe}}(t) = Z_{\text{electrode}} + Z_{\text{interface}}(t) + Z_{\text{bulk}};\ Z_{\text{probe}}(0) = Z_{\text{electrode}} + \frac{Z_0}{N} + Z_{\text{bulk}} \tag{2}$$

where N is the number of active binding sites on the chip. Assuming no nonspecific coupling, N corresponds to the number of Ab present at the electrode surface. The term $Z_{\text{electrode}}$ in Eq. (1) represents the impedance of the sensor that is not affected by the Ag–Ab coupling. It consists in the impedance of the metal, functionalization layer and of entrapped Ab not affected by Ag coupling.

During the process of Ab–Ag interaction, we consider that the impedance, Z_1, of any newly bound antigen, replaces the impedance, Z_0, of the electrolyte that has previously occupied that locus. In the particular case of a one to one binding scheme, for N_1 the number of active Ab present at the surface of the working electrode, and n(t) denoting the number of Ag bounded at time t, the impedance, $Z_{interface}$ and admittance, $Y_{interface}$ of the interface, are given by:

$$\begin{gathered}\frac{1}{Z_{\text{interface}}(t)} = \frac{n(t)}{Z_1} + \frac{N_1 - n(t)}{Z_0} \Leftrightarrow Y_{\text{interface}}(t) = n(t)Y_1 + (N_1 - n(t))Y_0 \\ dY_{\text{interface}}(t) = dn(Y_1 - Y_0)\end{gathered} \tag{3}$$

Therefore, the larger the real and imaginary components of the difference of $Y_1 - Y_0$ become the better the sensitivity of this method. Assuming the following time dependence:

$$\frac{dn}{dt} = K\left(N_1 - n(t)\right) \Rightarrow n(t) = N_1\left(1 - e^{-K \cdot t}\right)$$

$$\text{if, } K = K_a \left(N_V \cdot V - n(t)\right)\Big/S \Rightarrow n(t) = N_1 \frac{1 - e^{-\frac{K_a\left(N_V \cdot V - N_1\right)}{S} t}}{1 - N_1\Big/\left(N_V \cdot V\right) \cdot e^{-\frac{K_a\left(N_V \cdot V - N_1\right)}{S} t}} \tag{4}$$

Where, K_a represents the association constant, N_V is the volume concentration of antigens at sensor surface, V is the volume of the flow-through channel and S denotes sensor's area.

One can derive the dynamics of the process of binding in relation to the concentrations of Ag/Ab in the experimental set-up. When a differential measurement of the working electrode (WE) versus a blank electrode (BK) is carried out, the differential admittance can be obtained from:

$$\Delta Y = \frac{Y_{BK}(t)}{Y_{WE}(t)} - 1 = \frac{Z_{WE}(t) - Z_{BK}(t)}{Z_{BK}(t)} = \frac{Y_0}{Y_1} \cdot \frac{1}{n/N_1 + \left(1 - n\big/N_1\right) \cdot \frac{Y_0}{Y_1}} - 1, \tag{5}$$

Consequently, the progress of the Ab–Ag reaction can be revealed directly by rearranging Eq. (5) to give:

$$\frac{n(t)}{N_1} = \frac{\Delta Y(t)}{\left(1 + \Delta Y(t)\right) \cdot \left(1 - Y_1\big/Y_0\right)}, \tag{6}$$

where $\Delta Y(t)$ is the measured data and Y_0 and Y_1 are the admitances of the bulk electrolyte and the related, newly bound Ag respectively. The ratio Y1/Y0 depends on the chosen pair Ab, Ag, as well on the entrapment procedure (providing different orientations of the active sites of the Ab). One should expect different values of Y_1/Y_0 for Ag with different molecular weights (e.g. IgG and cyanazine). The left hand side of Eq. (6) represents the ratio of bounded Ag versus surface-bound Ab, while right hand side comprises the measured admittance values (ΔY) using IS. The sign of ΔY is related to the ratio Y_1/Y_0 whether below or above unity.

While surface plasmon resonance is already a well-established technique for the probing of protein–protein or antigen–antibody recognition processes, and various biosensors are based on this method, the present study has demonstrated the application of differential impedance spectroscopy in the low frequency range, for the appraisal of bio-interfaces. Impedance/dielectric spectroscopy is used to assess changes underwent by transducer–probe interface due to biomolecular reaction between an immobilized compound and its pair (e.g., antibody against a target analyte and its antigen binding partner). The key idea is to reveal the presence of target analyte, through differential measurement, by investigating the dynamics of the impedance changes at the interfaces between bulk and specific/reference transducers, during the process of hydration, specific and non specific binding.

This study emphasizes the capabilities of differential impedance spectroscopy on modified sensors as an alternative route, more affordable than SPR, for interrogation of bio-recognition events and as a general transduction method for biosensing purposes. It must be emphasized that impedance determinations provide similar pattern of evolution during injection and rinsing steps, as well as similar detection limits as SPR systems.

Despite the advantages of the direct assay: small reagent consumption and no sample treatment, due to increased stability and larger signals, the inhibition assay is preferred.

Both experimental and theoretical approaches have proven the capabilities of differential impedance interrogation of modified electrodes with immobilized (immune) compounds (Ab/Ag) to detect minute amounts of analytes (Ag/Ab), enabling real time monitoring of the binding events in conjunction with analyte concentration in both direct and competitive approaches. Modeling the dynamics of impedance in relation to the amount of target analyte(s) and sensor's active surface, this study presents further developments of our approach described previously [1], stressing on the possibility to gain information on the concentration of target analytes, faster, prior to the occurrence of "plateaus" of the measured signals.

With appropriate design of both the electrode system and the measurement set-up, DIS can be applied to a wide range of analytes (including living cells) hence complementing the SPR measurements.

Combining the differential impedance spectroscopy (DIS) with surface plasmon resonance (SPR) provide inner validation and expand the analyte detection range while enabling sensor characterization during functionalization, as well as effective analyses.

2.2. DEVELOPMENT OF A DUAL ANALYTICAL SYSTEM, SPR-DIS

2.2.1. *Fluidics*

Sensitive assessment of bioaffinity reactions requires a fine control of the flow of the sample onto the sensitive area, fostering analyte–ligand binding. Design of the flow-through chambers should enable efficient mass transport without any resting region.

The system has two parallel flow channels connected to independent flow circuits. This allows for simultaneous, as well as independent analyses. The flow rate range is 10–1.000 µl/min with increments of 5 µl/min.

The pumps and valves are controlled through a computer interface. Sample loading, injections and washing protocol are preprogrammed and the user has merely to set the sample volume, the channel(s) to be addressed and the corresponding flow rates.

2.2.2. *Sensor design*

The surface used for SPR sensing undergoes functionalization steps and is suitable for electric connections to enable simultaneous SPR (optical) and DIS (electrical) measurements on the same chip.

For bioaffinity investigations the gold layer is functionalized to present carboxylic groups further modified to bind the ligand (e.g., antibody). The sensor can be fully regenerated.

2.2.3. *Equipment*

The dual measurement system is presented in Fig. 1. The SPR assays are performed using the 3 channel SPREETA sensor (Texas Instruments) with the control box from Nomadics Inc. The functionalization and sensing protocols have been developed using the Biacore 3000 SPR system. Similar sensitivities are achieved providing that the flow conditions and temperature be strictly controlled. The SPREETA sensor has a refractive index measurement range from 1.32 to 1.36 RIU (refractive index units). This allows measurements of various liquid samples, from water to ethanol.

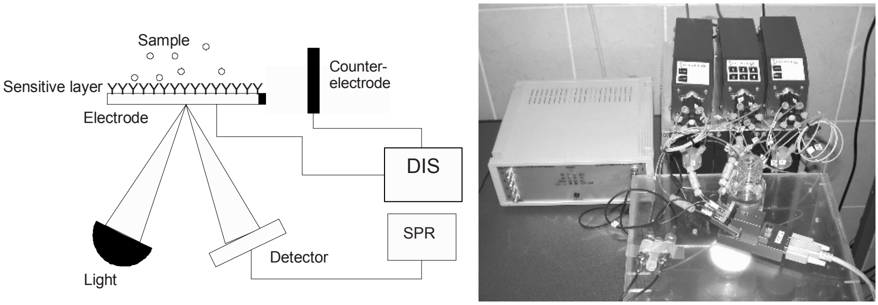


Figure 1. Schematic and actual representation of the dual system

Differential approach was chosen to increase the accuracy of the determination and to minimize the stray effects (temperature, medium composition), while the low frequency range was addressed since this domain is mainly affected by interfacial effects of the bioaffinity reactions that take place in at the sensor surface. We are using the low frequency differential impedance spectrometer (LFDIS) custom developed by ICB, Romania, to monitor the differential impedance (magnitude and phase) between the reference and up to eight working channels, as well as individual impedances of each channel. The control and acquisition software allows a real time fitting of the complex impedance data using equivalent circuit models.

2.2.4. *Experimental*

The capabilities of the system were investigated by addressing bioaffinity reaction using modified gold sensors.

Customized SPR gold sensors were purchased from Ssens NL and functionalized to allow protein immobilization.

Bovine seric albumine at concentration 1mg/ml was injected with the help of the automated flow injection module. The response of both SPR and DEI modules were recorded. Normalized values were plotted on the same graph. The result, a typical one presented in Fig. 2, shows a similar behavior of the SPR and impedance signals during the adsorption, confirming the sensitivity of both methods to the interface changes.

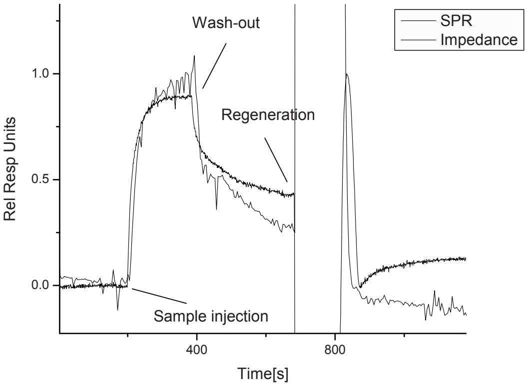


Figure 2. Dual, SPR and Impedance response at protein adsorption (BSA 1 mg/mg on gold)

The sensitivity of the system was investigated for low molecular analytes (gentamicin) using a competitive assay. In this format, the sensing surface is functionalized with the target analyte (or a derivative of it) and signal attenuation of a given amount of specific antibodies due to the presence in solution of various amounts of target analyte is used for detection and calibration purposes. It is preferred since aminoglycosides, broad-spectrum antibiotics most commonly used in veterinary drug medicine in the treatment of infections caused by aerobic Gram-negative bacteria are low molecular weight compounds. The presence of residues of these drugs in food is considered a high risk to the consumer; therefore maximum residue limits (MRLs) have been established: in the European Union (EU), the MRLs for gentamicin, is 100 ng/ml, while in US, a safe level of 10 ng/ml is recommended. The gentamicin (Sigma) was immobilized on the surface of the sensor and the sample containing the anti-gentamicin monoclonal antibody (Rikilt NL) and given concentrations of gentamicin were injected.

The calibration curve, Fig. 3, shows an appropriate sensitivity in the domain of interest (100 ng/ml – EU regulation limit) with a limit of detection of 10 ng/ml.

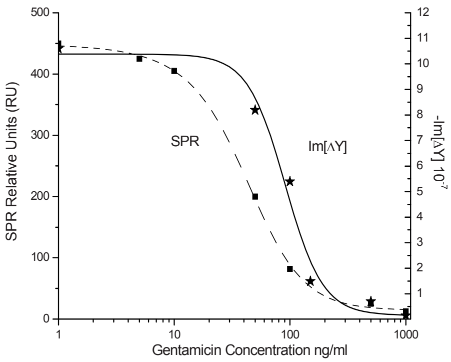


Figure 3. SPR and DIS calibration curves for gentamicin detection in a competitive assay

Cell assessment is another important issue we advanced in fostering appraisal of biological impact of various agents, including engineered nanoparticles. One should take into account that measuring cell suspensions in a flow-through system raises the problems of clogging and contamination. Carefully tailored experiments, involving intensive washing and an optimal flow-though chamber design, have been considered for cell analyses.

Using functionalized sensors, the impedance capabilities of the system to investigate *E. coli* in suspension was addressed. The anti-*E. coli* antibody was immobilized on the sensor surface and cell suspensions, with different concentrations, were injected. The changes of the impedance were monitored and the response plotted against time. Preliminary results, Fig. 4, show a sensitivity of ~10^5–10^6 cells/ml better than the ones provided using bench top SPR instrumentation.

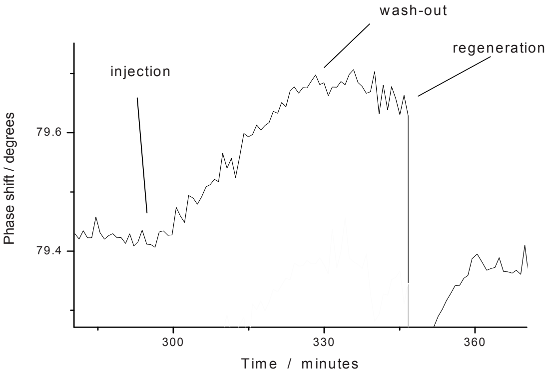


Figure 4. Monitoring phase shift during the injection of a *E. Coli* suspension (10^6 cell/ml)

3. Dielectric Models of Non Speroidal Cells

Non-invasive appraisal of cellular systems raises challenging issues. Impedance/ dielectric spectroscopy is not only a non-invasive technique (given the tiny relative perturbation of the potential across cell membrane induced by the applied electric field, [5]) but also a “mature” field as regards availability of both appropriate instrumentation and, to some extent, of theoretical findings. Obviously, data interpretation requires a model, and since we are interested in assessment of cell status (and dynamics) via shape and electrical parameters a microscopic model has to be available.

Exact analytical solutions of Poisson equation can only be obtained for spheroidal shapes. However, we stress on the possibility to derive analytical solutions of Poisson/ Laplace equation, not exact but truncated, still able to accurately describe the dielectric behavior of non-spheroids (with errors much less than the experimental ones).

This approach has been applied to describe a large variety of shapes from those exhibited by budding yeasts during cell cycle, to red blood cells and gap-junction connected cells.

To compute the complex permittivity of a suspension of cells we consider the following assumptions [6, 7]:

A uniform electrical field, $\vec{E}_0 = E_0\vec{N}$, is applied to a regular distribution of particles, i.e., the suspension is equivalent to a rectangular lattice containing one particle (of volume V_p) in the centre of each element.

Suspension permittivity, which relates the volume averages of the displacement and electrical field on a lattice unit:

$$\left\langle \vec{D} \right\rangle = \varepsilon_{sus} \left\langle \vec{E} \right\rangle, \tag{7}$$

$$\varepsilon_{sus} \cdot \left\langle \vec{E} \right\rangle = \frac{1}{V} \int\limits_{\vec{r} \in V} \varepsilon(\vec{r})\, \vec{E}(\vec{r})\, dV, \tag{8}$$

is derived using the mean field method, by taking into account the mutual dipole–dipole interaction between all suspended particles.

The (total) electrical field is assumed to exhibit the same distribution regardless the lattice unit emplacement and is given by:

$$\left\langle \vec{E} \right\rangle = \left\langle \vec{E}_e \right\rangle + \left\langle \vec{E}_1 \right\rangle, \tag{9}$$

where, $\vec{E}_e$ stands for the effective field, due to the external sources (including the dipoles of the particles outside the respective lattice unit), while $\vec{E}_1$ represents the electrical field of the induced dipole by cell polarisation in the effective field.

By subtracting the permittivity of the medium, ε_O, from both sides of Eq. (8) and by performing the average over all orientations, Ω, of the particle, noticing that the integrand vanishes outside the particle, after introducing the volume fraction, $p = {}^{V_p}\!/_{V}$, one obtains:

$$\left(\varepsilon_{sus} - \varepsilon_O\right)\left\langle \vec{E} \right\rangle = \frac{p}{V_p}\,\frac{1}{4\pi}\int\limits_{V_p}\int\limits_{\Omega}\left(\varepsilon - \varepsilon_O\right)\vec{E}\cdot\vec{N}\ dV\cdot d\Omega\,, \tag{10}$$

Considering the single layer (polarization) charge distribution $\mu\left(\vec{r}\right)$ on the surface Σ of the particle, one obtains the polarization, $\vec{P}$ due to the effective field in the lattice element, averaged over all orientations of the particle:

$$\left\langle \vec{P} \right\rangle = \frac{1}{4\pi V}\int\limits_{\Omega}\int\limits_{\Sigma}\mu\left(\vec{r}\right)\ \vec{r}\ dS\ d\Omega = \frac{1}{4\pi V}\int\limits_{V_p}\int\limits_{\Omega}\left(\varepsilon - \varepsilon_O\right)\vec{E}\cdot\vec{N}\ dVd\Omega\,, \tag{11}$$

Introducing particle's polarizability, α,

$$\left\langle \vec{P} \right\rangle = \frac{V_p}{V}\cdot\ \varepsilon_O\cdot\alpha\cdot\left\langle \vec{E}_e \right\rangle\,, \tag{12}$$

one obtains suspension permittivity derived as a function of particle polarizability:

$$\varepsilon_{sus} = \varepsilon_O + p\frac{\alpha\cdot\varepsilon_O}{1 - p\cdot\dfrac{\alpha}{3}} \tag{13}$$

Similarly with Eq. (13), the complex permittivity of a dilute suspension, is given by:

$$\varepsilon^*_{sus} = \varepsilon^*_O + p\frac{\alpha\left(\varepsilon^*_O\right)\cdot\varepsilon^*_O}{1 - p\cdot\dfrac{\alpha\left(\varepsilon^*_O\right)}{3}}\,, \tag{14}$$

where, ε^*_O stands for the complex permittivity of the medium and $\alpha\left(\varepsilon^*_O\right)$ is the polarizability specific to respective shape and electrical properties:

$$\alpha\left(\varepsilon^*_O\right) = \frac{1}{4\pi V_p\varepsilon^*_O\left\langle E_e \right\rangle}\int\limits_{\Omega}\int\limits_{\Sigma}\mu\left(\vec{r}\right)\ \vec{r}\ dS\ d\Omega\,, \tag{15}$$

The problem is now restricted to a proper way to compute the polarizability of an arbitrarily shaped particle. By assuming the usual boundary conditions [7] one obtains an integral equation for the surface charge distributions. The key idea to solve the integral equation is to transform it into an algebraic one using the spectral decomposition on the eigen vectors of the integral operator. We have restrained our calculations to particles with shapes exhibiting axial symmetry but the formalism is general. Consequently, the polarizability of a homogenous particle is given by an expression of the following type, [6]:

$$\alpha\left(\varepsilon_o^*\right)=\sum_{n=1}^{L}\frac{\alpha_n}{\frac{1}{2\lambda}-\chi_i}, \tag{16}$$

With α_n and χ_i purely geometrical (shape) factors and λ merely dielectric:

$$\lambda=\frac{\varepsilon^*_{\mathrm{i}}-\varepsilon^*_{\mathrm{o}}}{\varepsilon^*_{\mathrm{i}}+\varepsilon^*_{\mathrm{o}}}, \tag{17}$$

When considering a double shell particle, as the case for budding yeasts where besides cell membrane the cell wall has to be considered as well, the equivalent polarizability becomes:

$$\alpha\left(\varepsilon^*_{\mathrm{O}}\right)=\frac{1}{3}\sum_{\mathrm{i=1}}^{3}\sum_{\mathrm{j=1}}^{\mathrm{n}}\frac{\mathrm{A_{ij}}}{\mathrm{B^*_{ij}}-\mathrm{C_{ij}}} \quad , \tag{18}$$

where summations are made in relation with the three orthogonal directions and the matrix elements of the integral operator. The more intricate the shape, the larger the rank of matrix of the integral operator we have to cope with. Terms $\mathrm{A_{ij}}$, $\mathrm{C_{ij}}$ are purely (shape) numbers and $\mathrm{B_{ij}}$ terms depend both on shape through $\mathrm{C_{ij}}$ and on shell sizes and dielectric properties of the constituents of shelled particles, by means of $\mathrm{D_{ij}}$.

$$\mathrm{B^*_{ij}}=\frac{\mathrm{D^*_{ij}}}{2\,(\mathrm{D^*_{ij}}-2\cdot\varepsilon^*_{\mathrm{o}})}, \tag{19}$$

with

$$\mathrm{D^*_{ij}}=\varepsilon^*_{\mathrm{o}}+\varepsilon^*_{\mathrm{w}}\left(1+\left(-1/2+\mathrm{C_{ij}}\left(1-\delta_2\right)+\frac{\delta_2\left(\mathrm{NN}+\varepsilon^*_{\mathrm{w}}\right)}{2\left(\mathrm{NN}-\varepsilon^*_{\mathrm{w}}\right)}\right)^{-1}\right); \tag{20}$$

$$\mathrm{NN}=\varepsilon^*_{\mathrm{m}}\left(1+\frac{1}{-1/2+\mathrm{C_{ij}}\left(1-\delta_1\right)+\frac{\delta_1\,(\varepsilon^*_{\mathrm{i}}+\varepsilon^*_{\mathrm{m}})}{2(\varepsilon^*_{\mathrm{i}}-\varepsilon^*_{\mathrm{m}})}}\right)$$

$\varepsilon_k^* = \varepsilon_k - j\frac{\sigma_k}{\omega \cdot \varepsilon_v}$, where k stands for o (outer medium), i (inner medium), m (membrane), w (cell wall, i.e., external shell); shell sizes are given by the following relations on the volumes of different cell constituents:

$$\delta_1 = \frac{V_{\text{inner}}}{V_{\text{inner}} + V_{\text{membrane}}};\ \delta_2 = \frac{V_{\text{inner}} + V_{\text{membrane}}}{V_{\text{inner}} + V_{\text{membrane}} + V_{\text{wall}}}, \tag{21}$$

3.1. RESULTS ON SELECTED CELLULAR SYSTEMS

3.1.1. *Red blood cells, RBC*

The entering and localization of different nanoparticles consisting of differing materials and of different charges were studied in human red blood cells [8]. As these cells do not have any phagocytic receptors on their surface, and no actin-myosin system, they can be considered as a model for nonphagocytic cells for studying how nanoparticles penetrate cell membranes. Though the entry mechanism remains rather obscure, the process is already established and recent data [9] suggest that the attachment of the nanoparticles to the red blood cells could extend their circulation time and their ability to evade the immune system. Direct visualization of the nanoparticles within the RBC is the general approach but is limited to particles larger than 100 nm. The ability to derive shape changes and modifications of the electric parameters of the intact membranes is of considerable interest when assessing "gentle" bioeffects of nanoparticles.

Aiming to describe the dielectric β dispersion of red blood cells we have considered the shapes given by the following expression:

$$\mathrm{R}(\theta) = \sqrt{-\mathrm{A} \cdot \mathrm{Cos}(2\ \theta) + \sqrt{\mathrm{C}^2 - (\mathrm{A}\ \mathrm{Sin}(2\ \theta))^2}}, \tag{22}$$

with

$$\mathrm{A} = \frac{(\mathrm{d}^2 - \mathrm{t}^2)}{8}; \mathrm{C} = \frac{(\mathrm{d}^2 + \mathrm{t}^2)}{8} \tag{23}$$

where, d is the diameter and t the least thickness of the red blood cell. Figure 5 presents the three and bi dimensional representation of a RBC.

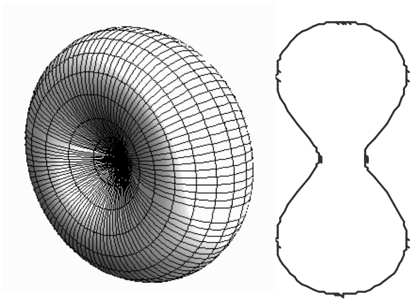


Figure 5. 3 and 2 D representation of a red blood cell according to Eqs. (22) and (23), with d = 7μm and t = 0.8 μm

Figure 6 presents the permittivity spectrum for a RBC with d = 7 μm and t = 0.8 μm and the corresponding oblate spheroid when the electric field is perpendicular to the cell rotation axis.

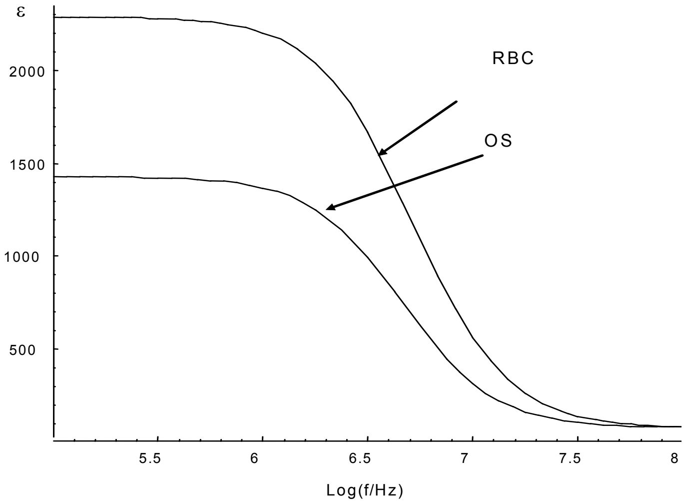


Figure 6. Permittivity spectrum for the considered RBC and the corresponding oblate spheroid (OS) when the electric field is perpendicular to the cell rotation axis

This approach provides the ability to extract the information regarding the shape of the cell and to separate the electric information from the one concerning cell morphology as imposed when assessing the possible influence of nanoparticles on the blood cells.

3.1.2. *Interconnected cells*

Tissue integrity and functionality requires the cooperative behavior of constituent cells as functional syncytia and/or dynamic barriers. This is achieved by complex, dynamic, connecting architectures (such as the gap junctions). These areas of cell to cell communication are possible entry routes for nanoparticles.

Aiming to assess the dielectric behavior of gap junction connected cells, we have considered ensembles of interconnected cells generated from the shape (corresponding to two interconnected cells) described by:

$$R(\theta)=\frac{a_0+\cos^2(\theta)}{1-a_1\cdot\cos^2(\theta)}, \tag{24}$$

A pair of gap junction connected cells, as described by Eq. (24) is shown in Fig. 7.

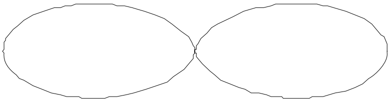


Figure 7. An example of two gap junction connected cells, given by Eq. (24) assuming: $a_0 = 0.001$ and $a_1 = 0.8$

Figure 8 presents the spectrum of the permittivity (relative units) of two gap connected cells and the related individual cells; cells are oriented parallel to the electric field.

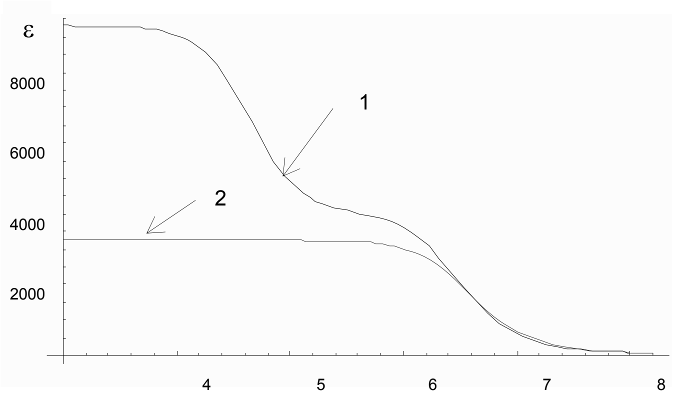


Figure 8. The spectrum of the permittivity (relative units) of two gap connected cells and the related individual cells; cells are oriented parallel to the electric field, (1) represents the spectrum of gap junction connected cells and (2) represents the spectrum of individual cells

This behavior has been already identified in real tissue samples [10] subjected to environmental stress (ischemic insult), revealing the process of closure of gap junction communication as a relevant marker of sublethal bioeffects.

4. Appraisal of Cell-Substrate Interaction

Development of topography controlled structures with biological relevant scale (nano-micro structures), similar with the ones that we can find *in vivo* and the characterization of the interaction of human cells and bacteria with these surfaces, is a hot topic.

Orchestration of these topographies in conjunction with modulation of the hydrophilic/hydrophobic properties of substrata is a promising avenue to obtain high biocompatibility and selective growth (the improvement of the growth conditions for target cells and rejection/non-proliferation of the unwanted cells or bacteria) [11].

Development of "smart" surfaces can find a large scale of applications from tissue engineering, prosthetic applications to optimization of cells cultures used for development of biosensors [12] and advanced analytical platforms.

Cultivation of cells in conditions close to the tissue or organ structure permits a better translation of the *in vitro* results to the potential, in vivo, ones. The elimination of contamination risk factor raises the accuracy of determinations and the stability of the bioanalyses platforms.

Our study aims at development of a modified ECIS [13] method to appraise cell–substrate interaction based on impedance spectroscopy.

4.1. ELECTRODE AND SUBSTRATE PREPARATION

Experiments involved (interdigitated) gold electrodes on a glass substrate. To facilitate the complementary optical (TIRF) analyses, the substrate was made by optical glass and the thickness of the gold substrate was 50 nm.

We used SiOMMA (polisiloxan methyl metacrilate) polymer from ICMPP, Romania. The polymer was spin coated (SCS model P6708) to the gold–glass substrate 1500 rps for 120 s.

4.2. BIOLOGICAL MATERIAL

Madin–Darby Canine Kidney (MDCK) cells are frequently utilized as a general model for epithelial cells [14]. In the body, epithelial cells are tightly packed into contiguous sheets called epithelia. The cells that comprise an epithelial sheet are linked together by unique specialized junctions called tight junctions. Epithelial sheets function in a number of ways, but are especially important as barriers to the diffusion of various molecules. The epithelial cells that line the kidneys also are involved in the temporary storage and secretion of wastes. In culture, epithelial cells tend to experience strong contact inhibition of migration and form monolayer similar to the epithelial sheets that occur ***in vivo***.

For these experiments, MDCK cells were used as a model of collecting duct cells grown in α-MEM medium (Life Technologies, Rockville, Maryland, USA) modified according to Gibson d'Ambrosio, supplemented with 10% fetal calf serum and grown until confluence (~ 6 days). The MDCK cells were cultivated 3 days at 37°C, on the polymer substrate.

4.3. MEASUREMENTS: IMPEDANCE SPECTROSCOPY

The gain-phase/impedance analyzer Solartron 1260 has been used to perform time based impedance spectroscopy assays for assessment of cell–substrate interaction within the frequency range: 1 Hz–10 MHz, at a constant amplitude of the applied signal of 50 mV. The measuring chamber for impedance assays (tailored made) allowed flow-though measurements (Fig. 9).

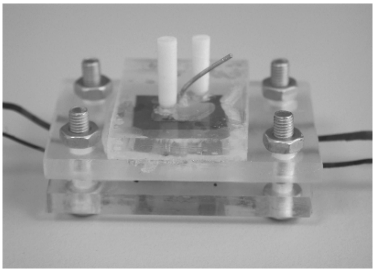


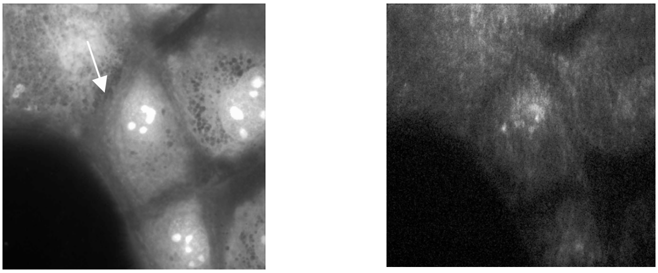
Figure 9. Flow-through measuring chamber

We measured the following (modified) electrodes: 1 – gold on glass; 2 – a SiOMMA layer on top of gold layer on glass and 3 – same set-up with MDCK cells cultured on top of the SiOMMA layer.

The first two types of electrodes were used to develop the equivalent circuit. Therefore, five different saline solutions with given conductivities (S1 = 0.76 S/m, S2 = 0.98 S/m, S3 = 1.21 S/m, S4 = 1.42 S/m and S5 = 1.66 S/m) and the culture medium with a conductivity of 1.2 S/m have been addressed. In the case of cell-coated electrodes, the culture medium has been solely used.

A home made procedure implemented in Mathematica able to fit simultaneously the real and imaginary impedance data has been used for data analysis.

Figure 10 presents MDCK cells adhered to SiOMMA substrate. To obtain the information on the presence of the MDCK cells on the SiOMMA substrate, we derived a model that can support data provided by impedance measurements of five saline solutions and culture medium using bare gold electrodes and the same electrodes with SiOMMA polymer substrate spincoated on top.



a b

Figure 10. a – Epi-fluorescence 488 nm; b – Laser TIRF – 488 nm

In a first step, the circuit elements that model the electrodes, the solution, the contacts and the cables have been derived (Fig. 11).

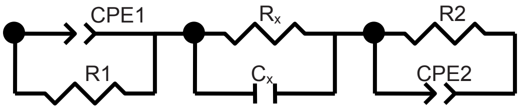


Figure 11. The equivalent circuit for the gold electrodes

The gold electrodes are not symmetrical therefore, two parallel circuits R-Z_{CPE}, one for each electrode, have been considered.

Figure 12 presents the measured and fitted spectra on gold electrodes.

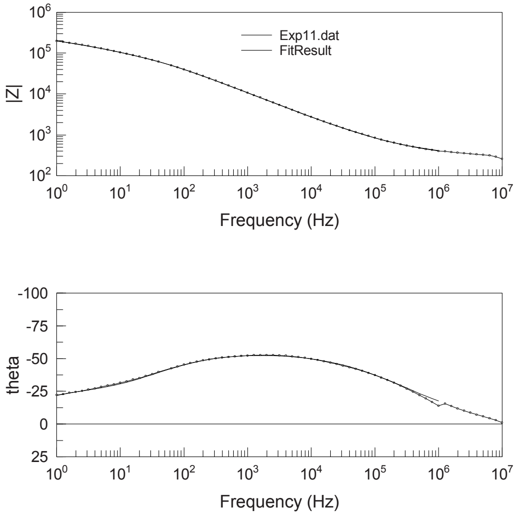


Figure 12. Fitted (using the model in Fig. 11) and the measured data on gold electrodes in culture medium

CPE represents the Constant Phase Element due to electrode polarization at one electrode. The circuit elements related to the impedance of saline solutions are given by R_x and C_x.

Figure 13 presents the equivalent circuit for polymer coated electrodes. Rx and Cx are related to the saline solutions. The values for the C1 and C2 are similar. Both are related to the capacitance of the polymer layer, spin coated over the gold in a uniform layer. Since the polymer layer exhibits pores, of resistance R1 and R2 for the two electrodes respectively, constant phase elements have to be considered, as well.

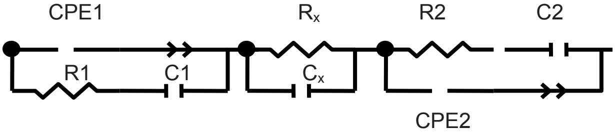


Figure 13. The equivalent circuit for the SiOMMA polymer layer on top of the gold electrodes

Figure 14 presents the measured and fitted spectra on gold electrodes on electrodes coated with SiOMMA polymer.

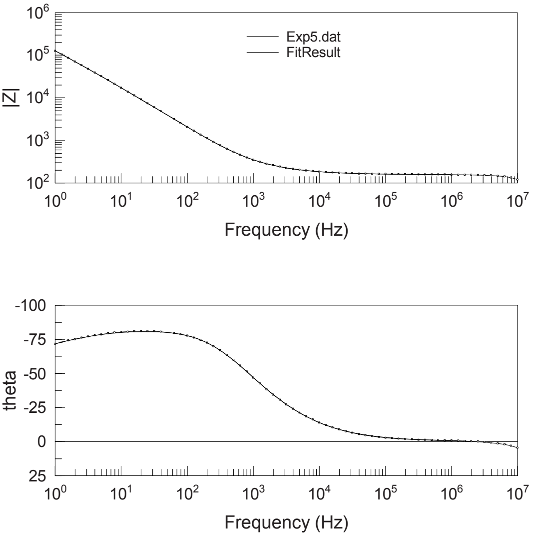


Figure 14. Fitted (using the model in Fig. 13) and the measured data on electrodes coated with SiOMMA polymer layer in culture medium

As the optical, fluorescence experiments revealed, the MDCK cells have grown in mono-stratum over the SiOMMA layer.

Coping with the equivalent circuit derived for the electrodes with polymer with/without adhered cells the impedance spectra of MDCK cells layer has been derived as shown in Figs. 15 and 16.

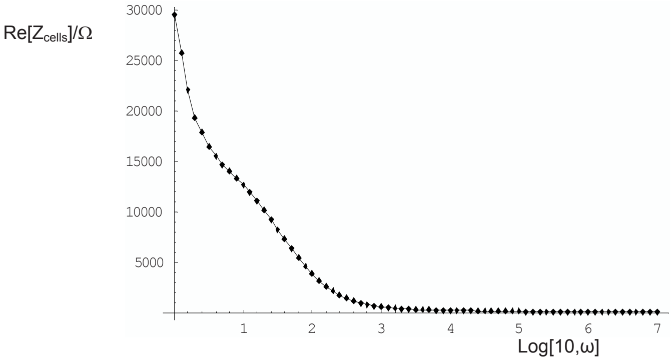


Figure 15. Real part spectra of the MDCK monolayer cells impedance

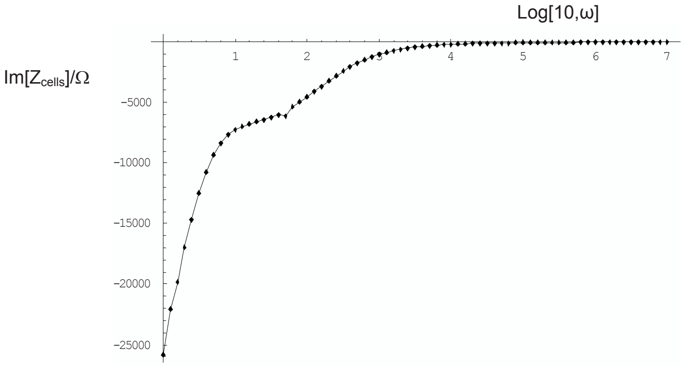


Figure 16. Imaginary part spectra of the impedance exhibited by a monolayer of MDCK cells

Cole-Cole spectrum (Fig. 17) shows two principal dispersions, the one at the low frequencies is incomplete.

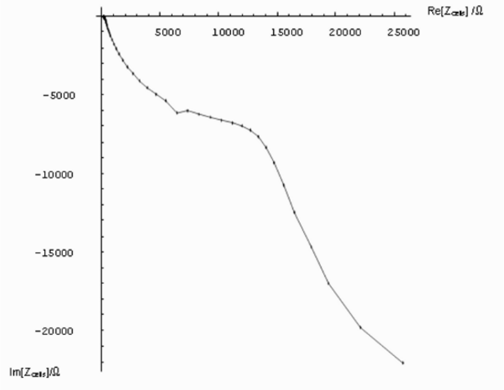


Figure 17. Cole-Cole representation of the impedance exhibited by a monolayer of MDCK cells

Formally relating the impedance of cellular layer to an equivalent R||C circuit, Fig. 18 illustrates the non-monotonous effect of addition of a pore forming compound (e.g., Triton X100) on the evolution of ΔRr, i.e., R(t)/R(0) − 1 at several frequencies. We noticed a similar behavior exhibited by artificial membranes.

The impedance measurements revealed that cell adhesion is able to be described within a rather low frequencies domain, from 100 Hz to 10 kHz. Beyond 10 kHz, the effect of cells becomes negligible. Further studies are in progress to relate the impedance spectra to microscopic models on interconnected cells.

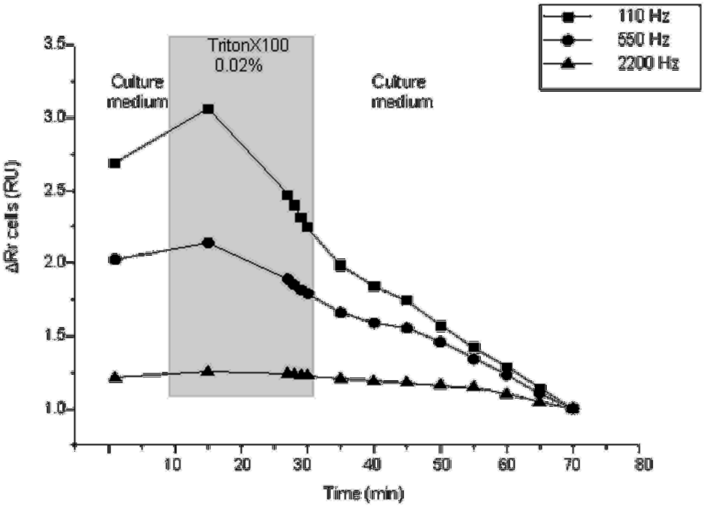


Figure 18. The non-monotonous effect of addition of a pore forming compound (Triton X100) revealed by time evolution of ΔRr cells at different frequencies

5. Discussions

This study advances the state of the art regarding assessment of bioaffinity and cellular platforms using SPR and DIS by providing a dual measurement set-up with appropriate sensorics and flow through measurement channels. While both systems have separately proven valuable for biosensing, the combination enables accurate assessment of bio-interfaces providing means to reduce if not eliminate the nonspecific influences, provide mutual validation and expands the analyte detection range, from low molecular weight compounds to cells.

When addressing the dielectric behavior of cells exhibiting given non-spheroidal shapes, in comparison with computational methods which provide numerical solutions for Poison/Laplace equation, that can be applied to intricate shapes but requires significant computing facilities and do not allow separation of shape factors from electrical parameters, our approach (actually restricted to shapes with rotational symmetry) can provide an analytic expression of the complex permittivity of ensembles of particles exhibiting any orientation, volume concentration, number of shells or last but not least electric properties. This study allows the appraisal of the errors related to the use of spheoridal approximation, which are especially large when oriented cells are considered.

It is worth emphasizing the applicability of this approach to cell suspensions (from assessment of cell cycle to RBC analyses) and interconnected cells – tissue like structures.

The study on cell adhered on a substrate revealed that cells prefer different spots of the polymer substrate depending on the surface properties (hydrophilic properties, roughness).

By suitable use of the models of electrical circuits we were able to derive the impedance spectra of cells adhered on top of polymeric substrata. This procedure will be further developed by considering not phenomenological approaches but microscopic models, such as to appraise both the interaction between selected cells and "smart" substrata as well as the environmental and biological risks of nanobiotechnology using cellular platforms.

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SYNTHESIS AND UTILIZATION OF HYPERBRANCHED POLY(AMINO ACIDS) AS CARRIERS OF BIOLOGICALLY ACTIVE SUBSTANCES: PROBLEMS AND SOLUTIONS

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Abstract. Current tendencies of development of synthetic approaches for the creation of biocompatible and biodegradable polymer carriers of biologically active substances (BAS) are examined. Specifically, the utilization of carriers based on of lysine dendrimers and hyperbranched poly(lysines) as analogues of high molecular weight dendrimers for targeted delivery of BAS is discussed. Possible means of overcoming the problems associated with their preparation and application are also elucidated.

Keywords: biocompatible and biodegradable polymer, carriers of biologically active substances, dendrimers, lysine dendrimers, hyperbranched poly(lysines)

1. Introduction

The design of polymer carriers for binding and delivery of biologically active substances (BASs) have long been one of the high priority in the field of BAS chemistry [1]. The polymer carrier should provide a rapid and efficient delivery of BAS to the site of its utilization. Moreover, it should be nontoxic and nonimmunogenic, and its constituents should be biocompatible and biodegradable. Among the polymer carriers which have been obtained and studied in the laboratory of Biologically Active Polymers (Institute of Macromolecular Compounds of Russian Academy of Sciences), those that most closely correspond to this set of conditions are starlike polymer–protein conjugates (1) [2], lysine dendrimers and their derivatives (2) and hyperbranched poly(amino acids) (3) (Fig. 1). All these carriers have one more feature in common, their spatial structures are close to spherical [3, 4].

In this review the problems associated with preparation, optimization of structure and properties of these three types of polymers based on lysine dendrimers and their derivatives such as hyperbranched poly(lysines) and also their utilization as BAS carriers will be discussed.

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Dendrimers (“starburst” dendrimers, cascade polymers), synthetic macromolecules containing a dense core [1], can be considered as synthetic protein models. The introduction of functional groups into these compounds makes it possible to bind different BAS including DNA [2–7]. It was poly(amidoamine) (PAMAM) dendrimers which have been initially and most extensively investigated as DNA carriers. It was shown that PAMAM dendrimers cause the haemolysis of erythrocytes [4]. One of the first examples of successful use of lysine dendrimers for the BASs transport was their utilization as carriers of peptide antigenic determinants for the antibody generation using so-called multiple antigenic peptide system (MAP) [8].

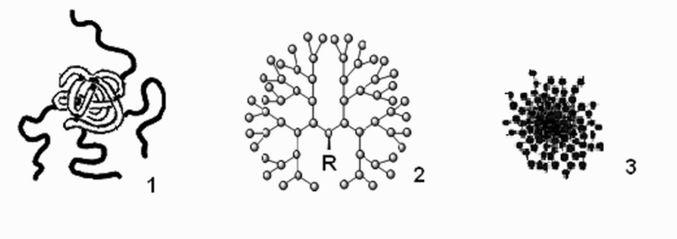


Figure 1. Biocompatible and biodegradable polymer carriers of BAS studied in Laboratory of Biologically Active Polymers (Institute of Macromolecular Compounds, Russian Academy of Sciences)

We synthesized lysine dendrimers using a divergent strategy (macromolecules were formed beginning from the core) [9] by the method of solid phase peptide synthesis (SPPS) and analyzed more thoroughly the problems of synthesis of first–fifth generation lysine dendrimers (Fig. 2). Use of divergent strategy synthesis of lysine dendrimers allowed us to evaluate the correlation of fullness of amino acyldendrimer polymer acylation with the number of dendrimer generation and chemical nature of amino acids entering into dendrimer. Homodendrimer contains only lysine at the “branching” points.

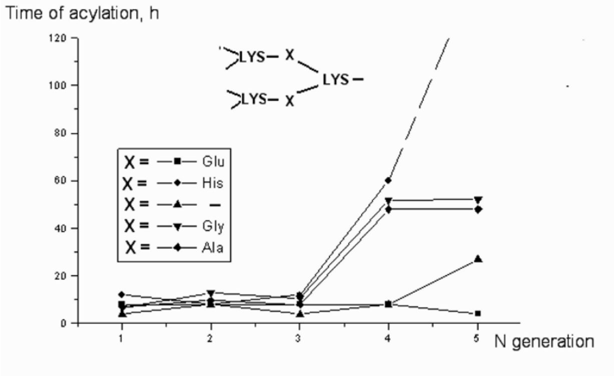


Figure 2. Influence of number of generation, chemical structure and character of dendrimer (homotype or heterotype) on the acylation stage of N-terminal aminogroups of lysine dendrimers (solid phase dendrimer synthesis)

Heterodendrimers during the creation of each generation contain additional amino acids between lysine residues at the “branching points”. These amino acids may contain different side radicals, particularly, alanine, glutamic acid, histidine, and the glycyl–glycine dipeptide are utilized.

During the synthesis of a homodendrimer at the fourth generation stage, it was necessary to increase the acylation time to 20 h against 10 h for the synthesis of the first–third generations. During the synthesis of heterodendrimers containing alanine and diglycine between the “branching” points (residues of diacylated lysine), the acylation time at the fourth and fifth generation stages increased to 50 h (Fig. 2). More serious problems arose at the fourth generation stage during the synthesis of a histidine-containing dendrimer. In order to attach lysine at the fourth generation stage, we had to increase the acylation time to 60 h, and histidine was attached at this fourth generation stage by long-term (more than 100 h) acylation (Fig. 2).

However, the attachment of lysine for the synthesis of the fifth generation practically did not occur even after the addition of 4-(N,N-dimethylamino) pyridine as a catalyst. This data has been confirmed by mass-spectrometry and amino acid analyses (Table 1). Results shown in Table 1 demonstrate that for the most part heterodendrimers of fifth generation are “inperfect” dendrimers.

TABLE 1. Molecular weight (theoretical and experimental) for lysine homo- and heterodendrimers [9]

Dendrimer[a]	Structure	M theoret., (g mol^{-1})	M exp., (g mol^{-1})
D1	(Lys)$_2$ Lys-Ala-NH$_2$	473	–
D3	(Lys)$_8$(Lys)$_4$(Lys)$_2$ Lys-Ala-NH$_2$	2,011	2,011
D4	(Lys)$_{16}$(Lys)$_8$(Lys)$_4$(Lys)$_2$Lys-Ala-NH$_2$	4,061	4,062
D5	(Lys)$_{32}$(Lys)$_{16}$(Lys)$_8$(Lys)$_4$(Lys)$_2$-Lys-Ala-NH$_2$	8,162	8,163
D5-H	(Lys-His)$_{32}$(Lys-His)$_{16}$(Lys-His)$_8$ -(Lys-His)$_4$(Lys-His)$_2$-Lys-Ala-Ala-Lys(ClAc)[b]Ala-NH$_2$	17,004	11,540[c]
D5-E	(Lys-Glu)$_{32}$(Lys-Glu)$_{16}$(Lys-Glu)$_8$ (Lys-Glu)$_4$(Lys-Glu)$_2$Lys-Ala-Lys(ClAc)[b] -Ala-Ala-NH$_2$	16,506	15,226
D5-A	(Lys-Ala)$_{32}$(Lys-Ala)$_{16}$(Lys-Ala)$_8$ (Lys-Ala)$_4$(Lys-Ala)$_2$Lys-Ala-Lys(ClAc)[b] -Ala-Ala-NH$_2$	12,962	12,915
D5-GG	(Lys-Gly-Gly)$_{32}$(Lys-Gly-Gly)$_{16}$ (Lys-Gly-Gly)$_8$(Lys-Gly-Gly)$_4$(Lys-Gly-Gly)$_2$Lys-Ala-Lys(ClAc) [b]Ala-Ala-NH$_2$	15,626	15,166

(MALDI TOF method; H – histidine; E – glutamic acid; A – alanine; GG – diglycine

[a] cipher – number of generation

[b] N$^{\varepsilon}$-chloroacetyl

[c] mole ratio Ala/His/Lys (amino acid analysis: 3/62/64 (theor.), 3/52/32 (exper.)

2. Optimisation of Dendrimer Structure

Optimization of dendrimer structure has been achieved by modification of amino groups of N-terminal lysine fragments of dendrimers with carbon-chain polymers or polylysine and C-terminal group by lysine dipeptide containing lipophilic palmitoyl lysine residues (**R**=(N$^{\varepsilon}$-palmitoyl)-Lys-(N$^{\varepsilon}$-polmitoyl)-Lys, **D2**, Table 2).

TABLE 2. The structure of a trispherical lysine-based dendrimer of third generation (**D3)**, its lipophilic derivative (**D3Lyp)**, and starburst polymeric **(pVIm)$_8$-D3** and **(pLys)$_n$-D3** derivatives [10]

Structure of lysine dendrimer of third-generation and its derivatives	Abbreviation
(NH$_2$)$_{16}$(Lys)$_8$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_4$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_2$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)-Ala-NH$_2$	**D3**
(NH$_2$)$_{16}$(Lys)$_8$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_4$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_2$- (N$^{\alpha}$,N$^{\varepsilon}$-Lys)-Ala-[Lys(Plm)]$_2$-Ala-NH$_2$	**D3Lyp**
(pVIm)$_8$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_8$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_4$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_2$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)-Ala-NH$_2$	**(pVIm^{a})$_8$D3**
(pLys)$_n$-(N$^{\alpha}$,N$^{\varepsilon}$ -Lys)$_8$-(N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_4$-(N$^{\alpha}$,N$^{\varepsilon}$ (N$^{\alpha}$,N$^{\varepsilon}$-Lys)$_2$- (N$^{\alpha}$,N$^{\varepsilon}$-Lys)-Ala-NH$_2$	**(pLys^{b})$_n$-D3**

[a] Poly(N-vinylimidazole)
[b] Poly(lysine)

The starlike poly(N-vinylimidazole) conjugate of lysine dendrimer of third-generation in which the modifying poly(*N*-vinylimidazole) was attached to N$^{\alpha}$- or N$^{\varepsilon}$-amino groups of lysine of the third sphere of dendrimer via one of its termini was synthesized in two stages [6] (Fig. 3). At the first stage, the amino groups of dendrimer (Fig. 3, (1)) were modified by 2,2'-azobisisobutyric acid dimethylimidate (2).

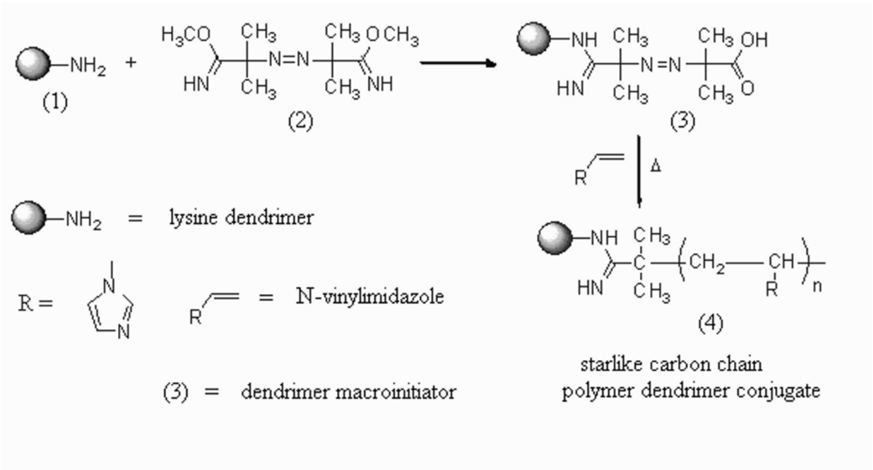


Figure 3. Scheme of synthesis of starlike poly(N-vinylimidazole) lysine dendrimer conjugate

The titration by trinitrobenzenesulfonic acid of free amino groups of the dendrimer that did not enter into the modification reaction indicated that at this stage eight residues of 2,2'-azobisisobutyric acid were attached. The resulting dendrimeric “macroinitiator” (3) containing 2,2'-azobisisobutyric acid residues linked through amidine bonds to the amino groups of the dendrimer was used at the second stage for the polymerization of *N*- vinylimidazole to form a starlike poly(*N*-vinylimidazole) conjugate of lysine dendrimer of third generation **[(pVI)$_8$-D1]** (Fig. 3, (4) and Table 2). The molecular mass of the starlike poly(*N*-vinyl-imidazole) lysine dendrimer conjugate was 80 kDa (determined by gel chromatography on a protein-calibrated Sephadex G-150 column). Considering the number of 2,2'-azobisisobutyric acid residues linked with dendrimer at the first stage (eight residues) and, accordingly, the number of grafted polymer chains, this corresponds to the mean degree of polymerization of each poly(N-vinylimidazole) chain of conjugate equal to 125.

A starlike poly(lysine) conjugate of third generation dendrimer (Table 2; **(pLys)$_n$-D3**), was synthesized analogous to the preparation of poly(amino acid) derivatives of proteins [10]. This was done by polymerization of *N*-carboxyanhydride of N^{ε}-benzyloxycarbonyl-L-lysine at the N-terminal amino groups of lysine residues as initiating groups of the previously synthesized third generation dendrimer **D3**. Removal of protecting Z-groups from the N^{ε}-amino groups of poly(L-lysine) chains grafted at one point to the dendrimer by the action of gaseous hydrogen bromide in trifluoroacetic acid resulted in generation of polylysine conjugate **(pLys)$_n$-D3**. In this conjugate, poly(lysine) chains are linked to lysine α-and/or ε-amino groups of the third sphere of lysine dendrimer (Table 2, **D3) via** their *C*-termini. Amino acid analysis of the starlike poly(lysine) derivative dendrimer showed that 157 lysine residues were additionally introduced into dendrimer. This corresponds to the molecular mass of the conjugate being 22 kDa and to the average degree of polymerization (**n**) of grafted polylysine chains (pLys)$_n$ being 20, assuming that, as it is in the case of grafting the poly(*N*-vinylimidazole) fragments, only 50% of the lysine amino groups of dendrimer could act as initiating groups.

Although this strategy of dendrimer synthesis affords products that are, as expected, a structurally uniform and perfectly monodisperse, it is not very attractive for large-scale preparation of high molecular weight dendrimers as well as for production of dendrimers of elevated generation number. Our data (Table 1) demonstrate that as number of dendrimer generation is increased the chemical structure of amino acids between the points of “branching” becomes more complex. This, in turn, leads to emergence of problems, which may make synthesis of structurally uniform and perfectly monodisperse dendrimers unachievable. Therefore, it is necessary to investigate alternative synthetic routes that will facilitate the preparation the high molecular weight dendrimers.

3. Synthesis of High Molecular Weight Dendrimers

The first approach for the synthesis of high molecular weight lysine dendrimer includes combination of stages of polymerization of N-carboxyanhydride of N^{ε}-carbobezoxy-L-lysine (1), modification of amino groups of N-terminal lysine residues of poly(lysine) with N^{α}, N^{ε}-di(9-fluorenylmethoxycarbonyl (Fmoc)-lysine (2), selective removal of two Fmoc-groups from N-terminal lysine residues of poly(L-lysine) chains (3) and polymerization on amino groups of N-terminal lysine residues of poly(lysines) derived from blocked polymer of new portion of N-carboxy-anhydride of N^{ε}-carbobezoxy-L-lysine (4). Repeated carrying out of these stages allows production of high molecular weight lysine dendrimers of desired generation number [11]. Resulting dendrimers contained poly(lysine) chains of smaller or greater polydispersity between points of “branching”.

3.1. SYNTHESIS OF DENDRIGRAFTS

The second approach for preparation of high molecular weight lysine dendrimers is preparation of “dendrigrafts” based on lysine [12]. Polymerization of N-carboxyanhydride N^{ε}-trifluoroacetyl-L-lysine in water results in formation of olygo(N^{ε}-trifluoroacetyl)-lysine (1). After removal of N^{ε}- trifluoroacetyl groups from olygo(N^{ε}- trifluoroacetyl)-lysine with piperidine (2) its amino groups were used for polymerization of new portion of N-carboxy-anhydride N^{ε}-trifluoroacetyl-L-lysine.

Repeated application of these stages resulted in formation of high molecular weight lysine dendrimers. The quantity of repeated stage determines number of dendrimer generation and their molecular weight. Still, both of these variants of synthesis of hyper branched poly(lysines) include repeated step-by-step synthesis. This leads to defects in polymer structure when its generation number is increased.

3.2. SYNTHESIS OF HYPER BRANCHED POLY(LYSINES)

Since 2004 my laboratory is investigating new, alternative routes for preparation of high molecular weight lysine dendrimers [13, 14]. Two variants of one-step synthesis of hyperbranched poly(lysines) were proposed using either hyperbranched homopoly (lysines), which contain only lysine residues both at “branching” points and outside of them or utilizing hyperbranched heteropoly(lysines), which outside of the “branching” points possess polymeric chains containing other amino acids in addition to lysine. Scheme of preparation of hyperbranched poly(lysines) is rather simple [14] (Fig. 4). Hyperbranched polyamino(acids) were synthesized under the conditions of removal of protecting benzyloxycarbonyl (Z)-group from *N*-carboxyanhydride of N^{ε}-benzyloxy-carbonyl(lysine) by hydrogenolysis over an activated palladium catalyst. After the removal of the Z-group from the N^{ε}-amino group of lysine *N*-carboxyanhydride (1), the resulting free ε-amino groups act as initiators for polymerization of new *N*-carboxyanhydrides of N^{ε}-Z-lysine, producing the poly(lysine) chains linked with the N^{ε}-amino groups of lysine. This is followed by removal of poly(lysine) chains Z-groups. Polymerization of new portion of *N*-carboxyanhydrides of N^{ε}-Z-lysine on new amino groups leads to elongation of polymeric chains, producing hyperbranched homopo (lylysine). Outside of the branching points (lysine fragments built into the polymeric chain with their N^{α}- and N^{ε}-amino groups and the α-carboxyl group), the resulting polymer contains lysine residues that incorporate into the polymeric chain with N^{α}- as with N^{ε}-amino- groups and α-carboxyl groups., If *N*-carboxyanhydrides of other amino acids, e.g., the *N*-carboxyanhydride of γ-*tert*-butyl-L-glutamic acid, which γ-*tert*butyl-group is stable under the conditions of catalytic hydrogenation, or the *N*-carboxyanhydride of alanine are added to reaction medium prior to the onset of catalytic hydrogenation along with the *N*-carboxyanhydride of N^{ε}-Z-lysine, then a hyper branched heteropoly (lysine) is formed. Outside of the branching points of lysine residues such polymer contains polymeric fragments composed either of lysine and glutamic acid or of lysine and alanine, respectively. The structure of hyperbranched heteropoly(lysine) may be regulated by appropriate choice of N-carboxyanhydride of N$^{\varepsilon}$-Z-lysine and N-carboxyanhydride of other amino acids. That makes possible generation hyperbranched poly(lysines) of various structure and therefore of different properties (see below).

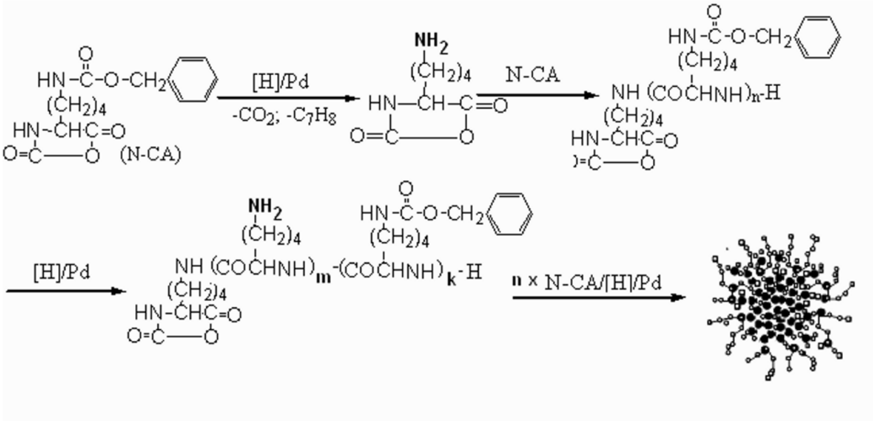


Figure 4. Scheme of hyperbranched homopoly(lysine) synthesis [14]. Designations: N-CA=N-carboxyanhydride N$^{\varepsilon}$-carbobenzoxy-lysine; N-carboxyanhydride N$^{\varepsilon}$-carbobenzoxy-lysine; dark circle – lysine at the "branching" point incorporated into the polymeric chain with its α- and ε-amino group and α-carboxyl group; the gray square denotes alanine or glutamic acid.

4. Molecular Characteristics of Hyperbranched Poly(lysines)

Light scattering characterization demonstrates (Table 3) that macromolecules of the linear poly(lysine) with $M_w = 10 \times 10^5$ (molecular mass was determined by gel-chromatography with the use of a column calibrated relative to proteins yields $M_w = 95 \times 10^4$) and $R_H \approx 400$ nm occur in a strongly asymmetric conformation similar to rodlike. For the hyperbranched homopoly(lysine) with $M_w = 195 \times 10^4$ (molecular mass determeined by gel chromatography with the use of the column calibrated relative to proteins is 95×10^4), parameters were as follows: R_H=(100 ± 20) nm and Rg=(110 ± 30) nm. As a result, Rg /R_H appeared to be almost identical. Taking into account this data

TABLE 3. Characteristics of linear and hyperbranched homopolylysines determined by light scattering [14]

Polymer	$M_w \times 10^{-4a}$	R_H, nm	R_g, nm
p(K) – 100[b]	9.5/10.0	400	–
hbp(K)[c]	9.5/19.5	100 ± 20	110 ± 30

[a] Values of Mw obtained by gel filtration and light scattering are in the nominator and denominator, respectively

[b] Linear poly(lysine) prepared by the polymerization of N-CA using isopropylamine as an initiator

[c] Hyper**b**ranched poly(**K**) (lysine)

and relatively low values of R_H, one may infer that the density of macromolecules of hyperbranched homopoly(lysine) in water is rather high and their shape is close to spherical.

5. Secondary Structure of Linear and Hyperbranched Homo- and Heteropoly(Lysines)

Hyperbranched homo- and heteropoly(lysines) were studied by the method of circular dichroism (Table 4). It was shown that the hyperbranched homopoly(lysine), compared to the linear poly(lysine) samples that have two different molecular masses, predominantly occurs as random-coil and partially is present in β-structural conformation. This demonstrates that only short oligo(lysine) fragments exist between branching points.

Examination of the circular dichroism data for the hyperbranched heteropoly(lysine) (Table 5) polymers comprised of L-alanine and lysine and L-glutamic acid and lysine units between the "point of branching" shows that secondary structure of polymers strongly depends both on chemical structure and the ratio of lysine and other amino acids to new amino acids introduced.

TABLE 4. Elements of the secondary structure of linear and hyperbranched homopoly(lysines) [14]

Polymer	$M_w \times 10^{-4}$	Solvent	Elements of secondary structure, %	
			α-helix	β-struicture, (antipallel)
p(K)	10[a]	0.1 н. NaOH	40.1 ± 4.84	6.5 ± 4.84
		80% TFE	66.0 ± 4.84	3.3
p(K)	14[a]	0.1 н. NaOH	33.9 ± 4.84	7.7 ± 4.84
		80% TFE	66.1 ± 4.84	3.3
hbp(K)	19.5[b]	0.1 н. NaOH	9.9 ± 6.94	28.0 ± 6.39
		80% TFE	14.6 ± 6.43	24.7 ± 6.39

[a] Determined by gel chromatography
[b] Determined by light scattering

A study of synthesized poly(amino acids) showed that their structure is close to the structure of lysine dendrimers [9]. Attempts to regulate molecular mass and size of the polymer as well as modification of amino groups located on its *N*-terminal lysine residues were undertaken. These attempts included the reductive removal of an N^{ε}-carbobenzoxy group of *N*-carboxyanhydrides of N^{ε}-Z-lysine by hydrogen over activated palladium in the presence of a chain termination agent, which was an activated pentafluorophenyl ether of N^{α}-*tert*-butyloxycarbonylhistidine or trifluoroacetic acid.

TABLE 5. Elements of the secondary structure of linear and hyperbranched heteropoly(lysines) [14]

Polymer	Elements of secondary structure (% of α-helix and β-structure)	
	α-helix	β-structure, (antiparallel)
hbp(K,A)-1.30[a]	7.5 ± 6.20	26 ± 6.20
hbp(K,A)-2.26	3.4	25.5 ± 6.20
hbp(K,A)-0.26	80.5 ± 6.39	0.5
hbp(K,E)-1.96	32.4 ± 6.20	7.8 ± 6.20
hbp(K,A)-1.30	12.3 ± 6.39	24.5 ± 6.39
hbp(K,A)-2.26	6.4 ± 6.39	32.1 ± 6.39
hbp(K,A)-0.27	83.8 ± 6.39	0.3
hbp(K,E)-1.96	37.7 ± 6.45	5.7
hbp(K,A)-1.30	45.7 ± 6.60	8 ± 6.60
hbp(K,A)-2.26	42.9 ± 6.45	6.6 ± 6.45
hbp(K,A)-0.27	89.2 ± 6.60	0.2
hbp(K,E)-1.96	3.6	43.4 ± 6.60
hbp(K,A)-1.30	56.7 ± 6.39	4.0
hbp(K,A)-2.26	87.6 ± 6.60	0.3
hbp(K,A)-0.27	93.4 ± 6.60	0.1
hbp(K,E)-1.96	87.2 ± 6.39	0.4

[a] Ratio of amino acids based on amino-acid analysis data

6. Elucidation of Mechanism of Hyperbranched Polyamino Acids Synthesis to Optimize Their Structure and Properties

It is known that linear polylysines may be used for binding and compaction of DNA during its delivery to the cell nucleus [15]. However, the level of transfection activity of DNA complexed with the linear polylysine appears to be very low. It has been established that transfection activity of DNA complexed with linear poly(lysine) may be enhanced through modification of its side N^{ε}-amino groups by histidine residues [16]. Based on this, we developed a method for preparation of hyperbranched poly(lysine) via the polymerization of N^{ε}-carbobenzoxy-lysine *N*-carboxyanhydride (Fig. 5). This approach permitted to regulate the molecular mass and size of this polymer and at the same time to modify amino groups of its *N*-terminal lysine residues. This method includes the reductive removal of an N^{ε}-carbobenzoxy by hydrogen over activated palladium in the presence of a chain termination agent, activated pentafluorophenyl ether of N-α- *tert*-butyloxycarbonyl-(N^{Im}-benzyloxymethyl)-histidine (BOC- (N^{Im}-Bom)- His- OPFP) [17].

As is seen in the scheme (Fig. 5), the amino group of lysine-*N*-carboxyanhydride, which is released during catalytic removal of the of N^{ε}-carbobenzoxy- blocking group from N^{ε}-carbobenzoxy-carboxyanhydride-lysine *N*-carboxyanhydride immediately initiates the polymerization of *N*-carboxyanhydride, thereby causing the growth of oligomer (polymer) chains. Then the removal of carbobenzoxy blocking groups from N^{ε}-amino groups of the resulting oligomer (polymer) chains continues to occur. Once a certain length of polymer chains is achieved, provided that the initial ratio between *L*-lysine-*N*-carboxyanhydride and the activated hystidine ether is changed, the activated pentafluorophenyl ether of N-α-*tert*-butyloxycarbonyl(N^{Im}-Bom)-histidine present in the reaction system begins to compete with N^{ε}-carbobenzoxy-lysine-*N*-carboxyanhydride. It modifies the amino groups of *N*-terminal lysine residues of growing polymer chains and thereby ceases the growth of polymer chains. To ascertain whether the molecular mass and size of hyperbranched polylysines may be regulated, hyperbranched poly(lysines) were synthesized at weight ratios of N^{ε}-carbobenzoxy-lysine-*N*-carboxyanhydride to pentafluorophenyl ether of N-α-*tert*-butyloxycarbonyl(N-Im-Bom)histidine equal to 1 : 1 and 10:1, respectively, (Table 6, polymers 1, 2). These values correspond to lysine-*N*-carboxyanhydride- to -activated histidine ether molar ratios equal to 1.8:1 and 17:1 for the first and second polymers, respectively. As evidenced by amino acid analysis of the polymers being formed, the real lysine-to-histidine ratios are 5.6:1 and 75.3:1, respectively (Table 6).

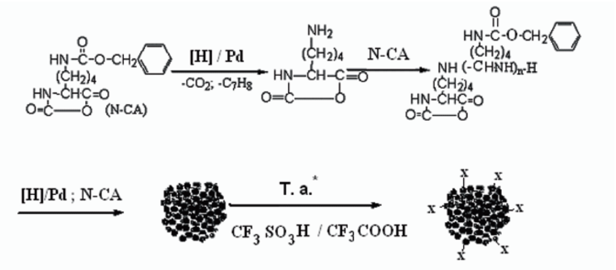


Figure 5. Scheme of synthesis of hyperbranched poly(lysines) modified on N-termini with histidine. Designations: N-CA=N-carboxyanhydride Nε-carbobenzoxy-lysine; N-carboxyanhydride Nε-carbobenzoxy-lysine; T.A.=termination agents (BOC- (NIm-Bom)- His- OPFP or CF3COOH); X=His or NH_3^+

TABLE 6. Conditions of synthesis of histidine-modified hyperbranched polylysines and their structure according to the aminoacid analysis and capillary electrophoresis [17]

Polymer	L-lysine-N-carboxyanhydride: activated histidine ether, mol/mol		Amino acids (lysine:histidine, mol/mol)[a]	N-terminal amino acids (lysine:histidine, mol/mol)[b]
	Weight	Molar		
1	1:1	1.8	5.6	1:34
2	10:1	17.5	75.3	1:14

[a] According to the amino-acid analysis

[b] Capillary electrophoresis

The quantitative determination of *N*-terminal amino acid residues in the hyperbranched poly(lysines) by means of capillary electrophoresis made possible the estimation of histidine fraction linked to the terminal amino acid groups of lysine of the hyperbranched polylysine and to trace how a change in their ratio affects the structure of the polymers. It turned out that upon the passage from the L-lysine-N-carboxyanhydride- to-activated histidine ether ratio from 10:1 to 1:1 (Table 6, polymers 2, 1), the molar ratio of *N*-terminal hystidine residue incorporated into the hyperbranched polylysine to the remaining N-terminal lysine residues increases from 14:1 to 34:1. This implies that, actually, the fraction of histidine linked to the amino groups of lysine of the outer sphere of the hyperbranched polylysine grows when concentration of activated histidine ether in reaction media increases.

7. Secondary Structure of Hyperbranched Polylysine Modifed with Histidine

The secondary structure of the polymers, namely, the ability of oligo(lysine) or poly (lysine) chains located outside "branching" points (diacylated lysine residues) to form the ordered secondary α-helical structure was studied by the method of circular dichroism [17]. According to Table 7, in water (pH 6.4) and dilute hydrochloric acid (pH 2.0), all polymer samples assume the disordered coil structure with a substantial amount of the β structure.

TABLE 7. Elements of the secondary structure of hyperbranched polylysine modified with histidine via N-terminal amino groups [17]

Polymer	Secondary structure elements, %	
	α-helix	β-structure[b]
	Water (pH 6.4)	
1	4.9	39.6/4.1
2	4.4	37.3/3.5
	HCl (pH 2.0)	
1	6.8	45.2/5.2
2	6.9	43.6/5.1
	NaOH (pH 10.0)	
hbp(K)[a]	9.9	28.0/4.8
1	13.8	19.5/4.8
2	40.7	6.8/5
	80% – trifluoroethanol	
hbp(K)[a]	14.6	24.7/28.0
1	21	18.3/6.1
2	47.6	6.1/5.4

[a] hbp(K) is the hyperbranched polylysine (K designates lysine in the one-letter code) synthesized without any chain-terminating agent [20]

[b] Antiparallel and parallel are in the nominator and denominator, respectively

Under these conditions, an α-helicity is almost absent. This phenomenon is associated with the presence of cation charges on the ε-amino groups of lysine residues that occur outside the “branching” points and that in turn give rise to the disordered coil. In an alkaline solution (pH 10), where the ε-amino groups of lysine are deprotonated and polylysine can occur as an α-helix, the fraction of the % α-helicity for polymer 1 is 13%, whereas for polymer 2, the % α-helicity increases by more than three times up to 41%. In a good solvent (trifuoroethanol), the fraction of α-helicity for the same polymers increases as well: for polymers 2 and 1, these values are 49% and 21%, respectively. A comparison of these results with the data of N-terminal analysis performed by capillary electrophoresis permits to suggest that an increase in the proportion of the terminating agent in the reaction system causes the formation of the polymer in which only short oligolysine fragments, which are incapable of forming stable α- helical structures occur outside of branching points Conversely, a reduction in the proportion of the terminating agent produces polymers with longer polymer chains outside the branching points; these chains are able to form a stable α-helix.

8. Molecular Characteristics of Hhyperbranched Polylysine in Which Amino Groups of N-Terminal Lysine Residues Are Modified with Histidine

Molecular conformational characteristics of hyper branched poly(lysines) with modifications introduced at amino groups of N-terminal lysine residues were investigated by molecular hydrodynamic and optic methods. The employment of dynamic light scattering allowed the determination of two modes (rapid and slow) in solution containing one of the test samples (Table 8, polymer 2). The size of particles corresponding to the slow mode is in the order of 300 nm. Probably, these species provide the major contribution to M_w values estimated by light scattering. The sizes of this species corresponding to the rapid mode is smaller than 10 nm.

TABLE 8. Hydrodynamic and molecular characteristics of the hyperbranched polylysine in 0.2 M aqueous solution of NaCl [17]

Polymer	[η], cm^3/g (at 21°C)	k′	$\bar{v}$, cm^3/g	S_0, Sv	$D_0 \times 10^7$, cm^2/s	$M_{SD} \times 10^{-3}$	$M_w \times 10^{-3}$
1	24	0.30	0.669	1.2	7.5	12	110
2	52	0.29	0.617	1.4	3.1	30	600

9. Investigation of Mechanism Hyperbranched Poly(Lysine) Synthesis

The question concerning the origin of the slow and the rapid modes was elucidated in the course of further synthesis and investigation of hyperbranched poly(lysines) under condition of termination reaction of N-carboxyanhydride N^{ε}-Z-lysine polymerization by addition of trifluoroacetic acid (Fig. 5). It was possible to conclude that rapid mode of polymer is hyperbranched low molecular weight poly(lysine) formed in the beginning of process of N-carboxyanhydride polymerization. High molecular weight polymer molecules may be either aggregates of these low molecular molecules [18] or constitute the product similar to starlike polylysine conjugates of lysine dendrimers in which large polylysine chains are grafted to a strongly branched core via one point [6]. We then undertook to prove the mechanism of both proposed modes. For this, the formation the investigation of hyper branched polylysine synethis under the condition of termination polymerization by trifluoroacetic acid was carried out by addition (at 1, 2, 4, 24 and 96 hours) of trifluoroacetic acid into reaction medium [19] (Fig. 5). It was found that at the first stage low molecular weight (molecular weight is 2,000–8,000) hyper branched poly(lysine) forms. Then polymerization of new portion of N-carboxyanhydride N^{ε}-carbobenzoxy-lysine continues utilizing amino groups of N-terminal lysine residues. That results in formation of high molecular weight polylysine structure of which reminds the structure of starlike poly(lysine) lysine dendrimer [6].

10. Determination of Molecular Weight of Hyperbranched Poly(lysines) Prepared Under Reaction Termination of Polymerization of N-carboxyanhydride with Trifluoroacetic Acid

With the help of chromatography method (GPC) it was found that during first 1–2 h of reaction polymers with molecular masses 6,000–9,000 are formed that possess rather narrow molecular weight distribution, which is close to Poisson distribution (Fig. 6a and b). Polymer prepared during 96 h of polymerization of N-carboxyanhydride shows bimodal distribution (Fig. 6c) [19]. This polymer consists of two modes – low molecular mode (MW ≈ 10 kDa) and high molecular weight mode (MW ≈ 170 kDa).

N-terminal polymer analysis with the help of capillary electrophoresis. CEPCEP allowed to estimate quantities of N-terminal amino lysine groups in polymer and therefore quantities of polymer point of “branching” depending on the time of polymerization (Table 9).

TABLE 9. Quantities of N-terminal lysine groups determined with the help of CEP (time of termination of reaction polymerization of N-carboxyanhydride 1, 2, 96 h) [19]

No	Time of termination of reaction polymerization of N-carboxyanhydride, h	Polymer molecular weight, 10^3	Quantities of N-terminal lysine groups[a]
1	1	6	16
2	2	9	17
3	96	10–170	27

[a] Data for DNP derivatives of lysine residues (capillary electrophoresis data)

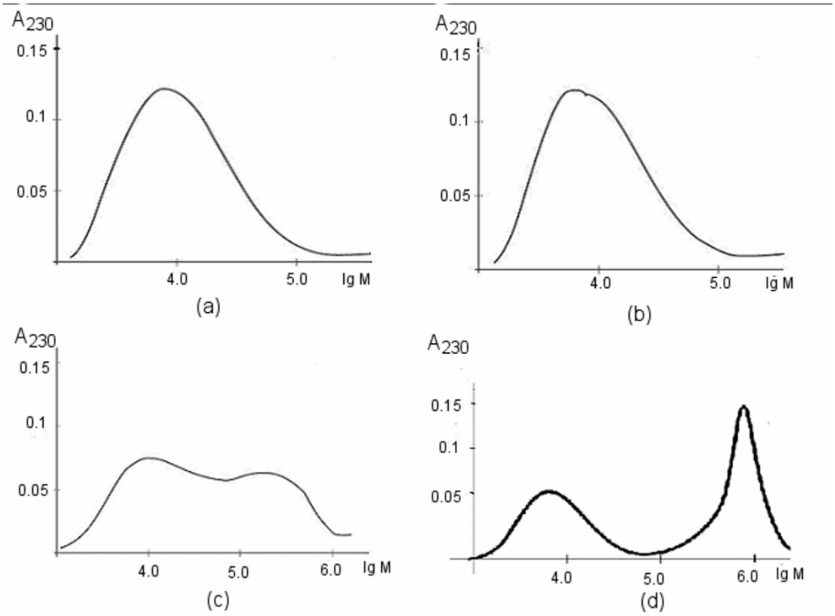


Figure 6. Analytical GPC of hyperbranched poly(lysines) prepared under termination reaction of N-CA polymerization with CF_3COOH ($HCOOH/Pd$): in 1 (a), 2 (b), 96 h (c), and without termination of N-CA polymerization (H_2/Pd), 96 h. Sepadex G-50. Column (1.5 × 42 cm)

Data presented in Table 9 demonstrate that during the first 1–2 h of polymerization process 16 to 17 N-terminal lysine residues are formed. Process of polymer "branching" continues and at 96 h time-point quantities of N-terminal lysine residues grow up to 27.

11. Secondary Structure of Hyperbranched Polylysines

In Table 10 the data regarding the fraction of α-helicity for hyper branched poly(lysines) is presented. It shows that in polymer formed during 1–2 h the percentage of α-helicity is very low. Polymer is practically disordered. But in polymer formed during 24–96 h the percentage of α-helicity grows and it actually very close to that of for high molecular weight linear poly(lysine).

This data confirms that at the first stage of polymer synthesis a low molecular weight hyper branched polymer core is formed In it only short lysine-lysine chains can be found between the point of "branching". These polymers exist predominantly in disordered conformation.

TABLE 10. Percentage of α-helicity of hyper branched poly(lysines) prepared by termination of reaction of polymerization of N-carboxyanhydride [19]

No	Time of polymerization of N-carboxyanhydride, h	% α-helicity
1	1	7 ± 4.8
2	6	10 ± 4.8
3	24	55 ± 4.8
4	96	60 ± 4.8
5	168	60 ± 4.8
6	Linear poly(lysine)[b]	66 ± 4.8[b]

[a] In TFE/H_2O (v/v 80/20)

[b] MW 100 и 140 kDa [14]

12. Enzymatic Hydrolysis of Hyper Branched Polylysines

The presence of relatively short poly(lysine) fragments in hyper branched poly(lysines) between the points of branching was confirmed via analysis of polymer enzymatic hydrolysis.

TABLE 11. Michaelis–Menten constants of enzymatic hydrolysis of hyper branched poly(lysines) (condition of experiments: pH 7.6, [0.1 M NaCl], trypsin, $[E_0] = 8.7 \times 10^{-7}$ M) [19]

Polymer	#	Time of polymerization, h	MW, kDa	Km(app) &, M, 10^5
hbpK[a]	1	1	6	120
hbpK[a]	2	2	9	26
hbpK[b]	3	6	6	45
hbpK[a]	4	96	(10–170)	5.2
Linear poly(lysine)	5	–	450[c]	1.1
Lysine dendrimer of fifth generation	6	–	8,162	Stable

[a] hbpK – hyperbranched poly(lysine) prepared with the utilization of formic acid/Pd hydrogenolysis system

[b] hbpK – hyperbranched poly(lysine) prepared with the utilization of H2/Pd hydrogenolysis system [14]

[c] Linear poly(lysine) [14]

Earlier we had used enzymatic (trypsin) hydrolysis of starlike carbon-chain polymer insulin conjugates [20] in which polymer chain is connected to amino group of hormone with one of its end groups. The same approach was used for determination of ability of hybrid block-copolymers of A-B and A-B-A types consisting of carbon-chain polymer (B) and polypeptide (poly(lysine)) (A) blocks [21, 22] to hydrolyze upon the action of enzyme. In the present work we have used that approach to determine the structure of hyperbranched poly(lysines) and also their biodegradability (Table 11).

Data presented in Table 11 shows that hyperbranched poly(lysines) prepared in the period of 1 h of polymerization of N-carboxyanhydride (#1) has worse Michaelis–Menten (app) constant of hydrolysis whereas polymers prepared in 96 h (#4) the Km constant is close to that of for linear poly(lysine) (#5). The polymers prepared in 2 (#3) and 6 (#3) h of polymerization of N-carboxyanhydrides have Michaelis–Menten (app) constants intermediate to that of for other polymers. As expected, lysine dendrimer of fifth generation, molecular weight of which effectively coincides with that of low molecular weight polymers, is stable under these conditions.

13. Complex-Forming Ability of DNA-binding Polymer Carriers

The one of the main requirements for DNA carriers is the ability to form stable complexes with DNA. The special features of binding of the synthetic carriers to plasmid DNA were studied by agarose gel electrophoresis (gel retardation) that enables visualizing of changes in the electrophoretic mobility of plasmid DNA/carrier in agarose gel.

Lysine dendrimer of the third generation and its derivatives were investigated as DNA carriers (Table 2). These investigations [6, 7] showed that the effective binding of DNA plasmid molecules to lysine dendrimers strongly depends on dendrimer structure. The formation of the DNA/dendrimer of third generation (**D3**) complex occurs at 1:1 (w/w) DNA/carrier ratio (Fig. 7a, lane 4). The onset of complex formation (with **D3**) is demonstrated by disappearance of free conformational isoforms typical of intact plasmid DNA (Fig. 7a, lane 1) and the formation of complexes with heterogeneous charge (lanes 2, 3). It should be noted that increase in the carrier concentration did not result in any changes in the fluorescence of the complexes at the loci of application (lanes 5–9) and that no effect of fluorescence decay of the intercalating stain was noticed. This effect may indirectly indicate that DNA/D1 complexes formed are rather "loose". In the case of dendrimer, which contains two Lys residues modified by lipophilic palmitoyl fragments at the C-terminus (**D3Lip**, Fig. 7b), the complete binding of the plasmid occurs, just as with **D3**, at a DNA/**D3Lip** ratio of 1:1 (w/w) (Fig. 7b, lane 4). A specific feature of complexes with **D3Lip** is an increase in the density of the resulting complexes parallel with increasing dendrimer concentration. This is demonstrated by almost complete and nearly complete disappearance of ethidium bromide fluorescence in the gel wells (lanes 5 and 6–9, correspondingly). Earlier, a similar effect has been described for other DNA carriers [21]. It was shown for the starlike poly(N-vinylimidazole) derivative of **D3** (**(pVIm)$_8$D3**), Fig. 7c) that the formation of complexes with DNA occurs at the same mass ratios as in the case of dendrimer D3 and that the structure of these complexes is also rather "loose". It was found that in complexes of the starlike poly(lysine) (**(pLys)$_n$-D3**) derivative of **D3** with DNA complete DNA binding occurs at a ratio of the components of the complex 1:0.5 to 1:1 (Fig. 7d, lanes 3, 4). With the carrier concentration increase, the complex is condensed (lane 5) and becomes compact (lanes 6–9); it do not permit the intercalation of the staining compound, as found for the DNA/**D3Lip** complex (Fig. 7b).

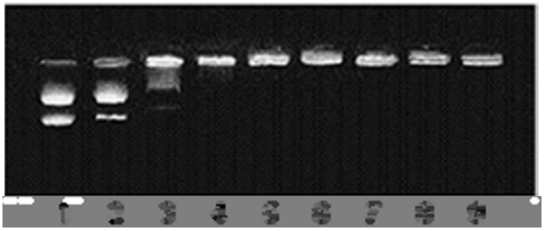


Figure 7a. Formation of plazmid DNA-D3 complex at DNA: D3 ratios of (2) 1:0.1; (3) 1:0.5; (4) 1:1; (5) 1:2; (6) 1:4; (7) 1:6; (7) 1:8; (8) 1:10; (9) 1:10. Hereinafter lane 1 is free (unbounded) DNA

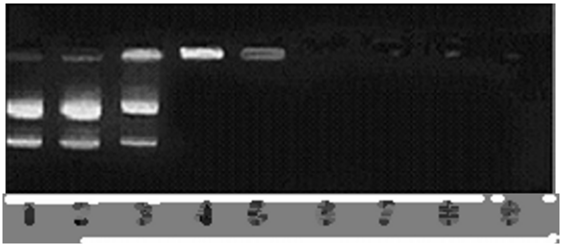


Figure 7b. Formation of plazmid DNA-D3Lip complex at DNA: D3Lip ratios of (2) 1:0.1; (3) 1:0.5; (4) 1:1; (5) 1:2; (6) 1:4; (7) 1:6; (7) 1:8; (8) 1:10; (9) 1:10. Hereinafter lane 1 is free (unbounded) DNA

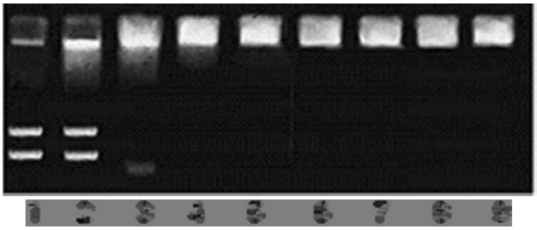


Figure 7c. Formation of plazmid DNA-$(pVim)_8$D3 complex at DNA: $(pVIm)_8$D3 ratios of (2) 1:0.1; (3) 1:0.5; (4) 1:1; (5) 1:2; (6) 1:4; (7) 1:6; (7) 1:8; (8) 1:10; (9) 1:10. Hereinafter lane 1 is free (unbounded) DNA

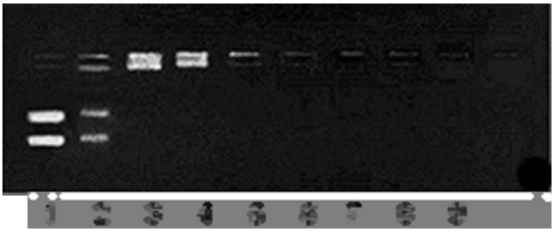


Figure 7d. Formation of plazmid DNA-$(pLys)_n$D3 complex at DNA: $(pLys)_n$D3 ratios of (2) 1:0.1; (3) 1:0.5; (4) 1:1; (5) 1:2; (6) 1:4; (7) 1:6; (7) 1:8; (8) 1:10; (9) 1:10. Hereinafter lane 1 is free (unbounded) DNA

Hyperbranched polylysine carriers. To enhance the transfection activity of hyperbranched homopoly(lysine), its N-terminal amino groups were modified by His residues. Data in Fig. 8 show that the formation of a stable complex begins even at a DNA/hyperbranched poly(lysine) ratio of 1:0.3 and stops at 1:0.6, i.e., at a lowest concentration of the polymeric carrier as compared with all the previously examined DNA carriers.

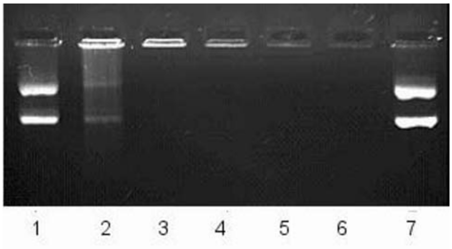


Figure 8. Gel electrophoresis of DNA complexes with hyperbranched homopoly(lysine) modified by histidine DNA/hyper-branched homopoly(lysine) ratio: (1) 1:0.1, (2) 1:0.3, (3) 1:0.6, (4) 1:1, (5) 1:1.5, (6) 1:2, and (7) DNA [23]

As the concentration of the carrier in the complex increases, a stable complex is formed, which leads to the termination of intercalation of ethidium bromide, just as it was observed for dendrimer D3Lip and the starlike polylysine conjugate p(Lys)n-D3 [6].

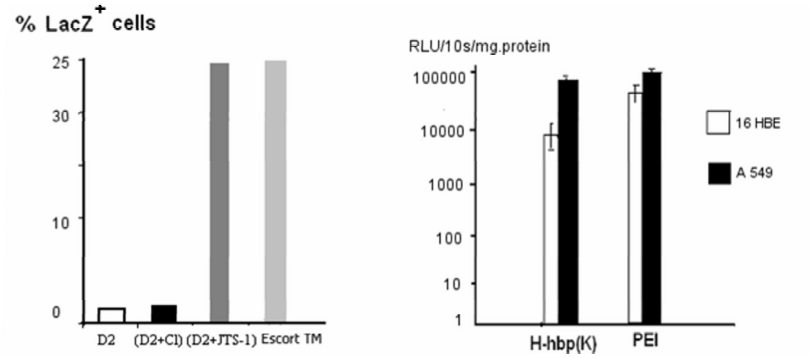
14. The Efficiency of Transfection by DNA Complexes with Lysine Dendrimers and the Hyberranched Polylysine Modified with Histidine

Lysine dendrimer of the third generation (Table 2, D1) and its C-terminal lypophilic analog (Table 2, D2) (Fig. 9a). The efficiency of transfection by the complexes containing dendrimers **D3** and **D3Lip** and the reporter plasmid pCMV-nlsLacZ was determined using HeLa or HepG2 cell lines and compared to that achieved with the use of the commercial carrier Escort^{TM} for complex formation with DNA. Complexes of DNA with **D3** and **D3Lip** had low transfection efficiency. This may be explained by DNA destruction in endosomes by endosomal enzymes. Introduction of the endosome destroying amphipathic anionic peptide JTS-1 peptide(H-Gly-Leu-Phe-Gly-Ala-Leu-Leu-Glu-Leu-Leu-Gly-Ser-Leu-Trp-Gly-Leu-Leu-Glu-Ala-OH) [15], into the preliminarily formed **D2**/DNA complex reliably increased the transfecting activity of DNA/**D3Lip** and allowed to obtain maximum transfection efficiency of 25 ± 1.5% (Fig. 11a). Efficiency of expression of this complex was comparable with that of commercial carrier EscortTM (positive control).

Hyperbranched homopolylysine modified by hisidine. In order to increase the efficiency of transfection by the complexes containing hyperbranched polylysine and hyperbranched homopolylysine the amino groups of N-terminal lysine residues of polymer were modified by histidine fragments. According to the preliminary results the transfection efficiency of the DNA complex with this modified homopolylysine was very high (Fig. 9b) [23].

It was comparable with the one of DNA/polyethylenimine complex in lung carcinoma cells (16HBE line) and their immortalized forms (line A549). Importantly, in this case no additional optimization of the DNA-containing complex by introduction of chloroquine or nonapeptide JTS-1 into transfection protocol was needed.

One should stress that the main difference between these two complexes is that hyperbranched polylysine is biodegradable polymer but polyethylenimine is non-degradable and, moreover, toxic.



a

b

Figure 9a. Transfection efficiency (in HepG2 cells) of DNA/lysine dendrimer **D3Lip** complexes in the absence of chloroquine or nonadecapeptide JTS-1, in the presence of chloroquine (**D3Lip**+Cl) and in the presence of the nonadecapeptide (**D3Lip** + JTS-1) [6]; b. Transfection efficiency of DNA complex with hyperbranched homopolylysine modified at the N-termini by histidine residues (to the left) and ofDNA complex with polyethylenimine (to the right). Y axis – cell number; lung carcinoma (16HBE) cells and their immortalized forms (A549) were used for transfection. Designations: RLU, relative light units; PEI, polyethylenimine [23]

15. Conclusion

Data presented in this paper distinctly shows the tendency of evolution of synthetic approaches for preparation of biocompatible and biodegradable hyperbranched polymer carriers based on amino acids. These studies have evolved from the synthesis of relatively artless low molecular weight dendrimers to the creation of high molecular weight dendrimer analogs. It is beyond any question that this same tendency will furthermore aim at the development of novel variants of hyperbranched polymer carriers in which molecular weight will be strongly controlled. Another goal is to improve the architecture of hyperbranched polymer carriers with the aim to enable controlled drug release for targeted delivery of biologically active compounds to specific cell types.

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BIODEGRADABLE AND BIOCOMPATIBLE CARBON-CHAIN POLYMER–PROTEIN CONJUGATES AS CARRIERS OF BIOLOGICALLY ACTIVE SUBSTANCES: PROBLEMS OF SYNTHESIS, RISKS OF APPLICATION AND HOW TO OVERCOME THEM

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Abstract. Problems of preparation, properties and probable avenues of application of starlike carbon-chain polymer–protein conjugates as carriers of biologically active substances are presented and discussed. Special attention is directed to methodology of conjugate preparation, possible means of optimization of conjugate properties and routes of their application.

Keywords: starlike carbon-chain polymer–protein conjugates, carriers of biologically active substances

1. Introduction

Current stage of medicinal science produces a strong demand to create new variants of biologically active compounds. The new generations of polymer-based drugs seem to be of a particular interest. At the present time this field is undergoing a new phase of development. The binding of biologically active substances (BAS) possessing anticancer, antiviral, and antimicrobial activities to carriers via chemical (covalent) or physical (ionic or hydrophobic) bonds, as well as their incorporation into polymeric networks or liposomes enables direct modulation of BAS properties, including their targeting and controlled release. Furthermore, this permits to reduce the concentration of active substances in the organism, thereby reducing their toxic effects (if any) [1]. The carrier protects BAS from enzymes and inhibitors and decreases their possible neutralization by the immune system. Collectively, a manifest optimization of medically important BAS becomes possible. Search for new BAS polymer carriers and studies aimed at improving their structures and extending the spectra of their application have been carried out for

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more than 50 years. During the last decade, the main attention of researchers in this field was attracted to the synthesis of carriers for the intracellular delivery of genetic material [2]. The desired characteristics of BAS polymer carriers are the following: biocompatibility, biodegradablity and the lack of immunogenicity [3]. If even one of those is missing, the use of a particular polymer as BAS carrier becomes impossible.

Many BAS polymer modifiers were employed, including carbon-chain and heterochain polymers, polysaccharides, polypeptides, and proteins. The carbon-chain and hetero-chain polymers such as carbon-chain polymers or polyethyleneimine (PEI) are not biodegradable and, therefore, can be accumulated in organism, which leads to undesirable side-effects [4]. Therefore, only low molecular weight carbon-chain polymers, not exceeding 30–40 kDa, could be utilized. Their half-life in the organism is short and they are removed from the organism via kidneys. Conversely, proteins are biodegradable; and therefore they have been predominantly utilized for the production of conjugates used for the introduction of BAS into the organism. Proteins differ from other polymer carriers. They possess intrinsic biological activity. Therefore, in addition to the targeted transport they also produce other effects, which are not always desirable. They can activate the immune system of organism, inducing the production of antibodies to themselves and the biologically active component of the conjugate. This may be viewed as an advantage of protein carriers when they are utilized to induce the production of antibodies to low-molecular and weakly immunogenic compounds. However, if proteins are used as carriers for the delivery of therapeutic BAS to a cell target, their immunogenicity is a clearly negative factor, since it can lead to the BAS immunological inactivation and the reduction of its efficiency.

Taking into account the biodegradability of proteins and their ability to provide the conjugate targeting the studies of synthesis and biological properties of starlike carbon-chain polymer–protein conjugates will be discussed herein (Fig. 1). Main attention will be devoted to the optimization of synthetic approaches to preparation of starlike carbon-chain polymer–protein conjugates, the influence of chemical nature and molecular weight of carbon chain polymer moiety of conjugate on spatial structure and biological properties of polymer–protein conjugate, ability of conjugate protein moiety to be enzymatically destroyed in a controlled fashion and the possibility of regulating the immunogenicity of conjugate protein moiety.

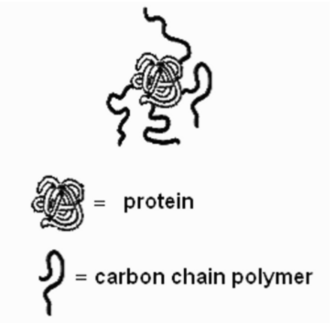

Figure 1. Polymer–protein conjugates

2. Synthetic Approaches for the Preparation of Starlike Polymer–Protein Conjugates: Advantages and Shortages

Many attempts were made to generate polymer–protein conjugates [5]. These strategies included the interaction of proteins with carbon-chain polymer, which is prepared in advance and contains activated side groups (Fig. 2, path 1). The main disadvantage of this approach is multipoint bonding of proteins with carbon chain polymers, which results in formation of polymer–protein conjugates of uncontrolled structure, molecular weight and unpredictable biological activity [1].

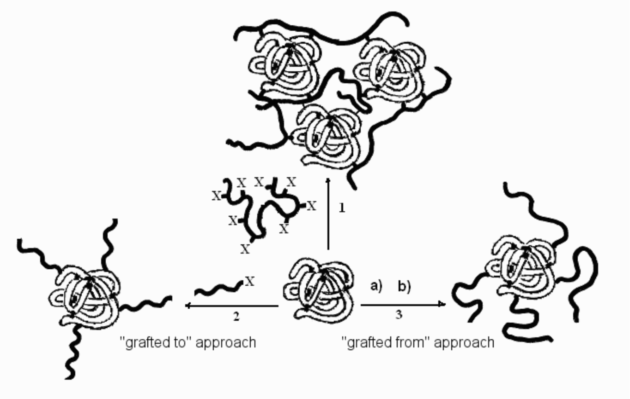

Figure 2. Approaches to synthesis of polymer–protein conjugates: X = activated group; (a) 2,2-azobisisobutyric acid dimethylimidate (diazide); (b) polymerization of vinyl monomers

Taking into account the biodegradability of proteins and their ability to provide the conjugate targeting the studies of synthesis and biological properties of starlike carbon-chain polymer–protein conjugates will be discussed herein (Fig. 1). Main attention will be devoted to the optimization of synthetic approaches to preparation of starlike carbon-chain polymer–protein conjugates, the influence of chemical nature and molecular weight of carbon chain polymer moiety of conjugate on spatial structure and biological properties of polymer–protein conjugate, ability of conjugate protein moiety to be enzymatically destroyed in a controlled fashion and the possibility of regulating the immunogenicity of conjugate protein moiety.

3. Synthesis of Polymer–Protein Conjugates for DNA Binding and Its Targeted Delivery

Polyethylenimine or polylysine-modified proteins (transferrin and insulin) were used for DNA delivery [12, 13]. The iron transporter transferrin and pancreatic hormone insulin can provide the site-specific targeting of resulting protein–polymer conjugate. At the same time, polycationic modifiers, polyethylenimine and polylysine, have been widely used for complex formation with DNA on their own. They provide the formation of a complex with DNA, which is capable of reverse ionic dissociation. It should be noted that polycation protein carriers of DNA were synthesized using a protein preliminarily modified with dialdehyde with polylysine or polyethylenimine (Fig. 2, path 1). A substantial drawback of this method consists in a multipoint binding of reaction components due to the interaction of two polymeric constituents (a preliminarily activated polymer carrier and protein that carries many amino groups), which leads to generation of conjugates possessing noncontrolled structure [1]. This may be alleviated by utilization of starlike carbon-chain polymer–protein conjugates [14–16] in which modifying polymer is connected with one of its termini to a single point of modified protein. In case of starlike carbon-chain polymer–protein conjugates, there is an additional possibility for the directed regulation of the structure and properties of polymer–protein conjugates. This is accomplished by varying the number of attached polymer chains, their molecular weights and immunogenicity. In principle, there are two possible approaches to the synthesis of starlike polymer–protein conjugates. First approach, “grafted from” (Fig. 3) [2], involves the modification of protein (I) with 2,2'-azobisisobutyric acid dimethylimidate (II), a derivative of 2,2'-azobisisobutyric acid, a widely known initiator of polymerization of vinyl monomers (stage 1). The resulting protein-based macroinitiator (III) is used as a polymerization base for a vinyl monomer (stage 2), e.g., N-vinylimidazole (the macroinitiator method). This reaction leads to the formation of starlike poly(N-vinylimidazole) protein conjugates (IV) in which the modifying carbon-chain polymer is coupled with one of its termini to a single point of modified protein. The choice of poly(N-vinylimidazole) as a polymer attached to the protein is governed not only by its ability to bind DNA (the first prerequisite to the formation of a DNA carrier), but also by the fact that it enables DNA release from lisosomes, thus facilitating lisosomal degradation.

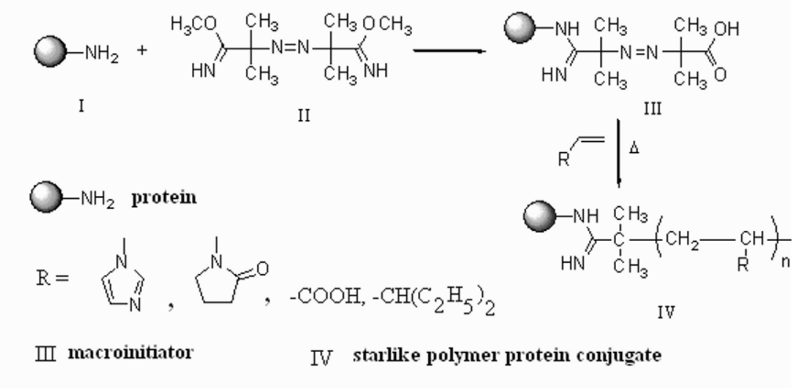

Figure 3. Scheme of synthesis of starlike carbon-chain polymer–protein conjugates (“grafted from” approach, Fig. 1, path 3)

The second approach (Fig. 4) to starlike carbon-chain polymer–protein conjugate synthesis [2] involves a preliminary synthesis of a carbon-chain polymer, poly(N-vinylimidazole) (VI), which provides the DNA binding and possesses a hydrazide group at one of its termini, which is capable of further modification. The 2,2'-azobisisobutyric acid hydrazide (V) serves as initiator in the polymerization of N-vinylimidazole.

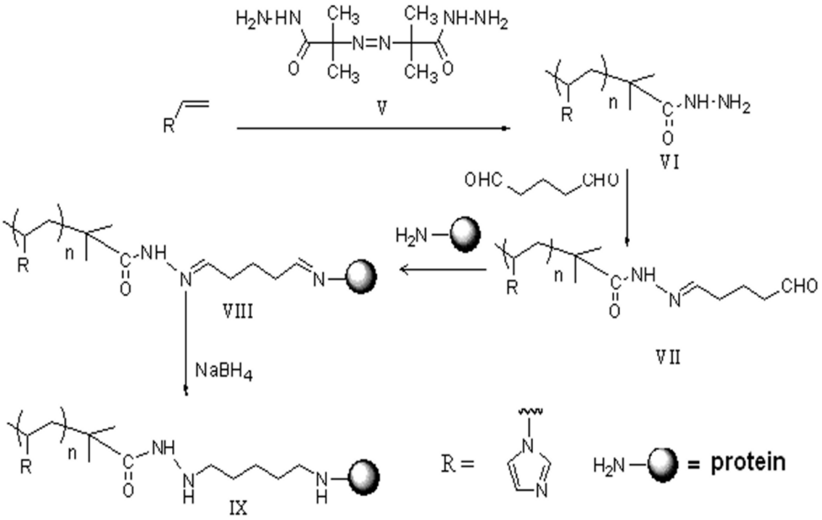

Figure 4. The scheme of synthesis of a starlike carbon-chain polymer–protein conjugate (“grafted to” approach, Fig. 1, path 2)

The hydrazide group in (VI) is modified by glutaraldehyde, resulting in generation of polymer (VII). It contained a reactive aldehyde group at one of its ends and formed a starlike polymer–protein conjugate (VIII) as a result of its reaction with protein amino groups. The reduction of double bonds in (VIII) with $NaBH_4$ leads to the formation of starlike carbon-chain polymer–protein conjugates (IX) in which the modifying carbon-chain polymer is attached with one of its termini at a single point of the modified protein (the macroreagents method using).

These two approaches to the synthesis of starlike polymer–protein conjugates: macroinitiator and macroreagents methods lead to identical final product, a starlike polymer–protein conjugate. The difference between those approaches is that, in the first method, the molecular weight of the polymer modifying the protein can be regulated at the stage of polymerization of vinyl monomer on the macroinitiator by choosing the appropriate monomer-to-initiator ratio. However, in this case, it is almost impossible to regulate the molecular weight distribution of grafted polymer chains. In the macroreagents method, the protein-modifying polymer is obtained at the preliminary stage; it can be prepared with the required polymerization degree and molecular weight distribution. However, the synthesis of relatively low-molecular polymers having an activated terminal group is a laborious task. This makes this avenue of producing starlike polymeric proteins with relatively low-molecular polymer chains not feasible.

4. The Influence of Carbon-Chain Polymer Moiety of Protein–Polymer Conjugate on Protein Biological Activity, Secondary Structure, Immunogenicity and Life Time

One of the advantages of starlike carbon-chain polymer–protein conjugates is the possibility of controlling the number and molecular weight of the polymer chains grafted to the protein. Similarly, the location of modification for low molecular weight proteins may be also controlled, e.g. for insulin [14]. Starlike polymer-insulin conjugates presents a possibility of decreasing the hormone immunoreactivity while preserving a considerable hormonal activity. The data of Table 1 shows that poly(N-vinylimidazole)-insulin conjugates are generally more active then other conjugates. However, the chemical nature of the modifying polymer influences the biological activity of the conjugates up to 4–5 kDa.

If polymer modifier of the higher molecular weight is utilized only molecular weight and position of modified amino acid inside the hormone influence its activity. One can see from the data of Table 1 that changes of biological activity and immune reactivity (ability to interact with anti-insulin antibodies) of conjugates correlate with changes of their α-heliclity. However, immune reactivity of conjugates falls more sharply than their biological activity. There may be two reasons for this. First is the shielding of antigenic determinants of hormone with polymer chains and, the second is the change of insulin spatial structure as a result of modification of its amino groups, which leads to the diminished ability to interact with hormonal receptors.

5. Immunogenicity of Starlike Polymer–Protein Conjugates

Absence of immunogenicity of polymer–protein conjugates along with their biocompatibility and biodegradablity is the prerequisite the utilization of polymer–protein conjugates. If any of these properties is missing, polymer–protein conjugates may not be used as BAS carriers. The problem of immunogenicity and approaches to its modulation were studied using starlike carbon-chain polymer-bovine serum albumin (BSA) conjugates containing bradykinin hormone. The preparation of starlike polymer-protein BSA-based conjugate based was carried out by polymerization of comonomers (acrolein diethyl acetal with methacrylic acid, acrolein diethyl acetal with N-vinylpyrrolidone and acrolein diethyl acetal and N-2-methyl-vinylimidazole) using BSA-macroinitiator prepared by modifying of BSA with 2,2'-azobisisobutyric acid dimethylimidate (Fig. 4). Unprotecting of reactive aldehyde groups in acrolein diethyl acetal fragments of the polymer moiety of conjugate by HCl and following interaction of conjugates with bradykinin allowed to synthesize bradykinin-containing conjugates. Their titer was determined by ELISA. Data of Table 2 demonstrate that chemical structure of the polymer moiety of conjugates determines conjugate immunogenicities.

TABLE 1. Biological activity (decreasing of glucose level in rabbit blood), secondary structure and immune reactivity of starlike carbon-chain polymer insulin conjugates [14]

Starlike carbon chain polymer insulin conjugates	M of polymer moiety, 10^{-3}	α-heliclity %, pH			Biological properties of conjugates	
		1.5	9.0	11.5	Diminishing of the glucose level in blood of rabbits, %	Immune reactivity, %
Insulin	–	42	40	24	100	100
A1,B29-AIB[a]	0.2	38	38	24	100	44
A1,B29-PVI[b]	1.5	32	–	27	150	1.5
A1,B29-PVI[b]	14	32	–	32	45	0.5
A1,B29-PVP[c]	3	32	–	27	70	2.0
A1,B29-PVP[c]	6	32	–	33	50	0.0
A1,B29-PAA[d]	4	30	–	22	80	2.5
A1,B29-PAA[d]	10	–	–	–	48	0.2
A1,B29-PA[e]	2.5	–	–	–	56	3.5
A1,B29-PA[e]	12	–	–	–	20	0.0
B1-PVI	1	–	–	–	95	5.0
B1-PVI	8	–	35	34	70	1.3
B1-PAA	5	–	32	20	65	3.0
B29-PVI	2	–	–	–	–	3.2
B29-PVI	6	–	35	33	–	2.0
B29-PAA	10	–	31	21	–	1.2
A1,B1,B29-PVI	4	–	35	35	0	0.0
A1,B1,B29-PAA	11	–	31	21	40	2.4

[a] 2,2′-azobutyryl- intramolecular cross-linked A1, B29-insulin
[b] PVI – poly(N-vinylimidazole)
[c] PVP-poly(N-vinylpyrrolidone)
[d] PAA – polyacrylic acid
[e] PA – poly(acrylamide)

The strongest antibody response against both bradykinin and BSA was produced by those starlike polymer conjugates, in which bradykinin present in the polymethacrylic acid moiety of the conjugate was additionally modified with succinic acid. Augmented immune response against the both components of such starlike polymer conjugates confirms the well-known ability of polyanionic polymers to activate immune system, i.e. to function as an adjuvant [17]. Starlike polymer BSA-based conjugates containing bradykinin in poly(N-vinylpyrrolidone) moiety also generated high titers of anti-bradykinin antibodies, coupled with less antibody activity against BSA. Thus, poly(N-vinylpyrrolidone) moiety of conjugate does not possess adjuvant properties. In this case polymer chains shield protein moiety, whereas bradykinin attached to polymer chains is more actively recognized by the cells of immune system. Starlike polymer BSA-based conjugates containing bradykinin in the poly(N-2-methyl-vinylimidazole) moiety (4)

TABLE 2. Antibody titer against bradykinin and bovine serum albumin [16]

Immunogen	Antigen			
	Immunization with Freund adjuvant		Immunization without Freund adjuvant	
	BKOva	BSA	BK-Ova[c]	BSA
Poly(MAA_k, $DEAA_l$, BK_h)-BSA(Suc)[&]	5,120	102400	320	2,560
Poly(MAA_k, $DEAA_l$, BK_h)-BSA[&]	1,280	[a]	[a]	[a]
Poly(VP_k, $DEAA_l$, BK_h)-BSA(Suc)[&]	2,560	3,200	[a]	160
Poly(VMI_k, $DEAA_l$, BK_h)-BSA(Suc)[&]	40	640	[b]	[b]
BK_{hc}[****]–BSA(Suc)[&]	2,560	6,400	320	2,560

[a] Titer was not determined.

[b] Immunization was not done.

[c] Prepared with the help of glutaraldehyde; BK – bradykinin; Ova – ovalbumin; BSA – bovine serum albumin [&]MAA – methacrylic acid; VP – vinylpyrrolidone; VMI – vinyl-N-methylimidazole; DEAA – acrolein diethylacetal; Suc – succinic acid.

produced the lowest level of antibodies against both bradykinin and protein moiety even after additional modification with succinic acid. In this case poly(N-2-methyl- vinylimidazole) moiety inhibits immune response. Therefore, changes of chemical structure of polymer moiety of polymer–protein conjugates enables two-way modulation of immune response against low molecular weight compounds introduced into conjugate polymer moiety and polymer carrier itself. This possibility of regulating the immunogenicity of carbon-chain polymer–protein conjugates allows their two-pronged utilization. First option is to use them for targeted BAS delivery without its loss of activity due to the reaction of immune system. Second option envisions the use of carbon-chain polymer–protein conjugates for the augmentation of immune response against low molecular weight compounds connected with the polymer moiety of conjugate, thus resulting in the creation of synthetic or semi-synthetic vaccines.

6. Optimization of Resistance of Starlike Carbon-Chain Polymer–Protein Conjugates to Enzyme Hydrolysis

Functional state of polymer–protein conjugates in the organism (its “life time”) is the major factor for the determination of its usefulness and practicality. Experiments on enzyme hydrolysis *in vitro* with Al, B29-carbon-chain polymer–insulin conjugates indicate its life-time (utilizing degradation by a model protease, trypsin) depends on chemical nature of the modifying polymer (Table 3).

The choice of Al, B29-polymer insulin conjugate and the use of highly specific trypsin digestion allowed to study the kinetics of the peptide bond hydrolysis in a single position. This is the B22-B23 bond between arginine and glycine (Arg-Gly) insulin residues. It was also possible to determine the effect of the chemical nature and molecular weight of the polymer modifier on the formation of Michaelis–Menten enzyme-substrate complex (K_m(app)). The data of Table 3 show that there is a great difference between K_m(app) for different conjugates. These depend on the chemical nature of the polymer modifier and their molecular weight. In this respect, PAA and PVP derivatives differ from PVI derivatives by three orders of magnitude. To explain this phenomenon, it is necessary to take into account that interaction of polyacrylic acid–insulin conjugate with trypsin is more favorable (diminishing of $K_{m(app)}$) as a result of electrostatic attraction of components.

TABLE 3. Michelis–Menten constants for trypsin hydrolysis of two-point (Al, B29) starlike carbon-chain polymer insulin conjugates [16]

Insulin conjugate[a]	M modifier $\times 10^{-3}$	$K_{m(каж)} \times 10^6$, M
Insulin	-	4500.0
A1,B29-AIB[b]	0.3	2200.0
A1,B29-PVI[c]	0.6	3500.0
A1,B29-PVI[c]	10.0	2000.0
A1,B29-PVI[c]	14.0	6300.0
A1,B29-PAA[d]	4.0	1.8
A1,B29-PAA[d]	6.0	6.6
A1,B29-PAA[e]	8.0	5.4
A1,B29-PVP[f]	6.0	1.3
A1,B29-PVP[f]	22.0	3.8

[a] Al, B29-polymer insulin conjugates

[b] 2,2′-azobutyryl- intramolecular cross-linked A1, B29-insulin

[c] PVI – poly(N-vinylimudazole)

[d] PAA – polyacrylic acid

[e] PA- polyacrylamide

[f] PVP-poly(N-vinylpyrrolidone)

Similarly, unfavourable interaction of trypsin with poly(N-vinylimudazole) insulin conjugate (growthing of $K_{m(app)}$) is a result of electrostatic repulsion of these components. Values of $K_{m(app)}$ in the case of trypsin – poly(N-vinylpyrrolidone) insulin conjugate may be explained by the ability of poly(N-vinylpyrrolidone) to form complexes with proteins and polymers.

7. Fine Analysis of Interaction of Polymer–Protein Conjugates with DNA

The main requirement for the DNA carriers is the ability to form stable complexes with DNA at the low ratio of interactive components. The special features of binding of the synthetic carriers to plasmid DNA were studied by agarose gel electrophoresis (gel retardation) via analyzing the changes of the electrophoretic mobility of plasmid in agarose gel (Fig. 5a and b). DNA-carrier complex was formed for 1 h. Equal amounts of DNA (1.0 µg) and different (w/w) amounts of the DNA-binding carriers were added into each well. Free DNA and DNA-carrier complexes were visualized by ethidium bromide staining. The efficiency of DNA binding to starlike poly(N-vinylimidazole) protein conjugates was examined in conjugates containing transferrin, ovalbumin, trypsin, and bovine serum albumin. Data presented in Table 4 shows that the ability to form complexes with the starlike poly(N-vinylimidazole) protein (ovalbumin and trypsin) conjugates [2] conjugates depends on the number and molecular weight of conjugate polycationic components.

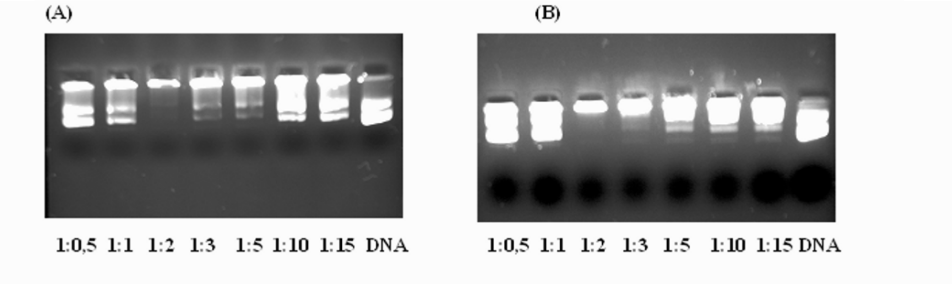

Figure 5. Gel electrophoresis of DNA complexes with starlike carbon-chain protein conjugates: (a) DNA – poly(N-vinylimidazole) ovalbumin conjugate; (b) DNA – poly(N-vinylimidazole) trypsin conjugate. DNA-to-polymer ratio in each lane is shown

Polymer–transferrin conjugates form complexes at a rather high conjugate concentration. It is likely that relatively low-molecular weight polymer chains do not provide good association of DNA with transferrin conjugates. At the sane time, the complex-forming ability of poly(N-vinylimidazole) ovalbumin conjugate as well as of poly(N-vinylimidazole) trypsin conjugate is higher. These conjugates, which contain polymer moiety with the MW of 70 kDa start to bind DNA at DNA-to-polymer ratio of 1 to 2. However, a further increase in the concentration of the polymer carrier/protein results in the destruction of complexes with DNA. The reasons for this bell-shaped correlation of the stability of the complex with DNA with the concentration of the binding polymer are unclear. Such correlation was observed by us many times over [13, 15], are unclear.

TABLE 4. Starlike carbon-chain polymer conjugates of proteins and their DNA binding efficiency (retardation test) [2]

Protein	Number of poly(N-vinyl imidazole) chains	M of one poly(N-vinyl-imidazole) chain, Da	Total M of a polymer, Da	DNA binding efficiency (Ratio DNA/conjugate)
Transferrin[a]	6	3,000	18,000	1/500
	14	3,800	53,200	1/50
	15	2,000	30,000	1/50
	15	5,300	79,500	1/50
	15	6,000	90,000	1/10
Ovalbumin[b]	5	70,000	350,000	1/2
Trypsin[b]	3	70,000	210,000	1/2

[a] Prepared using "grafted from" approach

[b] Prepared using "grafted to" approach

8. Conclusion

Two original methods of starlike carbon-chain polymer–protein conjugates synthesis were proposed for optimizing of carbon-chain polymer–protein conjugate structure. These methods of synthesis of starlike carbon-chain polymer–protein conjugates make it possible to adjust their structure and properties. They had allowed, on one hand, to obtain conjugates in which protein moiety fulfill function of biodegradable and biocompatible spacer between relatively short carbon-chain polymers, which can be used as carriers of biologically active substances. On the other hand, chemical nature of carbon-chain polymer moiety of protein conjugates can be used for creation of polymer modified proteins with determined organism life-time. In such conjugates protein moiety will be protected from enzyme action as well from immune system as a result of its shielding with carbon-chain polymer. Therefore, a novel approach of regulating immune properties of polymer–protein conjugates is proposed.

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MODERN RISKS OF ANTHROPOGENIC INFLUENCE ON LIVING SPECIES: NANO-LEVEL FLUCTUATION

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Abstract. Taking into consideration oncoming global change, basic researches, concerning prospects of the use the modern methods of modeling in such important aspect as reactions of living organism on miscellaneous level hierarchy on risks, appearing as a result these change become exceedingly actual. Using different methods of modeling, generalized experimental material, we managed consider in detail some changes of the biological processes on different hierarchy levels (cellular, organism and population) in response to risks, appearing in ecosystems. In particular, processes of the shaping new desert in context of global desertification were modeled; possible mechanisms of speciation of living organism in radiation–chemical stress and mutation are described. The enzymes degradation models were worked out. On base of these experimental results the phenomena of negative geotropism of root system at influence of specifically dangerous xenobiotics (in particular, chlororganic) and thick water insoluble polymeric covering is considered. Besides, attempt of modeling of complex interaction in ecosystems in condition ecological crisis is realized. In spite of different levels of models, they, on our point of view, can illustrate the interaction of nanoworld with sharply changing condition of the environment and give the approaches to creation new technology. Consideration of these models is important and with standpoint of the estimation of risk and that difficulties, which faces the mankind at period of the oncoming global change of ecosystems under influence of different "on its nature" calls.

Keywords: risks, anthropogenic, fluctuation, cellular, radiation–chemical stress, mutation, global desertification, enzymes degradation, negative geotropism, ecological crisis

1. Introduction

Modern external negative influence on ecosystems and risks connected them leads to local and global changes the living organism environment, loss the quality and yield of agricultural production, therefore the creation of new technology have needed. At that

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researchers activity have directed on shaping the new methodology based on nano-, bio, and information technologies. Besides, toward forecast calls and risks certain of forestalling is noted due to ordered system of the monitoring. Though modern development of the global processes does not give the possibility to realize the reliable forecast more then for 5–10 years. Use biological and other sensor allows only to identify the situation since biological sensors are subjected to the mutation themselves. Regrettably, except forecast and ubiquitous introduction of modern technology for obtaining "full-fledged" and sufficient for consumer market of the products of the feeding, little that changed in such scale process as interaction of the organism with new substrate, inwardly- and inter-population interactions, understanding the adaptation mechanism in new condition of the environment, determination the correlation between got to know stressful factors and change, occurring in living systems using the most important variables for modeling.

As a rule, living organism reactions on stresses reveal on all hierarchical levels – micro-, meso- and macro. It is supposes, that micro - and mesoscopic levels of organizations of the living systems may be referred to nanolevel – an assembly and destruction and again assembly. Practically all structured and information formations of the cell have nanosizes that provided their functional particularities, including lability to environmental factors and complementarily to areas of biomacromolecules. Other word, exactly on them "collapse" blows of the external ambience through soma, which under determined condition may be a "good" solvent or a "bad". At that, physical and physic-chemical parameters of the environment in which nanostructures work, change. With standpoint of living systems hierarchy, the separations of the subsystems, which nonlinear functioning between itself in nanoscale, it may be supposed that, first, biological nanosystems may possible consider in naturephylosophic context, but in – second, – mean the relative magnitudes (for instance, to soma, population and more large inter-populational interactions) formed, stabilized and functioning biological nanostructures. Really, the cell reaction on stress spreads on more high level of the hierarchies.

Taking into consideration oncoming global change, basic researches, concerning prospects of the use the modern methods of modeling in such important aspect as reactions of living organism on miscellaneous level hierarchy on risks, appearing as a result these change become exceedingly actual. Herewith, it is important to select the role of anthropogenic factor in such dynamically developing situation as global warming and desertification on example of the interaction of old and new deserts, radiation–chemical influence and the other risk, existing in ecosystems. Under these risk influence the environment of these organisms is essentially change up to critical parameters. In these critical points intraspecific changes can appear and appear in metabolism and life-support processes of living cells, as well as speciation is occur.

Using different methods of modeling, generalized experimental material, we managed consider in detail some changes of the biological processes on different hierarchy levels (cellular, organism and population) in response to risks, appearing in ecosystems. In particular, processes of the shaping new desert in context of global desertification were modeled; possible mechanisms of speciation of living organism in radiation-chemical stress and mutation are described. The enzymes degradation models were worked out. On base of these experimental results the phenomena of negative geotropism of root system at influence of specifically dangerous xenobiotics (in particular, chloroorganic) and thick water insoluble polymeric covering is considered. Besides, attempt of modeling of complex interaction in ecosystems in condition ecological crisis is realized. In spite of different levels of models, they, on our point of view, can illustrate the interaction of nanoworld with sharply changing condition of the environment and give the approaches to creation new technology. Consideration of these models is important and with standpoint of the estimation of risk and that difficulties, which faces the mankind at period of the oncoming global change of ecosystems under influence of different "on its nature" calls [1–18].

2. Modeling of New Deserts Formation in Global Desertification Context – Synergetic Approach

As a result of ecological crisis, possessing the different nature, the change of Earth's geographic landscape is observed. In particular, the process of certain territories desertification as well as formation of new deserts, takes place.

We assume that old and new deserts at the certain conditions can interact with each other intensively enough especially if they are located rather in plainly part of territory.

Very often, by virtue of anthrophogeneous or other factors, new deserts are formed on the boundary with the territories of the human cultural activity. These territories are a kind of division between the old and new deserts. By understandable reasons the reclaimed territories susceptible to influence both old and new deserts, especially in bordering zones. In this case territories separating the desert are carrying the role of hamper extinguishing deserts aggressivity.

It is necessary to assume that old and new deserts distinguished one from another, mainly, by a whole number of signs. For example, the old sandy deserts have a wide specific variety of living organisms. Here the trophic chains have been formed, their movement is restricted in time and in conditions of the certain human cultural activity.

They may be maintained in definite limits. New salt deserts characterized by minimal species variety; trophical chains are destroyed, new ones have formed, they are more aggressive. Their movement is very intensive and territories capture is realized fairly fast. The territories located between the new and old deserts in due time begin to get the signs both new and old deserts. In this case, in virtue of the greater new deserts aggressivity their signs begin to dominate on territories occupied. They eventually may lead to capture of before human reclaimed zones, closing with old deserts and attack on them.

3. The Interaction of Old and New Deserts

The naturally developed interaction between the old and new desert will prevail. The impact of old desert degradation on a new desert must be considered and to be taken into account. The remedy for this interaction between the old and new desert should be considered at an early stage through an intensive investigation to the cause or causes of the degradation of both deserts. Therefore, the following three mathematical models will be discussed [2, 3].

3.1. MODEL 1

Let us consider one example of possibility to retard the process of new desert attack on zones of human cultural activity. Let us assume the territory reclaimed by human and surrounded with desert. It is characterized by substrate (*S*) so that functioning of human reclaimed zones is symbate to *S* value. The kinetics of so-called useful territory degradation described by differential equation:

$$\frac{\delta S}{\delta t} = \Theta - \frac{S}{\tau} \tag{1}$$

where *S* – unit time, the velocity of substrate renewing; *t* – time of system "useful territory – desert" relaxation; If at initial condition $S(t = 0) = S_0$ the solution (1) will be: τ – unit time, Θ – substrate per unit time

$$S(t) = \Theta * \tau + (S_0 - \Theta * \tau) * \exp(-\frac{t}{\tau}) \tag{2}$$

Add the condition of old desert uptake useful territory. When substrate value became less than S^* very rapid, catastrophic degradation territory occurs, in the time:

$$t^* = \tau * \left| \frac{S_0 - \Theta * \tau}{S^* - \Theta * \tau} \right| \tag{3}$$

It will be noted that relaxation time is determined both the external influences (for example wind etc.) and internal reasons (substrate serves as food for existing trophical chains). The question is if it to slow down by any way the degradation of new territories (i.e. to increase time t^*). Impose on the useful territory the trophical pair "beast of prey – victim" (PBV) with the values stationary populations X_0 and Y_0, correspondingly. In this case, the added PBV properties is such that for already functioning trophical chain the nearest to substrate element of trophical chain is the "victim's" substrate itself when adding PBV. From Eq. (2) one would expect, that increased population Y_0 decreases S and vice versa, – Y_0 decrease leads to enrichment of useful territory (substrate increasing). Indeed, t* is defined as:

$$t^* = \tau * \left| \frac{S_0 - \Theta * \tau}{S^* - \Theta * \tau} \right| \tag{4}$$

It is necessary to note that when description of useful territory degradation processes kinetics as well as the methods which stop this processes we solve the problem inverse to that of describes the trophical chains in certain ecological systems. So the processes of degradation useful territories can be stopped and supporting its quantity on the definite level. In this case, it would be reasonable not to consider that critical situations when on the useful territories a new sign is fixed spontaneously due to powerful ejection from new desert of that or other activity products on the useful territory, e.g. salts, sands, living organisms, etc.

3.2. MODEL 2

Let’s assume that there is a useful territory where the living organisms population a concentration (X_0). The useful territory surrounded by two types of desert – “old” “new”. When the first type desert (“old”) and the useful territory (including its population) exist dynamic equilibrium, the population feeding useful territory occurs in settled relations population annually has the changing quantity describing by logistic law.

$$X_{n+1} = r * x_n * (1 - x_n) \tag{5}$$

But processes in the new desert, bordering with useful territory (saltmarshes type regions) in virtue of their novelty are far from equilibrium; so the population responds to “instantaneous” parameters of new desert.

All together it leads to dependence of population functioning parameters depends on desert influence factor differently:

$$r = f(y_0 y_n); \frac{\delta r}{\delta y_0} = 0; \frac{\delta r}{\delta y_n} \neq 0 \tag{6}$$

So, the population concentration “catches” is an immediate influence factor, while to “old” factors, adapts as average values. Then population function on useful territory influences the properties of oasis itself by such a way that copulation grows in n – generations leads to critical state of useful territory. This state is such that at some duration t^* of critical state of useful territory may be destroyed by attacking of “old” desert. The value of critical state duration is controlled by the desert influence factor. Therefore, new desert controlling the n – parameter grows, introduce populations in state of determinated chaos (as it usually occurs with logistic law).

Considerable by time ejection in $\{X_i\}$ allows the process of fixation on new critical level for degradation parameters of useful territory to be combined together (old desert fix the changes). Let’s assume that population turn into by scenario of alternating (see [4]). If it is so then the population size distribution by determinated state longitude (t) is $P(t)$.Then the probability that determinated, (non-chaotic) state will be last more than t, is:

$$\Omega = \int_{\tau^*}^{00} P(t)dt \tag{7}$$

The possibility of chaotic state for population value will be respectively:

$$W(r^*) = 1 - \Omega(\tau^*) = 1 - \int_{\tau^*}^{00} P(t)dt \tag{8}$$

So, for the time τ^* with probability $W(r^*)$ critical state has time to fix when old desert time to do the critical degradation of old territory. Under experimental investigation of actual degradation, it's very interesting to reveal the parameters of ecosystem to be investigated (r, t^*): from here the model discussed may describe the real mechanisms of degradation of ecosystem such as "old desert – useful territory – new desert. Now, let's consider the case of the desert "old" and "new" deserts of direct interaction and he rule of their division boundary.

3.3. MODEL 3

We consider boundary between old and new desert. The expression

$$V_1(X) = N_1 \exp(-(x+S_1)^2) \tag{9}$$

is the distribution of some parameter V characterizing old desert fauna similarly:

$$V_2(X) = N_2 \exp(-(x+S_2)^2) \tag{10}$$

is the distribution of new desert dimensional coordinate along direction which normal to the boundary between the S_1, S_2, N_1, N_2 are parameters of the distributions). Evidently, that both these parameters reflect the possibility of penetration in region f opposite parameter predomination. If $x = 0$ is the strict disposition of the boundary between old and new desert; than S_1 and S_2 demonstrate the character of diffuse penetration of two deserts one in another. Interpretation of these two parameters is determined by product v^*, v.

For simplicity assume that: $S_1 = S_2$ we obtain the distribution of route mutating living organisms:

$$V_3(X) = N_1 * N_2 \exp(-(x+S)^2 - (x-S)^2) \tag{11}$$

This result is easily generalized if as property of every desert to choose (9) and (10). It's not difficult to show that in this case the product of these two Action is such that it's maximum account for the region near $X = 0$; moreover maximum coordinate is restricted by S_1 and S_2 values. Starting from this, rather common result has been obtained, showing especially active mutagenious region near the boundary regions of old and new desert.

Thus on interaction of old and new deserts as well territories of human cultural activity, situation may appear when progress of territories degradation get intensive character. In this case territories also get new uninherent for them signs, these may fix, causing the essential flora and fauna changes up to mutation accumulation and fixation.

Evidently, it all concern not only desert territories but also the others which are different by genesis species composition of living organisms, as for example in the case of forest and tundra interaction.

4. Modeling of the Speciation in Radiation–Chemical Stress Condition – Biophysical Aspect

When powerful fluctuations, caused different stressful factor arise, for instance, caused by remaining amounts of pesticides, ultraviolet radiation and some type of radiation, changes on qualitative level are possible, which can lead to formation and fastening new signs of living organisms, up to arising of new species [4–10].

Trying to explain this phenomenon, let define two planes of mutations: horizontal and vertical. We shall consider some possible mechanisms of mutations.

On horizontal type due to changing environment conditions accumulation of mutations takes place. At reduction of ecological loading or their complete exclusion on horizontal line rehabilitation is possible due removal of defects, caused by mutagenic factors. Similar “transformations” are observed in case of influence on micro-organisms by mutagenic factors with the view of obtaining opportunity varieties for solution of any biotechnological tasks.

Similar “Conversions” are observed in case of influence of mutagenic factors on microorganisms with the view of obtaining opportunity varieties for solution of any biotechnological tasks. In some time at removal of the factors stimulated varieties by phenotypic displays begins to correspond to initial ones.

One the molecular level situation may be presented as follows factors, causing mutations, and acting any fragments of DNA, change configuration of this part. If the changes are not essential, the structures forming repatriation system, probably coming to spoiled fragment copy and, processing memory, correct a defect of the fragment. Let’s note that at complex radiate–chemical stress radiate changes in DNA fragments can’t be corrected by reparative fragments, if activity is modeled simulated by chemical agents. Situation may be imagined, whereat by such mechanism conformation of many DNA fragments is spoiled due to influence of multiple mutagenic factors. In this case sum of local conformation changes of macromolecule may influence on conformation of the whole molecule. This, alongside with other mechanisms should lead to fixing of mutations. From the same time, according to our ideas, transition from horizontal plane to vertical one is carried out. We suppose that at realization of such transition new type is formed.

These ideas are confirmed by American botanists, which at nuclear ground in Washington states discovered new type of mustard species. If the considered approach is correct in principle, than in biological sphere alive systems, being both on horizontal plane and on vertical plane should be present simultaneously. Herewith alive organisms, present in vertical plane as the mist adaptive to real existence conditions, probably will control the whole substrate. In other words, on population level “breaches” of trophic chains and establishment of new relations between species of alive organisms may be expected. The proposed mechanism of transfer with formation of a new type and evolution may be modeled.

A problem of micro-macroevolution processes of biological systems interaction is far from its solution. It is not clear, for example, what principle ways of molecular mutations mechanisms interaction are with new types formation. It is rare threshold collective process, protected against external initiation. Proceeding from this it can be supposed that of the modern theory of co-operative process can be useful here.

Let's suppose that the appearance of the new type is connected with the certain molecular reconstruction of the genome, covering large number of DNA fragments. It can be supposed that it is possible if firstly number of such fragments is more than some threshold N_A^*, and then if the arrangement of similar measured fragment is topological determined $(\{j\})$, and at third the transformation of the normal fragments to mutated one is carried out if the change of this fragment properties is higher than the certain threshold $\left(M_j^*\right)$.

Then connecting some parameter of order is naught for stable genome and is not naught at the type formation with co-operative molecular reconstruction the Landau–Ginsburg equation can be written down for type-forming process:

$$\delta\eta / \delta t = \delta(F(\eta)) / \delta\eta \tag{12}$$

Here $F(\eta) = F_0 + (Q/2)\eta^2 + (b/4)\eta^4$ - is Landau–Ginsburg functional (13)

We will link the stable state of genome, keeping the type, with $a > 0$ and $b > 0$ values. Then stationary state $\delta\eta/\delta t$ will be realized at $\eta = 0$ i.e. when there is no type formation.

Mutation process in fragments changes their properties, so gradually instability conditions for all co-operative molecular rearrangement are being prepared. Such rearrangement are possible at $a < 0$ as then $\delta\eta/\delta t = 0$ give

$$|\eta| = \sqrt{a/b} > 0 \tag{14}$$

When is it possible? Let's consider the simplest model, demonstrating such situation. In each fragment the elementary configuration is stable until the selection instability is not realized, caused by the rearrangement of the highest occupied and the lowest free molecular orbits (HOMO and LFMO correspondingly). The last is realized as at pure election excitation (for example, ionization radiation) and the change of nucleotide bases sequence. Conditions of single-hole potential (SP) transformation to double-hole one (DH) will have the type:

$$\Delta < C / K$$

where Δ – is distance by energy between LFMO and HOMO, K – local (for the fragment) elastic constant of molecular rearrangement, C – vibrating constant. The following shall be noted the fragment stability outsize of mutation conditions means $\Delta_0 > C / K$; the reaching of the reverse process is the threshold process, which can be realize, for example, by such regrouping of nucleotide bases, which give:

$$\Delta_0(\rangle C / K) \to \Delta(\langle C / K) \tag{15}$$

Thus the transition of single-hole potential to double-hole potential must be carried out in many fragments.

Let's the interaction between fragments is realized at the distance of $R < R^*$, i.e. R^* – a bound between interfragment interaction. Then if the average concentration of modified ($SP - OP$) fragments is N_A, the condition of the cooperative rearrangement possibility will have a form: $[\eta = 0] - [\eta = 0] N^{-\frac{1}{3}} < R^*$, so the bound threshold concentration of mutated fragments has the following form:

$$N * A = \left(R^*\right)^{-3}$$

In this case the model of co-operative rearrangement can be seen is scheme as congerent transfer of unstable fragments structures to the common state.

The following can be put to terms of our model:

$$a = a_0(1 - N_A / N_A^*) = a_0\left[1 - N_A (R^*)^3\right] \tag{16}$$

so at the low concentration of mutated fragments when $N_A^* = (R^*)^{-3} < 1$, we have $a > 0$ and $h = 0$, i.e. type formation is impossible; at the larger concentration of such fragments when $N_A^* = (R^*)^{-3} > 1$ we have $\eta = \sqrt{a / b} > 0$ and type formation is possible.

Medium properties change where above mentioned process takes place R^* determines the value (for example pH of the ambience), so the increase simplifies the type formation, requiring the less for N_A realization.

The proposed scheme allows to think about reverse process of movement downward of the type stairs. However, the particular ways are required for these way firstly realization of the transfer from $N_A > (R^*)^3$ to the conditions $N_A < (R^*)^3$ and that geometrical "separation" of genome with the violation of the condition $R < R^*$ is possible or the reduction of the number of mutated fragments due to the liquidation in the part of their vibrating instability ($N_A > (R^*)^3$).

The combination of three states (MSM) – metabolism, self reproduction and mutability is the basis for various approaches to the understanding of interaction of micro-macroevolution processes. It should noted that the realization of each of base positions (MSM) requires very strong conditions as they are threshold by corresponding characteristics (degree of unbalance, reagent concentration, external disturbances) whereas the situation with simple probability exhaustive search, being realized in any conditions is soft. The question is: are there any possible modes, intermediate between soft and strong which, from one hand, allows the realization of MSM triad, and from the other hand don't require such strong conditions.

We think that such modes are possible and correspond the entry of complex non-liner system to the mode so-called dynamic chaos. The essence of the idea is in the following. Let's consider the complex molecular system in the state to the equilibrium, i.e. when the creation of complex structures is determined by the combinatorics and is extremely impossible due to the system complexity. As it is known and weak external effect the system first enters the Onzager unbalance state, characterized by relaxation behavior and then at the increase of unbalance to the particular state of alteration, combining chaos and determinism in its behavior. When system enters to one or other state the time of stay in each of them has probability character.

The probability density of system existence $\Phi(\tau, \varepsilon)$ in determined state during the time τ depends on the parameter ε, characterizing its distance from the equilibrium $\delta\varepsilon / \delta\eta < 0$ where η is proportional to unbalance degree.

Then if for the strengthening of the ordered state of the system the inclusion of the molecular process is required t_+ then the probability of this qualitatively new state will be

$$\Lambda(t_+) = 1^{-t} + \Phi(t_{+0}) d\tau$$

This probability characterizes the to the higher hierarchy level in the case of vibration only mode of the molecular system to the critical alteration area: herewith the values caricatures the features of molecular system structure, reflecting the intensity of its parts interaction. The dependence of the system's unbalance degree Λ_j is important; it grows with the increase of $\eta : d\Lambda_j / d\eta > 0$.

The proposed ideology naturally interprets the series of traditionally difficult moments of biological evolution problems.

Thus the appearance of the new types connected with the accumulation of the critical modification, value in the critical number of DNA fragments extracted doesn't require extremely strong mutagen influences: their number sufficient for the genome introduction to the alteration state can be reached, when very sharply but insufficiently time for fixing (by any molecular process of the type system τ_+ remains belonging to the new type to remain in it. It is carried out with the probability Λ_j (*). The reverse process is possible by similar way, weakening of the features by mutation can introduce system to alteration, when it "goes back" to the former state for the short period of time τ_+, if for time the molecular mechanisms can be implemented, which put off the fixation of the new type, then the system remains on the level of the former type.

Thus the possibility of the new type formation was proposed on the basis of the analysis of the ecological situation and some experimental factors. Possible mechanisms of unfavorable environmental factors were considered on the DNA level both organism and population. Herewith the sum of factors of anthropogenic and space character was considered.

The proposed model describes the transfer of living organisms with determined horizontal plane to vertical. Features, connected with the accumulation and fixation of mutations can be described within this model. Herewith the latter stipulates the new type formation.

5. Thermal Mechanism of Radiation-Stimulated Mutations – Microscopic Approach

In radiation–chemical influence condition on ecological system it is necessary to analyze completely the situations, connected to functioning of living systems [11]. It is known that radiation is one of the mutagenic factors. This is explained by multi-channel arrival of radiation energy to biological objects. In the given approach heat mechanism of radiation-stimulated mutation, based on the idea of "hydrogen key" formulated by Watson–Crick–Lyovdin is considered, according which the mutations are conditioned by hit hydrogen atom, connecting A and T, G and C bases of DNA in "wrong" positions in untwisting of DNA double spiral. Let consider the fluid ambience, containing DNA with replicative forks density equal to γ. We shall assume that at the beginning initially coordinates ($r = 0$) at initial moment of time ($t = 0$) the energy release as a result of interactions to radiation with substance, characterized by integral section δ. Considering the dissipation of energy Q within the framework of model θ – flash, shall link radiation-stimulated redistribution of hydrogen atoms with passing of the heat wave, coming from the centre of energy releasing site according to law of heat conductivity:

$$\frac{\delta T}{\delta t} = D_T v^2 T \,, \tag{17}$$

where ambiences temperature conductivity, $T(r,t)$ describes the field of the temperatures.

If the hierarchy of the energy states of hydrogen atom in molecule DNA is entered $\left(E_j^S\right)$ (the indexes j and s numbered the tautomer forms and types bases pairs ($s = 1 -$ AT; $s = 2 -$ GC), that probability to occupations of j – position of hydrogen atom, residing on distance r from the centre of energy releasing, will is:

$$\xi(r) = \int_0^{\tau} P\left[\frac{E_j^S}{kT(r,T)}\right] dt / \tau \,, \tag{18}$$

τ – time, during which any atom of the hydrogen, found at moment $t = 0$ in replicative fork mouth remains in reactionary volume; V – a velocity of DNA untwisting.

$T(r, t)$ – it is defined by decision of the Eq. (1) for event of the uniform ambience (c – heat capacity, d – density of the ambience):

$$P\left[\frac{E_j^S}{kT(r,T)}\right]=\exp\left[-E_j^S / kT^*(r,t)\right]/\sum_j \exp\left[-E_j^S / kT^*(r,t)\right], \tag{19}$$

In heat peaks theory two possible variants are realized: study of the processes on distance, greater typical sizes of the initial heat releasing area, and in the energy releasing area. In the first event the temperature is described by the formula (4), in the second – in formula (4) it is suppose that $r = 0$ and the temperature becomes the function only from time.

Summarizing the probability of j-mutations for these two variants and averaging on replicon volume with probabilistic masses shall get:

$$\xi_{jtot}^S = \xi_{jin}^S - \xi_{jout}^S \tag{20}$$

$$\xi_{jin}^S = \xi_j^S(0,t)*\frac{\exp}{\exp-1}*(1-\exp(-\Omega_0\gamma)), \tag{21}$$

$$\xi_{jout}^S = \xi_j^S(\vec{r},t)\frac{\exp}{\exp-1}*(\exp(-\Omega_0\gamma)-\exp(-1)), \tag{22}$$

Where $\vec{r}$ – certain average value within replicon radius.

In obtaining of these results we use as probabilistic masses the probability of next-door neighbor:

$$W(r)=\frac{\exp}{\exp-1}*4\pi r^2\gamma\exp(-\frac{4}{3}\pi r^2\gamma),$$

In approach, when one high energy particle causes one θ – flash, it is possible to calculate the amount of induced mutations of given type in the volume:

$$N_p = V\delta JtN_0\xi_{jtot}^S, \tag{23}$$

where V – irradiated volume, δ – a section of the heat peak formation, J – an integral flow of the particles, t – time of the irradiation, N_0 – an average atoms concentration in unit of the volume of the irradiated ambience.

For number of common thermodynamic mutations we have

$$N_{T0} = VN_0\xi_{j0}^S, \tag{24}$$

where $\xi_j^S T_0$ is defined according to formula (2).

The number of mutations is defined as $N_{tot} = N_p + N_{T_0}$ and radiation factor reinforcement of mutation – on the following formula:

$$\chi = N_{tot} / N_{T_0} = 1 + N_p / N_{T_0} = 1 + \sigma Jt \xi^S_{jtot} / \xi^S_{jT_0} \tag{25}$$

Consequently, radiation mutations are essential in doses:

$$\Phi = Jt > \xi^S_{jT_0} / \xi_{jtot^\delta} \tag{26}$$

It is notes that in given approach two admissions are used – uniformity of the replicons distribution in the volume and time, and homogeneity of the ambience. Actually as hutch itself, and space-temporary distribution of replicons are not uniform. Taking into consideration these circumstances it will present more high approach in contrast with used approaches.

Undoubted interest presents the modeling of the cellular solutions water sorption processes by macromolecules, since the initiating stages of the metabolism in cell are bounded to them, and also a number of intermediate stages of functioning. Unconditional interest presents the influence of mutagenic factors, and particularly low doses of radiation (radiation background) on processes of the water binding by biopolymers of cell protoplast (the hydratation).

6. To Mechanism of Water Sorption by Biomacromolecules in vivo and in High Radiation

On established conceptions the colloidal-bounded water (water bound to polymers of cell protoplast) is an element fine regulatory mechanism of the direction and velocities of life-supporting processes [12, 13]. Any change connected with sorption of water by biomacromolecules can change essentially the picture of the metabolism and finally influence on growing and development of the biological systems. Let consider the hypothetical mechanism of water sorption by macromolecules.

Model 1. As well known, macromolecules swelling process is accompanied by merge entropy ΔS_s increasing resulted in decreasing of thermodynamic potential of the solution. However, number of the molecules of the solvent N_s occupies the part of biomacromolecule's volume, making its inaccessible for nodes of own biopolymer. Hereupon, at expansion of the volume, entropy of the system decreases on ΔS_p. Finally, this brings the balance of polymer-solvent system by fluctuations around balance saturation level $N_0 \sim n^{9/5}$ (from formula of Flory (where n – number of the nodes). The deviation from balance leads to arising of the force $\frac{dU}{dN} = F$, that prevents absorption of the solvent. Here:

$$U = kT\Delta S = kT(\Delta S_s + \Delta S_p) = kT(n - \frac{n^2}{N} + 1nN - \frac{3}{2}1nn - \frac{3N^{2/3}}{2n} - \frac{3}{2}) \tag{27}$$

For smaller deviations it is equitable the following expression

$$U(N) - U(N_0) \approx \frac{d^2U}{dN^2}|_{N_0}\ (N - N_0)^2 \tag{28}$$

Considering that variable number of the molecules of the solution is a single degree of the freedom, possible write systems Langrajian

$$\xi = \frac{mV_3^{2/3}N^2}{2} - \frac{1}{2}\frac{d^2U}{dN^2}|_{N_0}\ (N - N_0)^2 \tag{29}$$

where m and V_s – molecular mass of the solvent and volume of the molecules of the solvent accordingly, whence easy to get the frequency of free fluctuations ω_0 of numbers of the molecules of the solvent:

$$\omega_0 = \left[\frac{d^2U}{dN^2}|_{N_0}\ / mV_s^{2/3}\right]^{1/2} = \left[\frac{kT}{3n^{13/5}mV_s^{2/3}}\right]^{1/2} \tag{30}$$

Model 2. If the sorption of the solvent occurs in radiation condition, absorption process changes. Radiation breaking chemical bonds, is promote the formation of new bonds, enlarging number of the nodes (cross-links) in polymeric net. Hereupon, the sorption ability of macromolecule changes, since balance number of the molecules of the solvent is defined by number of the nodes in polymer.

As well known, in linear approach the number of nodes generated by radiation, can be described drawn near by equation:

$$\frac{dn}{dt} = \sigma In \tag{31}$$

where σ – section of defect formation, I – an intensity to radiation, n – a number of the nodes. The equation, describing fluctuations to water concentrations near new balance value, will:

$$\dddot{N} + \frac{kTN}{mn_0^{13/5}}\exp\left[\frac{13\sigma It}{5}\right] = 0\,, \tag{32}$$

decision which is defined by expression

$$N_s \approx N_0 \cos\left[\frac{10}{13(\sigma I)}\left[\frac{kT\exp(-2,6I\sigma t)}{mn_0^{13/5}}\right]^{1/2}\right] \quad (33)$$

Thereby, radiation not only changes biopolymers sorption possibility, but also exponentially smoothes the fluctuations of concentrations of water near balance value. Above brought analysis is actual for small doses of radiation. As a result of realization of radiation-induced sorption the possible scenario is breaking life-support processes and, in particular, processes of biopolymer hydrolysis and inclusion of the products of hydrolysis in metabolism. Coming from conducted analysis it becomes clear the insofar significant role of small influence on living organisms. So, in “grading” of calls small influences must be taken into account as leading to big risk. In this context, on our view, appropriately consider the possible mechanisms of enzymes degradation.

7. Models of Enzyme Degradation – Microscopic Approach

Under mutagenic factors influence it is interesting the consideration more deep hierarchy of the mechanism of the operation enzyme–substrate complex [14, 15]. Among the varied physical characteristic of enzymes one of background is reproducing the enzyme molecule after termination of the catalytic reaction. Also inhibition effects are well known, when other molecules interfere in different stages of enzymatic process inhibiting the reaction. However it is possible to select a number of experimental situations, when the efficiency of enzyme actions falls without visible reasons in the presence of new component in reacting mixture. One of the more impressive phenomena’s of the similar kind – some types of the biological objects ageing.

The subject of given approach is development of the mechanism of such biopolymer enzymatic activity fall. This effect hereinafter we shall name electronic-stimulated enzyme auto degradation (ESEAD).

The microscopic model 1. Among different microscopic theory of enzyme catalytic action, the motivated Blumenfield–Chernavskiy model, according to which catalytic reaction S + E ‘ESC EPC’ R + E includes four consequent stages: (1) quick, on which enzyme E and substrate S are formed enzyme–substrate complex (ESC), containing electronic radiation less transition in resting nuclei (the principle of the Franc–Kondon); (2) slow; when the geometric relaxation of ESC appears and ESC converts into enzyme-productive complex (EPC); (3) quick, on which electronic radiation less transition occurs under frozen EPK geometries, so the system moves to final therms of the reactions; (4) slow, when EPC disintegration occurs with forming the product R and reproducing the enzyme E. Obviously, scheme does not consider the enzyme degradation process, however, it allows to conduct the certain natural generalization, within the framework of which putted problem turns out to be allowed.

We shall come from fairness of using the adiabatic approach of Born–Oppenhamer to ESC, i.e. characterized ESC by wave function

$$\phi(q,\{Q_j\}) = \phi(q\{Q_j\})X(\{Q_j\}) \,, \tag{34}$$

where q – an electronic coordinates; $\{Q_j\}$ – an oscillatory modes. Wave function $\phi(q,\{Q_j\})$ describes the condition of the electron under frozen frames $\{Q_j\}$; wave function X($\{Q_j\}$) –frames (“nuclei”) oscillatory condition.

Unlike, we shall suppose that all oscillatory degrees of freedom are possible to divide into slow $\{Q_M^j\}$ and quick $\{Q_\delta^j\}$ modes. In a result of radiationless transition 1 stage current with probability

$$W_1 = \frac{2\pi}{\hbar} < \phi(q_1\{Q_j\}) \,|\, \hat{L} \,|\, \phi(q_1\{Q\}) > \prod_j < X(\{Q_j\}) \,|\, X(\{Q_j\}) > , \tag{35}$$

involving as slow, as quick modes.

Due to their typical time $(\tau_\delta^j << \tau_M^j)$ differences the electronic transition will bring fluctuations of the quick modes on background of the dullard relaxation of slow (structurally it can correspond to the fluctuations of the macromolecule separate fragment, including S-degrees of freedom, on background of the large-scale relaxation of the whole macromolecule). At that if ΔE_e – part of electron radiation less transition energy released on quick modes, then in processes of the quick fluctuations of macromolecule fragment can interfere and composed displacements along a certain coordinate of the reactions, corresponding to, for instance, turn of the macromolecule fragment (figuratively, on macromolecule “is tied nodule”). If energy barrier for realization of specified reactions is E_m, than, using Kossel approach, probability of this electronic-stimulated reaction is determined as

$$(1 - \frac{\Delta E_e}{E_T})^{S-1} e^{-\frac{E_T - \Delta E}{kT}} \equiv \beta \tag{36}$$

After overcoming the barrier E_T by electronic-stimulated way ESC will slowly relax on therm. If on this stage the catalysis occurs, that realization of the transition does not disturb the catalysis and transition to ESC formation. However on the following quick stage enzyme renewing is possible only at presence of “scythe” electronic-oscillatory transition, since for vertical turning the energy may be fall. “Sidelong” transition includes configuration change on quick modes $\{Q_{\delta_0}^j\} \to \{Q^j\}$ in $\{Q_{M_0}^j\} = const,$ that sharply reduces the probability a bit the factor of the Franc–Kondon on quick modes

$$(W_3 \sim \prod_j < X(\{Q_\delta^j = 0\}) \,|\, X(\{Q_{\delta_0}^j\}) > << 1) \tag{37}$$

Consequently, probability that enzyme will remain undegradable in act of one reactions will $\Omega^{(1)} = 1 - (1 - \gamma)\beta$. If enzyme completely useless in K-local electronic-stimulated conformations, that probability of remaining of catalytic activity is

$$\Omega^{(1)} = 1 - \left[(1-\gamma)\beta\right]^{k} \tag{38}$$

The obtained $\Omega^{(1)}$ values allow to separate all reaction classes with given enzyme on easy- ($\Omega^{(i)} << 1$) and difficult degraded ($\Omega^{(i)} \sim 1$). We shall note, that a number of important circumstance corresponds to degradation difficulty: first, than more degrees of freedom S includes the local conformation change, than Ω is higher; secondly, dimensionality and quality of the contact in FSC greatly influence on Ω, as with improvement of the contact a big part of released electronic energy ΔE_e dissolves in heat conducting process, so Ω increases.

Kinetics. Existence of electronic-stimulated degradation channel of enzyme greatly reflected on kinetics of the reactions and its velocity.

Let consider the manifestation of this effect on simple scheme.

$$\text{(a) } F_0 \xrightarrow{k_1}\xleftarrow[k_{-1}]{\quad} F_1 \xrightarrow{K_2} F_2 \xrightarrow{k_3} P\ ;$$

here F_0 – a concentration of the enzyme in initial condition; F_1 – a concentration of ESC; F_2 – a concentration EPC; P – a concentration of the products; the corresponding to constants of the reaction are specified beside arrows.

Let suppose now, that as a result of electronic stimulation a part of ESC occurs with formation of such degraded state, when realization even stage 2 is impossible. This corresponds to the scheme of reactions:

$$F_0 \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} k_4 \underset{F_3}{\overset{F_1}{\Updownarrow}} k_{-4} F_1 \overset{k_3}{\rightarrow} F_2 \overset{k_3}{\rightarrow} P$$

Concentration of degraded ESC is marked through F_3.

Let consider, that whole enzymatic reaction scheme 1→2→3→4 is realized, at that stage 1-electronic-stimulated, and on stage 3 (because of "scythe of" transition) return in condition F_0 is possible. Scheme is of the form of

$$F_0 \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} k_4 \underset{F_3}{\overset{F_1}{\Updownarrow}} k_{-4} F_1 \overset{k_3}{\rightarrow} F_2 \overset{k_3}{\rightarrow} P(+F_0)$$

$$\tilde{k}_{-1} \xrightarrow{\substack{\uparrow \mid \tilde{k}_4 \\ \rightarrow}} \tilde{F}_3 \frac{k_3 \rightarrow \tilde{P}(+F_0)}{\tilde{k}_4 \rightarrow P\left(+\tilde{F}_0\right)}$$

For all these events possible to write system of the kinetic equations

$$\text{(a)}\ F_0 = -kF_0S + k_{-1}F_1 + k_3F_3\,, \tag{39}$$

$$F_1 = k_1F_0S - (k_{-1} + k_3)F_1\,, \tag{40}$$

$$F_2 = k_2F_1\,; \tag{41}$$

$$\text{(b)}\ F_0 = -kF_0S + k_{-1}F_1 + k_3F_2 \tag{42}$$

$$F_1 = k_1F_0S - (k_{-1} + k_2 + k_4)F_1 + k_{-4}F_2 \tag{43}$$

$$F_2 = k_2F_1 - k_3F_2 \tag{44}$$

$$F_3 = k_4F_1 - k_{-4}F_3 \tag{45}$$

$$\text{(c)}\ F_0 = -(k_1 + \overline{k_1})SF_0 + k_{-1}F_1 + \overline{k_{-1}}\,\overline{F_1} + k_3F_2 + \overline{k_3}F_2 + k_4\overline{F_0} \tag{46}$$

$$F_1 = k_1F_0S - k_2F_1\,, \tag{47}$$

$$\overline{F_1} = \overline{k_1}SF_0 - \overline{k_2}\,\overline{F_1} \tag{48}$$

$$F_2 = k_2F_1 - k_3F_2\,, \tag{49}$$

$$\overline{F_2} = \overline{k_2}F_1 - \overline{(k_2} + \overline{k_3})\overline{F_2}\,, \tag{50}$$

$$\overline{F_0} = \overline{k_3}\,\overline{F_2} - k_4\overline{F_0} \tag{51}$$

For total stationary state with consideration of enzyme mass keeping $(E = \sum_i F_j) : F_j = 0$ we shall get reaction velocity

$$\text{(a)}\ v = \frac{k_2SE}{\dfrac{k_{-1}}{k_1} + \dfrac{k_2}{k_1} + (1 + \dfrac{k_2}{k_3})S}\,, \tag{52}$$

$$\text{(b)}\ v = \frac{k_2SE}{\dfrac{k_{-1}}{k_1} + \dfrac{k_2}{k_1} + \left[1 + \dfrac{k_2}{k_3} + \dfrac{k_4}{k_{-4}}\right]S}\,, \tag{53}$$

$$\text{(c)}\ v = \frac{\left(k_1 + \overline{k_2}\right)SE}{1 + \left[\dfrac{k_1}{k_2} + \dfrac{\overline{k_1}}{k_2} + \dfrac{k_1}{k_3} + \dfrac{\overline{k_1}}{\overline{k_3} + \overline{\overline{k_2}}} + \dfrac{k_1\overline{\overline{k_3}}}{k_2k_3}\right]S}\,. \tag{54}$$

Obviously that enzyme degradation role is more significant: in all events the velocity of reaction sharply falls from (a) to (b) and (c). In absence of the degradation effect $v_a = v_b = v_c$.

Such findings are equitable and for the other types of enzymatic kinetics.

Model 2. For maintenance of quasi-equilibrium state of the living system with environment work made due to energy-mass-exchange. It is interesting not only quantitative estimation of living system functioning, but also those qualitative changes, which accompany its vital activity and lead to ageing.

Let consider enzyme degradation and try to build the microscopic model of this process, basing on the most consequent beliefs about process of enzymatic catalysis.

As well known, full cycle of enzymatic reactions $E + S \rightarrow E + P$ includes the sequence of two pairs (four stages) "quick → slow" processes, moreover act of the stimulation occurs on the second stage during slow relaxation. The absence of degradation is provided by energy equality, i.e. returning of the system from relax state on initial therm under quick electronic transition (on the third stage). Unlike Blumenfeld, let take into account the presence in macromolecule not only slow $\left(Q_j^M\right)$, but also quick $\left(Q_j^\delta\right)$ of the degrees of freedom. Quick electronic transition on the first stage switch the system $\left\{Q_j^M;Q_j^\delta;\right\}$ from initial therm to final.

$$U_i\{Q_j^M;Q_j^\delta\} \rightarrow U_i\{Q_j^M;Q_j^\delta\} \tag{55}$$

Energy of the first electronic transition is distributed between Q_j^M and Q_j^δ thereby, that slow modes accumulate the potential energy, whereas quick – oscillate after receiving total energy E. Further two ways of the electronic transition are possible. In first the energy quickly relax for time

$$\tau_\delta \approx E/(dE/dt) << \tau_M\ , \tag{56}$$

where τ_M – time to relaxations of the slow modes. After "cooling" of quick modes the system slowly relax on coordinate Q_j^M, exactly on this stage the stimulation to reactions occurs. Return on initial therm carried on direction of the arrow. At the second way the energy E is distributed on modes Q_j^δ, but in these fluctuations their interference and act of concentration to whole energy on coordinate of the reactions occurs, corresponding to conformational transition in local area. If barrier of this transition − E_K, and a number of the quick modes is S, than probability of reactions is proportional to $(1 - (E_K/E(t)))^{S-1}$, that is leads from Kossel–Race–Ramsprager theory for gas monomolecular reaction. Release energy E can "dissolve" in ambience and so depend on time (for instance, for "outtake" of energy according heat conductivity law should to take into account that $E(t) = E/(\alpha t)^{3/2}$. After energy dissolution the relaxation on Q_j^M carried already on the other "nearby" groove along energy surface:

$$U_f\{Q_j^\delta = Q_{j_0}^\delta;Q_j^M\}\ , \tag{57}$$

where $Q^{\delta}_{j_0}$ – new positions of “quick” modes. The end of relax configuration after completion of the second stage is characterized by energy $U_f\{Q^{\delta}_{j_0};Q^{M}_{j_0}\}$. It is clear, that energy of the electronic transition on the third stage $\left(E_e^{(3)}\right)$ can be fail for probable transition:

$$E_e^{(3)} < U_i\{Q^{\delta}_{j_0};Q^{M}_{j_0}\} - U_{j_0}\{Q^{\delta}_{j_0};Q^{M}_{j_0}\}, \tag{58}$$

that will mean nonrepairability of initial state, i.e. enzyme degradation. Possible, however, indirect transition, for which:

$$E_e^{(3)} = U_i\{Q^{\delta}_{j};Q^{M}_{j}\} - U_f\{Q^{\delta}_{j_0};Q^{M}_{j_0}\} \tag{59}$$

At that inter-atomic distances change during electronic transition, that sharply reduces probability of radiation less transition due to the reduction of the Franc–Kondon factor:

$$\gamma = \frac{\prod_j \left\langle Q^{M}_{j} \mid Q^{M}_{j_0}\right\rangle \left\langle Q^{\delta}_{j} \mid Q^{\delta}_{j_0}\right\rangle}{\prod_j \left\langle Q^{M}_{j} \mid Q^{M}_{j_0}\right\rangle} \approx \left[\prod_j \left\langle Q^{\delta}_{j} \mid Q^{\delta}_{j_0}\right\rangle\right] < 1 \tag{60}$$

Under significant displacement of equilibrium positions of the quick modes from zero at realization of conformational transition on modes Q^{δ}_{j} value $\gamma << 1$.

Thereby, the probability of less degradation cycle of the enzyme functioning is:

$$W = W_1 + W_2 = P_1P_2\left[1-(1-E_K/E)^{S-1} + \gamma(1-E_K/E)^{S-1}\right] \tag{61}$$

where first component is correspond to the way without conformational transition on $\left\{Q^{\delta}_{j}\right\}$, the second – with consideration of local conformation, but with indirect electronic-oscillatory transition on the third stage. Here P_1 and P_3 – probability of electronic transition on stages 1–3 under resting atoms of macromolecule. Probability that enzyme, participating in N acts of enzymatic reaction, will remain undegradable, is

$$W_N = W^N = (P_1P_3)^N\left[1-(1-E_K/E)^{S-1} + (1-E_K/E)\gamma\right]^N \tag{62}$$

This formula is shown that small values E_K and γ, greater E and S promote the stability of the enzyme to degradation. With physical standpoint this corresponds to the level of small conformational barrier, great energy releasing on quick modes, strong displacement of equilibrium positions of these modes under local conformational transition to their greater number. These conditions can serve as criterion for division of enzymes on quickly and slowly degrading, and factor of resistance to degradation will be defined by equation:

$$\Omega = \left[1-(1-E_K / E)^{S-1} + (1-E_K / E)^{S-1}\gamma\right] = 1-(1-\gamma)(1-E_K / E)_{S-1} \tag{63}$$

Let consider the following events:

$E_K = 0.1$ eV; $E = 1$ eV; $S = 6$; $\gamma = 0.1$, then
$\Omega = 1 - 0.9(1 - 0.1)5 = 1 - 0.96 = 0.48$;
$E_K = 0.1$ eV; $E = 1$ eV; $S = 6$; $\gamma = 0.9$, then $\Omega = 1 - 0.1(1 - 0.1)6 = 0.95$.

So, in the first event strong degradation occurs, whereas in the second – weak. Necessary to note the dependency of enzyme degradation velocity from degree of substrate bounded and enzyme in kinetics in vivo. Reduction to dimensionality of the contact from three-dimensional (three-dimensional) to two-dimensional (surface) one-dimensional (linear) reduces the velocity to relaxations of free energy released on quick degrees of the freedom that enlarges the velocity of degradation.

The considered changes in biological system, caused, on the one hand, by enzymatic systems aging, from other hand – by influence of risk factors on living systems, are indicative on exclusive lability of biological life-support systems and “quick” response reactions on stressful factors. The most complex interactions, occurring in living systems in risk conditions, cannot be not reflected on the whole collections of the interconnected processes, running in organism. It is difficult to select the main and the secondary sections of the metabolism and pool processes, defining high functionality of living systems and their adaptability to condition of environment.

Let once again stop on the role of the small influences, in this instance chemical, on living systems. At that we use as example the experimentally obtained effect of negative root geotropism of the plants (tropisms – moving of the plants) [1, 16–18], which is described in term of the theories of the catastrophes.

8. Model of the Effect Negative Root Geotropism of the Plants – Phenomenological Approach

Certainly that phenomena of induced negative root geotropism can not be is uniquely interpreted in consequence of multistage and complexity of processes, leading to arising of the phenomenon. On these circumstance, the theoretical analysis of induced negative geotropism is possible to carry out on the base of phenomenological approach, taking into consideration greatly general features of the phenomena, for which the theories of catastrophes apparatus is adequate.

This theory has well proved in area of the studies with weakly developed mathematical structure. We shall translate the main regularities experiments on induced negative geotropism on topological language, i.e. having selected “flags of the catastrophe”.

First, in experiments it is obvious the existence of two steady directions of the growing: along and against the direction of gravity – shall name this as bimodality. Secondly, horizontal direction of the root growing does not observed in usual condition, in situation at least, when this possible observes – name this characteristic as unattainability. Thirdly, except chemical activator induced negative geotropism a number of additional factors exist, which in presence of inductor as stimulate, or suppress the growing against gradient of gravity – shall name this characteristic a divergence (for instance, raised concentration of the carbon dioxide in seeds growth chamber). Fourth, there are indications in experiments on possibility of reversibility of the change of the growing direction on the inverse phenomena, however under differing influenced factors in our experiments there is certain initial trend in the root growing downwards, and then upwards – shall name this characteristic an hysteresis. Fifth, in the experiments obtained, that amount of the negative geotropism inductor on seed surfaces may influence on the moment of the transition from normal growing root to anomalous (this is reflected on nature of curve), that may be connected to such characteristic as value of jumping and regime approaching to unceasing change of the growing direction.

Thus, these five characteristics – bimodality, unattainability, divergence, hesteresis and coexistence of jumps and unceasing regimes allow to consider the induced negative geotropism from positions of the theories of catastrophes. These characteristic are flags of the Toma's peak catastrophe on Witney surfaces of "assembly" type.

For Witney surface the canonical record is exists:

$$\chi^3 + \chi U_1 + U_2 = 0 \tag{64}$$

We shall produce the necessary adaptation of the values χ_1, U_1, U_2 to experiments on induced negative geotropism. Let χ – a velocity of the growing root toward gravity gradient field ("downwards") or against it ("upwards"). At that χ is less and more zero accordingly. Further, let control parameter U_2 is connected with concentration of the inductor (C_g) of certain smooth function:

$$U_2 = -f(C_g) \tag{65}$$

The function $f\,(C_g)$ must possess by several characteristics: she must be monotonous from variable $\eta = C_g - C_g^0$, where C_g^0 – certain threshold value; it must null at $C_g = C_g^0$. The suitable form of the expression can be the following:

$$f(\eta) = \sum_j a_j \eta^j \tag{66}$$

where $j = 1, 2, 3, 2n + 1$

For controlling parameter U_1 let place its equality to certain function $U_1 = \Phi(\xi)$ from generalized parameter ξ, formed from rest features of all growing conditions (moisture, the temperature, luminosity, composition of the soil solution, etc.).

Structure ξ is such, that ξ is simbatical to factor of the stimulation of the root growing. Function $\Phi(\xi)$ must possess the following characteristic. It should be positive at $\xi > \xi^0$, where ξ^0 is a certain threshold value; it should increase when $\xi - \xi^0$ increases. Suitable record can be the following:

$$\Phi(\xi) = e^{f(\xi-\xi^0)} - 1 \tag{67}$$

where

$$f(\xi-\xi^0) = \sum_j b_j(\xi-\xi^0);\ \mathrm{j = 1, 3, \ldots\ 2n + 1; j = 1, 3, 2n + 1} \tag{68}$$

So, we have:

$$U_1 = 1 - e^{\sum\limits_j b_j(\xi-\xi^0)^j} \tag{69}$$

$$U_2 = \sum_j a_j(C_g - C_g^0)^j \tag{70}$$

$$j = 1, 3, \ldots\ 2n + 1$$

The presented model works as follows. The effective root growing (upwards, downwards) is possible only $U_1 < 0$, $\xi > \xi^0$, i.e., when level of the stimulation by moisture, the temperature etc. is sufficient. Under small level of the stimulation ($\xi < \xi^0$) of the growing is absent. When there is growth ($\xi > \xi^0$), it is possible, two directions of the growing – up and downwards depending on concentrations of the inductor and, probably, a number of other factors – thick polymeric covering under essential participation of the inductor. If concentration is small $(C_g > C_g^0)$, that possible only growing downwards (the upper sheet of surface $U < 0$). If concentration of the inductor is great $(C_g > C_g^0)$, that possible growing root upwards (the lower sheet to surfaces under $U < 0$).

So, we get, that at $U_1 > 0$ and any U_2 no root growing at any concentrations of the inductor; at $U_1 < 0$ и $U_2 < 0$ – is realized growing downwards.

The built scheme modeled all five characteristics of the experiment. First, possibility of the growing only upwards and downwards – existence of two surfaces sheets. Secondly, impossibility of the horizontal growing – an unattainability of the condition along lines on surface. Thirdly, qualitative change the nature of the growing ("upwards-downwards") is realized in small variation of concentrations of the inductor (the deflection on U_2 relatively $C_g = C_g^0$ concentrations). Forth, existence on root "threshold", characterized the change of geotropic reaction ("upwards-downwards"), – histeresis nature of the transition from sheet on sheet of the Witney surface and jumping on it.

9. Conclusion

In conclusion it should be noted the following. In spite of the fact that phenomena's, which are described by presented models, have, at first thought, small resemblance, however they anyway illustrate the possible situations, which can appear under essential changes of environmental factors, risks connected with global climatic and ecological change, as well as participation of micro,- and mesoscopic level, responding on appearing risks. At that anthropogenic factor (as one of the risks) possible consider with standpoint of the trigger mechanism ("cock"). In this mechanism abrasion the marked and real existing new signs of the system – "inner planetary" are dominated, translating the system on new level. Other word, for formation of the new system and fastening new signs can be at sufficient small influences, to which the anthropogenic influence is possible refer. At that the role of nanolevels is concluded in forming of adaptation systems, which can change their functionality after determined limit. In these cases (the critical points) it is possible to expect changes an fractal dimensionality of macro particles (proteins, sugars and others), compression of genome, change of conformational mobility of genome fragments and possible transition in until understandable new types of quasi-chemical reactions.

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APPLICATION OF FULLEROID NANO-CARBON IN SORPTION TECHNIQUES

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Abstract. In the review article two main courses of application of the fullerene containing materials in sorption technology are examined. The first course is represented by nano-porous materials based on the fullerene soot, molded with various bonding materials. The second one is connected with modifying of traditional sorbents, such as active carbon, silica gel, zeolite, hopkalite and ion exchange resins with micro quantities of nano-carbon submitted by fullerenes, which provides for considerable improvement of sorption properties. Application of fulleroid nano-carbon in sorption techniques does not lead to increase of biological risks.

Keywords: sorption technology, nano-porous materials, sorbents

1. Introduction

Fullerene (in the condensed state – fullerite) is a comparatively lately synthesized material [1] with a unique structure resulting in specific properties, which define the ability to be used in various fields. Fullerenes are closed spheres (C_{60}) or spheroids (C_{70}, C_{84}), with their surface being formed by pentagons and hexagons. At the vertex of every penta- and hexatomic element atoms of carbon are situated. The central position among fullerenes occupies the C60 molecule, which is of maximum symmetry, leading to maximum stability.

In scientific publications information concerning application of fullerenes in construction of photodetectors, optoelectronic devices, superconductive materials, diamond and diamondlike films and also as dyes for copy devices are given [2]. The bulk of the publications deals with the ability of using fullerenes as a base for producing accumulator batteries [3, 4] with the principle of operation is settled on the reaction of hydrogen addition. This would provide for higher effectiveness, comparing to nickel accumulators, which are used nowadays, because fullerenes' hydrogen addition capacity is 5 times

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better at the expense of possible addition reaction. The possibility of using fullerenes as an admixture for propellants and lubricants is being discussed.

Fullerenes solutions in nonpolar solvents are characterized by nonlinear optical attributes, e.g. by abrupt decrease of transparency of the solution at specific conditions, which sets conditions for the possibility of application of fullerenes as optical limiters of laser emission intensity [5, 6].

Serious attention is paid to the problems of using fullerenes in medicine and pharmacology. E.g. the idea of invention of anticancer medicinal substances based on fullerenes' water-soluble endohedral compounds is being studied. One of the main problems is invention of non-toxic water-soluble fullerenes compounds that can be inserted into human organism and brought with blood to a certain organ [7].

So, we may say that range of fields for fullerene materials to be used in is rather broad.

In the present article authors are giving consideration to the possibility of using fullerene materials as adsorbents. Let's point out, that fullerene soots (FS), which are the products of carbon half-decay in a voltaic arc during the fullerene obtaining process and also depleted FS by fullerene extraction and which are by-products, possess the expressed sorption activity. Depending on the fullerene production technology and on the residual fullerene content in the FS, its sorption properties considerably vary. E.g. gas phase benzol sorption capacity (*Ws*) is 0.5–0.9 cm^3/g, while specific surface is (*Sspec)* 50 m^2/g. On the Tables 1 and 2 sorption properties of FS with various fullerenes content are given [8].

TABLE 1. Specific surface of FS with various fullerenes content

Fullerenes content in the initial soot, mass%	1.0	6.1	6.5	9.6	10.0
Argon-defined specific surface, m^2/g	600.0	187.0	287.0	268.0	350.0

Thus, fullerene materials can be regarded as sorbents, which are not inferior to active coils in some characteristics of pore structure.

TABLE 2. FS and activated carbon AG-3 porous structure parameters, estimated using the TDMFT (three-dimensional micropore filling theory) according to benzol vapors adsorption isotherms

Specimen	Ws	Vmi	Vme	Eo, kJ/mol
$FS_{10,0}$[a]	0.55	0.41	0.14	22.7
$FS_{0,1}$	0.93	0.83	0.10	21.8
АГ-3	0.51	0.31	0.21	19.7

Vmi. Vme – micro- and mesopores volume respectively; Eo – characteristic energy of adsorption

[a] The index mark hereinafter defines the mass concentration of the fullerenes in the carbon soot residue estimated using spectrophotometric method

2. Fullerene Materials Obtaining Technology and Courses of Their Usage as Sorbents

The usage of fullerene materials for sorption purposes is divided into two main courses. *First one* is connected with the usage of FS proper, as well as its derivates in a molded form as sorbents and sorptive products components. *Second one* is that of using fullerenes to modify different sorbents. The ways of using fullerenes to obtain adsorbents are schematically depicted in the Fig. 1.

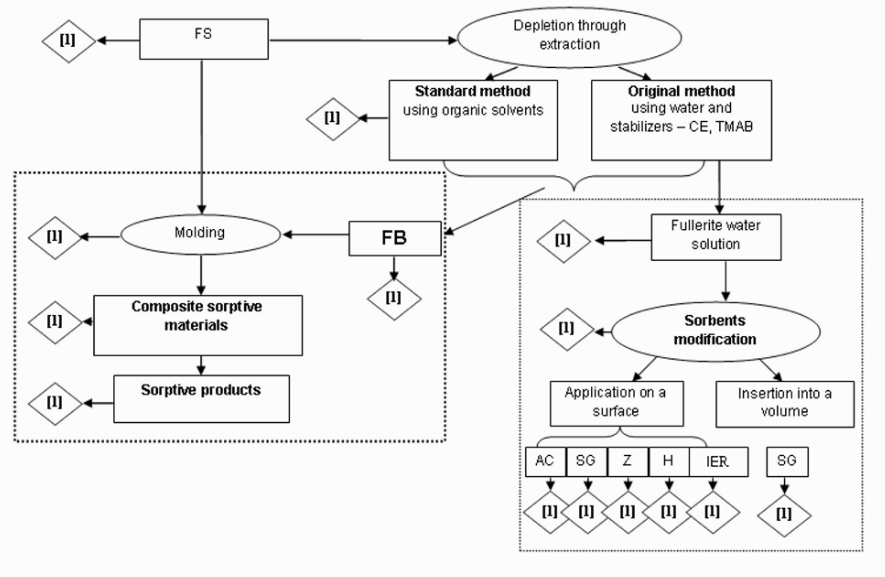

Figure 1. Main ways of obtaining fullerene containing materials and their usage for producing sorbents. AC – active carbon. SG – silica gel. Z – zeolite. H – hopkalite. IER – ion exchange resins. FS – fullerene soot; FB – fullerene black (soot after fullerene extraction)

3. Fullerene Containing Sorbents Obtaining Technologies

3.1. FULLERENE SOOTS MOLDING

As mentioned above. FS has considerable sorption properties [8]. But its direct usage as a sorbent is rather difficult either in static or in dynamic conditions. In the first case it is connected with expressed hydrophobic properties and bad moistening by water, in the second – with high dispersiveness of soot of 0.5–20 μm, that makes transmission of gas or liquid stream through it difficult. That’s why molding FS into granules or some other forms are necessary. Lately various technological methods are brought about aiming at obtaining composite sorptive materials (CSM) using different types of binding agents

[9], preferably polymeric systems. On the Table 3 the connection between dispersiveness of the polymeric system and the structure of the CSM obtained is depicted.

TABLE 3. The connection between the CSM structure and sizes of particles of polymeric systems used as binding agents

Polymeric system	Molecular	Colloidal	Coarse-dispersed
	Polymeric solutions	Latexes, fine dispersed emulsions, suspensions	Cross-linked polymeric forms, dispersive suspensions, emulsions, powders
Particle size	d < 10 Nm	d < 1 μm	d > 1 μm
CSM structure			

In the works [9, 10] sorption properties are given concerning materials that were obtained on the basis of binding agents that have different sizes of polymeric particles in the polymeric systems used. Depending on the size of the polymeric system particles represented by three types of polymers – solution, emulsion and coarse-dispersed powder three types of CSM can be pointed out. Their schematic structure is given on the Table 3. The size of binding agent and of filler is one of the main factors that influence the technological process of production in particular the time of components mixing process as well as the material structure at the expense of “filler-binding agent” interaction. Seems quite natural that changing of the sorbent structure one may intentionally change the field of usage.

FS was included by us into the CSM content using the following polymeric systems: polyacrylamide (PAA) molecular solution, fluoroplastic emulsion and coarse-dispersed phenylone powder.

CSM obtaining technology with selection of optimal conditions of producing them is rather well worked through and in a simple form is given on the scheme (Fig. 2).

During CSM production using polymeric molecular solutions a thin film forms that limits diffusion of adsorbate molecules which decreases sorption activity of the material. That’s why additional steps of the process take place that aim at protection of the fillers’ active surface [9, 11]. Particularly the usage of so-called “preservative agent” during the process of mixing of the components allows to protect the filler active centers from lockup during the interaction “polymer – soot” when being mixed and thus save high sorption properties of the material obtained. Surface-active agents (SAA) were used as such an agent. Their usage allowed not only to reduce the “polymer – soot” interaction, but also to decrease having increased effectiveness of the mixing duration at the expense of improving the soot moistening and uniformity of distribution of the filler in the polymeric component.

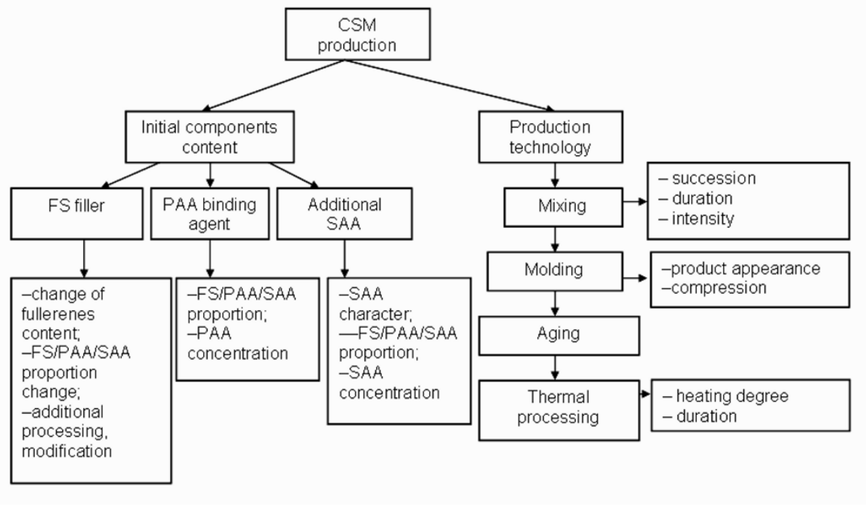

Figure 2. CSM obtaining scheme by the example of fullerene soot and polyacrylamide with surface-active agents. Selection of optimal conditions for molded material obtaining

Sorption properties of the CSM produced using various polymeric systems are given on the Tables 4–6 [12].

Table 4 shows that the fullerene material has high sorption properties. Benzol adsorption amount values are superior to those of active carbons. Besides that the solidity of such composite sorption materials is superior to solidity of technological active carbons seems to be worth pointing out.

TABLE 4. Sorption properties of the FS molded using the PAA water solution

Sorption material type	Ws C_6H_6, cm^3/g	X^{mb}, mg/g	E^{Cu}, mg/g	Sspec, M^2/g	Solidity, %
Molded FS_2	0.86	139	206	283	75
Molded $FS_{8.5}$	0.94	146	231	320	80
Molded $FS_{10.0}$	0.52	138	240	142	80
Molded $FS_{12.5}$	0.73	139	266	194	80
Active carbon SCT-6A	0.78	171	50	1250	≥ 67
Silica gel KSK-1	0.95	132	10	170	≥ 70
Active carbon OC-A	0.49	225	–	600	–

X^{mb} – methylene blue capacity; E^{Cu} – copper cations capacity

TABLE 5. Sorption properties of the initial FS and of CSM based on it and molded using fluoroplastic dispersion

Material	E, kJ/mol	Ws cm^3/g	Vmi	Vme	Vma	Y	Sspec, m^2/g
$FS_{4.2}$	20.8	0.67	0.22	0.52	0.86	1.00	310
CSM	20.1–23.0	0.30-0.45	0.03–0.05	0.25–0.42	0.21–0.27	0.89	130–158

Y – material hydrophobic properties

Fullerene soots molding with using fluoroplastic emulsion leads to considerable change of material properties (Table 5), e.g. fullerene soots thus molded are characterized by 1.5–2.0 times decreased volume of Ws mainly because of decrease of microporosity. The volume of micropores thus processed becomes 4–7 times smaller, specific surface becomes 2.0 – 2.4 times smaller compared to initial soot characteristics.

TABLE 6. Characteristics of porous structure of CSM based on FS and coarse-dispersed powder of fenilone SF-2

Material	E, kJ/mol	Vmi cm^3/g	Vme	Sspec, m^2/g
$FS_{4.2}$	20.8	0.22	0.45	366
80 % $FS_{4.2}$ + 20 % SF-2	19.2	0.16	0.37	285
70 % $FS_{4.2}$ + 30 % SF-2	18.0	0.14	0.33	244
60 % $FS_{4.2}$ + 40 % SF-2	16.9	0.11	0.29	205

Table 6 shows that the sorption properties decrease after coarse-dispersed powder-like polymer insertion is practically additive to the amount of the polymer inserted. The decrease of adsorption capacity practically equal to the amount of the polymer inserted characterized by absence of sorption pores is based on the presence in the content of CSM nonporous, coarse-dispersed binding agent not locking up the porosity of sorbent-filler as it is clear from the given estimations.

Thus by using various polymeric systems sorbents of different structure and with different sorption properties can be obtained.

It’s necessary to point out that in spite of rather good sorption properties. These materials are inferior to traditional sorbents such as active carbon and silica gel mainly in terms of cost price what is connected with high price of FS. That’s why the usage of such sorbents is reasonable only in highly specific matters where the price of materials wouldn’t be so important.

One of the fullerene materials interesting properties that may be used in specific sorption processes is their ability to change sorption activeness depending on the conditions of illumination [13]. On the Table 7 fullerite and FS benzol sorption capacity is given. Obviously the adsorption amount in the light is 1.5–2 times increased comparing to that estimated in the absence of lighting.

Such effect is characteristic only for fullerenes containing materials while sorption properties of traditional sorbents do not depend on the lighting conditions.

TABLE 7. The influence of visible lighting on the fullerene materials and traditional sorbents benzol sorption capacity

Material	Illumination rate	$A(C_6H_6)$, g/g
C_Σ	Light absence	0.15
	Light	0.38
$FS_{4.2}$	Light absence	0.40
	Light	0.63
Active carbon	Light absence	0.38
	Light	0.38
Industrial carbon	Light absence	0.34
	Light	0.33
Silica gel	Light absence	0.68
	Light	0.69

As mentioned above. FS is a highly disperse powder that makes its usage considerably more difficult. That’s why sorption products based on an optical element were introduced to carry out sorption processes in the conditions of changing illumination (Figs. 3 and 4).

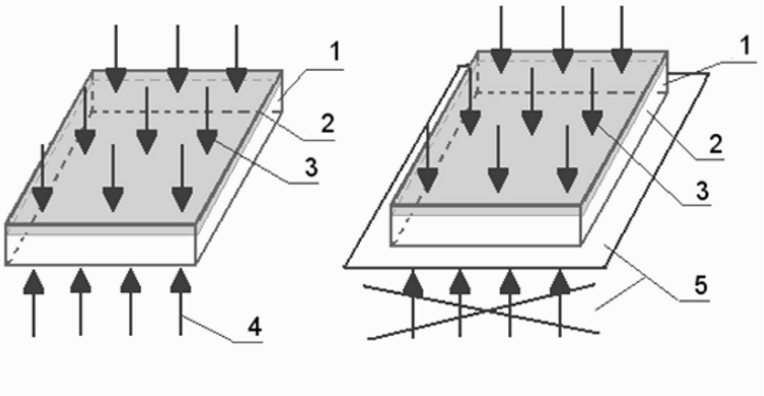

Figure 3. Schematic picture of sorption process with and without lighting
(1) sorption product CSM; (2) applicated on a lightguiding plate (glass). CSM consists of fullerene soot and fluoroplastic emulsion; (3) input and output of adsorbate (gas mixture); (4) lighting – light source; (5) light isolation

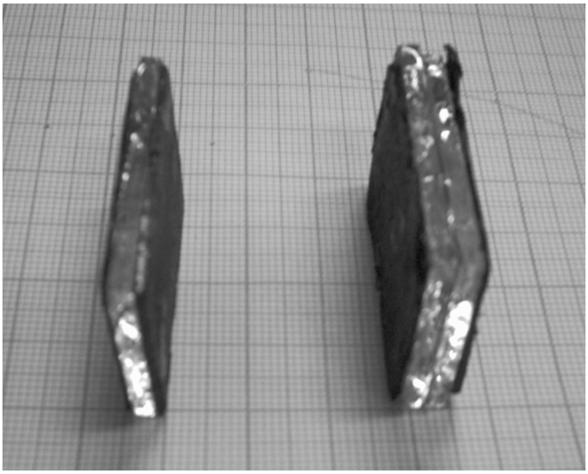

Figure 4. Photo of sorbent products based on the fullerene soot

Sorption process experiments in different lighting condition with these products showed that volume of sorption capacity at constant volume of organic compounds (benzol) vapor pressure can be varied by transmitting the light in the sorption system through a lightguide. As the Table 8 shows carrying on the process while the light power is transmitted through the lightguide results in 1.6–2.3 times increase of material sorption capacity. Thus by changing the rate of illumination the processes of sorption-desorption in carbon materials of fulleroid type can be controlled.

TABLE 8. Volume of sorption units sorption capacity in various conditions. The duration of the experiment is 24 h

Experiment conditions	Sorption volume, g/g at the sorbent layer thickness:	
	0.5 mm	2.0 mm
Lighting absence	0.32	0.21
Lighting by four diodes	0.50	0.44

Along with the usage of FS for obtaining CSM the usage of depleted FS also called fullerene black (FB) is also perspective way. On the Fig. 5 two methods of fullerene extraction from soot are given. The first of them is traditional using organic solvents (e.g. o-xylol) in the Soxhlet's apparatus. It's based on high fullerene solubility in these substances. The second one which is original method is based on fullerene solution in the water using various stabilizers [15, 16]. Steps of conducting these processes are schematically depicted on the Fig. 5.

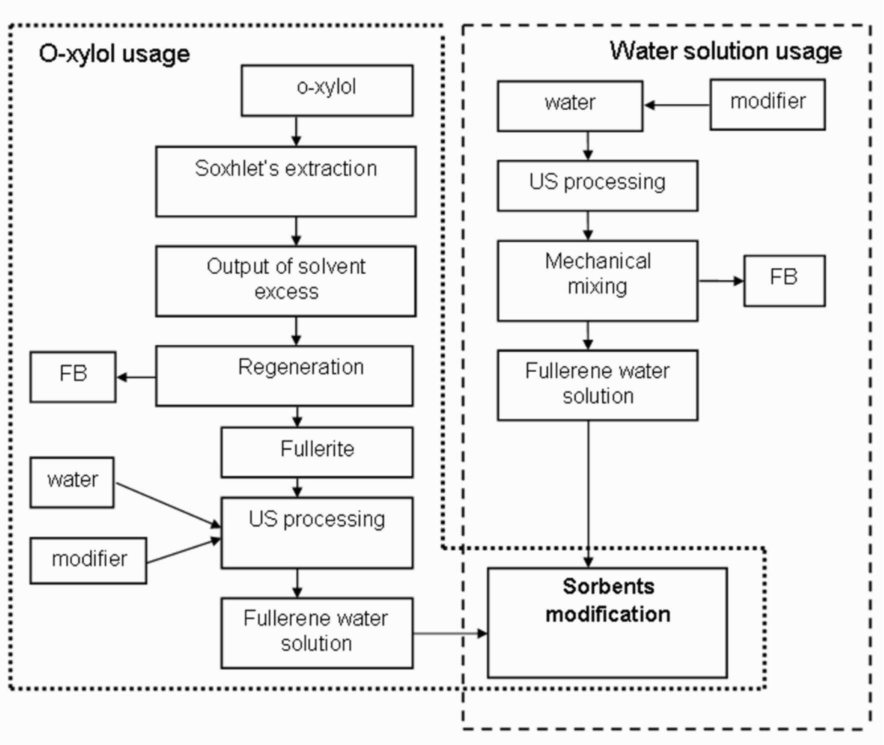

Figure 5. Scheme of fullerene extraction from FS using water solutions and o-xylol for obtaining FB and adsorbents modifying solutions

Optimal parameters of carrying out the process of extractions using water solutions were worked out by authors what allowed to obtain FB with 1.3% of mass fullerene content that is characterized by good sorption properties. In spite of o-xylol being more effective as extractant (0.1% of fullerene in FB) the FB obtained by water extraction is not inferior to initial FS and industrial sorbents in sorption properties. Sorption properties of FB which are obtained according to these two methods are given below in the part dealing with perspective fields of fullerene containing sorption-active material usage (Table 11).

The advantage of water systems for fullerene extraction from FS is a by-product of the process being fullerene water solution which can be used for sorbents modifying aiming at improvement of their sorption activity.

3.2. FULLERENE MODIFICATION OF ADSORBENTS

The second field of using fullerene containing materials in sorption technology is adsorbent modifying for effectiveness improvement. As it was shown by us [17, 18] insertion of fullerenes into adsorbents results in considerable improvement of their sorption properties. On the basis of broad range of porous adsorbents such as active carbons zeolites, silica gels, hopkalite, ion exchanging resins high-quality sorbent materials are obtained by modifying with fullerenes micro admixtures at the amount of (5–20) × 10^{-3}%. At the first step various organic solvents were used to apply fullerene on a porous carrying unit. Next one was conversion to more ecological technologies allowing to use for these purposes fullerene containing water systems where crown ether (CE) and tetraalkylammonium derivates. E.g. tetramethylammonium bromide (TMAB) were used as organic admixtures-stabilizers of fullerenes in the water [15, 16]. The technology of obtaining fullerenes water solution using CE lies in the interaction according to the “host–guest” principle. Depending on the size of the CE cavity the structure can form where per one CE molecule there is one to two fullerene molecules or per one fullerene molecule there are two ether molecules. Formation of fullerene compound with tetraalkylammonium salt comes as a result of electrostatic interaction. Thus formed two structured are water-soluble and thus fullerenes come to water solution.

The processes of application of modifying admixture on a porous surface are equal to that of obtaining carbons-catalysts [19] and consist of range of steps consisting of impregnation of sorbent with fullerenes solution and thermal processing aiming in removal of the solvent surplus.

Besides fullerene application on the surface of the sorbent hereinafter referred to as surface modification within the course of works the insertion of fullerene into the sorbent volume during its obtaining was exercised on the example of silica gel (three-dimensional modification [Fig. 6]).

During such modification fullerene is mainly situated inside the globular silica gel structure that to a certain degree eliminates the direct contact between adsorbat and fullerene-modifier.

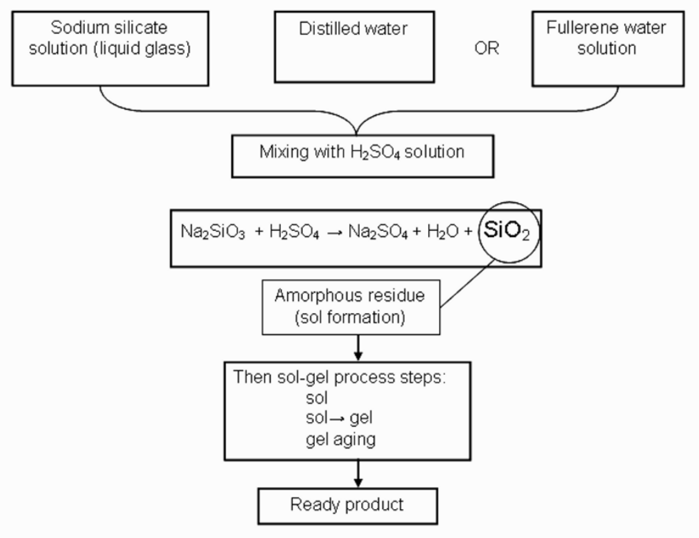

Figure 6. Obtaining of “three-dimensionally modified” with fullerenes silica gel from sodium silicate

3.3. THE USAGE OF FULLERENE CONTAINING MATERIALS IN SORPTION TECHNOLOGIES

Depending on various properties revealing fullerene containing materials can be used in different fields of sorption technology. On the scheme (Fig. 7) main fields of their usage together with technology of their obtaining.

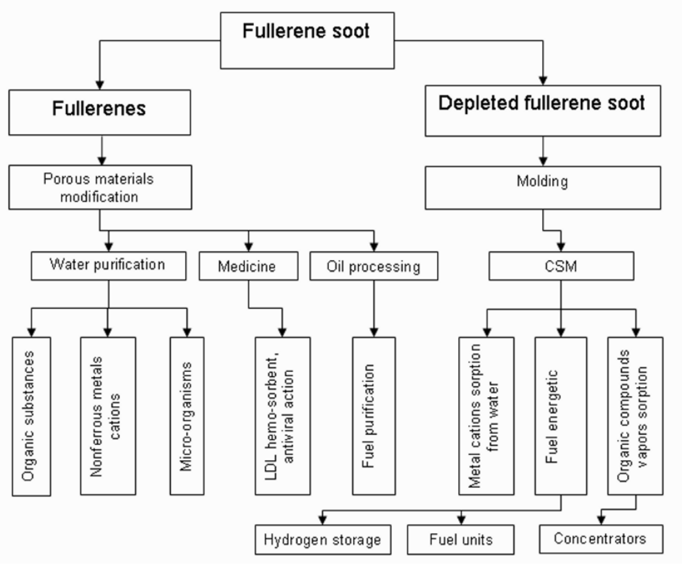

Figure 7. Fullerenes containing materials usage in sorption technology

Dealing with fullerene modified materials according to the type of porous carrier also fields can be pointed out that depend on the type of adsorbate what is shown on the Table 9.

TABLE 9. Fields of usage of fullerene containing materials

Field of usage	Sorbent	Medium	Adsorbate components
Water processing (potable water. wastewaters. galvanic)	Active carbon	Water	Organic compounds Metal ions Microorganisms
Medicine (blood plasma LDL purification)	Silica gel	Blood	Colloid systems – LDL
Oil processing (fuel purification)	Zeolite	Paraffin’s	Aromatic compounds/sulfur
Life-support systems	Active carbon	Gas–air	Organic compounds vapor
	Catalyst – hopkalite	Gas–air	Catalytic oxidation CO

Let us give more detailed consideration to fullerene containing materials usage in sorption technologies.

3.3.1. *Fullerene containing materials usage in sorption from aqueous mediums*

Fullerene modified active coil can be used for complex purification of water mediums from organic compounds metal cations and microorganisms. In [20] is shown that fullerenes application on active carbon results in its sorption capacity increasing with respect to metal cations: copper (1.5–2 times increase), silver (2–2.25 times) and lead (40–60% increase) and the maximum increase is observed in the specimen with fullerene content of 20 µm/g. Modified by fullerenes active carbons also are characterized by high antibacterial activity on *E. coli* (Table 10).

TABLE 10. Sorption properties of active carbons modified with water solution fullerenes with stabilizers: crown-ether (AC-F-crown) or tetramethylammonium bromide (AC-F-TMAB)

Specimen	Sorption ability according to substances, mg/g					*E. coli*,
	Cu^{2+}	Pb^{2+}	Butanol-1	o-xylol	Chlorben-zene	Pcs/ml
AC init.	53	110	0.3	0.69	1.35	30
AC-F-crown	200	–	0.9	0.99	1.83	1
АУ-F-TMAB	230	160	0.9	0.78	1.83	0

Composite sorbent products based on FS with different fullerene content possess high volumes of sorption capacity with respect to copper cations at low concentrations that are superior to traditional sorbents that is shown on the Table 11.

TABLE 11. FS and FB based CSM properties

Filler	Fullerene soot %	Soot processing Solvent (stabilizer)	Binding agent	W_S, cm^3/g acc. to C_6H_6	Sspec, m^2/g	A (Cu^{2+}), mg/g		
						$C_0 = 0.05$ g/l	$C_0 = 0.1$ g/l	S, %
Initial FS	7.8	–	–	0.51	310	4	66	–
			PAA	0.48	265	3	52	80
			FE	0.38	220	3	20	65
Depleted FS	1.3	Water(CE)	–	0.98	460	14	78	–
			PAA	0.50	340	16	64	85
			FE	0.30	250	8	24	65
	3.8	Water (TMAB)	–	0.65	420	10	72	–
			PAA	0.45	320	8	59	85
	0.1	O-xylol	–	0.86	460	10	74	–
			PAA	0.55	340	10	58	85
Silica gel	–	–	–	0.45	400	3	57	–
КУ-23	–	–	–	–	30	5	31	–
AC	–	–	–	0.68	1,000	8	64	–

S – abrasion solidity; КУ-23 – cation-exchange pitch

3.3.2. *Fullerene containing materials usage for sorption from non-aqueous liquid mediums*

The example of sorbent usage for purification of non-aqueous liquid mediums is paraffin hydrocarbons purification from aromatics, e.g. motor oil. The experiments results in dynamic conditions and process of adsorbent regeneration influence are shown on the Table 12.

Table 12 shows that fullerenes application on zeolite NaX results in a considerable increase (1.7–2.0 times) of volume of hydrocarbons purified and duration of protection time (2.0 times) compared to initial zeolite in dynamic conditions. That points out the considerable advantage of using fullerene modified adsorbents (V cm^3 – volume of n-alkanes (saturated hydrocarbons). $A_{d\,0.01}$. mg/g – materials dynamic adsorption capacity up to the 0.01 % mass concentration. $K_d = A_{d\,0.01}/A_b$ – balanced dynamic adsorption capacity usage coefficient $K_{0.01}$ % mass part – 0.01% aromatics containing production obtaining coefficient.

TABLE 12. Techno-economic and operational characteristics of paraffin hydrogen dynamic purification process

Cycle No	V, cm^3	$A_{d\,0.01}$, mg/g	$K_d = A_{d\,0.01}/A_b$	$K_{0.01}$, % mass part	K_Σ, % mass part
1	1,000	4.50	0.77	414	966
5	1,100	5.00	0.83	462	1,007
11	970	4.50	0.80	414	938
1[a]	590	2.65	0.51	241	569

[a] non-modified zeolite

3.3.3. *Fullerene containing materials usage for medical sorption*

Fullerenes modified silica gels can be used as medical sorbents first in atherosclerosis treatment at the expense of showing sorption activity on low density lipoproteins (LDL) (Fig. 8), second as antiviral material which is allowed by the possibility of singlet oxygen obtaining which leads to elimination of virus.

During LDL sorption from blood plasma sorption capacity improvement is observed under fullerene insertion (Fig. 8), but in this case the amount of fullerenes applied must be 1–5%. Probably for given large-sized object the dispersion interaction pattern does not appear under the low content of fullerenes in the system. Silica gel sorption capacity improvement with respect of LDL is connected with adhesion improvement or colloid adsorption directly on the fullerene situated directly on the silica gel surface.

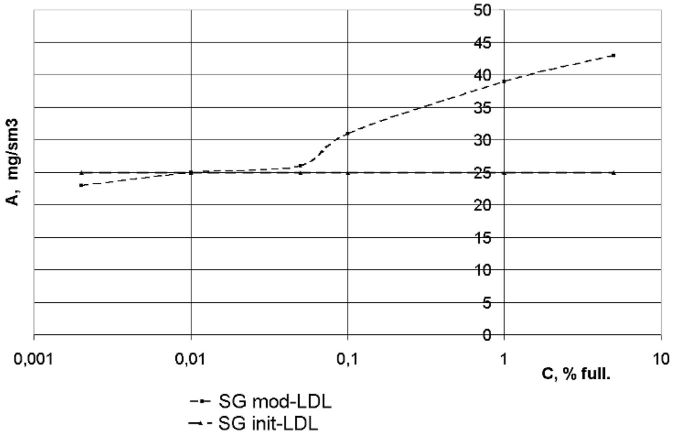

Figure 8. Silica gel KSK-1fullerene content influence on its sorption properties with respect to LDL

Besides mentioned above fullerene modified materials are characterized by high selectivity with respect of LDL and do not sorption high density lipoproteins (HDL). Materials obtained are also characterized by high biological concordance.

3.3.4. *Fullerene containing materials usage for sorption from gas mediums. Sorption chromatographic concentrators*

The phenomenon expressed by influence of illumination intensity on fullerene materials sorption properties can be used in various technologic fields, e.g. as concentrators in chromatography. One of the imperfections of concentrators is using temperature for desorption that in some cases may result in destruction of adsorbate. Under desorption using illumination changes such phenomenon does not appear.

The illumination influence on sorption process can be observed on the example of a chromatographic curve given on the Fig. 9.

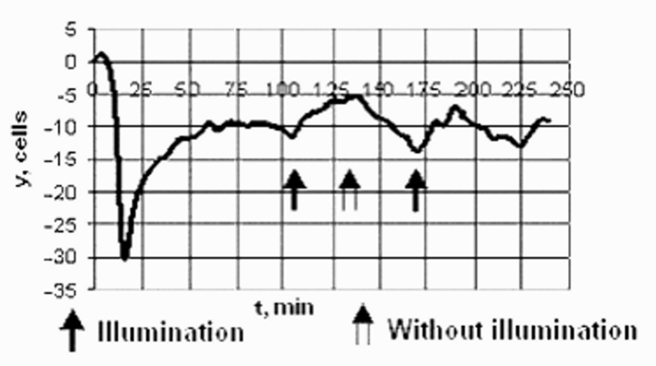

Figure 9. Chromatographic curve of illumination conditions influence on benzol sorption–desorption from gas phase

Figure 9 shows that under the illumination adsorbate accumulation occurs (benzol in this case) in the material and under change of conditions desorption takes place with gas phase adsorbate increasing which is registered by hydrogenic-ionization detector. Figure 10 obviously shows the rate of potentiometer analog recorder response with and without light.

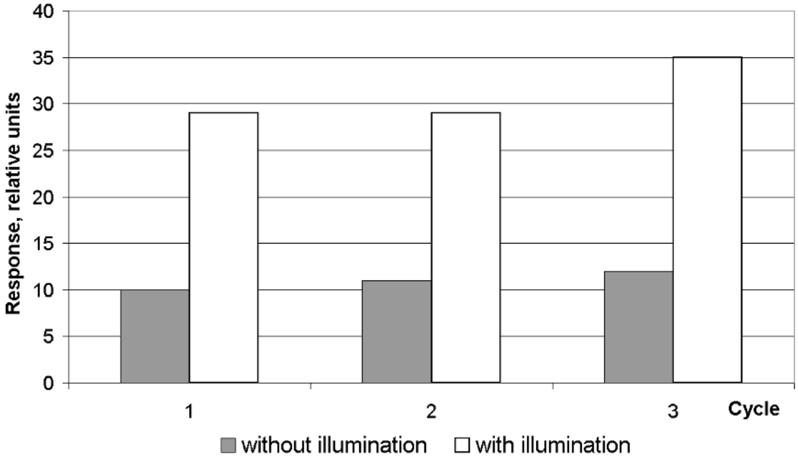

Figure 10. Benzol sorption rate response to the change of lighting

3.3.5. *Sorption in the moist mediums*

Fullerene modified materials can also be used for sorption from gas mediums. E.g. adsorption of organic microadmixtures on the active carbon from moist gases is one of considerable problems of life support. On the Fig. 11 dynamic curves of active carbons are given that characterize the effectiveness of gas mediums purification from micro amounts of organic compounds under stream high density conditions. Such researches were carried out for AG-5 and SKT-6A types of coil with fullerene content of 20 µm/g. given volumetric consumption of 0.5 dm^3/min. relative humidity 93% with initial benzol vapor concentration of 0.1 mg/dm^3.

Basing on the given diagram a conclusion can be made that under fullerenes application on the porous surface of active carbons (AG-5 and SCT-6A) considerable improvement (2 times) of adsorbent charge protection time with respect of benzol vapors under dynamic conditions and high (93 %) stream humidity. Given effect is probably connected with adsorbent hydrophobic properties improvement.

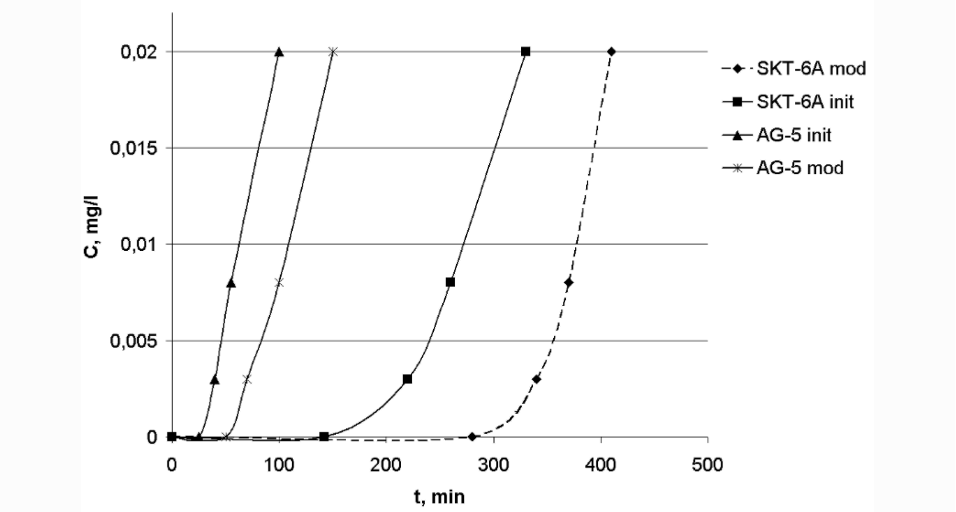

Figure 11. Diagram of benzol vapor concentration behind the active carbon layer AG-5 and SCT-6A dependency on duration under the initial concentration of 0.1 g/dm^3 and high (93%) stream humidity

4. Conclusions

Two main ways of obtaining fullerite-based sorption materials are settled. The first one is connected with depleted fullerene soots producing using water solutions containing fullerenes organic stabilizers with further molding into nano-carbon sorption products. The second one is represented by porous and massive adsorbents and catalysts modifying by nano-carbon submitted by fullerenes micro amounts under their insertion at the time of producing into material volume as well as on the porous adsorbent active surface. The fields of fullerene materials usage are represented by sorption processes, either in gas or in liquid (including aqueous) mediums where fullerene containing materials possess considerable advantage over the analogs. Application of fulleroid nano-carbon in sorption techniques does not lead to increase of biological risks.

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ASPECTS OF MICROPARTICLE UTILIZATION FOR POTENTIATION OF NOVEL VACCINES: PROMISES AND RISKS

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Abstract. Many recombinant vaccines against novel (HIV, HCV) or ever-changing (influenza) infectious agents require the presence of adjuvants/delivery vehicles to induce strong immune responses. The necessity of their improvement led to the major effort towards development of vaccine delivery systems that are generally particulate (e.g., nano- and microparticles) and have comparable dimensions to the pathogens (viruses or bacteria). The mode of action of these adjuvants is not fully understood but implies the stimulation of the innate or antigen-specific immune responses, and/or the increase of antigen uptake or processing by antigen-presenting cells (APC). Moreover, enhancement of adjuvant activity through the use of micro- and nanoparticulate delivery systems often resulted from the synergistic effects producing immune responses stronger than those elicited by the adjuvant or delivery system alone. Among particulate adjuvants, biodegradable micro- and nanoparticles of poly(D,L-lactide-*co*-glycoside) (PLGA) or poly(D,L-lactide) (PLA) have been reported to enhance both humoral and cellular immune responses against an encapsulated protein antigen. Cationic and anionic polylactide *co*-glycolide (PLG) microparticles have been successfully used to adsorb a variety of agents, which include plasmid DNA, recombinant proteins and adjuvant active oligonucleotides and are also currently tested in several vaccine applications. Another approach envisions specific targeting of APC, especially peripheral DC and exploitation of particulate systems that are small enough for lymphatic uptake (polystyrene nanobeads). Micro- and nanoparticles offer the possibility of enhancement of their uptake by appropriate cells through manipulation of their surface properties. Still, questions regarding toxicity and molecular interaction between micro- and nanoparticles and immune cells, tissues and whole organisms remain to be addressed. These risks and other possible side effects should be assessed in detail especially if mass-production and massive administration of such preparations is to be considered.

Keywords: vaccine, adjuvant, targeted delivery, nanoparticle, microparticle

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1. Introduction: Vaccination Goes "Nano" – Why?

Prevention of infectious disease through vaccination is one of the most important achievements in the history of medicine. Its effects on the mortality reduction are enormous and may be compared only to those caused by the establishment of safe water supply [1]. Adaptive immunity against infectious disease, i.e. lack of infection in previously exposed individuals has been noted for a long time, most famously by Athenian historian Thucydides in 5th century BC. It is often said that first recorded attempts of vaccination against infectious disease (smallpox) go back to AD 1000. in China, but they cannot be verified till 16th—17th centuries, when the procedure of variolation started to be used on a reasonably large scale. In the end of XVIII pioneering works of Jenner and his less-known predecessor Jesty on vaccination against smallpox with cowpox paved the way to modern vaccination, whose true founder in a scientific sense was Louis Pasteur [1]. Interestingly, first successful vaccines were launched against two viral diseases, smallpox and rabies. Smallpox became first and only infectious disease to be eradicated in 1967–1977 [2]. It is commonly said that Jenner's work constitutes the first deliberate use of live virus vector as a vaccine, but we should also note that it was first recorded use of nanotechnology (virion size of a poxvirus is around 200 nm in diameter and 300 nm in length). We should also mention that the problems of unknown side effects, possibility of human infection with new or incompletely inactivated virus and as well as initial difficulties of social acceptance of vaccination that were faced by both Jenner and Pasteur are not dissimilar from the risks that nanotechnology of vaccination encounters today. In fact, these problems have persisted for more than 200 years and yet many other major diseases have been put under control with the help of vaccination. These include, to name just a few, diphtheria, tetanus, yellow fever, pertussis, poliomyelitis (currently targeted for eradication by WHO), measles, mumps and rubella. And this list is far from complete.

At the same time, it is important to remember that a number of vaccine-related disasters and incidents were caused over this period of time, all of them due to failures in vaccine manufacturing techniques. Specifically, during the 1st century of scientific vaccination (post-Pasteur) three types of vaccines were generally used: live-attenuated (weakened), killed viruses/bacteria and subunit or extract (chemically or biochemically processed and thus detoxified, the technique that mostly important in anti-toxin vaccination, i.e. against diphtheria). It is thus of no surprise that there were instances of incomplete attenuation, sterilization or detoxification of vaccine products (see [2] for details). While historical role of early-generation vaccines cannot be underestimated, current awareness of health and safety issues resulted in much higher standards of safety and it is true that many past vaccines would not even meet the minimum standards of today. New techniques of vaccine development that may enable a generation of safe, effective and economically feasible vaccines are being actively explored. Additionally, it is now clear that successful vaccination against several newly-discovered infectious agents as human immunodeficiency virus (HIV), hepatitis C virus (HCV) or severe acute respiratory syndrome (SARS) will require the development of radically new vaccine concepts and products.

There are several types of novel vaccines or vaccine components the utilization of which is not mutually exclusive. In fact, their complementary use may be even required in some cases. Firstly, there are recombinant molecules: proteins or nucleic acids (NA; DNA vaccines have been tested extensively over the last decade, RNA vaccines are now actively pursued in several experimental systems, but relevant information is scarce at the moment save for RNA alphaviral replicons). Protein antigens induce immune response directly, while NA vectors encode necessary antigens and produce them upon their introduction into organism. Secondly, these molecules may be carried or delivered by biological or chemically produced vectors, separately or in combination. These vectors are known to tremendously augment the immune response induced by proteins or nucleic acids used alone. Such augmentation is also called adjuvant effect. The size of these vectors is generally within 10–1000 nm and it is a specific mechanism by which our immune system recognizes such particles that underlies their adjuvant potencies (in addition, many carriers protect proteins/NA from rapid degradation *in vivo* and release them into the organism during prolonged periods of time, which also results in higher immunogenicity). Needless to say, many details of this mechanism remain to be elucidated, although current vaccine development fashion is definitely of "going small", i.e. toward micro- and nanoscale [3]. In this paper, I will briefly discuss the current state of the vaccine nanotechnology, promises of the new approaches as well as potential risks that these approaches may contain.

Both recombinant NA and protein vaccines have been designed to be safer than traditional vaccines based on whole viruses and bacteria, but their limited immunogenicity has so far hindered their development for clinical use. This led to the sustained research effort aimed at development of specific adjuvants that may make such vaccines more potent without compromising on their safety. Currently, only one adjuvant, alum (aluminum hydroxide or aluminum phosphate) is used worldwide in diphtheria, tetanus and hepatitis B vaccines. One of the proposed mechanisms for alum action is generation of small salt particles in which vaccinating agent is trapped and then preferentially taken up by cells of immune system, macrophages and dendritic cells (DC), which, in turn, leads to elevated immune response. Multiple attempts to create antigen-bearing particles that will be capable to imitate this suggested avenue of immunogenicity augmentation have been undertaken over the last decade and many of them have been useful. What may be the mechanism of higher immunogenicity exhibited by particulate antigens compared to soluble ones and does the size of these particles matter?

Adjuvanting effects of micro- and nanoscale particulates are now known to be a consequence of them being of suitable size for uptake by antigen-presenting cells (APC), such as DC and macrophages through phagocytosis or pinocytosis. APC then stimulate T-lymphocytes constituting cellular arm of immune response, which among others is responsible for specific antiviral immunity. This APC-mediated activation of T-cells initiates adaptive immune response. Antigens delivered in particulate form are preferentially processed by APC and via so-called MHC class I and II pathways and then presented to CD8+ (cytotoxic lymphocytes) and CD4+ (T-helpers) T-cells, which first serve as effector cells of immune response and then are instrumental in generation memory T-cells, those that are responsible for the defense of the organism in case of repeated exposure to the infectious agent bearing antigen in question. Those particulate antigens that are not directly taken up by DC, but by other cells of the organism (e.g., by muscle cells after intramuscular injection) may also stimulate immune response by two possible pathways. Either they eventually either find their way to DC after cell death followed by phagocytosis (if they are stable enough) or they may be processed to the cell surface and then recognized by already activated T-cells thus providing further stimulus for their activation and multiplication. Obviously, that particle-driven stability of delivered antigens is a very important part of such an equation.

Moreover, the surface of micro- or nanoparticle may be further modified to increase their targeting specificity, which can be also attained via simple size variation. It is now clear that different subtypes of DC, those residing in skin and in lymph nodes (LN) are differentially affected by nanoparticles of various size with smaller nanoparticles (10–100 nm) being capable of passive migration to lymph nodes and rapid activation of immature LN-resident DC, while particles of the larger sizes (100–1000 nm) are preferentially uptaked by DC at a vaccine injection site. Those skin or mucosal APC residing at those parts of the body where the contact with infectious agents is most likely constitute “the first line of defense” of the organism. It is more than probable that activation of several DC populations done sequentially or simultaneously is a process imperative for generation of potent immune response. Moreover, activation of DC does also trigger non-specific immune responses, known as innate (e.g., induction of interferons and other cytokines), which in turn may further potentiate generation of prolonged and strong specific immune response against vaccinating agent. All of these developments made by fundamental research are now actively transposed into the science of vaccine manufacturing.

2. Approach 1: Imitation or Modification of Nature - Viruses and, Rarely, Bacteria

There are two types of vectors of viral origin that have been extensively explored lately, first being viral vectors per se (replication-competent or -deficient) and second, virus-like particles (VLP). Viral vectors consist of replicating or non-replicating virus that contains genetic material (in form of DNA or RNA) encoding the desired antigen. These vectors maintain the ability to penetrate cells and disseminate in the organism and sometimes even replicate, but are rendered harmless by specific changes or mutations. Advantages of virally-vectored vaccines include their ease of production, a good safety profile (at least in some cases), ability to potentiate strong immune responses, potential for nasal or epicutaneous delivery and mucosal immunization [3]. They are also more potent than pure DNA vaccines (since DNA in this case is protected from degradation by viral capsid and directly delivered to virus-susceptible cells), but are especially good if used sometime after initial DNA immunization (in so-called prime-boost regimen).

Adenoviruses are probably among the best-studied viruses and they were heavily exploited for vaccine development over last two decades [4]. There are many promising experimental results using either replication-competent or -incompetent (the latter, by definition, are very safe) adenoviral vectors. However, consistent presence of adenoviruses (the agents of common cold) in human population resulting in pre-exisitng immunity (the ability of human immune system to recognize adenoviral vector and expeditiously remove it from the organism) has somewhat damped the enthusiasm for their clinical use. Still, experimental data, especially in the immunization against HIV and influenza were sufficiently promising to enable large-scale clinical trial of adenoviral-based HIV vaccine manufactured by Merck (USA). This, as we know, has recently ended in a complete failure. The trial was aborted [5, 6]. Importantly, not only this vaccine was not protective, it has apparently also increased risk of HIV infection in vaccinated subjects that were previously exposed to adenovirus (those with pre-existing immunity). Notably, we do not currently know the fundamental reason for the latter (and it was not foreseen by anyone based on current immunological knowledge). This example shows that vaccines of novel generation, however promising, may cause side effects of completely unpredictable nature.

Another type of viral vectors is based on various poxviruses, closely related to vaccinia virus that has been used for many years for vaccination against smallpox. It is known that immunization with vaccinia viruses induces potent immune response against recombinant antigen [7] and many experimental vaccines containing proteins from HIV, influenza, malaria, etc. have been produced and tested. It is important to stress that unmodified live vaccinia virus has never been proposed as delivery vehicle for vaccines aimed at general use (application of such vaccines as anti-cancer therapeutics is outside of this review) since the risks of its utilization would have been enormous. In particular, live vaccinia virus can not be used to vaccinate people with immune deficiencies, suffering from eczema, etc. However, its replication-deficient strain, called modified vaccinia virus Ankara (MVA) is much safer and still very immunogenic. Another approach envisions the utilization of avian poxviruses, e.g. fowlpox or canarypox viruses, which are also incapable of replication in humans, but still immunogenic. Similar to adenoviral vectors, the issue of pre-existing immunity should be addressed regarding poxviral-based vaccines since nearly all humans over 40 years old have been vaccinated against smallpox at least once and may therefore respond poorly to new poxviral vaccination. The possibility of adverse effects similar to the one observed in Merck anti-HIV vaccine trial can not be discounted as well, although what is true for one group of viruses may not be automatically applied to another. Many MVA-vectored vaccines have been already developed, but only one of them, against malaria, is now under active clinical investigation, which at the moment appears to be highly successful. In this case prime vaccination with DNA molecule is followed by boost immunization with recombinant poxvirus. Currently we do not know why poxviral-based vaccine is especially potent against malaria and if these results could be translated into other infectious systems.

Other replicating virus vectors are based on measles and vesicular stomatitis virus and they suffer from similar drawbacks: prior immunity and safety concerns. The same could be said about two more novel non-replicating viral vectors based on alphaviruses and herpesviruses [4]. It appears that viral vaccine vectors will require considerable breakthrough in order to enable their extensive clinical application.

Another approach envisions the utilization of VLPs. VLPs are non-infective virus particles (capsids) consisting of self-assembled viral proteins without NA, which mimic the structure of native virions [8]. These particles fall in the general size range of viruses (22–150 nm) [9], albeit it is fair to say that full viral size range is within 15–400 nm [10]. They also maintain a specific virus-like morphology and are effectively consumed by cells similarly to infective viral particles. They may be formed by a single viral protein or by co-expression of many, in the latter case creating complex virus-like structures. It appears that particulate nature of VLPs drives their efficient presentation to the cells of immune system. Moreover, those VLPs that closely resemble infectious viruses may trigger the same array of antiviral immune responses (e.g., via viral receptor) without causing immune suppression (as living viruses do).

VLPs can be produced in many expression systems, those of mammalian cells, yeast, bacteria, baculovirus (viruses of insects) and plants. They have been manufactured for many viruses including, but not limited to HIV, hepatitis B virus (HBV), HCV, Ebola, influenza, rotavirus, human papillomavirus (HPV) and Norwalk virus [8]. Several VLP-based vaccines have been licensed for general use, many of them against HBV, which are composed of HBV surface antigen (HBsAg), which is a main component of currently used protein-based, alum adjuvant-potentiated vaccine. Upon its production *in vitro* (e.g., in yeast) HBsAg protein aggregates in 22 nm particles (single-component VLP), which are both safe and highly immunogenic [11]. In fact, HBsAg is now actively pursued as molecular adjuvant on its own ("VLP as platform" approach). Fusion of several less immunogenic proteins to HBsAg, most notably, influenza M2 protein capable of cross-protective immunity, resulted in significant immunogenicity augmentation [12]. Similar data has been reported for HBV VLP containing proteins from the circumsporozoite stage of the malaria *Plasmodium* [13]. Improvements of single-protein HBV VLPs by inclusion of large and middle viral envelope proteins are also actively sought [9].

The most recently approved VLP vaccine is Gardasil that is protective against several types of HPV, which are known to be associated with cervical cancer and genital warts. This vaccine is composed of self-assembled particles of HPV major capsid protein [14–16] and it also contains an aluminum salt adjuvant. It has been shown to reduce infection of HPV by 90% and is almost 100% effective HPV types 6, 11, 16 and 18. This vaccine if administered early in life is expected to drastically reduce the occurrence of this life threatening disease in women and has generated significant excitement. Therefore, it is currently recommended that girls at 9–14 years group age are vaccinated and many U.S. states will likely make this vaccination mandatory. Anti-HPV vaccine is clearly the most dramatic example of recent success of recombinant vaccine developers. At the same time, there was a significant fight-back against general utilization of this vaccine stemming from different social groups that we will describe in the final part of this review.

Several other VLP vaccines are now close to clinical use, those against Norwalk virus and rotavirus (both causing acute gastrointestinal infections). Rotavirus is the leading cause of diarrhea-related deaths (400–600,000) in children worldwide and clinical trials of VLP-based vaccine against rotavirus has long been advocated [8]. VLP-based vaccine against Norwalk virus is now assessed in phase I clinical trials. A variety of other VLP vaccines have been evaluated in preclinical studies include HIV, influenza, HCV, Ebola and SARS coronavirus [9]. It should be added that non-vaccine nanoparticle VLP applications also exist such as using them as scaffolds to allow assembly of biopolymers (large plant virus-derived VLPs are utilized, notably from tobacco and cowpea mosaic viruses), including their utilization as templates to polymerize nanowires as building blocks for semiconductors or manufacture nanowires for the construction of smaller lithium ion batteries [10].

Liposomes (phospholipids-based vesicles) are roughly of the similar size as VLP (usually 50–200 nm) and they were used extensively as drug delivery vehicle for nearly four decades. Liposomes transport their contents across cellular membranes and release it following fusion with internal cellular compartments called endosomes. Thus, they are capable of delivering of encapsulated or adsorbed antigen for vaccine use and were investigated as adjuvants for vaccines against influenza, HIV and malaria, among others. However, it seems that no unmodified liposome-based vaccine possesses an adjuvant effect strong enough to substantiate its clinical development. Conversely, modified liposomal vaccines based on viral membrane proteins (virosomes) are sufficiently potent and are approved for use in Europe as vaccines against hepatitis A virus (HAV) and influenza [17]. Immunopotentiating influenza virosomes are liposomes containing main influenza surface protein hemagglutinin intercalated into their membrane. Their approximate mean diameter is 120–170 nm. The glycoproteins of influenza virus stabilize the liposomal particles and maintain their receptor-binding actrivities when reconstituted into such protein lipid vesicles and are therefore actively taken up by cells *in vivo* and actively conveyed to immunocompetent cells [18]. They have an excellent safety profile. Other virosomal vaccines produced include not only those against HAV, but also combined HAV-HBV vaccine in which inactivated HAV virions and HBV HBsAg cores were covalently coupled to the surface of virosome [18].

Adjuvant properties of virosomes can be further increased by integration of co-stimulatory molecules (immune response mediators and activators) or their specific targeting to particular DC subtype. Moreover, they can additionally carry DNA or RNA and thus provide for multifaceted immune stimulation via different pathways. Therefore, virosomes are becoming more and more popular in modern vaccine concepts since they combine the safety and flexibility of subunit vaccines with the biological and immunogenic properties of VLPs [10].

Another mode of imitating nature is the creation of sometime misleadingly called Proteosomes (note the capital “P”), nanoparticles composed of the outer membrane proteins (OMPs) of *Neisseria meningitides* and other *Neisseria*. Proteosome particles are considered to serve as potent vaccine delivery vehicles based on their nanoparticulate (20–800 nm size), vesicle-like nature [19]. In addition, hydrophobicity of Proteosomes may inhibit antigen degradation facilitate its uptake and processing by immunocompetent cells. OMPs have been used successfully in a marketed meningococcal vaccine since 1981 and are considered non-toxic and well-tolerated [3]. Meningococcal OMPs have been safely given parenterally to hundreds of million of children in a *Haemophilis influenza* Type b conjugate vaccine [19]. In several cases, a novel adjuvant known as

Protollin consisting of Proteosomes non-covalently complexed with immune stimulant lipopolysaccaride (LPS) has been used [20]. Proteosome-based influenza vaccines for nasal application have been also generated using this technology and successfully tested and many others (against *Shigella*, HIV, staphylococcal and *Brucella* toxins are under active development). There are other bacteria-based adjuvants, but they may not be called particles in a true sense of words, rather being biomolecules (modified proteins, peptides, components of bacterial wall). It is for their efficient delivery that some of synthetic micro- and nanoparticles can be successfully used.

3. Approach 2: Imitation or Modification of Nature via Physical Chemistry, Biochemistry or Natural Products Chemistry

The only nano-sized vaccine adjuvant that is approved for human use (in Europe, but not in the U.S.) as a vaccine component is MF59. It was the first new adjuvant to be licensed for human use (in 1997) 70 years after introduction of alum [21]. MF59 is an oil-in-water emulsion composed of <250 nm uniform and stable microparticles made by a drop of oil surrounded by a coat of water droplets held onto oil by surface detergents. Specifically, these droplets are formed when squalene (4.3% v/v) and two surfactants, polysorbate 80 (0.5% v/v, Tween 80) and sorbitan trioleate (0.5% v/v, Span 85) are emulsified in citrate buffer [3]. This oil is obtained from shark liver and is also found in humans as natural metabolite [21]. The strong immunogenicity enhancement of MF59 has been repeatedly demonstrated with some researchers showing an effect even stronger than that of alum. The mechanism of adjuvanticity of MF59 is believed to be through cytokine production, although no precise information is available as of yet. In general, it is thought that adjuvant emulsions potentiate immune responses via formation of antigen depots and stimulation of antibody-producin plasms cells. As noted above, an MF59-adjuvanted influenza vaccine, Fluad, is licensed in Europe and experimental vaccines for avian influenza have been produced. Their strong immunogenicity and protectivity has been demonstrated experimentally. Other vaccines strongly potentiated by MF59 include those against HBV, HCV, HIV, herpes simplex virus (HSV), *Haemophilis influenzae* type b and *N. meningitides*.

Montanide is a different, water-in-oil emulsion (one modification is a water-in-oil-in-water emulsion). Emulsions of Montanide51 and 720 are composed of a metabolizable squalene-based oil with a mannide monooleate emulsifier, which augments immunogenicity via formation of antigen depot at the site of injection [3]. While similar to Incomplete Freund's adjuvant (IFA), a well-known but extremely reactogenic adjuvant that contains a mineral oil and an emulsifying agent, in its physical character, Montanide is biodegradable. This eliminates many of the cytotoxic properties inherent for IFA. ISA 51 and 720 emulsions have been in phase I and/or II clinical trials for vaccines against malaria and HIV and various cancers and in most cases they were found to be safe and fairly well-tolerated.

Another particulate vaccine vehicle is immunostimulating complex (ISCOM). ISCOMs are based on triterpenoid saponins (Q saponins). They form particles of approximately 40 nm. These are essentially cage-like structures containing protein antigen, cholesterol, phospholipid and the saponin adjuvant Quil A or its purified component Quil21, which is derived from the aqueous extract from the bark of the South American tree *Quillaia saponaria Molina*. These components are held together by hydrophobic interactions. Saponins have been tested and used in both human and veterinary medicine for decades and they are known to efficiently induce T-helper responses. They have not been extensively used because of their reactogenicity (Quil A composed of more than 23 different saponins is too toxic for human use), although recently semi-synthetic saponins were created that are apparently less toxic [22]. ISCOM matrix traps the protein antigens (typically hydrophobic membrane proteins) through apolar interactions. A similar vaccine delivery vehicle and adjuvant has also been developed that uses the same material minus the antigen (ISCOMATRIX) and still possesses preferential targeting to APC [23]. A clinical study that compared a classical trivalent subunit influenza vaccine with an ISCOM adjuvanted version revealed a stronger immune response with the ISCOM vaccine eliciting rapid antibody responses as well as T helper (CD4+ T-cell) and some CTL (CD8+ T-cell) responses [24]. Additional ISCOM/ISCOMATRIX vaccines have been tested in the clinic for HIV, HSV, HPV and HCV [3]. In all cases, these studies have shown a good safety and tolerability profile in humans as well as effective induction of both humoral and cellular immune responses. Still, the actual use of ISCOMs in human vaccines has been deterred by concerns regarding safety since some saponins are toxic at elevated levels [3, 22].

Another completely new mode of biochemical modification of antigen is its attachment to so-called protein aggregating domains that form intracellular inclusions of several hundred nm. Such inclusions are then digested via the process called autophagy, which is now known to be linked to effective antigen presentation via MHC class II pathway. Initial data provided evidence of dramatic increase of immunogenicity when a test soluble antigen was attached to such aggregating domain [25], although this very promising approach is still in the very first stages of possible development.

There are several types of synthetic micro- and nanoparticles that are effective in vaccine delivery and potentiation. Calcium phosphate microparticles are relatively less-known. They can be generated by combining (while stirring) of calcium chloride, sodium phosphate and sodium citrate [3]. Since calcium phosphate is naturally occurring in the body, these materials are thought not to present a danger of significant side-effects. Calcium phosphate microparticles are less than ~1.2 μm in diameter (<1,000 nm according to other authors, [26]). Phase I study showed that these microparticles are safe and non-toxic when administered subcutaneously. Vaccines utilizing CaP, which are currently in preclinical studies include anthrax, HBV, influenza (H5N1 avian and seasonal) and HSV-2 [3].

Much better known are polymeric biodegradable microparticles. Those used most frequently are poly(D,L-lactide-*co*-glycolide) (PLG/PLGA) and polylactide (PLA) and their copolymers as well as polyorthoesters, polyanhidrids and polycarbonates [27]. Microparticles may be loaded by many types of recombinant vaccines, i.e., DNA (which is thus protected from degradation), proteins and also other adjuvants of smaller molecular size (of protein, peptide or oligonucleotide nature). These biodegradable, biocompatible polymers have been approved for use in humans (e.g., as sutures, bone implants, screws and implants for sustained drug delivery) and have been extensively studied for use in the formulation of vaccine antigens. PLG-based microparticles are the primary candidates for the development of microparticles as vaccine adjuvants since they have been safely used in humans for many years. The direct uptake of biodegradable microparticles into DC has been demonstrated both *in vitro* and *in vivo* and it appears that their appropriate size is within 1–3 μm range and that cationic microparticles are particularly effective in this regard [28]. In these formulations, antigen can be either entrapped or adsorbed to the surface of the particles. Furthermore, these particles can be tailored to degrade over a range of rates, which is especially important since several of those systems degrade rather slowly. Thus, additional triggering of their dissolution is necessary for efficient antigen delivery. On a positive side, they can therefore act as a depot from which the encapsulated antigen is gradually released [28]. Additionally, polymeric particles may offer high degree of protection to encapsulated antigens delivered orally and nasally and thus subjected to many degrading enzymes residing at these sites of the body. It appears that DCs respond to biomaterials via an innate immune response, which then stimulates an adaptive response to an antigen delivered by polymeric particles.

Biodegradable and biocompatible micro- and nanoparticles of PLGA or PLA have been reported to enhance both humoral and cellular immune responses against an encapsulated protein antigen. PLG nanoparticles can induce systemic antibody titers comparable to those of aluminum salts. It was demonstrated that PLG nanoparticles loaded with MPL (an immune stimulant composed of detoxified lipopolysaccharide (LPS) from *Salmonella minnesota*) were efficiently taken up by DC. Recently, it was shown that the adsorption of antigens at the surface of PLA particles also leads to elevated immune response. Cationic and anionic PLG microparticles have been successfully used to adsorb a variety of agents, including DNA, recombinant proteins and adjuvant active oligonucleotides and are also currently tested in several vaccine applications.

Another approach envisions specific targeting of APC, especially peripheral DC and exploitation of particulate systems that are small enough for lymphatic uptake (polystyrene nanobeads). These are in contrast non-degradable nanoparticles (represented also by gold, latex and silica beads). It appears that solid synthetic, particulate vaccines can induce strong immune responses imitating classical “danger signals” generated by infectious agents and microparticles. In this application 40–50 nm particles preferentially taken by some types of DC are often used and are known to generate potent and broad immune response [23]. Moreover, it was demonstrated that for polysterene beads even miniscule difference in size can influence the breadth and type of induced immune response [29].

Recently, ultra-small (25 nm) nanoparticle systems were shown to be capable of interstitial-to-lymphatic flow to deliver antigen and adjuvant to LN-resident DC via lymphatic capillaries, whereas 100 nm nanoparticles were only 10% as efficient [30]. Also, these ultra-small, ovalbumin-conjugated, polyhydroxylated nanoparticles based on Pluronic (a block copolymer of polyethylene glycol and polypropylene glycol) were shown to induce antigen-specific cellular immunity since their surface chemistry has activated complement system, a pathway of innate immunity that serves as a biochemical defense system that clears pathogens nonspecifically, but can also play a role in promoting antigen-specific responses.

In general, nanoparticles as vaccine vehicles might have three different advantages over microparticles. Most importantly, they have increased surface area for adsorption allowing for a higher antigen/polymer ratio and are also easier to prepare and process. As for their higher immunogenicity, the jury is still out since different groups of investigators are presenting conflicting evidence [31]. It should be also noted that sometimes the utilization of preposition “nano” to describe nearly any type of vaccine component is a bit overdone [3].

Since non-degradable nanoparticles may remain in the tissues for extended periods of time, it is thought that it will therefore enhance the time of immobilized antigen presentation and thus augment immunogenicity. Gold particles have been frequently described for vaccine delivery both with and without the aid of electroporation, a method which is unlikely to be employed in humans. An alternative approach to delivering DNA vaccines employing non-degradable nanoparticles is through particle bombardment also referred to as “gene gun” approach. This is essentially firing the DNA-coated gold nanoparticles into the epidermis. While the delivery efficiency of this technique is quite low, only small amounts of DNA are required to achieve a significant immune response. This method has been tested for vaccines against HBV, influenza and malaria.

Furthermore, micro- and nanoparticles offer the possibility of enhancement of their uptake by appropriate cells through manipulation of their surface properties. As delineated above, upon their inoculation, particulate compounds, microspheres or nanoparticles, must reach the secondary lymphoid organs, which are the sites of the immune response. This led to design of novel methods of dermal or transcutaneous vaccination, including the use of micro- and nano-particles to target the skin APC that will then deliver consumed antigens to the LN.

Finally, pulmonary delivery (which may be especially potent and useful against influenza and other respiratory viruses) requires dry forms of vaccines that are low cost, temperature-tolerant, efficiently aerosolized, and APC-directed. Therefore, nanoparticles can play a critical role in the formulation, development and delivery of needle-less pulmonary vaccines and these are now actively pursued as well. Additionally, nanoparticles containing vaccines for the oral delivery are also investigated. These particles are 100–200 nm in diameter and are likely needed to be targeted towards a special subtype of APC called M cells that reside within gut-associated lymphoid tissue.

4. Micro-/Nanoparticle-Based Vaccines – Is There Any Risk and Can We Foresee It?

It is apparent that novel micro- and nanoparticle-based delivery vehicles are being actively evaluated in many vaccine systems. Promising results have been reported from many directions. Still, questions regarding toxicity and molecular interaction between micro- and nanoparticles and immune cells, tissues and whole organisms remain to be addressed. There are many regulatory hurdles for new adjuvants and they are there for a reason. One of the greatest hurdles is the sheer size of population that needs to be tested to prove safety of a new adjuvant or vaccine. These numbers have dramatically increased in recent years since it became apparent that some approved drugs have rare serious and even fatal side effects that were not identified because of inadequate sample sizes during their clinical development [23]. During that time the association of adverse reactions with two vaccines resulted in their withdrawal from the market. These are nasal inactivated influenza vaccine associated with increase of cases of Bell's Palsy and also rotavirus vaccine, the administration of which lead to higher intussusception [23]. The case of adenoviral-based HIV vaccine has been mentioned above.

Reaction of parts of the society to a new vaccine may be also caused by imaginary side-effects. We have already noted that this is a case with Gardasil, a highly efficient anti-HPV vaccine, which is likely to tremendously diminish the incidence of cervical cancer and genital warts. Several conservative groups and think-tanks in the U.S. have questioned if such a vaccination will spark more promiscuity in young women. Statements like "What message are we sending to our elementary students when we inoculate them for a sexually transmitted disease in the third grade?" or "This means even Christian children who are brought up knowing that sexual activity before marriage is a sin would still be forced to be vaccinated against this STD or they could not attend school" [32] are not uncommon. But conservatives are not the only ones, who are in opposition to a mandatory vaccination against deadly disease and throughout the history of vaccination such reactions have been noted many times. It was aptly observed that groups fighting against Gardasil are very diverse and include Christian conservatives, who have long argued that safe sex encourages profligate sex, the growing antivaccine movement, which objects to all school-entry requirements and the parental-rights adherents, incensed by any mandates regarding their children's health [33]. These arguments may seem laughable or medieval to some, but they are very valid to others and it is advisable that the introduction of this great novel product of vaccine technology is done employing all possible precautions and public-relations instruments. Unquestionably, there is a lesson to be drawn. No new medicinal technology can be successful unless public is educated and well-informed of it.

It is apparent that nanotechnology is currently driving the development of novel vaccines and adjuvants. At the same time, some concerns regarding the toxicity of such small particles have appeared. Currently, there is a keen interest in nanotoxicology research since the processing of nanostructures in biological systems could lead to unpredictable and hence unknown toxic effects [34]. One may draw some lesson from the history of polio vaccine when during 1955–1963 more than 98 million Americans received one or more of its doses contaminated with polyomavirus SV40, which was then simply unknown being identified and isolated only in 1960. When it became apparent that under specific set of conditions SV40 may cause cancer in laboratory animals, this led to a serious public scare. Fortunately, subsequent studies of vaccinated humans over many years have shown that there was no causal relationship between receipt of SV40-contaminated vaccine and cancer. Such a completely unforeseen event should not be discounted when we in fact are actively engaged in genetical modification of humans (immunized individual always contains cells of immune system, which genome is partially rearranged in a way that cells of a non-immunized individual are not).

Other potential problems include high surface area and reactivity of small particles, their involvement in catalytic and oxidative reaction, ability to cross biological membranes as well as slow biodegradability of some materials used for their manufacturing. Possibility of all of these being potential toxicity issues are at least partially supported by data describing the effects of pollutants on human health [3]. Still, it seems reasonable to anticipate that in the case of vaccines, the infrequent and low-level exposure to nanoparticles that an individual will encounter during immunization is not enough to cause adverse health problems such as those potentially attributed to nanotoxicity effects. With that being said, the development of any novel vaccine adjuvant or delivery platform should undergo all the necessary safety tests. They will also need to withstand public and political scrutiny. Recently, regulatory authorities and the general public start to be concerned with products that cross traditional lines, i.e. combine biomaterials with cells, DNA or proteins as in non-viral polymeric carriers for vaccines [35].

Currently, the most probable reason for the micro- and nano-based vaccines not flooding the market is linked to the cost of their safety testing. Necessary clinical trials required for their approval are very long and difficult. Unlike animal studies, human trials often require significant waiting period before protection can be analyzed. Furthermore, since many vaccines are often administered to healthy individuals, and frequently to infants, it is critical that they are proven safe and well-tolerated in non-human primates before entering human trials.

These risks and other possible side effects should be assessed in detail especially if mass-production and widespread administration of novel preparations is to be considered. Currently, there is an uncertainty about nanoparticle processing *in vivo* and also near-complete absence of understanding of mechanisns of their interactions with biological systems (although the latter was never necessary in the history of medicine provided that the safety of this or that useful approach is demonstrated experimentally). Therefore, continued animal research dealing with nanoparticle *in vivo* pharmakinetics and tissue distribution, nanotoxicity investigated in the same vein as drug toxicity currently is, as well as human trials for the safety evaluation of the experimental micro- and nanoparticle-based vaccine regimens will be of immense importance.

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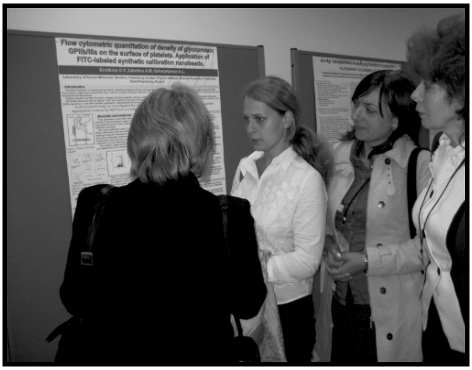
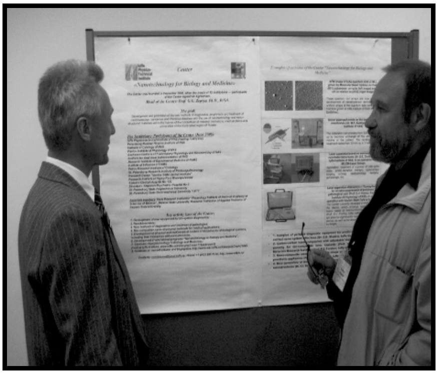
SUBJECT INDEX


NATO PROGRAMME SECURITY THROUGH SCIENCE ADVANCED RESEARCH WORKSHOP
Environmental and Biological Risks of Nanobiotechnology, Nanobionics and Hybrid Organic-Silicon Nanodevices (Silicon vs Carbon)
June, 18 - 20 2008
Saint-Petersburg


BON AQUA


Flow cytometric quantitation of density of glycoprotein GPIIb/IIIa on the surface of platelets. Application of FITC-labeled synthetic calibration nanobeads.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