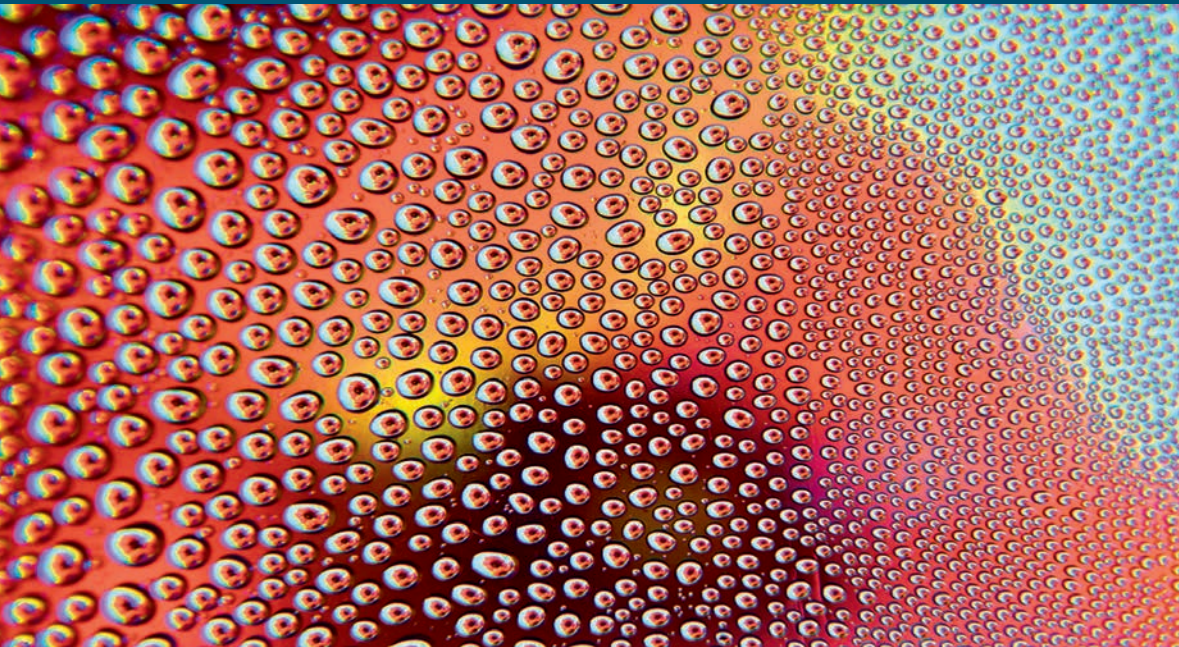


FLUID MECHANICS SERIES

Flows and Chemical Reactions in an Electromagnetic Field

Roger Prud'homme



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Preface

This book – a continuation of the previous publications *Flows and chemical reactions* [PRU 12], *Flows and chemical reactions in homogeneous mixtures* [PRU 13] and *Flows and chemical reactions in heterogeneous mixtures* [PRU 14a] – is devoted to *Flows and chemical reactions in an electromagnetic field*.¹

Part One, entitled Introduction, is made up of four chapters. *Chapter 1* gives an introduction to the equations of electromagnetism in the Minkowski timespace. This mode of presentation is extended to the balance equations, first in non-polarized homogeneous mixtures in *Chapter 2*, and then in a polarized homogeneous fluid medium in *Chapter 3*.

¹ Remember that the volume *Flows and chemical reactions* comprised three parts: 1. Fluid media with a single component, 2. Reactive mixtures, and 3. Interfaces and lines, that the volume *Flows and Chemical Reactions in Homogeneous Mixtures* comprised: 1. Pipe flows, 2. Chemical reactors, and 3. Laminar and turbulent flames, and that the volume *Flows and Chemical Reactions in Heterogeneous Mixtures* comprised: 1. Generation of multi-phase flows, 2. Problems at the scale of a particle, 3. Simplified model of a non-reactive flow with particles, 4. Simplified model of a reactive flow with particles, and 5. Radiative phenomena.

Chapter 4 is given over to heterogeneous media in the presence of an electromagnetic field. In that chapter, the balance equations at the interfaces are established.

Part Two of this volume is entitled Introduction. It too has four chapters. *Chapter 5* presents a study of the influence of diverse fields on flames; *Chapter 6* discusses a classic application of the Peltier effect; *Chapter 7* is devoted to metal/plasma interaction, and more specifically to the Langmuir probe, and finally *Chapter 8* discusses space propulsion by the Hall effect.

The *Appendix* gives supplementary information about the balance laws with an electromagnetic field, before going on to describe the methodology used to establish one-dimensional equations for a flow with active walls, as is the case with certain Hall effect thrusters.

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Roger PRUD'HOMME
September 2014

List of Main Symbols

Latin characters

A	chemical affinity; or monatomic species
A_2	diatomic species
\underline{A}	vectorial potential
A, B	Arrhenius coefficients
\mathbf{B}	magnetic field
c	speed of sound; or speed of light in a vacuum in the absence of a field
C	total number of moles per unit volume
C_j	molar concentration per unit volume
C_p, C_v	specific heat at constant pressure or constant volume respectively (c_p, c_v per unit mass)
d	distance; or differential
D	diffusion coefficient; or diameter
$D_{\alpha,i}$	diffusion coefficient of species α at quantum level i
\vec{D}	electric displacement
$\vec{\mathbf{D}}$	strain rate tensor

$\underline{\underline{4D}}$	four-matrix of the Lorentz special transformation
e	free electron; charge on the electron; or internal energy per unit mass
$e_{v,\alpha}$	vibrational energy of diatomic species α
e_e	mass internal energy of free electrons
$\bar{\mathbf{e}}_i$	orthonormal basis vector
E	internal energy (e per unit mass)
\mathbf{E}	electrical field
E_a	activation energy
f	parameter; reduced chemical production rate; or Blasius function
f', f''	Reynolds, Favre fluctuation, respectively
\mathbf{f}	force acting on each unit mass
\mathbf{f}_j	force acting on the unitary mass of species j
F	Helmholtz free energy (f for the unit of mass); generalized force; or any extensive value (f for the unit of mass);
\mathbf{F}	force of F_x, F_y, F_z components; or electromagnetic force
\mathcal{F}	source of momentum due to molecular collisions
$4\mathcal{F}, 4\mathcal{F}^*$	four-tensors of the electromagnetic field
G	Gibbs free enthalpy (g per unit mass)
\mathbf{g}	acceleration due to gravity (of modulus g)
g_j	chemical potential per unit mass of species j in a mixture
\tilde{g}_k	electrochemical potential per unit mass of species k in a mixture $g_k + z_k \phi$
H	enthalpy (h per unit mass)

H	magnetic displacement
${}^4\mathcal{H}$	four-tensor of electromagnetic displacement
I	unit tensor
i	intensity of the diffusion current
i	total current of conduction (or diffusion)
I	intensity of the electrical current equal to $ \mathbf{I} $
I	conventional electric current $\tilde{\rho}\underline{\mathbf{v}}$; or total current $\tilde{\rho}\underline{\mathbf{v}}+\underline{\mathbf{i}}$
4I	four-vector current
j, k	chemical species
J	total flux relative to a motionless reference frame
j	flux relative to the barycentric velocity in a composite fluid
\mathcal{J}_{Dk}	diffusion flux of species k equal to $\rho_k(\mathbf{v}_k - \mathbf{v})$
$\tilde{\mathcal{J}}_{Dk}$	diffusion current of species k equal to $\tilde{\rho}_k(\mathbf{v}_k - \mathbf{v})$
k	Boltzmann's constant; wave number; or kinetic energy $v^2/2$ $v^2/2$
$k(T)$	specific reaction rate
k_e	kinetic energy of the free electrons
K	kinetic energy (k per unit mass); heat exchange coefficient; or wave number
l	length; or mean free path
ℓ	transfer length; or integral scale of turbulence
ℓ_D	diffusion thickness of a non premixed flame
ℓ_f, ℓ_δ	respective thicknesses of preheating, of reaction of a premixed flame
ℓ_K	Kolmogorov length scales
L	length; molar latent heat; or phenomenological coefficient

Le	Lewis number
L_{ij}, l_{ii}	phenomenological coefficients
$\underline{\underline{\mathbf{L}}}$	matrix of phenomenological coefficients of chemical reactions
m	total mass; or mass of a material point m_0/α
m_0	mass of a material point in the Minkowski space;
M	molecular mass; diluent; Mach number; or material point
\mathcal{M}	molar mass
\mathbf{M}	magnetic polarization ($\mathbf{m} = \mathbf{M}/\rho$: per unit mass)
${}^4\mathbf{M}$	four-vector corresponding to a material point
${}^4\mathcal{M}$	four-tensor equal to ${}^4\mathcal{F} - {}^4\mathcal{H}$
m_j	mass of species j
\mathcal{M}_j	molar mass of species j
\dot{m}	unit mass flow rate; mass flow rate; or mass flow rate of a nozzle
n	total number of moles
n_j	number of moles of species j
N	number of species; number of molecules per unit volume; coordinate normal to an interface; or number of elements in a statistical calculus
\mathcal{N}	Avogadro's number
\mathbf{n}, \mathbf{N}	unitary normal to an interface; or to a surface
${}^4\mathbf{N}$	four-normal to a surface in Minkowski timespace
p	thermodynamic pressure
p_e	partial pressure of the free electrons
\mathbf{p}	momentum vector with coordinates p_x, p_y, p_z
$\bar{\mathbf{P}}$	electric polarization ($\mathbf{p} = \bar{\mathbf{P}}/\rho$: per unit mass)

\mathcal{P}	Poynting vector equal to $c \mathbf{E} \times \mathbf{B}$
$\bar{\mathbf{P}}$	pressure tensor
${}^4\mathcal{P}$	four-tensor of impulsion-energy
${}^4\mathcal{P}^{fld}$	four-tensor of impulsion-energy due to the electromagnetic field (or electromagnetic flux 4-tensor)
${}^4\mathcal{P}^{(m)}$	four-tensor of impulsion-energy due to mass
Pr	Prandtl number
q	parameter; or heat flux
\dot{q}	volume flow rate
\mathbf{q}	heat flux vector
Q	partition function; or quantity of heat
\dot{Q}	lateral heat flux in a nozzle
$(Q_f^0)_j = (H_f^0)_j$	molar enthalpy of formation of species j ($(q_f^0)_j$ per unit mass)
r	perfect gas constant per unit mass; or radius
R	molar universal gas constant; radius; or electrical resistance
\mathfrak{R}	reference frame
Re	Reynolds number
S	entropy (s per unit mass); area; or area of the cross section of a nozzle;
s	curvilinear abscissa
s_L, s_L^0, s_t	combustion velocity respectively laminar, standard, and turbulent
S, \mathcal{S}	surface
\mathbf{S}	symmetrical part of the velocity gradient tensor
Sc	Schmidt number

Sh	Sherwood number
t	time
T	absolute temperature
T_f	flame temperature
T_a, T_{ad}	activation temperature, adiabatic temperature of a reaction respectively
u, v, w	velocity \bar{v} components in Cartesian coordinates (v_r, v_θ, v_z in cylindrical coordinates)
\mathbf{U}, \mathbf{v}	velocity vector; velocity vector (components v_x, v_y, v_z or u, v, w in Cartesian coordinates and modulus v) of a material point; or barycentric velocity vector in a composite fluid
v, v'	velocity, turbulence intensity respectively
\mathbf{v}_k	velocity vector of species k
V	velocity; or volume in the phase space
$\bar{\mathbf{V}}, \mathbf{V}$	vector; velocity vector; or velocity vector in the phase space $(\bar{\mathbf{x}}, \bar{\boldsymbol{\zeta}})$; local velocity vector of a discontinuity
\mathcal{V}	volume; control volume
\mathbf{V}_k	diffusion velocity vector of species $\mathbf{v}_k - \mathbf{v}$
\mathbf{w}	velocity of a surface (normal component w); or $d\bar{\boldsymbol{\zeta}}/dt$ in the phase space
\mathbf{W}	local velocity vector of a discontinuity
\dot{W}_F	rate of production of the quantity F
\dot{W}_α	rate of production of species α
\dot{W}_{E_t}	rate of production of total energy
$\dot{W}_{E\alpha, \text{int}}$	rate of production of energy for the internal degrees of freedom of species α

$\dot{W}_{v,\alpha}$	rate of production of vibrational energy of species α
$\dot{W}_{\alpha,i}$	rate of production of species α at quantic level i
$\dot{W}_{E,a}$	rate of production of total energy per unit area and unit time at interface
x, y, z	Cartesian coordinates; x along a nozzle axis
$\bar{\mathbf{x}}$	position vector
X_j, Y_j	molar and mass fraction of species j respectively
$Y_{\alpha,i}$	mass fraction of species α at quantic level i
z	charge per unit mass $\sum_k z_k Y_k$ of the mixture
z_k	charge of species k per unit mass

Greek symbols

α	chemical species; or quantity $\sqrt{1-v^2/c^2}$
$\delta(x)$	Dirac distribution
Δ	difference; Laplacian; ΔH : heat of a reaction
ε	small dimensionless parameter; or electric permittivity
$\underline{\underline{\varepsilon}}$	dielectric tensor
ϕ	velocity potential; $\phi(\bar{\mathbf{x}}, t)$: weight function
φ	scalar potential
${}^4\Phi$	four-vector force
γ	isentropic coefficient c_p/c_v
${}^4\Gamma$	four-acceleration
η	bulk viscosity; shear viscosity; or reduced coordinate
η, π	thermo-electric coefficients

κ	heat diffusivity $\lambda/\rho c_p$; mean curvature of a surface
Λ	heat transfer coefficient
μ	coefficient of shear viscosity; Gibbs free energy per mole; or absorption coefficient per unit of wave length
μ_j	molar chemical potential of a species j in a mixture
ν	kinematic viscosity μ/ρ ; or light wavenumber
ν_j	algebraic stoichiometric coefficient $\nu_j = \nu''_j - \nu'_j$
ν'_j, ν''_j	stoichiometric coefficient of the direct reaction, or its inverse respectively
Π	viscous pressure tensor
Π_i	dimensionless group
θ	temperature; or angular coordinate
ρ	density (volumic mass)
ρ_j	partial density of species j
$\rho_{\alpha;i}$	partial density of species α at quantic level i
$\tilde{\rho}$	classical electric charge per unit volume $\tilde{\rho}_0/\alpha$
$\tilde{\rho}_0$	electric charge in the Minkowski timespace
$\tilde{\rho}_k$	electric charge of species k per unit volume
ρ	surface tension
Σ	surface; area of a surface; $\Sigma(x)$ area of the cross section of a nozzle
$\bar{\bar{\Sigma}}$	stress tensor
$\sigma_k, \sigma_\varepsilon$	Prandtl numbers of the $k - \varepsilon$ method
ϑ	volume per unit mass (inverse of the density)
τ	characteristic time; dimensionless energy of reaction $\tau = \Delta H/c_p T_1$; or proper time of a material point in the Minkowski timespace equal to αt

ω	speed of rotation; or pulsation of an oscillating wave
$\boldsymbol{\omega}, \boldsymbol{\Omega}$	rotation vector
Ω	speed of rotation; or solid angle
ξ	progress variable per unit mass; reduced coordinate; or correlation length
ψ	stream function; probability in the phase space
ζ	probability in the phase space; or reduced variable
$\dot{\zeta}$	rate of production of a chemical reaction
ζ	vector of the phase space

Subscripts, superscripts, and other symbols

a	of activation; relative to the quantities per unit area of the interface
ad	adiabatic
b	burned gases
chem	chemical
$CO-E_{pv}$	coupling CO molecule - vibrational energy
D	direct; of dissociation; diffusive
e	equilibrium flow
eff	effective
f	frozen composition; fresh gases; or flame
fld	field
$G, ^g$	gas
α, β, i, j	of species

<i>i</i>	internal; relative to imaginary part; or irreversible
<i>int</i>	internal degrees of freedom of a molecule
<i>l</i>	liquid
<i>L</i>	line; liquid; laminar
<i>m</i>	mixture; mass
<i>mec</i>	mechanical
<i>p</i>	at constant pressure
<i>r</i>	chemical reaction; reference
<i>R</i>	reverse; or recombination
<i>S</i>	steady state; surface; isentropic; or specific
<i>S</i>	surface; relative to the specific or intensive interfacial quantities
<i>st</i>	stoichiometric; or steady
<i>t</i>	for translational energy mode of a molecule; or turbulent
<i>T</i>	temperature; turbulent; or at constant temperature
<i>T</i>	transpose of a tensor
<i>°</i>	deviator of a tensor
<i>th</i>	thermal
<i>u</i>	unburned gases
<i>v</i> , or <i>v</i>	at constant volume
<i>V</i>	vapor
//	parallel to a surface
⊥	normal to a surface

0	standard reference value
\bullet	pure simple substance
\cdot	per unit time; or for a rate of production
$-$	average quantity; or Reynolds average
$'$	Reynolds disturbance in relation to an average value
$"$	Favre disturbance in relation to an average value
$s()$	symmetrical part of a matrix or a tensor
\sim	transpose of tensor; transpose of matrix; or Favre average
$\langle \rangle$	turbulent average
$()_T^0$	standard thermodynamic function
\times	vector product
\otimes	tensor product
\cdot	scalar product (singly-contracted tensor product)
$:$	dyadic product (doubly-contracted tensor product)
\wedge	exterior product
$*$	sonic conditions; or reference state; or virtual
$\bar{\nabla}$	nabla (gradient operator)
$[]^+$	jump of a quantity across an interface
d/dt	material derivative equal to $\partial/\partial t + \bar{\mathbf{v}} \cdot \bar{\nabla}$
$\partial/\partial t$	partial time derivative
d_w/dt	material derivative associated with the velocity $\bar{\mathbf{W}}$ equal to $\partial/\partial t + \bar{\mathbf{W}} \cdot \bar{\nabla}$
\rightleftharpoons	for a reversible chemical reaction

Part 1

Introduction

In this first part of this volume, Chapters 1-3 recap the fundamental equations for homogeneous media, mainly in the case of mixtures of conductive fluids in which chemical reactions do take place.

In Chapter 1, we look at the general principles which govern the establishment of the equations of electromagnetism in the case of a simple medium. These equations are expressed in the Minkowski space and then transferred into the usual three-dimensional space.¹ The quantities used in the four-dimensional space are the tensors of the electromagnetic field and the current 4-vector, the momentum-energy tensor. These quantities will also be presented in Chapter 4, where we shall establish the

¹ This way of working is not the only way. It is perfectly possible to study electromagnetism without operating in timespace in the domain of non-relativistic velocities (on this subject, see the remark made by Groot and Mazur [GRO 63, p. 376]; also see [CAB 70, ERI 90]). The method used here to establish the basic equations is, however, fairly conventional (for instance, see [LAN 69, LAN 82, GRO 69b, SAN 68]). In addition, it will enable us to seamlessly introduce interfacial heterogeneities in Chapter 3.

interfacial equations. First, we shall consider non-polarized media, followed by polarized media.

Reactive mixtures involved additional quantities such as the velocity 4-vectors associated with the chemical species and the force 4-vectors. The balance equations for conductive reactive fluid mixtures are first established in Chapter 2 in the absence of polarization.

Chapter 3 is dedicated to the case of conductive reactive fluid mixtures in the presence of electrical and magnetic polarization.

Additional information about the homogeneous balances with electromagnetic fields is presented in the Appendix. The primary objective is to establish the constitutive relations of these conductive homogeneous media, which we can only do if we specify the type of medium in which we are interested: metal, and then homogeneous plasma. We will need these constitutive equations in Chapter 4, when we look at interfaces, because on both sides of these interfaces, we have homogeneous media.

The balance equations of the electromagnetic field give us the two groups of Maxwell equations. The mass balances are established for the species and the mixture; that of the energy-momentum leads us to the equations of conservation of momentum and energy.

The case of non-polarized media is studied first followed by that of polarized media for which the constitutive equations are deduced from linearized TIP.² Attention is

² TIP: thermodynamics of irreversible processes.

drawn to the ambiguity of the definition of certain quantities in a polarized medium. This difficulty of definition arises particularly when we wish to separate the true electromagnetic effects from the mass effects.³

³ The simplest tensorial or matricial notations are used. Where there is no ambiguity, bold letters are used for all non-scalar quantities. However, if the same symbol is used for a 1st- or 2nd-order tensor, this is specified by a single arrow or bar below the symbol for a 1st-order tensor, and a double arrow or double bar below the symbol for a 2nd-order tensor. Thus, electrical polarization is represented by a vector $\vec{\mathbf{P}}$ or a column matrix $\underline{\mathbf{P}}$, whereas the pressure tensor, which is a 2nd-order tensor, corresponds to the tensorial notation $\vec{\vec{\mathbf{P}}}$ or matricial notation $\underline{\underline{\mathbf{P}}}$.

Relativistic Considerations

To begin with, here, we shall present the basic principles and the expressions of the classic quantities, such as the proper time and the universal velocity in the Minkowski timespace. The law of dynamics of the material point is then stated.

The expressions involved in continua, such as the electromagnetic field tensors and that of the electromagnetic momentum-energy, are presented in the case of media with a single component. The Maxwell equations are written, as are the balances of the electrical charge and the electrical momentum-energy in a polarized or non-polarized medium.

1.1. Recap of electromagnetics and mechanics in special relativity

We first recap the equations of electromagnetism, considering them to be deduced from the balance of various tensorial quantities in timespace [EIN 05, LAN 82]. Thus, the formulation is relativistic, but we believe this simplifies the reasoning process. The drawback is that the conventional balance equations in Aerothermochemistry are not relativistic. Hence, at first glance, this presentation seems non-homogeneous. In reality, though, it is not so at all: here, the homogeneity stems from a unique presentation

of the balance equation, relativistic or otherwise [GRO 69a, GRO 69b]. However, we shall limit ourselves to the relativity restricted to Galilean systems.¹

Let us recap some of the basic principles of our developments.

PRINCIPLE OF RELATIVITY.— All of the laws of nature are identical in all Galilean frames of reference; it follows that the equation of a law retains its form in time and space when we change the inertial frame of reference. The rate of propagation of the interactions is the same in all inertial frames of reference.

GALILEO'S PRINCIPLE OF RELATIVITY.— The rate of propagation of the interactions is infinite.

EINSTEIN'S PRINCIPLE OF RELATIVITY.— The rate of propagation of the interactions is constant and equal to the celerity of light c .

This principle leads us to work in timespace.²

1.1.1. *Minkowski timespace*

A point M of spacetime is represented by a complex vector $4\mathbf{M}$, with the associated column matrix:

$$4\mathbf{M} = \begin{bmatrix} x \\ y \\ z \\ ict \end{bmatrix} \quad [1.1]$$

1 The theory is called "special" because it applies the principle of relativity solely to the special case of inertial frames of reference.

2 In timespace, the elementary *interval* between events is defined by: $ds^2 = c^2 dt^2 - dl^2$, where dl is the elementary *distance* such that: $dl^2 = dx^2 + dy^2 + dz^2$.

where c is the celerity of light in a vacuum in the absence of a field. Here, the coordinates are indicated in a Galilean frame of reference.

If we wish to express these coordinates in another Galilean frame of reference of relative velocity $\underline{\mathbf{V}} = \begin{bmatrix} 0 \\ 0 \\ V \end{bmatrix}$ in relation to the first frame of reference, then we write:

$$\underline{\mathbf{4M}}' = \begin{bmatrix} x' \\ y' \\ z' \\ ict' \end{bmatrix} \quad [1.2]$$

and the relation dictating the change of frame of reference is found by way of the *special Lorentz transformation* – a linear transformation³:

$$\underline{\mathbf{4M}}' = \underline{\mathbf{4D}} \underline{\mathbf{4M}} \quad [1.3]$$

with the following $\underline{\mathbf{4D}}$ matrix:

$$\underline{\mathbf{4D}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1/\alpha & iV/c\alpha \\ 0 & 0 & -iV/c\alpha & 1/\alpha \end{bmatrix} \quad [1.4]$$

³ The *Lorentz transformation* preserves the *intervals* (whereas in conventional mechanics, the changes in the inertial reference frameworks preserve the *distances*). This transformation is, in fact, a rotation in the timespace. In our discussion below, we shall use the classic notations to denote tensors and matrices. In our calculations, we shall not use the “covariant/contravariant” notations which are often used in relativity.

where:

$$\alpha = \sqrt{1 - V^2/c^2} \quad [1.5]$$

In the three-dimensional space, the velocity \mathbf{v} of a material point can be defined at any given time. In order to define the velocity as an intrinsic quantity (i.e. one which is independent of the framework chosen to measure it with) in timespace, it is necessary to define a *proper time* (Figure 1.1).

At time t , the material point M has the velocity $\mathbf{v}(t)$ in the frame of reference \mathfrak{R} .

Now consider the Galilean frame of reference \mathfrak{R}' moving at a constant velocity \mathbf{V} such that, at time t , we have $\mathbf{V} = \mathbf{v}$. The time τ measured in relation to such a framework (one exists at all times) linked to the material point is called the proper time of that material point.

Suppose that the coordinates of M remain null; in the new frame of reference, we will have:

$$\begin{bmatrix} 0 \\ 0 \\ 0 \\ ic\tau \end{bmatrix} = \underline{\underline{4\mathbf{D}}} \begin{bmatrix} 0 \\ 0 \\ z \\ ict \end{bmatrix}, \quad \text{so: } \begin{cases} 0 = z - vt \\ c\tau = \frac{1}{\alpha} \left(-\frac{v}{c}z + ct \right) \end{cases}$$

From this, we deduce the expression of the proper time of the material point:

$$\tau = \frac{t}{\alpha} \left(1 - \frac{v^2}{c^2} \right) = \alpha t \quad [1.6]$$

Note that here, v and α , whilst they are variables, need to be considered to be constant when dealing with the

Galilean frame of reference which coincides with M and has the same velocity as M at time t .

The above relation is therefore, in fact, a differential relation linking the proper time to the time in the frame of reference \mathfrak{R} , and should, strictly speaking, be written:

$$d\tau = \alpha dt \quad [1.7]$$

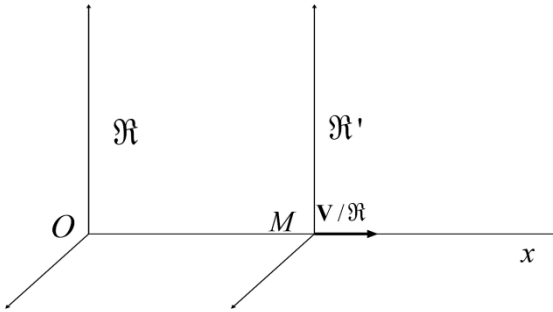


Figure 1.1. Galilean frames of reference. The frame of reference \mathfrak{R} is that in which we observe the events. At the point M moving at the instantaneous velocity \mathfrak{v} , we associate with time t the frame of reference \mathfrak{R}' moving at constant velocity $\mathbf{V} = \mathfrak{v}$

The *universe velocity* vector, or 4-velocity vector, of the material point M is defined as ${}^4\mathbf{V} = d{}^4\mathbf{M}/d\tau$ where, in matricial notation:

$$\underline{{}^4\mathbf{V}} = \frac{d\underline{{}^4\mathbf{M}}}{d\tau} \quad [1.8]$$

NOTE 1.1.— We can verify that ${}^4\mathbf{V}$ is indeed a 4-vector in the Minkowski space. If this is the case, then in relation to a new

Galilean frame of reference \mathfrak{R}_1 , of velocity $\underline{V}_1 = \begin{bmatrix} 0 \\ 0 \\ V_1 \end{bmatrix}$, constant

in relation to the frame of reference \mathfrak{R} (Figure 1.2), we must have: $\underline{4V}' = \underline{4D}_1 \underline{4V}$. This relation is written thus:

$$\begin{bmatrix} 0 \\ 0 \\ v'/\alpha' \\ ic/\alpha' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1/\alpha_1 & iv_1/c\alpha_1 \\ 0 & 0 & -iv_1/c\alpha_1 & 1/\alpha_1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ v/\alpha \\ ic/\alpha \end{bmatrix} \quad [1.9]$$

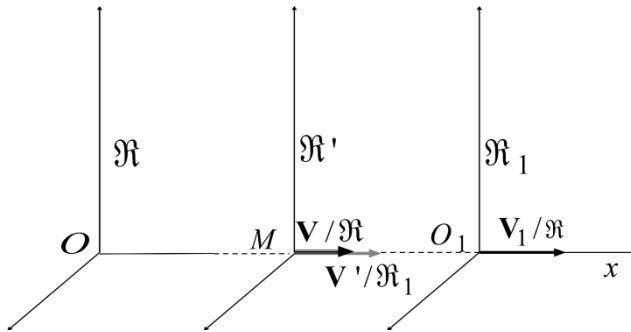


Figure 1.2. Change of the Galilean frame of reference. The new Galilean frame of reference \mathfrak{R}_1 has the velocity of translation \underline{V}_1 in the frame of reference \mathfrak{R}

We deduce from this that:

$$\frac{v'}{\alpha'} = \frac{v - v_1}{\alpha \alpha_1} \quad \text{and} \quad \frac{1}{\alpha'} = \frac{1 - v v_1 / c^2}{\alpha \alpha_1}$$

which has the consequence:

$$v' = \frac{v - v_1}{1 - v v_1 / c^2}$$

and:

$$\alpha'^2 = 1 - v'^2 / c^2$$

This conclusion is valid if ${}^4\mathbf{V}$ is indeed a 4-vector, which we shall verify by writing the expression:

$$\underline{{}^4\mathbf{V}'} = \frac{d\underline{{}^4\mathbf{M}'}}{d\tau'}$$

in view of the fact that $\underline{{}^4\mathbf{M}'} = \underline{\underline{\mathbf{D}}}_1 \underline{{}^4\mathbf{M}}$.

We obtain:

$$z' = \frac{1}{\alpha_1} (z - v_1 t), \quad t' = \frac{1}{\alpha_1} \left(t - \frac{v_1}{c^2} z \right)$$

and therefore:

$$\frac{dz'}{dt'} = \frac{dz - v_1 dt}{dt - \frac{v_1}{c^2} dz} = \frac{v - v_1}{1 - \frac{v v_1}{c^2}}$$

and finally:

$$v' = \frac{v - v_1}{1 - \frac{v v_1}{c^2}}$$

which does indeed correspond to the result found above.

We have:

$$\underline{{}^4\mathbf{V}'} = \begin{bmatrix} 0 \\ 0 \\ v'/\alpha' \\ ic/\alpha' \end{bmatrix}$$

with that value of v' .

NOTE 1.2.— v_x, v_y and v_z being the coordinates of the velocity \mathbf{v} in the three-dimensional space, the components of $4\mathbf{V}$ form the column matrix:

$$\underline{4\mathbf{V}} = \begin{bmatrix} v_x/\alpha \\ v_y/\alpha \\ v_z/\alpha \\ ic/\alpha \end{bmatrix} \quad [1.10]$$

and the following relation is always valid:

$$(4V)^2 = -c^2 \quad [1.11]$$

1.1.2. Law of dynamics for a material point

We define the mass m_0 of the material point M as being a scalar in the Minkowski space. The mass m_0 is therefore invariable when we change the Galilean frame of reference.

The universe momentum vector or 4-momentum is defined by:

$$4\mathbf{p} = m_0 4\mathbf{V} \quad [1.12]$$

$4\mathbf{V}$ being a 4-vector, $4\mathbf{p}$ is, of course, a 4-vector as well.

NOTE 1.3.— The first three coordinates of $4\mathbf{p}$ are the components p_x, p_y, p_z of the classic momentum \mathbf{p} and, for the mass of the material point moving at velocity \mathbf{v} , we have:

$$m = m_0/\alpha \quad [1.13]$$

Hence, the 4-vector ${}^4\mathbf{p}$ is written in matricial form:

$${}^4\mathbf{p} = \begin{bmatrix} p_x \\ p_y \\ p_z \\ imc \end{bmatrix} \quad [1.14]$$

We also define the force 4-vector ${}^4\mathbf{\Phi}$ of matrix:

$${}^4\mathbf{\Phi} = \begin{bmatrix} F_x/\alpha \\ F_y/\alpha \\ F_z/\alpha \\ -\mathbf{F} \cdot \mathbf{v}/ic\alpha \end{bmatrix} \quad [1.15]$$

on the basis of the coordinates F_x, F_y, F_z of the classic force vector \mathbf{F} . The *universe acceleration* ${}^4\mathbf{\Gamma}$ is also introduced:

$${}^4\mathbf{\Gamma} = d{}^4\mathbf{V}/d\tau \quad [1.16]$$

We observe that:

$${}^4\mathbf{V} \cdot d{}^4\mathbf{V}/d\tau = {}^4\mathbf{V} \cdot {}^4\mathbf{\Gamma} = 0 \quad [1.17]$$

In the Minkowski space, the formulas of the dynamics of the material point are condensed into one formula:

$$\frac{d{}^4\mathbf{p}}{d\tau} = {}^4\mathbf{\Phi} \quad [1.18]$$

This relation is also written as:

$${}^4\mathbf{\Phi} = m_0 {}^4\mathbf{\Gamma} = m_0 \frac{d{}^4\mathbf{V}}{d\tau} \quad [1.19]$$

It leads to the equations of mechanics in special relativity:

$$\mathbf{F} = \frac{d(m\mathbf{v})}{dt}, \quad \mathbf{F} \cdot \mathbf{v} = \frac{d(mc^2)}{dt} \quad [1.20]$$

from which we can deduce the classic formula: $W = \Delta(mc^2)$ where W is the work.

1.2. Electromagnetic quantities in a non-polarized medium

The equations of relativistic mechanics cannot easily be extended to *continuous media* (also known as *continua*). Indeed, in this case, we need to switch from looking at the material particle – a molecule, an electron or an ion, to looking at the ensemble formed by a very large number of particles, upon which we need to perform statistical calculations. Necessarily, therefore, we need to find the definition of a coherent relativistic thermodynamics if we wish to correctly describe the motion of the continuum. These problems are highly complex.

On the other hand, unlike the study of sets of particles, the study of an electromagnetic field is much easier, particularly when we are dealing with non-polarized media. Thus, we shall begin by looking at fields in the absence of polarization.

In a medium – be it polarized or otherwise – it is possible to define a current 4-vector. In order to do so, we introduce a scalar $\tilde{\rho}_0$, which is the electrical charge per unit volume.

Then, by definition, the current 4-vector 4I is:

$${}^4I = \tilde{\rho}_0 \frac{{}^4V}{c} \quad [1.21]$$

with ${}^4\mathbf{V}$ being the 4-velocity of the material point in question. Thus, we have:

$${}^4\mathbf{I} = \begin{bmatrix} \tilde{\rho}v_x/c \\ \tilde{\rho}v_y/c \\ \tilde{\rho}v_z/c \\ i\tilde{\rho} \end{bmatrix} = \begin{bmatrix} I_x/c \\ I_y/c \\ I_z/c \\ i\tilde{\rho} \end{bmatrix} \quad [1.22]$$

when we introduce the classic charge $\tilde{\rho}$ per unit volume:

$$\tilde{\rho} = \tilde{\rho}_0/\alpha \quad [1.23]$$

and the classic current density vector \mathbf{I} :

$$\mathbf{I} = \tilde{\rho} \mathbf{v} \quad [1.24]$$

The conservation of electricity expresses the fact that the integral of the charge flux 4I over an enclosed surface ${}^4S = \partial({}^4\mathcal{V})$ is null:

$$\int_{{}^4S} {}^4I \cdot {}^4N dS = 0 \quad [1.25]$$

With the divergence theorem, because of the conditions of continuity of the quantities, we can deduce that:

$$\int_{{}^4\mathcal{V}} {}^4\nabla \cdot {}^4I d\mathcal{V} = 0 \quad [1.26]$$

If no discontinuity surface exists in the 4-volume in question, we have:

$${}^4\nabla \cdot {}^4I = 0 \quad [1.27]$$

Immediately, we can deduce from this the classic relation:

$$\frac{\partial \tilde{\rho}}{\partial t} + \nabla \cdot \mathbf{I} = 0 \quad [1.28]$$

In a non-polarized medium, the electromagnetic field is defined by two matrices $\underline{\underline{4\mathcal{F}}}$ and $\underline{\underline{4\mathcal{F}^*}}$, depending on the six quantities $E_x, E_y, E_z, B_x, B_y, B_z$, such that in a given frame of reference:

$$\underline{\underline{4\mathcal{F}}} = \begin{bmatrix} 0 & B_z & -B_y & -iE_x \\ -B_z & 0 & B_x & -iE_y \\ B_y & -B_x & 0 & -iE_z \\ iE_x & iE_y & iE_z & 0 \end{bmatrix} \quad [1.29]$$

$$\underline{\underline{4\mathcal{F}^*}} = \begin{bmatrix} 0 & -iE_z & iE_y & B_x \\ iE_z & 0 & -iE_x & B_y \\ -iE_y & iE_x & 0 & B_z \\ -B_x & -B_y & -B_z & 0 \end{bmatrix} \quad [1.30]$$

As with the other quantities (scalars m_0 and $\tilde{\rho}_0$, vectors ${}^4\mathbf{V}, {}^4\Phi, {}^4\mathbf{p}, {}^4I$), the components of these tensors in relation to a new frame of reference satisfy the classic base-change relations, with the base-change matrix being that of the *special Lorentz transformation*.

This matrix is such that: $\underline{\underline{4\mathbf{D}^T}} = \underline{\underline{4\mathbf{D}^{-1}}}$, so, in the new base, we have:

$$\underline{\underline{4\mathcal{F}'}} = \underline{\underline{4\mathbf{D}}} \underline{\underline{4\mathcal{F}}} \underline{\underline{4\mathbf{D}^T}}, \quad \underline{\underline{4\mathcal{F}'}} = \underline{\underline{4\mathbf{D}^T}} \underline{\underline{4\mathcal{F}'}} \underline{\underline{4\mathbf{D}}} \quad [1.31]$$

The electromagnetic balance equations are expressed in the Minkowski space by:

$$\int_{\partial {}^4\mathcal{V}} \underline{\underline{4\mathcal{F}}} \underline{\underline{4\mathbf{N}}} dS = \int_{{}^4\mathcal{V}} \underline{\underline{4\mathbf{I}}} d^4\mathcal{V} \quad [1.32]$$

$$\int_{\partial {}^4\mathcal{V}} \underline{\underline{4\mathcal{F}^*}} \underline{\underline{4\mathbf{N}}} dS = 0 \quad [1.33]$$

By applying the divergence theorem, we obtain:

$$4\nabla \cdot 4\mathcal{F} = 4I \quad [1.34]$$

$$4\nabla \cdot 4\mathcal{F}^* = 0 \quad [1.35]$$

These two relations lead to the *two groups of Maxwell equations*:

$$\nabla \cdot \mathbf{E} = \tilde{\rho}, \quad \nabla \times \mathbf{B} = \frac{1}{c} \mathbf{I} + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} \quad [1.36]$$

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0}, \quad \nabla \cdot \mathbf{B} = 0 \quad [1.37]$$

where \mathbf{E} and \mathbf{B} have the respective components E_x, E_y, E_z and B_x, B_y, B_z .

1.3. Momentum-energy tensor in a non-polarized medium

We have expressed the fundamental law of dynamics for a material point, which has led us to the equations of mechanics for that material point. The momentum-energy of the electromagnetic field can also be defined. For a continuum characterized by the quantities introduced above, the electromagnetic momentum-energy flux is defined by the tensor $\underline{\underline{4\mathcal{P}}^{fld}}$ (the exponent “*fld*” denoting the field), with matrix:

$$\underline{\underline{4\mathcal{P}}^{fld}} = \begin{bmatrix} \vec{\mathbf{P}}^{fld} & i\mathbf{E} \times \mathbf{B} \\ i\mathbf{E} \times \mathbf{B} & -\frac{E^2 + B^2}{2} \end{bmatrix} \quad [1.38]$$

where:

$$\mathbf{P}^{fld} = \frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2} \mathbf{1} - \mathbf{E} \otimes \mathbf{E} - \mathbf{B} \otimes \mathbf{B} \quad [1.39]$$

is the *Maxwell pressure tensor*.

Let us calculate the integral of the momentum-energy flux on an enclosed surface ($\partial \mathcal{V}$) delimiting a volume (\mathcal{V}):

$$\int_{\partial \mathcal{V}} {}_4\mathbf{P}^{fld} \cdot {}_4\mathbf{N} dS = - \int_{\mathcal{V}} {}_4\mathbf{F} \cdot {}_4\mathbf{I} d\mathcal{V} \quad [1.40]$$

The right-hand side of this equation is obtained from the left-hand side, using only the Maxwell equations. It represents the resultant force exerted on the volume (\mathcal{V}) by the action of the electromagnetic field on the medium.

By applying the divergence theorem to the left-hand side, we obtain:

$${}_4\nabla \cdot {}_4\mathbf{P}^{fld} = - {}_4\mathbf{F}^* \cdot {}_4\mathbf{I} \quad [1.41]$$

or indeed:

$$\frac{1}{c} \frac{\partial \mathbf{E} \times \mathbf{B}}{\partial t} + \nabla \cdot \mathbf{P}^{fld} = - \left(\tilde{\rho} \mathbf{E} + \frac{1}{c} \mathbf{I} \times \mathbf{B} \right) \quad [1.42]$$

$$\frac{\partial \left(\frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2} \right)}{\partial t} + \nabla \cdot (c \mathbf{E} \times \mathbf{B}) = - \mathbf{I} \cdot \mathbf{E} \quad [1.43]$$

The first equation expresses the *electromagnetic momentum balance* $\frac{1}{c} \mathbf{E} \times \mathbf{B}$, whose flux density is \mathbf{P}^{fld} , the Maxwell pressure tensor, and whose production rate per unit volume is equal to the opposite of the Lorentz force $(\tilde{\rho} \mathbf{E} + \frac{1}{c} \mathbf{I} \times \mathbf{B})$ acting on the unit volume of the fluid. The second equation expresses the *electromagnetic energy*

balance $\left(\frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2} \right)$, whose flux density is the Poynting vector ($c \mathbf{E} \times \mathbf{B}$); the scalar product ($\mathbf{I} \cdot \mathbf{E}$) represents the power of the field.

1.4. Electromagnetic quantities in a polarized medium

The non-polarized medium is a special case. In general, polarization does take place, and the electromagnetic field is defined by two tensors ${}^4\mathcal{H}$ and ${}^4\mathcal{F}^*$, each dependent on six quantities which are the components of the vectors:

- \mathbf{H} : magnetic displacement vector⁴ (or magnetic induction, or indeed magnetic excitation – see Figure 1.3(a));
- \mathbf{D} : electrical displacement vector (or electrical induction – see Figure 1.3(b));
- \mathbf{B} : magnetic field;
- \mathbf{E} : electrical field

We have:

$$\underline{\underline{{}^4\mathcal{H}}} = \begin{bmatrix} 0 & H_z & -H_y & -iD_x \\ -H_z & 0 & H_x & -iD_y \\ H_y & -H_x & 0 & -iD_z \\ iD_x & iD_y & iD_z & 0 \end{bmatrix} \quad [1.44]$$

$\underline{\underline{{}^4\mathcal{F}^*}}$ is given by the law [1.30].

⁴ When a substance is introduced into a magnetic field created by electrical currents, the magnetic field changes. The substance becomes magnetized and creates its own magnetic field which, along with the primary magnetic field, forms the resultant field. Thus, we obtain the magnetic induction vector $\mathbf{H} = \mathbf{B} - \mathbf{M}$ where \mathbf{M} corresponds to the magnetization. That magnetization is caused by the preferential orientation of the individual magnetic moments of each molecule.

The electromagnetic balance equations then take the form:

$$\int_{4S} 4\mathcal{H} \cdot 4\mathbf{N} dS = \int_{4\mathcal{V}} 4I d\mathcal{V} \quad [1.45]$$

$$\int_{4S} 4\mathcal{F}^* \cdot 4\mathbf{N} dS = 0 \quad [1.46]$$

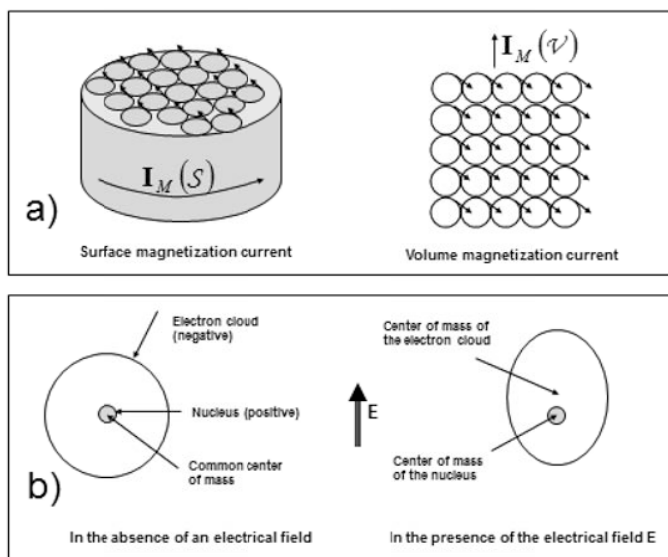


Figure 1.3. Electric and magnetic polarizations at the microscopic scale:
a) currents of magnetization of the surface (left), of the volume (right);
b) microscopic polarization induced by an electrical field

From this, we deduce the two groups of Maxwell equations for polarized media:

$$4\nabla \cdot 4\mathcal{H} = 4I \quad [1.47]$$

$$4\nabla \cdot 4\mathcal{F}^* = 0 \quad [1.48]$$

or indeed:

$$\nabla \cdot \mathbf{D} = \tilde{\rho}, \quad \nabla \times \mathbf{H} = \frac{1}{c} \mathbf{I} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} \quad [1.49]$$

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0}, \quad \nabla \cdot \mathbf{B} = 0 \quad [1.50]$$

For non-polarized media, we have:

$$\mathbf{D} = \mathbf{E}, \quad \mathbf{H} = \mathbf{B} \quad [1.51]$$

Generally, though, we define the electrical⁵ and magnetic polarizations:

$$\tilde{\mathbf{P}} = \mathbf{D} - \mathbf{E}, \quad \mathbf{M} = \mathbf{B} - \mathbf{H} \quad [1.52]$$

and the tensor:

$$4\mathcal{M} = 4\mathcal{F} - 4\mathcal{H} \quad [1.53]$$

The four vectors \mathbf{D} , \mathbf{H} , \mathbf{E} , \mathbf{B} are linked, two by two, and we can write the following formulas, for a medium at rest:

$$\underline{\mathbf{D}} = \underline{\underline{\epsilon}} \underline{\mathbf{E}} \quad [1.54]$$

$$\underline{\mathbf{H}} = \underline{\underline{\mu}}^{-1} \underline{\mathbf{B}} \quad [1.55]$$

⁵ The electrical polarization is not specific to conductive media. It plays a part, notably, in *dielectric* materials (or electrical insulators): these materials do not conduct electrical current, but they contain microscopic dipoles which are likely to move by small distances, or vibrate under the influence of an electrical field. The dipoles form in the atoms and the molecules, subject to electrical fields, when the barycenter of the negative charges (the electrons) shifts slightly in relation to that of the positive charges (the nuclei) (see Figure 2.3(b)).

ε being the *dielectric tensor* and $\underline{\mu}$ the *magnetic permeability tensor*. In the case of isotropic media, ε and $\underline{\mu}$ are reduced to scalars: ε the dielectric constant, and μ the magnetic permeability.

It must be noted here that, if the Maxwell relations are independent of the chosen Galilean frame of reference, the above relations are valid for a given fluid, and are written as follows, tracking the motion of that fluid:

$$\underline{\mathbf{D}}' = \underline{\varepsilon} \underline{\mathbf{E}}' \quad [1.56]$$

$$\underline{\mathbf{H}}' = \underline{\underline{\mu}}^{-1} \underline{\mathbf{B}}' \quad [1.57]$$

$\underline{\mathbf{D}}'$, $\underline{\mathbf{H}}'$, $\underline{\mathbf{E}}'$, $\underline{\mathbf{B}}'$ are expressed, in the framework with the same velocity as the fluid \mathbf{v} , thanks to the formulas of changing of the axes relating to the tensors ${}^4\mathcal{H}$ and ${}^4\mathcal{F}^*$:

$$\underline{\underline{{}^4\mathcal{H}}}' = \underline{\underline{{}^4\mathbf{D}}} \underline{\underline{{}^4\mathcal{H}}} \underline{\underline{{}^4\mathbf{D}}}'^T, \underline{\underline{{}^4\mathcal{F}}}'^* = \underline{\underline{{}^4\mathbf{D}}} \underline{\underline{{}^4\mathcal{F}}}'^* \underline{\underline{{}^4\mathbf{D}}}'^T \quad [1.58]$$

From these relations, when $v^2/c^2 \ll 1$, we deduce the following approximate formulas:

$$\begin{cases} \underline{\mathbf{D}}' = \underline{\mathbf{D}} + \frac{1}{c} \mathbf{v} \times \underline{\mathbf{H}}, \underline{\mathbf{E}}' = \underline{\mathbf{E}} + \frac{1}{c} \mathbf{v} \times \underline{\mathbf{B}} \\ \underline{\mathbf{H}}' = \underline{\mathbf{H}} + \frac{1}{c} \mathbf{v} \times \underline{\mathbf{D}}, \underline{\mathbf{B}}' = \underline{\mathbf{B}} + \frac{1}{c} \mathbf{v} \times \underline{\mathbf{E}} \end{cases} \quad [1.59]$$

Balance Laws for Non-polarized Reactive Mixtures

In this chapter, we shall first introduce the various quantities characterizing an electric medium with multiple components. These components are neutral or ionized chemical species and free electrons. Then, we shall recap on what is meant by a balance equation in three-dimensional space and in the Minkowski timespace.

We shall then move on to the balance equations for non-polarized composite media and describe a phenomenon typical of these media regarding electrical conduction.

2.1. Quantities characterizing a multi-component medium

If the medium is made up of multiple chemical species, then for each of those species, we define a charge per unit volume $\tilde{\rho}_k$, a specific mass ρ_k , and a velocity \mathbf{v}_k . If z_k denotes the charge per unit mass (constant for a given species), we have: $\tilde{\rho}_k = \rho_k z_k$. The mass flux of species k in relation to a fixed frame of reference is:

$$\mathbf{J}_k = \rho_k \mathbf{v}_k \tag{2.1}$$

and the flux of charge of species k , in relation to the same frame of reference, is:

$$\tilde{\mathbf{J}}_k = \tilde{\rho}_k \mathbf{v}_k \quad [2.2]$$

For the mixture, we introduce average values.

The charge per unit volume is defined by:

$$\tilde{\rho} = \sum_k \tilde{\rho}_k \quad [2.3]$$

The density is:

$$\rho = \sum_k \rho_k \quad [2.4]$$

and the total mass flux can be used to define the barycentric velocity of the fluid:

$$\mathbf{J}_M = \sum_k \mathbf{J}_k = \sum_k \rho_k \mathbf{v}_k = \rho \mathbf{v} \quad [2.5]$$

Thus, we have:

$$\mathbf{v} = \sum_k \frac{\rho_k}{\rho} \mathbf{v}_k = \sum_k Y_k \mathbf{v}_k \quad [2.6]$$

where Y_k denotes the mass fraction of the species.

The fluxes in relation to the barycentric motion are then defined, such as the diffusion flux (see Chapter 2 of [PRU 12]):

$$\mathbf{J}_{Dk} = \rho_k (\mathbf{v}_k - \mathbf{v}) \quad [2.7]$$

involving the diffusion rate:

$$\mathbf{V}_k = \mathbf{v}_k - \mathbf{v} \quad [2.8]$$

Of course, by definition, we have:

$$\sum_k \mathcal{J}_{Dk} = \mathbf{0} \quad [2.9]$$

The *diffusion current* of species k :

$$\tilde{\mathbf{J}}_{Dk} = \tilde{\rho}_k (\mathbf{v}_k - \mathbf{v}) \quad [2.10]$$

but this time we have $\sum_k \tilde{\mathbf{J}}_{Dk} \neq \mathbf{0}$, and we introduce the total conduction current \mathbf{i} :

$$\mathbf{i} = \sum_k \tilde{\mathbf{J}}_{Dk} = \sum_k \tilde{\rho}_k (\mathbf{v}_k - \mathbf{v}) \quad [2.11]$$

Given that the total current is equal to:

$$\mathbf{I} = \sum_k \tilde{\mathbf{J}}_k = \sum_k \tilde{\rho}_k \mathbf{v}_k \quad [2.12]$$

and the convection current is equal to $\tilde{\rho} \mathbf{v}$, we write:

$$\mathbf{I} = \tilde{\rho} \mathbf{v} + \mathbf{i} \quad [2.13]$$

From a thermodynamic point of view, the state of each chemical species is characterized by the same variables as in non-conductive media (see Chapter 2 of [PRU 12]). For example, species k is present at a concentration Y_k (mass fraction), a chemical potential g_k per unit mass. The *non-polarized conductive medium*, with internal energy

ε , entropy s and volume ϑ per unit mass, satisfies the relation:

$$de = T ds - p d\vartheta + \sum_k g_k dY_k \quad [2.14]$$

This result is no longer valid for polarized systems, as we shall see in Chapter 3. In a non-polarized medium, the Gibbs equation given above can be written as a function of other variables. Indeed, the Maxwell equations shown earlier enable us to write that the fields \mathbf{B} and \mathbf{E} depend on the scalar potential φ and the vector potential \mathbf{A} such that:

$$\mathbf{E} = -\nabla\varphi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \quad [2.15]$$

$$\mathbf{B} = \nabla \times \mathbf{A} \quad [2.16]$$

This potential φ can be used to define the electrochemical potential:

$$\tilde{g}_k = g_k + z_k \varphi \quad [2.17]$$

and the internal energy:

$$\tilde{e} = e + z \varphi \quad [2.18]$$

where:

$$z = \sum_k z_k Y_k \quad [2.19]$$

Thus, we obtain:

$$d\tilde{e} = T ds - p d\vartheta + \sum_k \tilde{g}_k dY_k + z d\varphi \quad [2.20]$$

If chemical reactions are present, we use the notation \dot{W}_k to denote the mass of species k produced by those reactions in the unit volume and per unit time. As the chemical reactions have algebraic stoichiometric coefficients ν_k , we have: $\dot{W}_k = \mathcal{M}_k \sum_r \nu_{kr} \dot{\zeta}_r$, where \mathcal{M}_k is the molar mass of the species in question, and $\dot{\zeta}_r$ is the production rate in moles for the reaction r .

2.2. General balance equation

Remember that the balance of a certain quantity F characteristic of a *fluid with a single chemical component* [PRU 12] expresses the fact that in a given volume (\mathcal{V}) delimited by a surface ($\partial\mathcal{V}$), any variation in F over time is the result of exchanges across ($\partial\mathcal{V}$) and production phenomena in (\mathcal{V}).

If we consider a fixed domain, we have:

$$\frac{\partial}{\partial t} \int_{\mathcal{V}} \rho f d\mathcal{V} + \int_{\partial\mathcal{V}} \mathbf{J}_F \cdot \mathbf{n} dS = \int_{\mathcal{V}} \dot{W}_F d\mathcal{V} \quad [2.21]$$

where f is equal to the mass value of F , \mathbf{J}_F is the total flux of the quantity F and \dot{W}_F is the production rate. From the above balance, in general, we can deduce the following balance equation for a homogeneous fluid:

$$\frac{\partial(\rho f)}{\partial t} + \nabla \cdot \mathbf{J}_F = \dot{W}_F \quad [2.22]$$

Another form of the balance equation is derived from the above equation, using the conservation of mass equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad [2.23]$$

by introducing the relative flux \mathbf{j}_F such that:

$$\mathbf{J}_F = \rho f \mathbf{v} + \mathbf{j}_F \quad [2.24]$$

We deduce:

$$\rho \frac{df}{dt} + \nabla \cdot \mathbf{j}_F = \dot{W}_F \quad [2.25]$$

where:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \quad [2.26]$$

for the time-derivative, following the barycentric motion.

For a *composite system*, we shall make an effort, in all cases, to obtain a balance equation with one of the forms shown above. When $\dot{W}_F = 0$ we say that we are dealing with a conservation equation.

From a *relativistic point of view*, the balance is expressed by means of the flux in the Minkowski space. A quantity F which has the flux ${}^4\mathbf{J}_F$ and the production rate ${}^4\dot{W}_F$ will be such that:

$$\int_{{}^4\partial\mathcal{V}} {}^4\mathbf{J}_F \cdot {}^4\mathbf{N} dS = \int_{{}^4\mathcal{V}} {}^4\dot{W}_F d\mathcal{V} \quad [2.27]$$

This equation is valid in any given frame of reference. When no discontinuity surface is present in the control volume (${}^4\mathcal{V}$), we can write:

$${}^4\nabla \cdot {}^4\mathbf{J}_F = {}^4\dot{W}_F \quad [2.28]$$

If we set:

$$\begin{bmatrix} {}^4\mathbf{J}_{Fx} \\ {}^4\mathbf{J}_{Fy} \\ {}^4\mathbf{J}_{Fz} \end{bmatrix} = \frac{1}{c} \mathbf{J}_F, \quad {}^4\mathbf{J}_{F\tau} = i\rho f, \quad {}^4\dot{W}_F = \frac{1}{c} \dot{W}_F \quad [2.29]$$

then we find ourselves with the balance equation:

$$\frac{\partial(\rho f)}{\partial t} + \nabla \cdot \mathbf{J}_F = \dot{W}_F \quad [2.30]$$

From this equation, at least for scalar values, we can derive a correspondence between the relativistic balance and the classic balance.

2.3. Mass balance and electrical charge balance

The mass flux density 4-vector is:

$${}^4\mathbf{J}_M = \rho_0 {}^4\mathbf{V} \quad [2.31]$$

where ${}^4\mathbf{V}$ is the 4-velocity.

For each species k , there will be a flux ${}^4\mathbf{J}_k = \rho_{0k} {}^4\mathbf{V}_k$, and the balance is written as:

$${}^4\nabla \cdot (\rho_{0k} {}^4\mathbf{V}_k) = {}^4\dot{W}_k \quad [2.32]$$

In the “laboratory system”, this equation gives us:

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k \mathbf{v}_k) = \dot{W}_k \quad [2.33]$$

with the mass production rate in relation to chemical reactions \dot{W}_k . Summation in relation to the index k gives us:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad [2.34]$$

or, in the Minkowski space:

$${}^4\nabla \cdot (\rho_0 {}^4\mathbf{V}) = 0 \quad [2.35]$$

in view of the conservation of overall mass, which is expressed chemically by:

$$\sum_k \dot{W}_k = 0 \quad [2.36]$$

or indeed:

$$\sum_k {}^4\dot{W}_k = 0 \quad [2.37]$$

By introducing the material derivative:

$$d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla \quad [2.38]$$

for a non-relativistic fluid, we obtain:

$$d\rho/dt + \rho \nabla \cdot \mathbf{v} = 0 \quad [2.39]$$

for the overall mass and, by combining this with the balance equations in the above form:

$$\rho dY_k/dt + \nabla \cdot \mathcal{J}_{Dk} = \dot{W}_k \quad [2.40]$$

As the electrical current is linked to the mass of the species and their charge, the charge balance equations will

be deduced from the mass balance equations. For the charge of species k , we need merely multiply by the charge z_k of the species per unit mass and divide by the celerity of light c . We obtain:

$${}^4\nabla \cdot {}^4\tilde{\mathbf{J}}_k = \frac{1}{c} z_k {}^4\dot{W}_k \quad [2.41]$$

where:

$${}^4\tilde{\mathbf{J}}_k = \frac{1}{c} z_k {}^4\mathbf{J}_k = \begin{bmatrix} \tilde{\rho}_k v_{kx}/c \\ \tilde{\rho}_k v_{ky}/c \\ \tilde{\rho}_k v_{kz}/c \\ i \tilde{\rho}_k \end{bmatrix} \quad [2.42]$$

for the total current, we have:

$$\tilde{\mathbf{J}} = \sum_k \tilde{\mathbf{J}}_k \quad [2.43]$$

so that:

$${}^4\nabla \cdot {}^4\tilde{\mathbf{J}} = \frac{1}{c} \sum_k z_k {}^4\dot{W}_k \quad [2.44]$$

or indeed:

$$\partial \tilde{\rho} / \partial t + \nabla \cdot \mathbf{I} = \sum_k z_k \dot{W}_k = 0 \quad [2.45]$$

because overall, there is *conservation of the electrical charge*; i.e. if, in the medium in question, a charged particle is produced, the particle of opposite charge is produced simultaneously. The right-hand side of this equation, which

only includes reactions involving charged particles, therefore, is null. We have:

$$\sum_k z_k \dot{W}_k = \sum_k z_k \mathcal{M}_k \left(\sum_r \nu_{kr} \dot{\zeta}_r \right) = \sum_r \dot{\zeta}_r \left(\sum_k \nu_{kr} z_k \mathcal{M}_k \right) \quad [2.46]$$

The product $z_k \mathcal{M}_k$ represents the charge of species k produced in the reaction r with the stoichiometric coefficient ν_{kr} . If species k is produced in this way, species k' , with the opposite charge, is simultaneously produced, so that:

$$z_{k'} \mathcal{M}_{k'} = -z_k \mathcal{M}_k, \quad \nu_{k'r} = \nu_{kr} \quad [2.47]$$

It follows from this that in the sum $\sum_k \nu_{kr} z_k \mathcal{M}_k$, there are only couples of terms such as: $\nu_{kr} z_k \mathcal{M}_k + \nu_{k'r} z_{k'} \mathcal{M}_{k'}$, which are, of course, equal to zero.

Given the definition of the conduction current \mathbf{i} , we also have:

$$\rho dz/dt + \nabla \cdot \mathbf{i} = 0 \quad [2.48]$$

2.4. Momentum and energy balances

We have expressed the energy-momentum tensor¹ due to the electromagnetic field for a simple system. The expression holds true in the case of a composite system. However, in

¹ This four-tensor is sometimes called “stress-energy tensor” or “stress-energy-momentum tensor”. It describes the density and flux of energy and momentum in spacetime, generalizing the stress tensor in Newtonian mechanics.

order to write the momentum-energy balance, we must be able to express the momentum-energy tensor due to the mass of the particles making up the fluid.

Steering clear of relativistic thermodynamics, as we decided to at the outset of this study, we shall content ourselves with using classic expressions. These expressions give us a pressure-energy 4-tensor² with the matrix:

$$\underline{\underline{{}_4\mathcal{P}^m}} = \begin{bmatrix} \rho \mathbf{v} \otimes \mathbf{v} + \vec{\vec{\mathbf{P}}} & ic \rho \mathbf{v} \\ \frac{i}{c} \left[\mathbf{q} + \vec{\vec{\mathbf{P}}} \cdot \mathbf{v} + \rho(e+k) \mathbf{v} \right] & -\rho(e+k) \end{bmatrix} \quad [2.49]$$

NOTE 2.1.— If we were dealing with a relativistic fluid, the tensor ${}_4\mathcal{P}^m$ could still be expressed in the form:

$${}_4\mathcal{P}^m = \rho {}_4\mathbf{V} \otimes {}_4\mathbf{V} + {}_4\mathcal{T} \quad [2.50]$$

where ${}_4\mathcal{T}$ is the relativistic generalization of the pressure tensor $\vec{\vec{\mathbf{P}}}$.

If forces other than those of the electromagnetic field are exerted on the species, we shall denote them by f_k for the unit mass. Thus, we shall have the generalized forces:

$$\underline{\underline{{}_4\mathcal{F}_k}} = \begin{bmatrix} \rho_k f_k \\ \frac{i}{c} \rho_k f_k \cdot \mathbf{v}_k \end{bmatrix} \quad \text{and: } {}_4\mathcal{F} = \sum_k {}_4\mathcal{F}_k \quad [2.51]$$

² Remember here that stresses and pressures have equal modulus but opposite signs. In fluid mechanics we generally use pressures instead of stresses. Therefore we have a pressure-energy tensor instead of a stress-energy tensor, and these four-tensors, written in bold, have opposite signs.

The energy-momentum balance equation is thus written as follows, in the 4D space:

$${}_4\nabla \cdot ({}_4\mathcal{P}^{ch} + {}_4\mathcal{P}^m) = {}_4\Phi \quad [2.52]$$

This equation gives us two relations in the 3D space:

$$\frac{\partial \left(\rho \mathbf{v} + \frac{1}{c} \mathbf{E} \times \mathbf{B} \right)}{\partial t} + \underline{\nabla} \cdot \left(\begin{array}{c} \rho \mathbf{v} \otimes \mathbf{v} + \bar{\bar{\mathbf{P}}} + \frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2} \\ \mathbf{1} - \mathbf{E} \otimes \mathbf{E} - \mathbf{B} \otimes \mathbf{B} \end{array} \right) = \sum_k \rho_k \mathbf{f}_k \quad [2.53]$$

$$\begin{aligned} & \frac{\partial \left(\rho(e+k) + \frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2} \right)}{\partial t} + \underline{\nabla} \cdot \left(\mathbf{q} + \bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \rho(e+k) \mathbf{v} + c \mathbf{E} \times \mathbf{B} \right) \\ &= \sum_k \rho_k \mathbf{f}_k \cdot \mathbf{v}_k \end{aligned} \quad [2.54]$$

We also deduce:

$${}_4\nabla \cdot {}_4\mathcal{P}^m = {}_4\mathbf{F} \cdot {}_4\mathbf{I} + {}_4\Phi \quad [2.55]$$

Hence, in addition to the electromagnetic momentum-energy equation, and the total energy balance equation, we can write the following momentum-energy balance equations applicable in the 3D space:

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot \left(\rho \mathbf{v} \otimes \mathbf{v} + \bar{\bar{\mathbf{P}}} \right) = \tilde{\rho} \mathbf{E} + \frac{1}{c} \mathbf{I} \times \mathbf{B} + \sum_k \rho_k \mathbf{f}_k \quad [2.56]$$

$$\frac{\partial \rho(e+k)}{\partial t} + \nabla \cdot \left(\mathbf{q} + \bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \rho(e+k) \mathbf{v} \right) = \mathbf{I} \cdot \mathbf{E} + \sum_k \rho_k \mathbf{f}_k \cdot \mathbf{v}_k \quad [2.57]$$

With scalar multiplication by \mathbf{v} of both sides of the first of these relations, we obtain the kinetic energy balance equation:

$$\frac{\partial(\rho k)}{\partial t} + \nabla \cdot (\rho k \mathbf{v} + \bar{\bar{\mathbf{P}}} \cdot \mathbf{v}) = \bar{\bar{\mathbf{P}}} : \nabla \otimes \mathbf{v} + \tilde{\rho} \mathbf{v} \cdot \mathbf{E} + \frac{1}{c} \mathbf{v} \cdot (\mathbf{I} \times \mathbf{B}) + \sum_k \rho_k \mathbf{v} \cdot \mathbf{f}_k \quad [2.58]$$

The second of these relations, when combined with the kinetic energy balance equation, gives us the internal energy balance equation:

$$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot (\mathbf{q} + \rho e \mathbf{v}) = -\bar{\bar{\mathbf{P}}} : \nabla \otimes \mathbf{v} + \mathbf{i} \cdot \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) + \sum_k \mathcal{J}_{Dk} \cdot \mathbf{v}_k \quad [2.59]$$

or indeed, in relation to the barycentric motion:

$$\rho \frac{de}{dt} + \nabla \cdot \mathbf{q} = -\bar{\bar{\mathbf{P}}} : \nabla \otimes \mathbf{v} + \mathbf{i} \cdot \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) + \sum_k \mathcal{J}_{Dk} \cdot \mathbf{f}_k \quad [2.60]$$

If we follow the particles in their motion, the momentum equation also becomes:³

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \bar{\bar{\mathbf{P}}} = \tilde{\rho} \mathbf{E} + \frac{1}{c} \mathbf{I} \times \mathbf{B} + \sum_k \rho_k \mathbf{f}_k \quad [2.61]$$

NOTE 2.2.— In cases where the non-electromagnetic forces \mathbf{f}_k derive from potentials ψ_k , we write: $\mathbf{f}_k = \nabla \psi_k$, and we can consider an average potential such that $\rho \psi = \sum_k \rho_k \psi_k$. This enables us to consider a total energy $(e + k + \psi)$ instead

3 The *thermodynamics of non-polarized media* does not involve electromagnetic variables, so there is no need, here, to write the electromagnetic balance equations following the motion of the fluid particles. However, it is possible to change the frame of reference, but as we can clearly see, this does not alter either the Maxwell equations or the law of dynamics. Hence, the expressions remain the same in variables \mathbf{E}' and \mathbf{B}' as in variables \mathbf{E} and \mathbf{B} .

of $(e+k)$, as we did with equation [2.54]. Furthermore, we establish the following balance equation for the potential [GRO 69a, DUD 82]:

$$\rho \frac{d\psi}{dt} = -\nabla \cdot \left(\sum_k \psi_k \mathbf{J}_{Dk} \right) - \sum_k \rho_k \mathbf{v}_k \cdot \mathbf{f}_k$$

2.5. Entropy flux and entropy production

The entropy flux is identical to the neutral gas flux, so we have:

$$\mathbf{J}_S = \frac{1}{T} \left(\mathbf{q} - \sum_k \mathbf{g}_k \mathbf{J}_{Dk} \right) \quad [2.62]$$

Also, the Gibbs law can be written thus, following the barycentric motion defined by d/dt :

$$T \frac{ds}{dt} = \frac{de}{dt} + p \frac{d\vartheta}{dt} + \sum_k \mathbf{g}_k \frac{dY_k}{dt} \quad [2.63]$$

The expressions for de/dt and dY_k/dt are given in the above discussion; $d\vartheta/dt$ is deduced from the mass balance because $\vartheta = 1/\rho$:

$$\rho d\vartheta/dt = \nabla \cdot \mathbf{v} \quad [2.64]$$

We now deduce the expression of the entropy production rate \dot{W}_S involved in the entropy balance equation:

$$\begin{aligned} \dot{W}_S = & -\frac{1}{T^2} \mathbf{q} \cdot \nabla T - \sum_k \mathbf{J}_{Dk} \cdot \nabla \left(\frac{\mathbf{g}_k}{T} \right) - \frac{1}{T} \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \frac{1}{T} \mathbf{i} \cdot \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) \\ & + \frac{1}{T} \sum_k \mathbf{J}_{Dk} \cdot \mathbf{f}_k - \frac{1}{T} \sum_k \mathbf{g}_k \dot{W}_k \end{aligned} \quad [2.65]$$

Maxwell equations	$\nabla \cdot \mathbf{E} = \tilde{\rho}, \quad \nabla \times \mathbf{B} = \frac{1}{c} \mathbf{I} + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t},$ $\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0}, \quad \nabla \cdot \mathbf{B} = 0$
Chemical species balance	$\rho \frac{Y_k}{dt} + \nabla \cdot \mathbf{J}_{Dk} = \dot{W}_k$
Continuity equation	$\frac{d\rho}{dt} + \rho \tilde{\nabla} \cdot \tilde{\mathbf{v}} = 0$
Electrical charge balance	$\rho dz/dt + \nabla \cdot \mathbf{i} = 0$
Momentum equation	$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \tilde{\mathbf{P}} = \tilde{\rho} \mathbf{E} + \frac{1}{c} \mathbf{I} \times \mathbf{B} + \sum_k \rho_k \mathbf{f}_k$
Internal energy balance	$\rho \frac{de}{dt} + \nabla \cdot \mathbf{q} = -\tilde{\mathbf{P}} : \nabla \otimes \mathbf{v} + \mathbf{i} \cdot \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) + \sum_k \mathbf{J}_{Dk} \cdot \mathbf{f}_k$
Entropy equation	$\rho \frac{ds}{dt} + \tilde{\nabla} \cdot \left[\left(\mathbf{q} - \sum_k g_k \mathbf{J}_{Dk} \right) / T \right] = \dot{W}_S$
Entropy production rate	$\dot{W}_S = -\frac{1}{T^2} \mathbf{q} \cdot \nabla T - \sum_k \mathbf{J}_{Dk} \cdot \nabla \left(\frac{g_k}{T} \right) - \frac{1}{T} \mathbf{\Pi} : \nabla \otimes \mathbf{v}$ $+ \frac{1}{T} \mathbf{i} \cdot \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) + \frac{1}{T} \sum_k \mathbf{J}_{Dk} \cdot \mathbf{f}_k - \frac{1}{T} \sum_k g_k \dot{W}_k$

Table 2.1. Balance equations of a non-polarized fluid mixture. \mathbf{B} magnetic field, \mathbf{E} electrical field, \mathbf{J}_{Dk} diffusion flux, \mathbf{q} heat flux, \mathbf{i} diffusion current, $\tilde{\mathbf{P}}$ pressure tensor, $\mathbf{\Pi}$ viscous pressure tensor, \dot{W}_k chemical production rate, \mathbf{f}_k remote forces other than those due to the electromagnetic field

This production rate is equal to:

$$\dot{W}_S = \rho \frac{ds}{dt} + \nabla \cdot \mathbf{J}_S \quad [2.66]$$

As for the tensor Π , it is equal to:

$$\Pi = \bar{\bar{\mathbf{P}}} - p\mathbf{1} \quad [2.67]$$

where p is the thermodynamic pressure, which is a common value between the pressure p as it appears in the Gibbs relation and the hydrodynamic pressure p .

The balance equations for a non-polarized medium are summarized in Table 2.1.

2.6. Electrical resistance

The entropy production rate is equal to a sum of products of generalized forces by generalized fluxes. The laws of thermodynamics of irreversible processes enable us to express these fluxes as functions of these forces. When we do not stray too far from the state of equilibrium, where the fluxes and forces are null, linear relations appear between these terms. The coefficients of these linear laws are the Onsager phenomenological coefficients: they are combinations of the coefficients of diffusion, viscosity, heat conduction, etc. In conductive media, the electrical resistance also appears as an Onsager coefficient.

In order to demonstrate this fact, we envisage an isothermal conductor made up solely of ions and electrons. This is illustrated well by a metal conductor, with the ensemble of ions (fixed) plus electrons (mobile) behaving like a fluid. No chemical reaction takes place, there are no forces \mathbf{f}_k at work, no viscosity, etc. Only an electrical current is liable to circulate.

In light of the above, we have:

$$T\dot{W}_S = -\sum_k \mathbf{j}_{Dk} \cdot \nabla g_k + \mathbf{i} \cdot \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) \quad [2.68]$$

However, we have: $\mathbf{v}_i = 0$, $\rho_e \mathbf{v}_e = \rho \mathbf{v}$, which, for the diffusion fluxes, gives us:

$$\mathbf{J}_{De} = -\mathbf{J}_{Di} = \frac{1 - Y_e}{z_e} \mathbf{I}$$

Because neutrality is assured, the total charge z is zero, and we have:

$$\mathbf{i} = \mathbf{I} = \rho_e z_e \mathbf{v}_e = \rho z_e \mathbf{v}$$

Additionally, in the absence of a temperature and pressure gradient, the Gibbs–Duhem equation gives us:

$$Y_e \nabla g_e + Y_i \nabla g_i = \mathbf{0} \quad [2.69]$$

where: $Y_i = 1 - Y_e$. From these equations, it results that:

$$T \dot{W}_s = \mathbf{I} \cdot \left[\mathbf{E} - \nabla \left(\frac{g_e}{z_e} \right) \right] \quad [2.70]$$

On the right-hand side of this equation, the generalized flux is the first factor of the product, and the generalized force is the second. We can write the following linear relation:

$$\mathbf{E} - \nabla \left(\frac{g_e}{z_e} \right) = \mathbf{R} \cdot \mathbf{I} \quad [2.71]$$

This is Ohm's law: the tensor \mathbf{R} is the electrical resistance tensor, which may not necessarily be isotropic.

If $|\nabla(g_e/z_e)| \ll |\mathbf{E}|$ and $\mathbf{R} = R \mathbf{1}$, we have $\mathbf{E} \propto \mathbf{I}$, and we find the familiar relation: $E = R I$.

Balance Laws for Polarized Reactive Mixtures

In this chapter, we shall begin by presenting the thermodynamic quantities which characterize a polarized medium. The relations between the various thermodynamic quantities will be written, and the laws of state established with reference to particular scenarios. We shall then establish the balance equations, as we did in regard to non-polarized media, and finally give two examples of non-equilibrium phenomena typical of polarized systems: dielectric relaxation and magnetic relaxation.

3.1. Thermodynamic relations in the presence of polarization

In order to characterize the polarization of the medium, we have previously introduced the electric and magnetic polarization vectors¹:

$$\vec{\mathbf{P}} = \mathbf{D} - \mathbf{E} \quad [3.1]$$

¹ The arrow over the polarization symbol $\vec{\mathbf{P}}$ is there, as previously noted, to clearly mark that it is a vector rather than a second-order tensor (remember that the pressure tensor is denoted $\vec{\vec{\mathbf{P}}}$).

$$\mathbf{M} = \mathbf{B} - \mathbf{H} \quad [3.2]$$

The mass volume of the medium being $\vartheta = 1/\rho$, we also introduce the vectors of polarization per unit mass:

$$\mathbf{p} = \vartheta \bar{\mathbf{P}} \quad [3.3]$$

$$\mathbf{m} = \vartheta \mathbf{M} \quad [3.4]$$

If the medium is moving, we can overlook the terms in v^2/c^2 to find:

$$\bar{\mathbf{P}}' = \bar{\mathbf{P}} - \frac{1}{c} \mathbf{v} \times \mathbf{M} \quad [3.5]$$

$$\mathbf{M}' = \mathbf{M} + \frac{1}{c} \mathbf{v} \times \bar{\mathbf{P}} \quad [3.6]$$

Similarly, with the same approximations, we have:

$$\mathbf{p}' = \mathbf{p} - \frac{1}{c} \mathbf{v} \times \mathbf{m} \quad [3.7]$$

$$\mathbf{m}' = \mathbf{m} + \frac{1}{c} \mathbf{v} \times \mathbf{p} \quad [3.8]$$

In the discussion which follows, we shall suppose that the frame of reference is linked to the fluid, but omit the prime for simplicity's sake. In any case, this makes no difference if we suppose that the transformations are reversible (and therefore slow) in the laboratory system.

A wide array of formulations exist in relation to the thermodynamics of equilibrium states.

3.1.1. Formulation advanced by de Groot and Mazur

S.R. de Groot and P. Mazur [GRO 69a] (formulas 70, p. 390) agree that the state of a composite system depends on $N + 4$ variables: $T, \vartheta, \mathbf{p}, \mathbf{m}, Y_1, \dots, Y_N$, and therefore write that the mass-free energy f is a function of those variables:

$$f = f(T, \vartheta, \mathbf{p}, \mathbf{m}, Y_1, \dots, Y_N) \quad [3.9]$$

We can just as well describe the system using the entropy or the internal energy instead of looking at the free energy. For example, with the mass internal energy e , we obtain:

$$e = e(s, \vartheta, \mathbf{p}, \mathbf{m}, Y_1, \dots, Y_N) \quad [3.10]$$

and the Gibbs relation is written as:

$$de = T ds - p d\vartheta + \mathbf{E}_{eq} \cdot d\mathbf{p} + \mathbf{B}_{eq} \cdot d\mathbf{m} + \sum_k g_k dY_k \quad [3.11]$$

\mathbf{E}_{eq} and \mathbf{B}_{eq} are therefore thermodynamic vectorial quantities defined by:

$$\mathbf{E}_{eq} = \left(\frac{\partial e}{\partial \mathbf{p}} \right)_{s, \vartheta, \mathbf{m}, Y_k} \quad [3.12]$$

$$\mathbf{B}_{eq} = \left(\frac{\partial e}{\partial \mathbf{m}} \right)_{s, \vartheta, \mathbf{p}, Y_k} \quad [3.13]$$

in the same way as we define the thermodynamic pressure:

$$p = - \left(\frac{\partial e}{\partial \vartheta} \right)_{s, \mathbf{p}, \mathbf{m}, Y_k} \quad [3.14]$$

If we move from one equilibrium state to another slightly different equilibrium state, the polarizations \mathbf{p} and \mathbf{m} respectively become $\mathbf{p} + d\mathbf{p}$ and $\mathbf{m} + d\mathbf{m}$. The corresponding variations $d\mathbf{E}_{eq}$ and $d\mathbf{B}_{eq}$ can easily be deduced, using relations [1.54] and [1.55] which, here, give us:

$$\mathbf{E}_{eq} = \rho \boldsymbol{\kappa}^{-1} \cdot \mathbf{p} \quad [3.15]$$

$$\mathbf{B}_{eq} = \rho(\boldsymbol{\chi} + \mathbf{1}) \cdot \boldsymbol{\chi}^{-1} \cdot \mathbf{m} \quad [3.16]$$

where:

$$\boldsymbol{\kappa} = \boldsymbol{\varepsilon} - \mathbf{1} \quad [3.17]$$

$$\boldsymbol{\chi} = \boldsymbol{\mu} - \mathbf{1} \quad [3.18]$$

A polarized fluid medium is such that *at equilibrium*, isotropy is ensured, so that $\boldsymbol{\varepsilon}$ and $\boldsymbol{\mu}$ are reduced to scalars, as are $\boldsymbol{\kappa}$ and $\boldsymbol{\chi}$. Thus, as a function of the electric and magnetic susceptibilities² κ and μ , we have:

$$\mathbf{E}_{eq} = (\rho/\kappa) \mathbf{p} \quad [3.19]$$

$$\mathbf{B}_{eq} = \rho(\chi + 1/\chi) \mathbf{m} \quad [3.20]$$

Non-equilibrium states, for their part, are characterized by the classic thermodynamic variables, in addition to which we need to consider the pressure tensor $\bar{\bar{\mathbf{P}}}$ including a

² Diamagnetic materials (alcohol, bismuth, carbon, copper, water, lead, mercury, silver) have a negative magnetic susceptibility, whereas the magnetic susceptibility of paramagnetic materials (air, tungsten, cesium, aluminum, lithium, magnesium, oxygen, sodium) is positive. When the magnetic permeability is much greater than one, we are dealing with a ferromagnetic material (cobalt, iron, nickel). It is null in a vacuum.

viscous part in the case of a fluid, the electrical field \mathbf{E} and the magnetic field \mathbf{B} , which may differ from \mathbf{E}_{eq} and \mathbf{B}_{eq} . The differences $\mathbf{E} - \mathbf{E}_{eq}$ and $\mathbf{B} - \mathbf{B}_{eq}$ induce the phenomena of *dielectric and magnetic relaxation*.

For example, dielectric relaxation (see section 3.5), in the simplest case (that of an isotropic system, with no magnetic field), gives us the expression of the production rate per unit volume (see equation [3.74] for the expression of the entropy production rate³):

$$\dot{W}_p = -\frac{L}{T} \frac{\partial \bar{\mathbf{P}}}{\partial t} \cdot (\mathbf{E}_{eq} - \mathbf{E}) \quad [3.21]$$

which, for a system at rest ($\mathbf{v} = 0$) gives us the *Debye equation*:

$$\frac{\partial \bar{\mathbf{P}}}{\partial t} = -\frac{L}{T} (\mathbf{E}_{eq} - \mathbf{E}) = -\frac{L}{\kappa T} (\bar{\mathbf{P}} - \kappa \mathbf{E}) \quad [3.22]$$

3.1.2. Kluitenberg formulation

Another formulation, advanced by C.A. Kluitenberg [KLU 73], presents the polarized system as the meeting of two polarized subsystems which may be in a state of mutual disequilibrium. This presentation is similar to that given by L.G. Napolitano [NAP 71] for the disequilibrium of the internal levels of vibration and translational motion in a gas, and for other systems with multiple levels of disequilibrium. For our purposes, we shall adopt the presentation given by Napolitano.

3 The entropy production rate used here, $\dot{W}_s = (\rho/T) (\mathbf{E}_{eq} - \mathbf{E}) \cdot d\mathbf{p}/dt$, is slightly different to that given by equation [3.74], which is based on the Kluitenberg formulation.

Suppose, for simplicity's sake, that we are dealing with a fluid with only one chemical component. The unit of mass of each subsystem is characterized by the relations:

$$\begin{cases} e_1 = e_1(s_1, \vartheta, \mathbf{p}_1, \mathbf{m}_1) = T s_1 - p \vartheta + \mathbf{E}_1 \cdot \mathbf{p}_1 + \mathbf{B}_1 \cdot \mathbf{m}_1 + g_1 \\ de_1 = T ds_1 - p d\vartheta + \mathbf{E}_1 \cdot d\mathbf{p}_1 + \mathbf{B}_1 \cdot d\mathbf{m}_1 \end{cases} \quad [3.23]$$

$$\begin{cases} e_2 = e_2(s_2, \mathbf{p}_2, \mathbf{m}_2) = T s_2 + \mathbf{E}_2 \cdot \mathbf{p}_2 + \mathbf{B}_2 \cdot \mathbf{m}_2 + g_2 \\ de_2 = T ds_2 + \mathbf{E}_2 \cdot d\mathbf{p}_2 + \mathbf{B}_2 \cdot d\mathbf{m}_2 \end{cases} \quad [3.24]$$

If we accept:

$$e = e_1 + e_2, s = s_1 + s_2, \mathbf{p} = \mathbf{p}_1 + \mathbf{p}_2, \mathbf{m} = \mathbf{m}_1 + \mathbf{m}_2, g = g_1 + g_2 \quad [3.25]$$

then, for the total system, we obtain:

$$e = e(s, \vartheta, \mathbf{p}, \mathbf{m}, \mathbf{p}_2, \mathbf{m}_2) \quad [3.26]$$

$$e = T s - p \vartheta + \mathbf{E} \cdot \mathbf{p} + \mathbf{B} \cdot \mathbf{m} - (\mathbf{E} - \mathbf{E}_2) \cdot \mathbf{p}_2 - (\mathbf{B} - \mathbf{B}_2) \cdot \mathbf{m}_2 + g \quad [3.27]$$

$$de = T ds - p d\vartheta + \mathbf{E} \cdot d\mathbf{p} + \mathbf{B} \cdot d\mathbf{m} - (\mathbf{E} - \mathbf{E}_2) \cdot d\mathbf{p}_2 - (\mathbf{B} - \mathbf{B}_2) \cdot d\mathbf{m}_2 \quad [3.28]$$

Let us illustrate these results with a concrete example: that of dielectric disequilibrium, mentioned above. In *Debye's theory*, the electrical polarization has two parts:

$$\mathbf{p} = \mathbf{p}^{def} + \mathbf{p}^{dip} \quad [3.29]$$

\mathbf{p}^{dip} is due to the orientation of the permanent dipoles in the molecules; \mathbf{p}^{def} is due to the deformation of the molecules.

We can consider \mathbf{p}^{dip} as an internal degree of freedom \mathbf{p}_2 liable to be in a state of disequilibrium with the rest of the fluid.

Thus, we have:

$$de = T ds - p d\vartheta + \mathbf{E} \cdot d\mathbf{p} - (\mathbf{E} - \mathbf{E}^{dip}) \cdot d\mathbf{p}^{dip} \quad [3.30]$$

At equilibrium, for given values of s , ϑ and \mathbf{p} , we have:

$$\underline{\mathbf{E}} - \underline{\mathbf{E}}^{dip} = \mathbf{0} \quad [3.31]$$

NOTE 3.1.— In his article, Kluitenberg [KLU 73] directly introduces the formula:

$$de = T ds - p d\vartheta + \mathbf{E} \cdot d\mathbf{p} + \mathbf{B} \cdot d\mathbf{M} - \mathbf{E}^{int} \cdot d\mathbf{p}^{int} - \mathbf{B}^{int} \cdot d\mathbf{m}^{int} \quad [3.32]$$

We feel it is more logical to employ formula [3.28]. Correspondence between these two formulas is obtained by setting:

$$\mathbf{p}^{int} = \mathbf{p}_2, \quad \mathbf{m}^{int} = \mathbf{m}_2, \quad \mathbf{E}^{int} = \mathbf{E} - \mathbf{E}_2, \quad \mathbf{B}_{int} = \mathbf{B} - \mathbf{B}_2 \quad [3.33]$$

Our formulation has the advantage of more clearly distinguishing exactly what is attributable to each subsystem. Indeed, in formula [3.32] it seems that $(-\mathbf{E}^{int})$ is the field of the subsystem (int), whereas in reality, the field of this subsystem is $(\mathbf{E} - \mathbf{E}^{int})$, as is shown by equation [3.33].

As we know the thermodynamic relations (equations [3.27] and [3.28]), we now need to determine the laws of state, or indeed the fundamental energy law [3.26].

Kluitenberg [KLU 73] defines the fundamental energy law based on the free energy:

$$f = e - Ts = f(T, \vartheta, \mathbf{p}, \mathbf{m}, \mathbf{p}_2, \mathbf{m}_2) \quad [3.34]$$

which he deconstructs into two parts for an isotropic medium:

$$f = f^{(1)}(T, \vartheta) + f^{(2)}(\vartheta, \mathbf{p}, \mathbf{m}, \mathbf{p}_2, \mathbf{m}_2) \quad [3.35]$$

the part $f^{(1)}$ corresponding to the non-polarized fluid, and the part $f^{(2)}$ having the form:

$$f^{(2)} = 0.5\rho(a_{00}\mathbf{p}^2 - 2a_{01}\mathbf{p} \cdot \mathbf{p}_2 + a_{11}\mathbf{p}_2^2 + b_{00}\mathbf{m}^2 - 2b_{01}\mathbf{m} \cdot \mathbf{m}_2 + b_{11}\mathbf{m}_2^2) \quad [3.36]$$

where the a_{ij} and b_{ij} are constant coefficients.

It is sufficient to know the law [3.34] to determine, at equilibrium, the dielectric constant ε and the magnetic permeability μ of the fluid, or indeed the electrical and magnetic susceptibilities κ and χ ; we have, successively:

$$\mathbf{E} = \partial f / \partial \mathbf{p} = \rho(a_{00}\mathbf{p} - a_{01}\mathbf{p}_2) \quad [3.37]$$

$$\mathbf{B} = \partial f / \partial \mathbf{m} = \rho(b_{00}\mathbf{m} - b_{01}\mathbf{m}_2) \quad [3.38]$$

$$\mathbf{E}_2 - \mathbf{E} = \partial f / \partial \mathbf{p}_2 = \rho(a_{11}\mathbf{p}_2 - a_{01}\mathbf{p}) \quad [3.39]$$

$$\mathbf{B}_2 - \mathbf{B} = \partial f / \partial \mathbf{m}_2 = \rho(b_{11}\mathbf{m}_2 - b_{01}\mathbf{m}) \quad [3.40]$$

At equilibrium:

$$\mathbf{E} - \mathbf{E}_2 = \mathbf{0}, \mathbf{B} - \mathbf{B}_2 = \mathbf{0} \quad [3.41]$$

From this, we deduce that at equilibrium:

$$\mathbf{p}_2 = \frac{a_{01}}{a_{11}}\mathbf{p}, \mathbf{m}_2 = \frac{b_{01}}{b_{11}}\mathbf{m} \quad [3.42]$$

and therefore that:

$$\mathbf{E} = \rho \left(a_{00} - a_{01}^2 / a_{11} \right) \mathbf{p} \quad [3.43]$$

$$\mathbf{B} = \rho \left(b_{00} - b_{01}^2 / b_{11} \right) \mathbf{m} \quad [3.44]$$

By comparing formulas [3.43] and [3.44] with relations [3.19] and [3.20], we deduce that:

$$\frac{1}{\kappa} = \frac{1}{\varepsilon - 1} = a_{00} - \frac{a_{01}^2}{a_{11}} \quad [3.45]$$

$$\frac{\chi + 1}{\chi} = \frac{\mu}{\mu - 1} = b_{00} - \frac{b_{01}^2}{b_{11}} \quad [3.46]$$

The fundamental energy law given by equations [3.35] and [3.36] lends itself well to the study of dielectric relaxation, as shown by Kluitenberg.

Other energy laws can be envisaged; thus, de Groot and Mazur [GRO 69a, p. 386] propose, for fluids, linear laws linking \mathbf{E} to \mathbf{p} and \mathbf{B} to \mathbf{m} , with the electrical and magnetic susceptibilities κ and χ depending solely on s and ϑ , or indeed [GRO 69a, p. 390], *for a composite fluid*, susceptibilities κ and χ depending only on T , ϑ and Y_k .

The thermodynamics of polarized media can also be described for elastic solids (see [GRO 69a, KLU 73]); the results are not hugely different in terms of the electrical and magnetic polarization vectors.

3.2. Momentum equation

The definition of the forces – and thus of the pressure tensor – poses a problem in a polarized medium. This stems,

in particular, from the *mathematical nature of quantities such as the electrical and magnetic displacements (or inductions)* (for example, see Jouguet [JOU 52, JOU 62], de Groot [GRO 69b], de Groot and Mazur [GRO 69a], de Groot and Suttrop [GRO 67a, GRO 67b, GRO 68a, GRO 68b, GRO 68c, GRO 68d, GRO 68e], or Fer [FER 71]). Let us take the example of electrical induction \mathbf{D} : this value is indeed equal to the sum $\mathbf{E} + \vec{\mathbf{P}}$, and does indeed satisfy the classic relation:

$$\nabla \cdot \mathbf{D} = \tilde{\rho} \quad [3.47]$$

The electrical induction \mathbf{D} corresponds, in fact, to a very particular measurement of the electrical field: \mathbf{D} is actually the electrical field measured in a flattened cylindrical cavity, whose axis runs in the same direction as the electrical polarization vector $\vec{\mathbf{P}}$.

This result stems, firstly, from the impossibility of directly defining the electrical field at a point in the polarized medium, and secondly from the fact that the field measured in the aforementioned cavity satisfies the classic Maxwell equations.

3.2.1. Impossibility of directly defining the electrical field in a polarized medium

The impossibility of making an absolute measurement of the field is apparent because of the expression of the potential, which involves the fictitious charges of volume $\tilde{\rho}'$ and of surface $\tilde{\rho}'_s$:

$$\tilde{\rho}' = -\nabla \cdot \vec{\mathbf{P}}, \quad \tilde{\rho}'_s = -\vec{\mathbf{P}} \cdot \mathbf{n} \quad [3.48]$$

where \mathbf{n} is the normal to the surface.

If a cavity is dug into a dielectric medium, the potential at a point M in that cavity is the sum of three integrals:

$$V(M) = \int_{\mathcal{V}} \frac{\tilde{\rho} + \tilde{\rho}'}{r} d\mathcal{V} + \int_S \frac{\tilde{\rho}_S + \tilde{\rho}'_S}{r} dS + \int_{S'} \frac{\tilde{\rho}'_S}{r} dS \quad [3.49]$$

In this expression, $\tilde{\rho}$ and $\tilde{\rho}_S$ denote the real volume and surface charges, $\tilde{\rho}'$ and $\tilde{\rho}'_S$ the corresponding fictitious charges, r the distance from the point M where the measurement is taken, (\mathcal{V}) denotes the outer volume of the cavity and (S) the surfaces situated in the same domain, and (S') is the surface delimiting the cavity. As the dimensions of the cavity tend toward zero, the potential tends toward a very clearly defined finite limit. However, the same is not true for the electrostatic field (∇V) because of the last integral, which depends on the form of the cavity as its dimensions tend toward zero.

Thus, for a small, highly-elongated cylinder whose axis is parallel to $\bar{\mathbf{P}}$, we obtain the electrical field \mathbf{E} ; for the flattened cylinder described earlier on, we obtain the field $\mathbf{E} + \bar{\mathbf{P}}$; and for a sphere, the field becomes: $\mathbf{E} + \frac{1}{3}\bar{\mathbf{P}}$.

The ambiguity relating to the measuring of the electrical field (and of the magnetic field) in a polarized medium of course arises once more when we wish to define the forces acting on the particle of fluid, and when we need to define the pressure tensor $\bar{\bar{\mathbf{P}}}$ of the fluid. The same issue presents itself with regard to the definition of the equilibrium hydrostatic pressure – i.e. the thermodynamic pressure.

We can show, for instance, that if \mathbf{F} , $\bar{\bar{\mathbf{P}}}$ and p are, respectively, the electromagnetic force, the pressure tensor

and the thermodynamic pressure, the following quantities are just as acceptable:

$$\mathbf{F}^* = \mathbf{F} + \frac{1}{2}\alpha \nabla \bar{\mathbf{P}}^2, \quad \bar{\mathbf{P}}^* = \bar{\mathbf{P}} + \frac{1}{2}\alpha \bar{\mathbf{P}}^2 \mathbf{1}, \quad p^* = p + \frac{1}{2}\alpha \bar{\mathbf{P}}^2 \quad [3.50]$$

they correspond to an effective electrical field: $\mathbf{E}^* = \mathbf{E} + \alpha \bar{\mathbf{P}}$.

We can see that, depending on the value of α (0, 1 or 1/3), we are dealing with the case of a measurement in a cylindrical cavity elongated in the direction of polarization $\bar{\mathbf{P}}$; with a flattened cylinder; or with a spherical cavity [GRO 69a, pp. 388–396].

3.2.2. Momentum as defined by de Groot and Mazur

Having clarified these details, we can now introduce the momentum as defined by de Groot and Mazur as being equal to:

$$\rho \mathbf{v} + \frac{1}{c} \mathbf{E} \times \mathbf{H} = \rho \mathbf{v} + \mathbf{Q}_v^{fd} \quad [3.51]$$

We then establish that:

$$\frac{\partial (\rho \mathbf{v} + \mathbf{E} \times \mathbf{H} / c)}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v} + \bar{\mathbf{P}} - \bar{\mathbf{P}}^{fd}) = \sum_k \rho_k \mathbf{f}_k \quad [3.52]$$

where:

$$\bar{\mathbf{P}}^{fd} = \left(\frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2} - \mathbf{M} \cdot \mathbf{B} \right) \mathbf{1} - \mathbf{D} \otimes \mathbf{E} - \mathbf{B} \otimes \mathbf{H} - \frac{\mathbf{v}}{c} \otimes (\bar{\mathbf{P}} \times \mathbf{B} - \mathbf{M} \times \mathbf{E}) \quad [3.53]$$

Equation [3.52] is the total momentum equation. For the electromagnetic momentum $\frac{1}{c}\mathbf{E}\times\mathbf{H}$, we have:

$$\frac{1}{c}\frac{\partial\mathbf{E}\times\mathbf{H}}{\partial t}+\nabla\cdot\bar{\bar{\mathbf{P}}}^{fld}=-\mathbf{F} \quad [3.54]$$

and for the momentum $\rho\mathbf{v}$:

$$\frac{\partial\rho\mathbf{v}}{\partial t}+\nabla\cdot\left(\bar{\bar{\mathbf{P}}}+\rho\mathbf{v}\otimes\mathbf{v}\right)=\mathbf{F}+\sum_k\rho_k\mathbf{f}_k \quad [3.55]$$

where \mathbf{F} is the force acting on the unit volume of the polarized medium:

$$\mathbf{F}=\tilde{\rho}\mathbf{E}+\frac{1}{c}\mathbf{I}\times\mathbf{B}+(\nabla\times\mathbf{E})\cdot\bar{\bar{\mathbf{P}}}+(\nabla\times\mathbf{B})\cdot\mathbf{M}+\frac{\rho}{c}\frac{d}{dt}(\mathbf{p}\times\mathbf{B}-\mathbf{m}\times\mathbf{E}) \quad [3.56]$$

Also, if we follow the motion, we have:

$$\rho\frac{d\mathbf{v}}{dt}+\nabla\cdot\bar{\bar{\mathbf{P}}}=\mathbf{F}+\sum_k\rho_k\mathbf{f}_k \quad [3.57]$$

It is evident, as noted above, that only the difference $\nabla\cdot\bar{\bar{\mathbf{P}}}-\mathbf{F}$ is perfectly defined once the forces \mathbf{f}_k are known, as we can control that fact using equation [3.50] in the case of the electrical field. Equation [3.57] was written in relation to the barycentric motion. Equation [3.54] can also be transformed to reveal the material derivative. We obtain:

$$\rho\frac{d}{dt}\left(\frac{\vartheta}{c}\mathbf{E}\times\mathbf{H}\right)+\nabla\cdot\left(\bar{\bar{\mathbf{P}}}^{fld}-\frac{\mathbf{v}}{c}\otimes(\mathbf{E}\times\mathbf{H})\right)=-\mathbf{F} \quad [3.58]$$

Similarly, equation [3.52] for the total momentum becomes:

$$\rho \frac{d}{dt} \left(\mathbf{v} + \frac{\partial}{c} \mathbf{E} \times \mathbf{H} \right) + \nabla \cdot \left(\rho \mathbf{v} \otimes \mathbf{v} - (\mathbf{E} \times \mathbf{H}) \otimes \frac{\mathbf{v}}{c} + \bar{\bar{\mathbf{P}}} + \bar{\bar{\mathbf{P}}}^{fld} \right) = \sum_k \rho_k \mathbf{f}_k \quad [3.59]$$

In these equations, the tensor:

$$\bar{\bar{\mathbf{P}}}^{fld} - (\mathbf{E} \times \mathbf{H}) \otimes \frac{\mathbf{v}}{c} \quad [3.60]$$

appears as the Maxwell pressure tensor in relation to the barycentric motion in the non-relativistic approximation (we discount the terms in v^2/c^2).

In reality, the Maxwell pressure tensor in relation to the Galilean frame of reference which, at time t and at the point in question, has the velocity \mathbf{v} of the fluid, is expressed not by equation [3.60], but rather:

$$\bar{\bar{\mathbf{P}}}^{\prime fld} = \bar{\bar{\mathbf{P}}}^{fld} + (\mathbf{E} \times \mathbf{H}) \otimes \frac{\mathbf{v}}{c} + \frac{\mathbf{v}}{c} \otimes (\mathbf{D} \times \mathbf{B}) \quad [3.61]$$

However, if we use this tensor $\bar{\bar{\mathbf{P}}}^{\prime fld}$, we also need to consider expressions of the momentum and of the electromagnetic force having been modified by that change of the frame of reference. We shall not go into detail about this issue, which is the problem of how to measure the Maxwell pressures in a shifting frame of reference.

3.3. Energy equation

By scalar multiplication by \mathbf{v} of both sides of equation [3.57], we obtain the kinetic energy balance equation:

$$\frac{\partial \rho k}{\partial t} + \nabla \cdot \left(\bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \rho k \mathbf{v} \right) = \bar{\bar{\mathbf{P}}} : \nabla \otimes \mathbf{v} + \mathbf{F} \cdot \mathbf{v} + \sum_k \rho_k \mathbf{v} \cdot \mathbf{f}_k \quad [3.62]$$

if we accept the hypothesis that the pressure tensor $\bar{\bar{\mathbf{P}}}$ is symmetrical.

By expressing the scalar product $\mathbf{F} \cdot \mathbf{v}$ as a function of the fields and the polarizations, the electromagnetic energy is introduced as:

$$E^{fld} = \frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2} - \mathbf{M} \times \mathbf{B} - \frac{\mathbf{v}}{c} \cdot (\bar{\bar{\mathbf{P}}} \times \mathbf{B} - \mathbf{M} \times \mathbf{E}) \quad [3.63]$$

if we discount the terms in v^2/c^2 . The electromagnetic energy flux becomes:

$$\mathbf{J}_E^{fld} = c(\mathbf{E} \times \mathbf{H}) - (\bar{\bar{\mathbf{P}}} \cdot \mathbf{E} + \mathbf{M} \cdot \mathbf{B}) \mathbf{v} \quad [3.64]$$

The balance equation for the sum of the kinetic energy and the electromagnetic energy is thus written as:

$$\begin{aligned} \frac{\partial(\rho k + E^{fld})}{\partial t} + \nabla \cdot (\bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \rho k \mathbf{v} + \mathbf{J}_E^{fld}) = \bar{\bar{\mathbf{P}}} : \nabla \otimes \mathbf{v} - \mathbf{i} \cdot \mathbf{E}' - \rho \mathbf{E}' \cdot \frac{d\mathbf{p}'}{dt} - \\ \rho \mathbf{B}' \cdot \frac{d\mathbf{m}'}{dt} + \sum_k \rho_k \mathbf{v}_k \cdot \mathbf{f}_k \end{aligned} \quad [3.65]$$

The quantities on the right-hand side bearing the exponent (') are local quantities obtained by following the fluid's motion. The expressions of these quantities are, in the non-relativistic approximation:

$$\mathbf{E}' = \mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B}, \quad \mathbf{p}' = \mathbf{p} - \frac{1}{c} \mathbf{v} \times \mathbf{m}, \quad \mathbf{B}' = \mathbf{B} - \frac{1}{c} \mathbf{v} \times \mathbf{E}, \quad \mathbf{m}' = \mathbf{m} + \frac{1}{c} \mathbf{v} \times \mathbf{p} \quad [3.66]$$

We know that the total energy is conserved, so we have:

$$\frac{\partial E}{\partial t} + \nabla \cdot \mathbf{J}_E = \sum_k \rho_k \mathbf{v}_k \cdot \mathbf{f}_k \quad [3.67]$$

where the right-hand side of the equation represents the power of the non-electromagnetic external forces. In this relation:

$$E = \rho(k + e) + E^{fld}, \mathbf{J}_E = \bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \mathbf{J}_E^{fld} + \mathbf{q} + \rho(e + k)\mathbf{v} \quad [3.68]$$

where e is the mass internal energy and \mathbf{q} is the heat flux. Equations [3.65] and [3.67] give us the internal energy balance equation:

$$\rho \frac{de}{dt} + \nabla \cdot \mathbf{q} = -\bar{\bar{\mathbf{P}}} : \nabla \otimes \mathbf{v} + \mathbf{i} \cdot \mathbf{E}' + \rho \mathbf{E}' \cdot \frac{d\mathbf{p}'}{dt} + \rho \mathbf{B}' \cdot \frac{d\mathbf{m}'}{dt} + \sum_k \mathcal{J}_{Dk} \cdot \mathbf{f}_k \quad [3.69]$$

3.4. Entropy flux and entropy production

Here we shall use the thermodynamic relations from section 3.1, considering the local thermodynamic quantities when we follow the motion of the unit mass of fluid. Thus, in light of equation [3.28], with the chemical terms added, the Gibbs equation is written as:

$$de = T ds - p d\vartheta + \mathbf{E}' \cdot d\mathbf{p}' + \mathbf{B}' \cdot d\mathbf{m}' - (\mathbf{E}' - \mathbf{E}'_2) \cdot d\mathbf{p}'_2 - (\mathbf{B}' - \mathbf{B}'_2) \cdot d\mathbf{m}'_2 + \sum_k g_k dY_k \quad [3.70]$$

The entropy flux is always taken as equal to:

$$\mathcal{J}_S = \frac{1}{T} \left(\mathbf{q} - \sum_k g_k \mathcal{J}_{Dk} \right) \quad [3.71]$$

and the entropy balance equation is of the form:

$$\rho \frac{ds}{dt} + \nabla \cdot \mathcal{J}_S = \dot{W}_S \quad [3.72]$$

Maxwell equations	$\nabla \cdot \mathbf{D} = \bar{\rho}, \nabla \times \mathbf{H} = \frac{1}{c} \mathbf{I} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}, \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0}, \nabla \cdot \mathbf{B} = 0$
Chemical species balance	$\rho \frac{Y_k}{dt} + \bar{\nabla} \cdot \bar{\mathcal{J}}_{Dk} = \dot{W}_k$
Continuity equation	$\frac{d\rho}{dt} + \rho \bar{\nabla} \cdot \bar{\mathbf{v}} = 0$
Electrical charge balance	$\rho dz/dt + \nabla \cdot \mathbf{i} = 0$
Momentum equation	$\rho \frac{d}{dt} \left(\mathbf{v} + \frac{\vartheta}{c} \mathbf{E} \times \mathbf{H} \right) + \nabla \cdot \left(\rho \mathbf{v} \otimes \mathbf{v} - (\mathbf{E} \times \mathbf{H}) \otimes \frac{\mathbf{v}}{c} + \bar{\bar{\mathbf{P}}} + \bar{\bar{\mathbf{P}}}^{fld} \right) = \sum_k \rho_k \mathbf{f}_k,$ $\bar{\bar{\mathbf{P}}}^{fld} = \left(\frac{E^2 + B^2}{2} - \mathbf{M} \cdot \mathbf{B} \right) \mathbf{1} - \mathbf{D} \otimes \mathbf{E} - \mathbf{B} \otimes \mathbf{H} - \frac{\mathbf{v}}{c} \otimes (\bar{\mathbf{P}} \times \mathbf{B} - \mathbf{M} \times \mathbf{E})$
Internal energy balance	$\rho \frac{de}{dt} + \nabla \cdot \mathbf{q} = -\bar{\bar{\mathbf{P}}} : \nabla \otimes \mathbf{v} + \mathbf{i} \cdot \mathbf{E}' + \rho \mathbf{E}' \cdot \frac{d\mathbf{p}'}{dt} + \rho \mathbf{B}' \cdot \frac{d\mathbf{m}'}{dt} + \sum_k \mathcal{J}_{Dk} \cdot \mathbf{f}_k$
Entropy equation	$\rho \frac{ds}{dt} + \bar{\nabla} \cdot \left[\left(\mathbf{q} - \sum_k g_k \mathcal{J}_{Dk} \right) / T \right] = \dot{W}_s$
Entropy production rate	$\dot{W}_s = -\frac{1}{T^2} \mathbf{q} \cdot \nabla T - \frac{1}{T} \sum_k \mathcal{J}_{Dk} \cdot \left[T \nabla \left(\frac{g_k}{T} \right) - z_k \mathbf{E}' - \mathbf{f}_k \right] - \frac{1}{T} \mathbf{\Pi} : \nabla \otimes \mathbf{v}$ $+ \frac{\rho}{T} (\mathbf{E}' - \mathbf{E}'_2) \cdot \frac{d\mathbf{p}'_2}{dt} + \frac{\rho}{T} (\mathbf{B}' - \mathbf{B}'_2) \cdot \frac{d\mathbf{m}'_2}{dt} - \frac{1}{T} \sum_k g_k \dot{W}_k$

Table 3.1. Balance equations for a polarized reactive fluid medium. \mathbf{H} magnetic displacement vector, \mathbf{D} electrical displacement vector, \mathbf{B} magnetic field, \mathbf{E} electrical field, $\bar{\mathbf{P}} = \mathbf{D} - \mathbf{E}$ electrical polarization (\mathbf{p} per unit mass), $\mathbf{M} = \mathbf{B} - \mathbf{H}$ magnetic polarization (\mathbf{m} per unit mass), (') following the motion, (2) relative to the dipoles (section 3.1), \mathcal{J}_{Dk} diffusion flux, \mathbf{q} heat flux, \mathbf{i} diffusion current, $\bar{\mathbf{P}}$ pressure tensor, $\mathbf{p}\mathbf{i}$ viscous pressure tensor, \dot{W}_k chemical production rate, \mathbf{f}_k distant forces other than those due to the electromagnetic field

By eliminating the material derivatives of the different variables and using the Gibbs relation, we find the following expression of the entropy production rate:

$$\begin{aligned} \dot{W}_s = & -\frac{1}{T^2} \mathbf{q} \cdot \nabla T - \frac{1}{T} \sum_k \mathcal{J}_{Dk} \cdot \left[T \nabla \left(\frac{g_k}{T} \right) - z_k \mathbf{E}' - \mathbf{f}_k \right] - \frac{1}{T} \mathbf{\Pi} : \nabla \otimes \mathbf{v} \\ & + \frac{\rho}{T} (\mathbf{E}' - \mathbf{E}'_2) \cdot \frac{d\mathbf{p}'_2}{dt} + \frac{\rho}{T} (\mathbf{B}' - \mathbf{B}'_2) \cdot \frac{d\mathbf{m}'_2}{dt} - \frac{1}{T} \sum_k g_k \dot{W}_k \end{aligned} \quad [3.73]$$

Table 3.1 summarizes the balance equations for a flow of a non-relativistic conductive fluid mixture with electric and magnetic polarizations.

3.5. Dielectric and magnetic relaxations

We shall only discuss dielectric relaxation, as magnetic relaxation is dealt with in identical fashion if we merely replace \mathbf{E}' with \mathbf{B}' and \mathbf{p}' with \mathbf{m}' . Suppose that we can neglect the heat transfer, diffusion, viscosity, magnetic relaxation and chemical reactions.

The entropy production rate is therefore reduced to:

$$\dot{W}_s = \frac{\rho}{T} (\mathbf{E}'_2 - \mathbf{E}') \cdot \frac{d\mathbf{p}'_2}{dt} \quad [3.74]$$

Thus, we can introduce a phenomenological coefficient L_p and express that there is a linear relation which exists between the polarization production rate $\rho \frac{d\mathbf{p}'_2}{dt}$ and the affinity of the electrical polarization $\frac{1}{T} (\mathbf{E}'_2 - \mathbf{E}')$; we find a relation identical to relation [3.21], which is now written as:

$$\rho \frac{d\mathbf{p}'_2}{dt} = \frac{L_p}{T} (\mathbf{E}'_2 - \mathbf{E}') \quad [3.75]$$

As the entropy production is positive, we deduce from relations [3.71] and [3.75] that the coefficient L_p is positive. Now envisage that we are dealing with a medium at rest, and express the law of state in the form [3.19] or [3.43].

Considering Debye's theory, we write:

$$\rho \frac{\partial \mathbf{p}^{dip}}{\partial t} = -\frac{L_p}{T} (\mathbf{E}^{dip} - \mathbf{E}) = -\frac{L_p}{T \kappa} (\bar{\mathbf{P}}^{dip} - \kappa \mathbf{E}) \quad [3.76]$$

where the internal degree of freedom $\mathbf{p}^{dip} = \mathbf{p}_2$ is due to the permanent dipoles in the molecules. As the medium is supposed to be incompressible, we can write:

$$\frac{\partial \bar{\mathbf{P}}^{dip}}{\partial t} + \frac{L}{T \kappa} (\bar{\mathbf{P}}^{dip} - \kappa \mathbf{E}) = 0 \quad [3.77]$$

This is the *Debye equation for dielectric relaxation*.

Interfacial Balances for Conductive Media

In this chapter, we look at the interface in media in the presence of an electromagnetic field. We use the macroscopic method, as we have done for most of other volumes in this series of books in the absence of an electromagnetic field [PRU 12, PRU 13, PRU 14]. We base our discussion on the knowledge of the simple media and homogeneous mixtures in the presence of a field, which were introduced in Chapters 2 and 3 of this volume.

The interface gradient operator ∇_s , which we have previously used in three-dimensional space, is generalized to apply to the Minkowski timespace. The general form of the interfacial balance is then established, using the surface operator ${}^4\nabla_s$.

In order to establish the interface balances, we shall proceed in the same way as we did with the homogeneous phase in Chapter 2, by analogy with the case of non-conductive media, drawing inspiration from the work of de Groot and Mazur, but in four-dimensional space.

The balances obtained in the timespace relate to tensorial quantities, and are similar in form to:

$${}^4\nabla_S \cdot {}^4\mathbf{J}_{vFa} + [{}^4\mathbf{J}_{vF\perp}]_{\perp}^+ = {}^4\dot{W}_{Fa} \quad [4.1]$$

where the respective terms represent:

1) the surface four-divergence of the flux of the property F internal to the 4-surface;

2) the jump in normal volume flux on crossing that surface;

3) on the right-hand side of the equation, the production rate.

These balances are then converted into the Euclidean space (see section 4.2.1).

They apply to the electromagnetic field¹, electrical current, total mass, mass of species k and the momentum-energy in the case of *non-polarized media*. The entropy production rate is also calculated.

With regard to *polarized media*², the Maxwell equations are used again; the other balance equations are then written in the simpler case of planar interfaces.

Here, we shall operate in the case of an interface with no thickness, with or without internal (or surfacic) properties, which moves and is deformed over the course of time. In terms of its shape, such an interface is perfectly comparable to a surface whose equation is time-dependent, so that we can very well describe the motion of the interface using an

1 The advantage to this method is that it enables us to consider the quantities of the electromagnetic field (fields and momentum-energy) in simple tensorial form in the Minkowski space, whereas they are not in such a simple form when examined in the Euclidean space.

2 This is the term we employ for conductive media where the fields – electric and magnetic – differ from the displacements.

equation in the Minkowski timespace. The interface thus constituted is made to support material; it is comparable to a curved 2-dimensional medium, either isotropic or otherwise, separating two 3-dimensional material domains. To move from one of these domains to the other, a particle must inevitably cross the interface, and *a priori*, there is no reason for the properties to vary continuously when that crossing is made, at least at the macroscopic scale with which we are concerned here. Thus, the very notion of an interface immediately introduced three material media whose properties are distinct, as continuity between those media can only be one very specific case. The 2-dimensional medium, therefore, is a material surface of discontinuity.

The analysis facilitated with such hypotheses depends, of course, on a scale factor. For example, the separation between a metallic solid and the liquid it forms when melted is discontinuous only if we do not look more closely at it. In reality, we are dealing with perfectly continuous changes, and the molecules, which are relatively free in the liquid, progressively rearrange to form the crystalline structure of the solid metal. Thus, when we accept that the separation between solid metal and liquid metal is a discontinuity, it simply means that the length scale on which we have chosen to operate is sufficiently large so that the continuous transition between the two phases is impossible to detect. At the mesoscopic scale, the same is absolutely not true, but it is important to note that at the molecular scale, the continuity is once again broken. However, it is often possible to justify the chosen macroscopic models using microscopic, or even molecular, arguments.

Under the auspices of this type of interfaces, we can cite the classic theory of shockwaves, surfacic chemical reactions, interfacial tension phenomena, etc.

Of course, there are cases where the above hypotheses are imperfectly, or simply are not, verified, where there is no

possible correspondence between so heavily simplified a theory and the facts observed experimentally. This is the risk we run when we envisage applying these concepts to polarized conductive media. Some authors refuse to do so (e.g. [FER 71]) and they are certainly right to refuse, in terms of the rigorousness of their demonstrations. Our approach will be to go as far as possible with material surfaces of discontinuity, whilst acknowledging that the correctness of our theories can only be confirmed or disproven by experimental verification.

Unlike the approach taken by many authors, for our 2-dimensional material medium, we introduce as many quantities as there are 3-dimensional media in contact with the surface in question. Thus, we will be dealing with internal surface energy, a given amount of entropy, a mass quantity (even if it is a very small one), chemical potentials, but also with electrical and magnetic polarizations. How are we to interpret quantities such as the electrical polarization of the interfacial material medium? Accepting the presence of electrical dipoles on a surface is not difficult to imagine, but measuring any polarization vector arising in the vicinity of a surface is no easy task, and might even be said to be rather unrealistic [FER 71]. In terms of accepting the existence of a polarization vector characterizing a 2-dimensional material medium, we do not yet have any satisfactory theoretical justification, or experimental measurements, to offer. Our only arguments are that, on the one hand, the material surfaces of discontinuity satisfactorily account for many phenomena; and on the other, there are still things that remain unexplained, or not explained to a sufficient degree of satisfaction in conductive media, and we need to make certain hypotheses to begin with, even if we later abandon them if they prove false or lead us to impossible or inaccurate results. After introducing the interface as a two-dimensional medium, we shall establish the balance equations in the absence of polarization, and

then later in the presence of electrical and magnetic polarization.

4.1. The shifting interface in the Minkowski space

Geometrically speaking, the material medium which we are about to describe is a deformable surface, which we shall now define in mathematical terms. The physical quantities used to describe the state of the material medium will then be introduced and, when we are dealing with tensorial quantities (pressure tensor, electrical and magnetic fields, momentum), compatibility conditions will need to be satisfied.

4.1.1. *Mathematical definition relative to the shifting interface*

A wide variety of definitions can be put forward to describe a surface (on this subject, see [GAT 01] and [PRU 12]). The parametric definition has the advantage of being applicable at a single point. The coordinates of any given point M are, at a given time, determined by taking the values of two parameters u and v . This lends itself very well to a material point on the surface. However, in order to define the surface as a geometric object, it is not necessary to resort to a single-point definition.

We shall use the notation x_1, x_2, x_3, x_4 to represent the coordinates of a point ${}_4M$ in the Minkowski space. By definition³, in matricial form, we have:

³ Where no ambiguity exists, simple symbols in **bold** text are used for all non-scalar quantities. However, where the same symbol is used for a 1st- or 2nd-order tensor, this is specified by the use of a single or double arrow. Such is the case of the electrical polarization $\vec{\mathbf{P}}$ and pressure tensor $\vec{\vec{\mathbf{P}}}$. See Chapter 3.

$$\underline{{}_4\mathbf{M}} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \\ ict \end{bmatrix} \quad [4.2]$$

or in the transposed, more compact form:
 $\underline{{}_4\mathbf{M}}^T = [x_1 x_2 x_3 x_4] = [x y z ict]$.

The equation for a surface (${}_4\Sigma$) in that four-dimensional space is:

$$f(x_1, x_2, x_3, x_4) = f({}_4\mathbf{M}) = 0 \quad [4.3]$$

This definition of a surface in the Minkowski space is, it should be pointed out, absolutely identical to that of a moving deformable surface in the three-dimensional space which is defined by the equation:

$$g(x, y, z, t) = 0 \quad [4.4]$$

and we simply have the correspondence:

$$g(x, y, z, t) \equiv f(x, y, z, ict) \quad [4.5]$$

Let us follow the motion of a fictitious material point M . If that fictitious material point remains on the 4-surface (${}_4\Sigma$), we shall have:

$$df = {}_4\nabla f \cdot d{}_4\mathbf{M} \quad [4.6]$$

Now we introduce the proper time τ of that moving point, so we have:

$$\frac{df}{d\tau} = {}_4\nabla f \cdot {}_4\mathbf{V} \quad [4.7]$$

where ${}^4\mathbf{V}$ is the universe velocity of the point in question.

The coordinates of ${}^4\mathbf{V}^T$, the row matrix transposed from the column matrix ${}^4\mathbf{V}$, are given by:

$${}^4\mathbf{V}^T = \left[\frac{v_x}{\alpha} \quad \frac{v_y}{\alpha} \quad \frac{v_z}{\alpha} \quad \frac{ic}{\alpha} \right], \quad \alpha = \sqrt{1 - \frac{|\mathbf{V}|^2}{c^2}} \quad [4.8]$$

with the vector \mathbf{V} in the 3-dimensional space itself being defined by its coordinates: $\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}$.

By expanding equation [4.7], we obtain the equivalent formula expressed in three dimensions:

$$\mathbf{V} \cdot \nabla g + \frac{\partial g}{\partial t} = 0 \quad [4.9]$$

where, in light of equation [4.5]:

$$\nabla g = \nabla f, \quad \frac{\partial g}{\partial t} = ic \frac{\partial f}{\partial x_4} \quad [4.10]$$

We shall indifferently write either equation [4.9] or the following:

$$\mathbf{V} \cdot \nabla f + \frac{\partial f}{\partial t} = 0 \quad [4.11]$$

In equation [4.7], we can see that ${}^4\mathbf{V}$ does not play its role entirely alone, but rather intervenes by its projection onto the 4-gradient of f ; additionally, we can see that $\frac{df}{d\tau}$ depends on the proper time, and therefore on the choice of the fictitious particle, moving with and on the surface.

In reality, the interfacial motion must not depend on the choice of a fictitious material point, but only on the point of the interface under consideration. Thus, there seems to be a problem, which we shall resolve as follows.

Let us introduce the unitary normal ${}^4\mathbf{N}$ into $({}^4\Sigma)$; we have:

$${}^4\mathbf{N} = {}^4\nabla f / |{}^4\nabla f| \quad [4.12]$$

Equation [4.7] becomes:

$${}^4\mathbf{V} \cdot {}^4\mathbf{N} = 0 \quad [4.13]$$

We shall therefore say that the surface has a motion such that any point which moves with the proper time τ , remaining on the surface with a 4-velocity whose projection, onto the normal ${}^4\mathbf{N}$ to the surface, is null. The problem of choosing the fictitious material point 4M on the 4-surface $({}^4\Sigma)$ is therefore resolved.

Let us now look again at the vector ${}^4\mathbf{N}$ defining the normal to the interface. We have:

$${}^4\underline{\nabla} = \begin{bmatrix} \frac{\partial}{\partial x_1} \\ \frac{\partial}{\partial x_2} \\ \frac{\partial}{\partial x_3} \\ \frac{\partial}{\partial x_4} \end{bmatrix} = \begin{bmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \\ \frac{1}{ic} \frac{\partial}{\partial t} \end{bmatrix}, \quad {}^4\underline{\nabla} f = \begin{bmatrix} \frac{\partial f}{\partial x_1} \\ \frac{\partial f}{\partial x_2} \\ \frac{\partial f}{\partial x_3} \\ \frac{\partial f}{\partial x_4} \end{bmatrix} = \begin{bmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \\ \frac{1}{ic} \frac{\partial f}{\partial t} \end{bmatrix} \quad [4.14]$$

$$|{}^4\underline{\nabla} f| = \left[(\nabla f)^2 - \frac{1}{c^2} \left(\frac{\partial f}{\partial t} \right)^2 \right]^{1/2}$$

For a point on the surface, we have: $\nabla f \cdot dx + \partial f / \partial t dt = 0$,
so:

$$\nabla f \cdot \mathbf{V} + \partial f / \partial t = 0$$

From this, it follows that:

$$|{}_4\nabla f| = \left[(\nabla f)^2 - \frac{1}{c^2} (\mathbf{V} \cdot \nabla f)^2 \right]^{1/2}$$

We can see that, in the non-relativistic case, where we can discount any influence of the terms in V^2/c^2 , we can write:

$$|{}_4\nabla f| \cong |\nabla f| \quad [4.15]$$

Let us now set:

$$\mathbf{N} = \nabla f / |{}_4\nabla f| \quad [4.16]$$

This definition enables us to write $\underline{{}_4\mathbf{N}}^T$ in the form:

$$\underline{{}_4\mathbf{N}}^T = \left[N_x \quad N_y \quad N_z \quad \frac{i}{c} \mathbf{V} \cdot \mathbf{N} \right], \quad |{}_4\mathbf{N}| = 1, \quad |\mathbf{N}| \neq 1 \quad [4.17]$$

Equation [4.13] is identically verified when we take care to write the components of the vector ${}_4\mathbf{N}$ in this way. With the non-relativistic approximation, equation [4.13] is the classic moving interface equation [PRU 71, GAT 01, PRU 12].

The operator ${}_4\nabla$ will, for discussions relating to the moving interface, generally be replaced by:

$${}_4\nabla_S = ({}_4\mathbf{1} - {}_4\mathbf{N} \otimes {}_4\mathbf{N}) \cdot {}_4\nabla \quad [4.18]$$

where $\mathbf{1}$ is the identity tensor in the timespace, in the same way as, in the three-dimensional space, we saw the intervention of:

$$\nabla_s = (\mathbf{1} - \mathbf{N} \otimes \mathbf{N}) \cdot \nabla \quad [4.19]$$

The properties of ∇_s are similar to those of ∇ . Remember that $\nabla \cdot \mathbf{N}$ represents the absolute value of the average normal curvature of the surface: $\left| \frac{1}{R_1} + \frac{1}{R_2} \right|$ (in particular, see Chapter 3 of Volume 1 [PRU 12]).

If we calculate $\nabla_s \cdot \mathbf{N}$, we obtain:

$$\nabla_s \cdot \mathbf{N} = \nabla \cdot \mathbf{N} + \frac{1}{c^2} \frac{\partial (\mathbf{V} \cdot \mathbf{N})}{\partial t} \quad [4.20]$$

We can see that in addition to the average surface curvature, the expression of the 4-divergence of the normal vector \mathbf{N} also contains a term representing interfacial acceleration. When $\mathbf{V} \cdot \mathbf{N} \ll c$, i.e. in non-relativistic cases, we find:

$$\nabla_s \cdot \mathbf{N} \cong \nabla \cdot \mathbf{N} \quad [4.21]$$

Expressed as a function of ∇_s , the operator ∇_s becomes the following, where $V_\perp = \mathbf{V} \cdot \mathbf{N}$:

$$\nabla_s = \left[\frac{\nabla_s}{ic} \left(\frac{\partial}{\partial t} + \mathbf{V}_s \cdot \nabla_s \right) \right] - \frac{1}{c^2} \left[\frac{\mathbf{N} \left(V_\perp \frac{\partial}{\partial t} + \frac{\partial V_\perp}{\partial t} \right)}{ic} \left(V_\perp \frac{\partial}{\partial t} + \frac{\partial V_\perp}{\partial t} \right) \right] \quad [4.22]$$

In the non-relativistic approximation, only the first part of the right-hand side of the equation remains, so we have:

$${}^4\nabla_S \cong \left[\frac{\nabla_S}{ic \left(\frac{\partial}{\partial t} + \mathbf{V}_S \cdot \nabla_{\perp} \right)} \right], |\mathbf{N}| \cong 1 \quad [4.23]$$

As is introduced with equation [4.3] or equation [4.4], note that the surface is defined with the sole exception of a certain amount of slip (with strain) over itself.

4.1.2. *Physical and thermodynamic quantities at the interface*

In this chapter, the assumption will be made that the material interface is in a state which can be characterized, locally, by physical and thermodynamic quantities, as can the media in contact with that interface. Thus, *in the absence of fields*, we had, for the internal surface energy $e_S = e_S(s_S, 1/\rho_a, Y_S^j)$ per unit mass (see Chapter 3 of [PRU 12]):

$$\begin{cases} e_S = T_S s_S + \sigma / \rho_a + \sum_{j=1}^N g_S^j Y_S^j \\ de_S = T_S ds_S + \sigma d(1/\rho_a) + \sum_{j=1}^N g_S^j dY_S^j \\ 0 = s_S dT_S + (1/\rho_a) d\sigma + \sum_{j=1}^N Y_S^j dg_S^j \end{cases} \quad [4.24]$$

where: $\rho_a = \int_{N^-}^{N^+} \rho dN$, $\rho_a f_S = \int_{N^-}^{N^+} \rho f dN$.

These equations remain valid for non-polarized conductive media. In the case of polarized conductors, we propose thermodynamic laws of the following type (in Chapter 3,

see the discussion of the Kluitenberg presentation and equations [3.26] and [3.28])⁴:

$$\left\{ \begin{array}{l} e_S = e_S(s_S, 1/\rho_a, Y_S^j, \mathbf{p}_S, \mathbf{m}_S, \mathbf{p}_{S2}, \mathbf{m}_{S2}) \\ de_S = T_S ds_S + \sigma d(1/\rho_a) + \mathbf{E}_a \cdot d\mathbf{p}_S + \mathbf{B}_a \cdot d\mathbf{m}_S \\ + (\mathbf{E}_{a2} - \mathbf{E}_a) \cdot d\mathbf{p}_{S2} + (\mathbf{B}_{a2} - \mathbf{B}_a) \cdot d\mathbf{m}_{S2} + \sum_{j=1}^N g_S^j dY_S^j \end{array} \right. \quad [4.25]$$

For the moment, we shall not go into great detail about the compatibility conditions which the vectorial quantities must satisfy. In the above equations, the interface is considered to be a two-dimensional fluid medium. This consideration is by no means obligatory, though. We could also envisage interfaces with the behavior of an elastic surface, for example. This exploits the product $\sigma d(1/\rho_a)$, which is transformed into a product of the pressure tensor by the strain rate tensor (see Chapter 3 of [PRU 12]). We retain the option of bringing these tensors into play in applications when it becomes necessary to do so. However, in the demonstrations given below, so as not to complicate the discussion, we shall suppose that the interface behaves like a fluid.

The motion of the material at the interface is characterized by physical quantities: particularly the fields, the momentum and the energy. These quantities will be characterized by 0, 1st- or 2nd-order tensors. However, most of the time, in addition to these physical quantities, we need to take account of the fluxes of those quantities across the surfaces in the 3-dimensional space. In the Minkowski space, these notions of quantities and fluxes associated therewith are replaced by a simpler concept: that of the flux across a

⁴ The electric and magnetic polarizations per unit mass \mathbf{p} and \mathbf{m} are defined by equations [3.3] and [3.4]. Here, we see the appearance of the corresponding interfacial quantities \mathbf{p}_S and \mathbf{m}_S .

4-surface in the *Minkowski timespace*. We can see this in Chapters 2 and 3 with regard to the balance equations written in this timespace.

For the surface electromagnetic field, we introduce a 4-tensor ${}^4\mathcal{F}_a$ and the corresponding tensor ${}^4\mathcal{F}_a^*$. In matricial notation, we have:

$$\underline{\underline{{}^4\mathcal{F}_a}} = \begin{bmatrix} 0 & B_{az} & -B_{ay} & -iE_{ax} \\ -B_{az} & 0 & B_{ax} & -iE_{ay} \\ B_{ay} & -B_{ax} & 0 & -iE_{az} \\ iE_{ax} & iE_{ay} & iE_{az} & 0 \end{bmatrix} \quad [4.26]$$

$$\underline{\underline{{}^4\mathcal{F}_a^*}} = \begin{bmatrix} 0 & -iE_{az} & iE_{ay} & B_{ax} \\ iE_{az} & 0 & -iE_{ax} & B_{ay} \\ -iE_{ay} & iE_{ax} & 0 & B_{az} \\ -B_{ax} & -B_{ay} & -B_{az} & 0 \end{bmatrix} \quad [4.27]$$

In the case of polarized media, the following tensor is also involved:

$$\underline{\underline{{}^4\mathcal{H}_a}} = \begin{bmatrix} 0 & H_{az} & -H_{ay} & -iD_{ax} \\ -H_{az} & 0 & H_{ax} & -iD_{ay} \\ H_{ay} & -H_{ax} & 0 & -iD_{az} \\ iD_{ax} & iD_{ay} & iD_{az} & 0 \end{bmatrix} \quad [4.28]$$

The interfacial material velocity 4-vector has the same definition as in the case of any given continuum (Chapter 1):

$${}^4\mathbf{v}_S = \begin{bmatrix} v_{Sx}/\alpha_S \\ v_{Sy}/\alpha_S \\ v_{Sz}/\alpha_S \\ ic/\alpha_S \end{bmatrix} = \begin{bmatrix} \underline{\mathbf{v}}_S/\alpha_S \\ ic/\alpha_S \end{bmatrix} \quad [4.29]$$

and the current 4-vector is written as:

$${}^4\mathbf{I}_a = \begin{bmatrix} \tilde{\rho}_a v_{Sx}/c \\ \tilde{\rho}_a v_{Sy}/c \\ \tilde{\rho}_a v_{Sz}/c \\ i\tilde{\rho}_a \end{bmatrix} = \begin{bmatrix} I_{ax}/c \\ I_{ay}/c \\ I_{az}/c \\ i\tilde{\rho}_a \end{bmatrix} \quad [4.30]$$

and involves the surface charge per unit area $\tilde{\rho}_a = z_S \rho_a$ where z_S is the surface charge per unit mass and ρ_a the surface mass, \mathbf{I}_a is the surface current. The current 4-vector represents the unitary flux density of electrical charge.

The momentum-energy flux is characterized by the pressure 4-tensor⁵:

$${}^4\mathcal{P}_a = {}^4\mathcal{P}_a^{ch} + {}^4\mathcal{P}_a^m \quad [4.31]$$

The tensors ${}^4\mathcal{P}_a^{fld}$ and ${}^4\mathcal{P}_a^m$, respectively representing the effects of the field and of the mass, are constructed on the basis of the interface quantities. In the case of a non-polarized medium, the tensors ${}^4\mathcal{P}_a^{fld}$ and ${}^4\mathcal{P}_a^m$ can easily be expressed with the non-relativistic approximation. In polarized media, the ambiguity relating to the forces and pressures renders the development more complex (see the note in section 3.1.3.5 on this subject).

4.1.3. Conditions relating to the tensorial quantities at the interface

By definition, the tensors representing the fluxes of interfacial quantities must be such that their components along the normal ${}^4\mathbf{N}$ to the 4-surface (${}^4\Sigma$) are zero.

⁵ The term “pressure” is sometimes introduced to avoid a possible confusion with the stress–momentum–energy tensor; we then speak of the pressure–momentum–energy tensor.

This stems from the very definition of the fluxes. The total flux is deconstructed into interface flux and flux across the interface, or in other words, tangential and normal flux. Of course, this separation between two types of flux is linked to the type of interface which we are envisaging: the notion of material surface of discontinuity.

Thus, ${}^4\mathcal{J}_{Fa}$ characterizes the tangential flux of the quantity F , whilst $[{}^4\mathcal{J}_{F\perp}]_{-}^{+} = ({}^4\mathcal{J}_F^{+} - {}^4\mathcal{J}_F^{-}) \cdot {}^4\mathbf{N}$ characterizes the normal flux, with ${}^4\mathcal{J}_F^{+}$ and ${}^4\mathcal{J}_F^{-}$ denoting the flux vectors of F into the two volumes in contact with the interface. The separation therefore implies that, using the notation \mathbf{V}_S for the surface velocity (which was written as \mathbf{V} in section 4.1.1), we have:

$${}^4\mathcal{J}_{Fa} \cdot {}^4\mathbf{N} = 0, \quad {}^4\mathbf{N} = \left[\begin{array}{c} \mathbf{N} \\ i \\ c \mathbf{V}_S \cdot \mathbf{N} \end{array} \right] \quad [4.32]$$

Applied to the mass, this condition gives us:

$$\rho_{a0} {}^4\mathbf{V}_S \cdot {}^4\mathbf{N} = 0 \quad [4.33]$$

or indeed:

$$\mathbf{v}_S \cdot \mathbf{N} - \mathbf{V}_S \cdot \mathbf{N} = 0 \quad [4.34]$$

which indicates that the normal projection of the particle velocity in the 3-dimensional space is equal to the normal velocity of the interface (Σ) (corresponding to the surface (${}^4\Sigma$) in the 4-dimensional space).

By applying the condition to the electrical charge, we find:

$$\mathbf{I}_a \cdot \mathbf{N} = \tilde{\rho}_a \mathbf{V}_S \cdot \mathbf{N} \quad [4.35]$$

This result indicates that the current normal to the interface is the result of a normal displacement of the charges contained in the interface, which is logical.

We also have:

$${}^4\mathcal{F}_a \cdot {}^4\mathbf{N} = \mathbf{0} \quad [4.36]$$

$${}^4\mathcal{F}_a^* \cdot {}^4\mathbf{N} = \mathbf{0} \quad [4.37]$$

and in the case of polarized media:

$${}^4\mathcal{H}_a \cdot {}^4\mathbf{N} = \mathbf{0} \quad [4.38]$$

It follows from this that *in the case of non-polarized media*:

$$\mathbf{N} \times \mathbf{B}_a + \frac{\mathbf{V}_s \cdot \mathbf{N}}{c} \mathbf{E}_a = \mathbf{0}, \quad \mathbf{E}_a \cdot \mathbf{N} = 0 \quad [4.39]$$

$$\mathbf{N} \times \mathbf{E}_a - \frac{\mathbf{V}_s \cdot \mathbf{N}}{c} \mathbf{B}_a = \mathbf{0}, \quad \mathbf{B}_a \cdot \mathbf{N} = 0 \quad [4.40]$$

In the case of polarized media, equation [4.40] is valid, but equation [4.39] is replaced by:

$$\mathbf{N} \times \mathbf{H}_a + \frac{\mathbf{V} \cdot \mathbf{N}}{c} \mathbf{D}_a = \mathbf{0}, \quad \mathbf{D}_a \cdot \mathbf{N} = 0 \quad [4.41]$$

Relations [4.39] and [4.40] show that, in the case of a non-polarized medium:

$$\mathbf{E}_a = \mathbf{0}, \quad \mathbf{B}_a = \mathbf{0} \quad [4.42]$$

Hence, when polarization is absent, *it is impossible* to introduce interfacial variables characterizing the fields in addition to the quantities that these fields have on either side of the interface.

In the case of a polarized interface, on the other hand, we have the relations:

$$\begin{cases} \mathbf{N} \times \mathbf{H}_a + \frac{\mathbf{V}_S \cdot \mathbf{N}}{c} \mathbf{D}_a = \mathbf{0}, & \mathbf{D}_a \cdot \mathbf{N} = 0, \\ \mathbf{N} \times \mathbf{E}_a - \frac{\mathbf{V}_S \cdot \mathbf{N}}{c} \mathbf{B}_a = \mathbf{0}, & \mathbf{B}_a \cdot \mathbf{N} = 0 \end{cases} \quad [4.43]$$

From this, we conclude that \mathbf{D}_a and \mathbf{B}_a are situated in the plane tangential to the interface, that \mathbf{H}_a is normal to \mathbf{D}_a , and that \mathbf{E}_a is normal to \mathbf{B}_a .

In the case of a non-polarized medium, the momentum-energy tensor due to the field is null. It follows from this that the only compatibility (or coherence) relations are given by:

$${}^4\mathcal{P}_a^m \cdot {}_4\mathbf{N} = \mathbf{0} \quad [4.44]$$

From this vectorial relation, we deduce:

$$\vec{\vec{\mathbf{P}}}_a \cdot \mathbf{N} = \mathbf{0}, \quad \mathbf{q}_a \cdot \mathbf{N} = 0 \quad [4.45]$$

These relations are well known, and mean that the surface tensions are exerted, for a fluid, in the plane tangential to the interface⁶, and that the interfacial heat flux introduced here is tangential.

In the case of a polarized medium, we can write:

$$\underline{\underline{{}^4\mathcal{P}}}_a = \left[\begin{array}{l} \rho_a \mathbf{v}_S \otimes \mathbf{v}_S + \vec{\vec{\mathbf{P}}}_a^m + \vec{\vec{\mathbf{P}}}_a^{fld} \quad ic \left(\rho_a \mathbf{v}_S + \frac{1}{c} \mathbf{E}_a \times \mathbf{H}_a \right) \\ \frac{i}{c} \left[\mathbf{q}_a + \vec{\vec{\mathbf{P}}}_a^m \cdot \mathbf{v}_S + \rho_a (e_S + k_S) \mathbf{v}_S + \mathbf{J}_{Ea}^{fld} \right] - \left[\rho_a (e_S + k_S) + E_a^{fld} \right] \end{array} \right] \quad [4.46]$$

⁶ We applied these compatibility relations previously, in Chapter 3 (section 3.2) of [PRU 12], to the surface tension tensor and the moment densities.

with:

$$\begin{cases} \bar{\bar{\mathbf{P}}}_a^{fld} = \left(\frac{E_a^2 + B_a^2}{2} - \mathbf{M}_a \cdot \mathbf{B}_a \right) \mathbf{1} - \mathbf{D}_a \otimes \mathbf{E}_a - \mathbf{B}_a \otimes \mathbf{H}_a - \\ \frac{\mathbf{v}_S}{c} \otimes (\bar{\mathbf{P}}_a \otimes \mathbf{B}_a - \mathbf{M}_a \otimes \mathbf{E}_a), \\ \mathbf{J}_{Ea}^{fld} = c \mathbf{E}_a \times \mathbf{H}_a - (\bar{\mathbf{P}}_a \cdot \mathbf{E}_a + \mathbf{M}_a \cdot \mathbf{B}_a) \mathbf{v}_S, \\ E_a^{fld} = \frac{E_a^2 + B_a^2}{2} - \mathbf{M}_a \cdot \mathbf{B}_a - \frac{\mathbf{v}_S}{c} \otimes (\bar{\mathbf{P}}_a \times \mathbf{B}_a - \mathbf{M}_a \times \mathbf{E}_a) \end{cases} \quad [4.47]$$

where the internal energy due to the field is denoted by E_a^{fld} .
The equation:

$${}_{4}\mathcal{P}_a^m \cdot {}_{4}\mathbf{N} = 0 \quad [4.48]$$

which is valid in the absence of external surface forces other than the electromagnetic forces, gives us:

$$\begin{cases} \bar{\bar{\mathbf{P}}}_a^m \cdot \mathbf{N} + \bar{\bar{\mathbf{P}}}_a^{fld} \cdot \mathbf{N} - \frac{\mathbf{v}_S \cdot \mathbf{N}}{c} \mathbf{E}_a \times \mathbf{H}_a = \mathbf{0}, \\ \left(\mathbf{q}_a + \bar{\bar{\mathbf{P}}}_a^m \cdot \mathbf{v}_S \right) \cdot \mathbf{N} + \mathbf{J}_{Ea}^{fld} \cdot \mathbf{N} - \mathbf{v}_S \cdot \mathbf{N} E_a^{fld} = 0 \end{cases} \quad [4.49]$$

4.2. Equations for non-polarized media at the non-polarized interface

4.2.1. General balance equation

In the Minkowski space, the balance of a quantity F at the interface expresses the fact that the flux of F at the borders of a four-dimensional spatial domain constituted by the surface (Σ) delimited by a closed two-dimensional manifold, is equal to the production of that quantity F within that domain.

With the interfacial flux being denoted by ${}^4\mathbf{J}_{\mathbf{v}Fa}$ at its edges and by ${}^4\mathbf{J}_{\mathbf{v}F}^+$ and ${}^4\mathbf{J}_{\mathbf{v}F}^-$ on its upper and lower faces (a direction from (-) to (+) has been set arbitrarily⁷ to orientate the normal ${}^4\mathbf{N}$), and the production rate being \dot{W}_{Fa} , we have:

$${}^4\mathbf{J}_{\mathbf{v}Fa} \cdot {}^4\mathbf{N} = 0 \quad [4.50]$$

$$\int_{\Sigma} {}^4\nabla \cdot {}^4\mathbf{J}_{\mathbf{v}Fa} d\Sigma + \int_{\Sigma} [{}^4\mathbf{J}_{\mathbf{v}F\perp}]_{-}^{+} d\Sigma = \int_{\Sigma} {}^4\dot{W}_{Fa} d\Sigma \quad [4.51]$$

The first integral in equation [4.51] represents the flux on the edge of (Σ), the second the flux on the faces of (Σ), and finally the third is the production of the quantity F within (Σ).

Equation [4.50] corresponds to equation [4.32], and expresses the compatibility condition according to our hypotheses. The operator ${}^4\nabla_S$, which represents the interfacial gradient, is defined by equation [4.18]. In the absence of discontinuities on (Σ), the balance equation for F becomes valid locally at every point, and is written as:

$${}^4\nabla_S \cdot {}^4\mathbf{J}_{\mathbf{v}Fa} + [{}^4\mathbf{J}_{\mathbf{v}F\perp}]_{-}^{+} = {}^4\dot{W}_{Fa} \quad [4.52]$$

where: ${}^4\mathbf{J}_{\mathbf{v}F\perp} = {}^4\mathbf{J}_{\mathbf{v}F} \cdot {}^4\mathbf{N}$.

⁷ The normal \mathbf{N}^- is orientated toward the volume in contact with the side (-), and the normal \mathbf{N}^+ is orientated toward the volume in contact with the side (+). Thus, we have $J_{F\perp}^- = \mathbf{J}_F \cdot \mathbf{N}^-$ and $J_{F\perp}^+ = \mathbf{J}_F \cdot \mathbf{N}^+$. If we choose to set $\mathbf{N} = \mathbf{N}^+$, we find $\mathbf{N}^- = -\mathbf{N}$. The unitary flux of F exiting through the faces of (Σ) is therefore $\mathbf{J}_F^- \cdot \mathbf{N}^- + \mathbf{J}_F^+ \cdot \mathbf{N}^+ = (\mathbf{J}_F^+ - \mathbf{J}_F^-) \cdot \mathbf{N} = J_{F\perp}^+ - J_{F\perp}^- = [J_{F\perp}]_{-}^{+}$. The important thing is to orientate \mathbf{N} away from (-) and towards (+), chosen arbitrarily.

By setting:

$$\underline{{}_4\mathbf{J}}_{vF} = \begin{bmatrix} \frac{1}{c} \underline{\mathbf{J}}_{vF} \\ i \rho f \end{bmatrix}, \quad \underline{{}_4\mathbf{J}}_{vFa} = \begin{bmatrix} \frac{1}{c} \underline{\mathbf{J}}_{vFa} \\ i \rho_a f_s \end{bmatrix} \quad [4.53]$$

we obtain the balance equation expressed in the three-dimensional space (see equation [3.5], and the section 3.2.2 of [PRU 12] for the velocity fields in the interfacial layer):

$$\frac{d_s(\rho_a f_s)}{dt} + \rho_a f_s \nabla_S \cdot \underline{\mathbf{V}}_S + \nabla_S \cdot \underline{\mathbf{J}}_{vFa} + [\underline{\mathbf{J}}_{vF\perp}]^+ = \dot{W}_{Fa} \quad [4.54]$$

where the material derivative $\frac{d_s}{dt} = \frac{\partial}{\partial t} + \underline{\mathbf{v}}_S \cdot \nabla$ plays a part, as do the fluxes:

$$\underline{\mathbf{J}}_{vF\perp} = \underline{\mathbf{J}}_{vF} \cdot \underline{\mathbf{N}}, \underline{\mathbf{J}}_{vF} = \underline{\mathcal{J}}_F + \rho f (\underline{\mathbf{v}} - \underline{\mathbf{V}}), \underline{\mathbf{J}}_{vFa} = \int_{N_-}^{N_+} \underline{\mathbf{J}}_{vF} dN \quad [4.55]$$

4.2.2. Maxwell equations at the interface

4.2.2.1. General relations without polarization

Given that in conductive media in the absence of polarization, it is impossible to introduce electrical and magnetic fields at the interface $\underline{\mathbf{E}}_a$ and $\underline{\mathbf{B}}_a$ which are non-null, it follows that the tensors ${}_4\mathcal{F}_a$ and ${}_4\mathcal{F}_a^*$ are identically null and that the Maxwell equations at the interface are obtained by way of two relations:

$$[{}_4\mathcal{F}]^+_{-} \cdot {}_4\mathbf{N} = {}_4I_a \quad [4.56a]$$

$$[{}_4\mathcal{F}^*]^+_{-} \cdot {}_4\mathbf{N} = \mathbf{0} \quad [4.56b]$$

We can immediately deduce the Maxwell equations at the interface:

$$\mathbf{N} \times [\mathbf{B}]_{-}^{+} + \frac{1}{c} \mathbf{V} \cdot \mathbf{N} [\mathbf{E}]_{-}^{+} = \frac{1}{c} \mathbf{I}_a, \quad [\mathbf{E}]_{-}^{+} \cdot \mathbf{N} = \tilde{\rho}_a \quad [4.57a]$$

$$[\mathbf{E}]_{-}^{+} \times \mathbf{N} + \frac{1}{c} \mathbf{V} \cdot \mathbf{N} [\mathbf{B}]_{-}^{+} = 0, \quad [\mathbf{B}]_{-}^{+} \cdot \mathbf{N} = 0 \quad [4.57b]$$

4.2.2.2. Specific case

When the interface is motionless and the charge and surface current are zero, we can see that there is no discontinuity in the electromagnetic field – i.e. $\mathbf{E}^{+} = \mathbf{E}^{-}$, $\mathbf{B}^{+} = \mathbf{B}^{-}$.

When the interface is motionless and the current and surface charge are non-zero, the discontinuity of the electrical field vector $[\mathbf{E}]_{-}^{+}$ is normal to the interface, and its normal projection onto \mathbf{N} is equal to the surface charge. Additionally, the discontinuity vector for the magnetic field $[\mathbf{B}]_{-}^{+}$ is located in the plane tangential to the interface at the point in question: it is perpendicular to the current vector \mathbf{I}_a (see Figure 4.1) and has the modulus $\frac{1}{c} |\mathbf{I}_a|$.

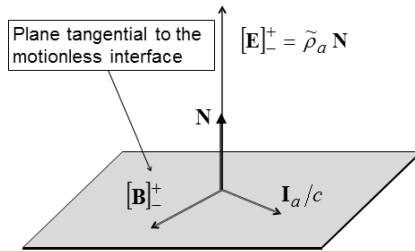


Figure 4.1. Arrangement of the vectors in the particular case of the motionless interface

Thus, we note that in the absence of polarization, the interface causes no discontinuities in the electrical or magnetic fields unless it carries a charge or a non-zero current. We shall see later on that even in the absence of charge and current, the *polarized* immobile interface induces such discontinuities.

In the absence of polarization, the discontinuities of the electrical and magnetic fields are given by:

$$\left(1 - \frac{(\mathbf{V} \cdot \mathbf{N})^2}{c^2}\right) [\mathbf{E}]_{-}^{+} = \tilde{\rho}_a \mathbf{N} - \frac{\mathbf{V} \cdot \mathbf{N}}{c^2} \mathbf{I}_a, \quad \left(1 - \frac{(\mathbf{V} \cdot \mathbf{N})^2}{c^2}\right) [\mathbf{B}]_{-}^{+} = \frac{1}{c} \mathbf{I}_a \times \mathbf{N} \quad [4.58]$$

In the non-relativistic approximation, we therefore obtain:

$$[\mathbf{E}]_{-}^{+} = \tilde{\rho}_a \mathbf{N} - \frac{\mathbf{V} \cdot \mathbf{N}}{c^2} \mathbf{I}_a, \quad [\mathbf{B}]_{-}^{+} = \frac{1}{c} \mathbf{I}_a \times \mathbf{N} \quad [4.59]$$

4.2.3. Conservation of electricity. Conservation of mass

Let us apply the balance equation [4.52] to the vectors:

$$\mathbf{J}_{aM} = \rho_{a0} \mathbf{V}_S, \quad \mathbf{J}_M = \rho_0 \mathbf{V} \quad [4.60]$$

or indeed the balance equation [4.54] to the quantities: $f = f_S = 1$, $\mathbf{J}_{aF} = \mathbf{J}_F = \mathbf{0}$. We obtain the classic global mass balance equation at the interface:

$$\frac{d_S \rho_a}{dt} + \rho_a \nabla_S \cdot \mathbf{V}_S + [\rho(\mathbf{v} - \mathbf{V})]_{-}^{+} \cdot \mathbf{N} = 0 \quad [4.61]$$

This equation can be deduced from the mass balances of the different chemical species which become:

$$\frac{d_S (\rho_a Y_{ks})}{dt} + \rho_a Y_{ks} \nabla_S \cdot \mathbf{V}_S + \nabla_S \cdot \mathbf{J}_{vka} + [\mathbf{J}_{Dk} + \rho Y_k (\mathbf{v} - \mathbf{V})]_{-}^{+} \cdot \mathbf{N} = \dot{W}_{ka} \quad [4.62]$$

with summation on the index k , and in view of the fact that:

$$\sum_k Y_k = \sum_k Y_{kS} = 1, \quad \sum_k \mathcal{J}_{Dka} = \sum_k \mathcal{J}_{Dk} = \mathbf{0}, \quad \sum_k \dot{W}_{ka} = 0 \quad [4.63]$$

Let us multiply both sides of equation [4.61] by f_S and subtract the equation thus obtained, term by term, from equation [4.54]. We find:

$$\rho_a \frac{d_S f_S}{dt} + \nabla_S \cdot \mathcal{J}_{Fa} + [\mathcal{J}_F + \rho(f - f_S)(\mathbf{v} - \mathbf{V})]_{-}^{+} \cdot \mathbf{N} = \dot{W}_{Fa} \quad [4.64]$$

Equation [4.64] is a general balance equation; it is simpler in form than is equation [4.54].

The charge of species k involves the 4-fluxes:

$${}^4\tilde{\mathcal{J}}_k = \rho_{k0} z_k {}^4\mathcal{J}_k = \begin{bmatrix} \tilde{\rho}_k \mathbf{v} \\ i c \tilde{\rho}_k \end{bmatrix} \quad [4.65]$$

$${}^4\tilde{\mathcal{J}}_{ka} = \rho_{k0} z_{kS} {}^4\mathcal{J}_{ka} \quad [4.66]$$

and, for the total charge:

$${}^4\tilde{\mathcal{J}} = \sum_k {}^4\mathcal{J}_k, \quad {}^4\tilde{\mathcal{J}}_a = \sum_k {}^4\mathcal{J}_{ka} \quad [4.67]$$

We obtain the equation:

$${}^4\nabla \cdot {}^4\tilde{\mathcal{J}}_a + [{}^4\tilde{\mathcal{J}}]_{-}^{+} \cdot {}^4\mathbf{N} = \sum_k z_k \tilde{W}_{ka} = 0 \quad [4.68]$$

Using the rate of production \dot{W}_k of the species:

$$\rho_a \frac{d_S z_S}{dt} + \nabla \cdot \mathbf{i}_a + [\mathbf{i} + \rho(z - z_S)(\mathbf{v} - \mathbf{V})]_{-}^{+} \cdot \mathbf{N} = 0 \quad [4.69]$$

This is the charge conservation equation. Indeed, we have:

$$\sum_k z_{ka} \dot{W}_k = \sum_k z_{ka} \mathcal{M}_k \sum_r v_{kr} \dot{w}_r = 0 \quad [4.70]$$

because any production of charge is compensated by the production of an opposite charge.

4.2.4. Momentum and energy

At the interface, the pressure-momentum-energy tensor is reduced to its mass part \mathcal{P}_a^m . Thus, we have the equation:

$${}^4\nabla_S \cdot {}^4\mathcal{P}_a^m + [{}^4\mathcal{P}^m + {}^4\mathcal{P}^{fld}]^+ \cdot {}^4\mathbf{N} = {}^4\Phi_a \quad [4.71]$$

where ${}^4\Phi_a$ represents the 4-vector corresponding to the non-electromagnetic external forces.

Let us recap the expressions of the different terms in this relation:

$${}^4\nabla_S = \left[\begin{array}{c} \nabla_S \\ \frac{1}{ic} \left(\frac{\partial}{\partial t} + \mathbf{V} \cdot \mathbf{N} (\mathbf{N} \cdot \nabla) \right) \end{array} \right], \quad {}^4\mathbf{N} = \left[\begin{array}{c} \mathbf{N} \\ \frac{i}{c} \mathbf{V} \cdot \mathbf{N} \end{array} \right] \quad [4.72]$$

$$\underline{\underline{\mathcal{P}}}_a^m = \left[\begin{array}{cc} \rho_a \mathbf{v}_S \otimes \mathbf{v}_S + \vec{\vec{\mathbf{P}}}_a & ic \rho_a \mathbf{v}_S \\ \frac{i}{c} \left[\mathbf{q}_a + \vec{\vec{\mathbf{P}}}_a \cdot \mathbf{v}_S + \rho_a (e_S + k_S) \mathbf{v}_S \right] & -\rho_a (e_S + k_S) \end{array} \right] \quad [4.73]$$

$$\underline{\underline{\mathcal{P}}} = \left[\begin{array}{cc} \rho \mathbf{v} \otimes \mathbf{v} + \vec{\vec{\mathbf{P}}}^m + \vec{\vec{\mathbf{P}}}^{fld} & ic \left(\rho \mathbf{v} + \frac{1}{c} \mathbf{E} \times \mathbf{B} \right) \\ \frac{i}{c} \left[\mathbf{q} + \vec{\vec{\mathbf{P}}} \cdot \mathbf{v} + \rho_a (e + k) \mathbf{v} + \mathbf{J}_E^{fld} \right] & -[\rho (e_S + k_S) + e^{fld}] \end{array} \right] \quad [4.74]$$

$$e^{fld} = \frac{E^2 + B^2}{2}, \quad \mathbf{J}_E^{fld} = c \mathbf{E} \times \mathbf{B}, \quad \vec{\vec{\mathbf{P}}}^{fld} = \frac{E^2 + B^2}{2} \mathbf{1} - \mathbf{E} \otimes \mathbf{E} - \mathbf{B} \otimes \mathbf{B} \quad [4.75]$$

By expansion, relation [4.71] gives us the momentum balance equation and energy balance equation:

$$\begin{aligned} & \rho_a \frac{d_S \mathbf{v}_S}{dt} + \nabla_S \cdot \vec{\vec{\mathbf{P}}}_a + \left[\vec{\vec{\mathbf{P}}} + \rho (\mathbf{v} - \mathbf{v}_S) \otimes (\mathbf{v} - \mathbf{V}) + \vec{\vec{\mathbf{P}}}^{fld} \right. \\ & \left. - \frac{1}{c} (\mathbf{E} \times \mathbf{B}) \otimes \mathbf{V} \right]^+ \cdot \mathbf{N} = \sum_k \rho_{ak} \mathbf{f}_{ak} \end{aligned} \quad [4.76]$$

$$\begin{aligned}
 & \rho_a \frac{d_S(e_S + k_S)}{dt} + \nabla_S \cdot (\mathbf{q}_a + \bar{\bar{\mathbf{P}}}_a \cdot \mathbf{v}_S) \\
 & + \left[\mathbf{q} + \bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \rho(e + k - e_S - k_S)(\mathbf{v} - \mathbf{V}) + \mathbf{J}_E^{fld} + e^{fld} \mathbf{V} \right]_+ \cdot \mathbf{N} \quad [4.77] \\
 & = \sum_k \rho_{ak} \mathbf{f}_{ak} \cdot \mathbf{v}_{Sk}
 \end{aligned}$$

The kinetic energy equation can be deduced from equation [4.76], both sides of which we multiply by \mathbf{v}_S in scalar fashion – we then have:

$$\begin{aligned}
 & \rho_a \frac{d k_S}{dt} + \nabla_S \cdot (\mathbf{v}_S \cdot \bar{\bar{\mathbf{P}}}_a) + \left[\mathbf{v} \cdot \bar{\bar{\mathbf{P}}} + \rho(k - k_S)(\mathbf{v} - \mathbf{V}) \right]_+ \cdot \mathbf{N} \\
 & = \bar{\bar{\mathbf{P}}}_a : \nabla \otimes \mathbf{v}_S + \sum_k \rho_{ak} \mathbf{v}_S \cdot \mathbf{f}_k \quad [4.78] \\
 & + \left[(\mathbf{v} - \mathbf{v}_S) \cdot \bar{\bar{\mathbf{P}}} + \frac{1}{2} \rho (\mathbf{v} - \mathbf{v}_S)^2 (\mathbf{v} - \mathbf{V}) \right]_+ \cdot \mathbf{N} + \dot{W}_{Ka}^{fld}
 \end{aligned}$$

where \dot{W}_{Ka}^{fld} is the production of kinetic energy due to the fields:

$$\dot{W}_{Ka}^{fld} = -\mathbf{v}_S \cdot \left[\bar{\bar{\mathbf{P}}}^{fld} - \frac{1}{c} (\mathbf{E} \times \mathbf{B}) \otimes \mathbf{V} \right]_+ \cdot \mathbf{N} \quad [4.79]$$

To simplify this expression, let us set:

$$\mathbf{E}^+ + \mathbf{E}^- = 2\mathcal{E}, \quad \mathbf{B}^+ + \mathbf{B}^- = 2\mathcal{B} \quad [4.80]$$

and take account of the relations:

$$[\mathbf{E}]_-^+ = \tilde{\rho}_a \mathbf{N} - \frac{\mathbf{V} \cdot \mathbf{N}}{c^2} \mathbf{I}_a, \quad [\mathbf{B}]_-^+ = \frac{1}{c} \mathbf{I}_a \times \mathbf{N} \quad [4.81]$$

Then, by omitting the terms in v^2/c^2 , we obtain:

$$\dot{W}_{Ka}^{fld} = \mathbf{v}_S \cdot \left(\rho_a \boldsymbol{\mathcal{E}} + \frac{1}{c} \mathbf{I}_a \times \boldsymbol{\mathcal{B}} \right) \quad [4.82]$$

Let us also give the expression of the field term appearing in the momentum expression:

$$\left[\bar{\bar{\mathbf{P}}}^{fld} - \frac{1}{c} (\mathbf{E} \times \mathbf{B}) \otimes \mathbf{V} \right]_+ \cdot \mathbf{N} = \rho_a \boldsymbol{\mathcal{E}} + \frac{1}{c} \mathbf{I}_a \times \boldsymbol{\mathcal{B}} \quad [4.83]$$

The internal energy equation becomes:

$$\begin{aligned} \rho_a \frac{d_s e_s}{dt} + \nabla_S \cdot \mathbf{q}_a + \left[\mathbf{q} + \rho(e - e_s)(\mathbf{v} - \mathbf{V}) \right]_+ \cdot \mathbf{N} = -\bar{\bar{\mathbf{P}}}_a : \nabla_S \otimes \mathbf{v}_S \\ + \sum_k \mathcal{J}_{Dka} \cdot \mathbf{f}_{ak} - \left[(\mathbf{v} - \mathbf{v}_S) \cdot \bar{\bar{\mathbf{P}}} + \frac{1}{2} (\mathbf{v} - \mathbf{v}_S)^2 (\mathbf{v} - \mathbf{V}) \right]_+ \cdot \mathbf{N} + \dot{W}_{Ea}^{fld} \end{aligned} \quad [4.84]$$

The expression of \dot{W}_{Ea}^{fld} :

$$\dot{W}_{Ea}^{fld} = \left[-\mathbf{J}_E^{fld} + e^{fld} \mathbf{V} + \mathbf{v}_S \cdot \left(\bar{\bar{\mathbf{P}}}^{fld} - \frac{1}{c} (\mathbf{E} \times \mathbf{B}) \otimes \mathbf{V} \right) \right]_+ \cdot \mathbf{N} \quad [4.85]$$

with the exception of the terms in v^2/c^2 , becomes:

$$\dot{W}_{Ea}^{fld} = \mathbf{i}_a \cdot \left(\boldsymbol{\mathcal{E}} + \frac{1}{c} \mathbf{v}_S \times \boldsymbol{\mathcal{B}} \right) \quad [4.86]$$

In order to obtain these results, we have used the relations:

$$\begin{cases} \mathbf{I}_a = \mathbf{i}_a + \tilde{\rho}_a \mathbf{v}_S, & \mathbf{v}_S = (\mathbf{V} \cdot \mathbf{N}) \mathbf{N} + \mathbf{N} \times (\mathbf{v}_S \times \mathbf{N}), \\ \mathbf{I}_a \cdot \mathbf{N} = \tilde{\rho}_a \mathbf{V} \cdot \mathbf{N}, & \text{or } \mathbf{i}_a \cdot \mathbf{N} = 0 \end{cases} \quad [4.87]$$

4.2.5. Entropy production rate

The equations of thermodynamics at the interface can be used to find the entropy balance equation on the basis of the other balance equations. The process is identical to that used in the absence of fields. The equation is written thus:

$$\rho_a \frac{ds_S}{dt} + \nabla_S \cdot \mathbf{J}_{Sa} + \left[\frac{\mathbf{q}}{T} - \sum_k \mathcal{J}_{Dk} \frac{\mathbf{g}_k}{T} + \rho(s - s_S)(\mathbf{v} - \mathbf{V}) \right] \cdot \mathbf{N} = \dot{W}_{Sa} \quad [4.88]$$

The entropy production rate \dot{W}_{Sa} is written:

$$\begin{aligned} \dot{W}_{Sa} = & \mathbf{q}_a \cdot \nabla_S \left(\frac{1}{T_S} \right) - \frac{1}{T_S} \sum_k \mathcal{J}_{Dka} \cdot \left(T_S \nabla_S \left(\frac{\mathbf{g}_{kS}}{T_S} \right) - \mathbf{f}_{ka} \right) - \frac{1}{T_S} \mathbf{\Pi}_a : \nabla_S \otimes \mathbf{v}_S \\ & - \sum_k \frac{\mathbf{g}_{kS}}{T_S} \dot{W}_{ka} + \left[\left(\frac{1}{T} - \frac{1}{T_S} \right) \mathbf{q} - \sum_k \left(\frac{\mathbf{g}_k}{T} - \frac{\mathbf{g}_{kS}}{T_S} \right) \mathcal{J}_{Dka} - \frac{1}{T} (\mathbf{v} - \mathbf{v}_S) \cdot \mathbf{\Pi} \right. \\ & \left. + \frac{\rho}{T} \left((T_S - T)s + \sum_k (\mathbf{g}_{kS} - \mathbf{g}_k) Y_k - \frac{1}{2} (\mathbf{v} - \mathbf{v}_S)^2 \right) (\mathbf{v} - \mathbf{V}) \right] \cdot \mathbf{N} + \dot{W}_{Sa}^{fld} \end{aligned} \quad [4.89]$$

The term \dot{W}_{Sa}^{fld} , attributable to the fields, is equal to:

$$\dot{W}_{Sa}^{fld} = \frac{1}{T} \dot{W}_{Ea}^{fld} \quad [4.90]$$

By replacing \dot{W}_{Ea}^{fld} with its expression, we therefore obtain:

$$\dot{W}_{Sa}^{fld} = \frac{1}{T_S} \mathbf{i}_a \cdot \left(\mathbf{E} + \frac{1}{c} \mathbf{v}_S \times \mathbf{B} \right) \quad [4.91]$$

with the exception of the terms in v^2/c^2 .

We can see that this quantity disappears in the absence of a surface current.

4.3. Interface with polarization

All of the interfacial equations in a polarized medium are given in Table 4.1. Thereafter, we give the explanations to aid the understanding of how this table has been compiled. However, as we shall see, *it has only been possible to follow through the calculations to their conclusion for the particular case of the flat, immobile interface* [PRU 78a, PRU 78b].

Maxwell equations	$\nabla_s \times \mathbf{H}_a - \frac{1}{c} \frac{\partial \mathbf{D}_a}{\partial t} - \frac{1}{c} (\mathbf{v} \cdot \mathbf{N})(\mathbf{N} \cdot \nabla) \mathbf{D}_a + \left[\mathbf{N} \times \mathbf{B} + \frac{1}{c} (\mathbf{v} \cdot \mathbf{N}) \mathbf{E} \right]_+ = \frac{1}{c} \mathbf{I}_a,$ $\nabla_s \times \mathbf{E}_a - \frac{1}{c} \frac{\partial \mathbf{B}_a}{\partial t} + \frac{1}{c} (\mathbf{v} \cdot \mathbf{N})(\mathbf{N} \cdot \nabla) \mathbf{B}_a + \left[\mathbf{N} \times \mathbf{E} - \frac{1}{c} (\mathbf{v} \cdot \mathbf{N}) \mathbf{B} \right]_+ = \mathbf{0},$ $\nabla_s \times \mathbf{D}_a + [\mathbf{E}]_- \cdot \mathbf{N} = \tilde{\rho}_a, \quad \nabla_s \times \mathbf{B}_a + [\mathbf{B}]_- \cdot \mathbf{N} = \mathbf{0}$
Chemical species balance	$\frac{d_s (\rho_a Y_{ks})}{dt} + \rho_a Y_{ks} \nabla_s \cdot \mathbf{v}_s + \nabla_s \cdot \mathbf{J}_{vka} + [\mathbf{J}_{Dk} + \rho Y_k (\mathbf{v} - \mathbf{V})]_- \cdot \mathbf{N} = \dot{W}_{ka}$
Continuity equation	$\frac{d_s \rho_a}{dt} + \rho_a \nabla_s \cdot \mathbf{v}_s + [\rho (\mathbf{v} - \mathbf{V})]_- \cdot \mathbf{N} = \mathbf{0}$
Electrical charge balance	$\rho_a \frac{d_s z_s}{dt} + \nabla \cdot \mathbf{i}_a + [\mathbf{i} + \rho (z - z_s) (\mathbf{v} - \mathbf{V})]_+ \cdot \mathbf{N} = \mathbf{0}$
Momentum equation	$\rho_a \frac{d_s \mathbf{v}_s}{dt} + \nabla_s \cdot \bar{\bar{\mathbf{P}}}_a + \left[\bar{\bar{\mathbf{P}}} + \rho (\mathbf{v} - \mathbf{v}_s) + \bar{\bar{\mathbf{P}}}^{fld} - \frac{1}{c} (\mathbf{E} \times \mathbf{B}) \otimes \mathbf{V} \right]_+ \cdot \mathbf{N}$ $= \sum_k \rho_{ak} \mathbf{f}_{ka}$
Internal energy balance	$\rho_a \frac{d_s e_s}{dt} + \nabla_s \cdot \mathbf{q}_a + [\mathbf{q} + \rho (e - e_s) (\mathbf{v} - \mathbf{V})]_+ \cdot \mathbf{N} = -\bar{\bar{\mathbf{P}}}_a : \nabla_s \otimes \mathbf{v}_s$ $+ \sum_k \mathbf{J}_{Dka} \cdot \mathbf{f}_{ka} - \left[(\mathbf{v} - \mathbf{v}_s) \cdot \bar{\bar{\mathbf{P}}} + \frac{1}{2} (\mathbf{v} - \mathbf{v}_s)^2 (\mathbf{v} - \mathbf{V}) \right]_+ \cdot \mathbf{N} + \dot{W}_{Ea}^{fld}$
Entropy production rate	<p>due to the mass: equation [4.123] due to the field: equation [4.124]</p>

Table 4.1. Interfacial balance equations in a polarized reactive fluid medium. Interfacial quantities: \mathbf{H} : magnetic displacement vector; \mathbf{D} : electric displacement vector; \mathbf{B}_a : magnetic field; \mathbf{E}_a : electric field; $\mathbf{P}_a = \mathbf{D}_a - \mathbf{E}_a$: electrical polarization (\mathbf{p}_s per unit mass); $\mathbf{M} = \mathbf{B} - \mathbf{H}$: magnetic polarization (\mathbf{m}_s per unit mass)

4.3.1. Maxwell equations

Let us apply the general balance equation [4.51] to the electromagnetic tensors \mathbf{F}_a^* and \mathcal{H}_a . We obtain [PRU 76, PRU 79]:

$${}^4\nabla_S \cdot {}^4\mathcal{H}_a + [{}^4\mathcal{H}]_-^+ \cdot {}^4\mathbf{N} = {}^4\mathbf{J}_a \quad [4.92]$$

$${}^4\nabla_S \cdot {}^4\mathbf{F}_a^* + [{}^4\mathbf{F}^*]_-^+ \cdot {}^4\mathbf{N} = \mathbf{0} \quad [4.93]$$

With the classic variables of time and space, these equations give us the Maxwell equations at the interface:

$$\left\{ \begin{array}{l} \nabla_S \times \mathbf{H}_a - \frac{1}{c} \frac{\partial \mathbf{D}_a}{\partial t} - \frac{1}{c} (\mathbf{V} \cdot \mathbf{N})(\mathbf{N} \cdot \nabla) \mathbf{D}_a + \left[\mathbf{N} \times \mathbf{B} + \frac{1}{c} (\mathbf{V} \cdot \mathbf{N}) \mathbf{E} \right]_-^+ \\ = \frac{1}{c} \mathbf{I}_a \\ \nabla_S \times \mathbf{D}_a + [\mathbf{E}]_-^+ \cdot \mathbf{N} = \tilde{\rho}_a \end{array} \right. \quad [4.94]$$

$$\left\{ \begin{array}{l} \nabla_S \times \mathbf{E}_a - \frac{1}{c} \frac{\partial \mathbf{B}_a}{\partial t} + \frac{1}{c} (\mathbf{V} \cdot \mathbf{N})(\mathbf{N} \cdot \nabla) \mathbf{B}_a + \left[\mathbf{N} \times \mathbf{E} - \frac{1}{c} (\mathbf{V} \cdot \mathbf{N}) \mathbf{B} \right]_-^+ = \mathbf{0} \\ \nabla_S \times \mathbf{B}_a + [\mathbf{B}]_-^+ \cdot \mathbf{N} = \mathbf{0} \end{array} \right. \quad [4.95]$$

Also remember that we have (system [4.43]):

$$\left\{ \begin{array}{l} \mathbf{N} \times \mathbf{H}_a + \frac{\mathbf{V}_S \cdot \mathbf{N}}{c} \mathbf{D}_a = 0, \quad \mathbf{D}_a \cdot \mathbf{N} = 0 \\ \mathbf{N} \times \mathbf{E}_a - \frac{\mathbf{V}_S \cdot \mathbf{N}}{c} \mathbf{B}_a = 0, \quad \mathbf{B}_a \cdot \mathbf{N} = 0 \end{array} \right. \quad [4.96]$$

4.3.2. Conservation of electricity; conservation of mass

There is no change in relation to the case without polarization discussed in section 4.2.3.

4.3.3. Momentum and energy

The media in contact with the interface are also supposed to be polarized, as the interface production of potential is non-null.

The development shown in section 4.1.2 is slightly modified by the polarization of the bulk and by the presence of a potential production term \dot{W}_ψ which (see [PRU 79]) verifies:

$$\frac{\partial \rho_a \psi_s}{\partial t} + \nabla_s \cdot \sum_j \rho_{ja} \mathbf{v}_{js} \psi_{js} + \left[\sum_j \mathcal{J}_{Dj} \psi_j + \rho \mathbf{v} \psi \right] \cdot \mathbf{N} = \dot{W}_{\psi_a} \quad [4.97]$$

In our discussion below, we shall limit ourselves to the case of a flat, motionless interface.

The tensorial momentum-energy equation is always written as:

$${}^4\nabla_s \cdot {}^4\mathcal{P}_a^m + \left[{}^4\mathcal{P}^m + {}^4\mathcal{P}^{ch} \right] \cdot {}^4\mathbf{N} = {}^4\Phi_a \quad [4.98]$$

and gives us the following two equations:

$$\begin{aligned} & \frac{\partial}{\partial t} \left(\rho_a \mathbf{v}_s + \frac{1}{c} \mathbf{E}_a \times \mathbf{H}_a \right) + \nabla_s \cdot \left(\rho_a \mathbf{v}_s \otimes \mathbf{v}_s + \bar{\bar{\mathbf{P}}}_a + \bar{\bar{\mathbf{P}}}_a^{fld} \right) \\ & + \left[\bar{\bar{\mathbf{P}}}_a + \rho \mathbf{v} \otimes \mathbf{v} + \bar{\bar{\mathbf{P}}} + \bar{\bar{\mathbf{P}}}^{fld} \right] \cdot \mathbf{N} = \mathbf{0} \end{aligned} \quad [4.99]$$

$$\begin{aligned} & \frac{\partial [\rho_a (e_s + k_s) + E_a^{fld}]}{\partial t} + \nabla_S \cdot (\mathbf{q}_a + \mathbf{v}_S \cdot \bar{\bar{\mathbf{P}}}_a + \rho_a (e_s + k_s) \mathbf{v}_S + \mathbf{J}_{Ea}^{fld}) \\ & + \left[\mathbf{q} + \underline{\mathbf{v}} \cdot \bar{\bar{\mathbf{P}}} + \rho (e + k) \mathbf{v} + \mathbf{J}_E^{fld} \right] \cdot \mathbf{N} = -\dot{W}_{\psi_a} \end{aligned} \quad [4.100]$$

By introducing the external force \mathbf{F}_a , equation [4.99] can be decomposed into two parts: one part due to the mass:

$$\rho_a \frac{d_s \mathbf{v}_S}{dt} + \nabla_S \cdot \bar{\bar{\mathbf{P}}}_a + \left[\bar{\bar{\mathbf{P}}} + \rho (\mathbf{v} - \mathbf{v}_S) \otimes \mathbf{v} \right] \cdot \mathbf{N} = \mathbf{F}_a \quad [4.101]$$

and another part due to the field:

$$\frac{1}{c} \frac{\partial (\mathbf{E}_a \times \mathbf{H}_a)}{\partial t} + \nabla_S \cdot \bar{\bar{\mathbf{P}}}_a^{fld} + \left[\bar{\bar{\mathbf{P}}}^{fld} \right] \cdot \mathbf{N} = -\mathbf{F}_a \quad [4.102]$$

Similarly, equation [4.100] can also be deconstructed into two parts, by introducing the production \dot{W}_a :

$$\begin{aligned} & \rho_a \frac{d_s (e_s + k_s)}{dt} + \nabla_S \cdot (\mathbf{q}_a + \mathbf{v}_S \cdot \bar{\bar{\mathbf{P}}}_a) + \left[\mathbf{q} + \mathbf{v} \cdot \bar{\bar{\mathbf{P}}} + \right. \\ & \left. \rho (e + k - e_a - k_a) \mathbf{v} \right] \cdot \mathbf{N} = \dot{W}_a \end{aligned} \quad [4.103]$$

$$\frac{\partial E_a^{fld}}{\partial t} + \nabla_S \cdot \mathbf{J}_{Ea}^{fld} + \left[\mathbf{J}_E^{fld} \right] \cdot \mathbf{N} = -\dot{W}_a - \dot{W}_{\psi_a} \quad [4.104]$$

The kinetic energy balance equation is obtained by scalar multiplication of equation [4.101] by \mathbf{v}_S – in this case, we have:

$$\rho_a \frac{d_s k_s}{dt} + \nabla_S \cdot (\mathbf{v}_S \cdot \bar{\bar{\mathbf{P}}}_a) + \left[\mathbf{v} \cdot \bar{\bar{\mathbf{P}}} + \rho (k - k_a) \mathbf{v} \right] \cdot \mathbf{N} = \dot{W}_{Ka} \quad [4.105]$$

$$\dot{W}_{Ka} = \mathbf{F}_a \cdot \mathbf{v}_S + \bar{\bar{\mathbf{P}}}_a : \nabla_S \otimes \mathbf{v}_S + \left[(\mathbf{v} - \mathbf{v}_S) \cdot \bar{\bar{\mathbf{P}}} + \frac{1}{2} \rho (\mathbf{v} - \mathbf{v}_S)^2 \mathbf{v} \right] \cdot \mathbf{N} \quad [4.106]$$

By subtraction of equations [4.103] and [4.105], we find the internal energy equation:

$$\rho_a \frac{d_s e_s}{dt} + \nabla_S \cdot \mathbf{q}_a + [\mathbf{q} + \rho(e - e_s) \mathbf{v}]_-^+ \cdot \mathbf{N} = \dot{W}_{Ea} = \dot{W}_{Ea}^m + \dot{W}_{Ea}^{fld} \quad [4.107]$$

the internal energy production rate being equal to:

$$\begin{aligned} \dot{W}_{Ea} = \dot{W}_a - \dot{W}_{Ka} = & -\bar{\bar{\mathbf{P}}}_a : \nabla_S \otimes \mathbf{v}_S - \left[(\mathbf{v} - \mathbf{v}_S) \cdot \bar{\bar{\mathbf{P}}} \right. \\ & \left. + \frac{1}{2} \rho (\mathbf{v} - \mathbf{v}_S)^2 \mathbf{v} \right]_-^+ \cdot \mathbf{N} + \dot{W}_{Ea}^{fld} \end{aligned} \quad [4.108]$$

The entropy production rate directly due to the field is written as:

$$\dot{W}_{Ea}^{fld} = -\dot{W}_\psi - \frac{\partial E_a^{fld}}{\partial t} + \nabla_S \cdot \mathbf{J}_{Ea}^{fld} - [\mathbf{J}_E^{fld}]_-^+ \cdot \mathbf{N} - \mathbf{F}_a \cdot \mathbf{v}_S \quad [4.109]$$

or indeed (see [PRU 79, p. 60] and [DUD 82, p. 148]):

$$\begin{aligned} \dot{W}_{Ea}^{fld} = & -\dot{W}_{\psi a} - \frac{\partial E_a^{fld}}{\partial t} + \nabla_S \cdot \mathbf{J}_{Ea}^{fld} - [\mathbf{J}_E^{fld}]_-^+ \cdot \mathbf{N} \\ & + \mathbf{v}_S \cdot \left(\nabla \cdot \bar{\bar{\mathbf{P}}}_a^{fld} + [\bar{\bar{\mathbf{P}}}^{fld}]_-^+ \cdot \mathbf{N} \right) \end{aligned} \quad [4.110]$$

The Maxwell equations form the following systems, respectively, for the volume:

$$\begin{cases} \nabla \times \mathbf{H} = \frac{1}{c} \mathbf{I} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} & \nabla \cdot \mathbf{D} + [\mathbf{D} \cdot \mathbf{N}]_-^+ = \tilde{\rho} \\ \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0} & \nabla \cdot \mathbf{B} = 0 \end{cases} \quad [4.111]$$

and for the interface, supposing the configuration to be flat as shown in Figure 4.1:

$$\begin{cases} H_{a,2} - \frac{1}{c} D_{a1,t} - [H_2]_-^+ = \frac{1}{c} I_{a1} \\ -H_{a,1} - \frac{1}{c} D_{a2,t} + [H_1]_-^+ = \frac{1}{c} I_{a2} \\ D_{a1,1} + D_{a2,2} + [D_3]_-^+ = \tilde{\rho}_a \end{cases} \quad [4.112]$$

(and from this, we deduce that $\tilde{\rho}_t + \nabla_S \cdot \mathbf{I}_S + [I_3]_-^+ = 0$) and:

$$\begin{cases} E_{a,2} + \frac{1}{c} B_{a1,t} - [E_2]_-^+ = 0 \\ -E_{a,1} + \frac{1}{c} B_{a2,t} + [E_1]_-^+ = 0 \\ B_{a1,1} + B_{a2,2} + [B_3]_-^+ = 0 \end{cases} \quad [4.113]$$

The electromagnetic interfacial vectors are such that:

$$\begin{cases} \underline{\mathbf{N}} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \underline{\mathbf{D}}_a = \begin{bmatrix} D_{a1} \\ D_{a2} \\ 0 \end{bmatrix}, \underline{\mathbf{B}}_a = \begin{bmatrix} B_{a1} \\ B_{a2} \\ 0 \end{bmatrix}, \mathbf{E}_a = E_a \mathbf{N}, \mathbf{H} = H_a \mathbf{N} \\ \underline{\mathbf{P}}_a = \underline{\mathbf{D}}_a - \underline{\mathbf{E}}_a = \begin{bmatrix} D_{a1} \\ D_{a2} \\ -E_a \end{bmatrix}, \underline{\mathbf{M}}_S = \begin{bmatrix} B_{a1} \\ B_{a2} \\ -H_a \end{bmatrix} \end{cases} \quad [4.114]$$

The tensor $\overline{\overline{\mathbf{P}}}_S^{fd}$ is given by the matrix [PRU 79]:

$$\underline{\underline{\mathbf{P}}}_a^{fd} = \begin{bmatrix} \frac{E_a^2 - B_a^2}{2} & 0 & 0 \\ 0 & \frac{E_a^2 - B_a^2}{2} & 0 \\ -\{E_a D_{a1} + H B_{a1} \\ + \frac{v_{S1}}{c} (D_{a1} B_{a2} - D_{a2} B_{a1})\} & -\{E_a D_{a2} + H B_{a2} \\ + \frac{v_{S2}}{c} (D_{a1} B_{a2} - D_{a2} B_{a1})\} & \frac{E_a^2 - B_a^2}{2} \end{bmatrix} \quad [4.115]$$

and $\nabla \cdot \vec{\mathbf{P}}_a^{fld}$ by:

$$\nabla \cdot \mathbf{P}_a^{fld} = \left[\begin{array}{l} \left(\frac{E_S^2 - B_S^2}{2} \right)_{,1} \\ \left(\frac{E_a^2 - B_a^2}{2} \right)_{,2} \\ - \left\{ \left[E_a D_{a1} + H_a B_{a1} + \frac{v_{S1}}{c} (D_{a1} B_{a2} - D_{a2} B_{a1}) \right]_{,1} \right. \\ \left. + \left[E_S D_{S2} + H B_{S2} + \frac{v_{S2}}{c} (D_{S1} B_{S2} - D_{S2} B_{S1}) \right]_{,2} \right\} \end{array} \right] \quad [4.116]$$

Additionally, we have:

$$\left[\underline{\mathbf{P}}^{fld} \underline{\mathbf{N}} \right]^+ = \left[\begin{array}{l} -[E_1 D_3 + H_1 B_3]^+ \\ -[E_2 D_3 + H_2 B_3]^+ \\ \left[\frac{E^2 - B^2}{2} - \mathbf{M} \cdot \mathbf{B} - E_3 D_3 - H_3 B_3 \right]^+ \end{array} \right] \quad [4.117]$$

The force \mathbf{F}_a is then deduced from equation [4.102], as follows:

$$\underline{\mathbf{F}}_a = \left[\begin{array}{l} - \left(\frac{E_a^2 - B_a^2}{2} \right)_{,1} + [E_1 D_3 + H_1 B_3]^+ \\ - \left(\frac{E_a^2 - B_a^2}{2} \right)_{,2} + [E_2 D_3 + H_2 B_3]^+ \\ \left[E_a D_{a1} + H_a B_{a1} + \frac{v_{S1}}{c} (D_{a1} B_{a2} - D_{a2} B_{a1}) \right]_{,1} + \\ \left[E_a D_{a2} + H_a B_{a2} + \frac{v_{S2}}{c} (D_{a1} B_{a2} - D_{a2} B_{a1}) \right]_{,2} - \\ \left[\frac{E^2 - B^2}{2} - \mathbf{M} \cdot \mathbf{B} - E_3 D_3 - H_3 B_3 \right]^+ \end{array} \right] \quad [4.118]$$

From this, we can deduce the scalar product $\mathbf{F}_a \cdot \mathbf{v}_S$:

$$\begin{aligned} \mathbf{F}_a \cdot \mathbf{v}_S = & \left[-\left(\frac{E_S^2 - B_S^2}{2} \right)_{,1} + [E_1 D_3 + H_1 B_3]_{-}^{+} \right] v_{S1} + \\ & \left[-\left(\frac{E_S^2 - B_S^2}{2} \right)_{,2} + [E_2 D_3 + H_2 B_3]_{-}^{+} \right] v_{S2} \end{aligned} \quad [4.119]$$

From equation [4.104], we deduce \dot{W}_a :

$$\begin{aligned} \dot{W}_a = & \rho_a \left(\mathbf{E}_a \cdot \frac{d\mathbf{p}_S}{dt} + \mathbf{B}_a \cdot \frac{d\mathbf{m}_S}{dt} \right) + (E_a^2 - B_a^2) [\rho v_3 / \rho_a]_{-}^{+} \\ & - \mathbf{v}_S \cdot \nabla (E_a^2 - B_a^2) / 2 - c [\mathbf{E} \times \mathbf{H}]_{-3}^{+} + [(\mathbf{P} \cdot \mathbf{E} + \mathbf{M} \cdot \mathbf{B}) v_3]_{-}^{+} - \dot{W}_{\psi a} \end{aligned} \quad [4.120]$$

Finally, we obtain:

$$\begin{aligned} \dot{W}_{Ea}^{fld} = & \dot{W}_a - \mathbf{F}_a \cdot \mathbf{v}_S = \rho_a \left(\mathbf{E}_a \cdot \frac{d\mathbf{p}_S}{dt} + \mathbf{B}_a \cdot \frac{d\mathbf{m}_S}{dt} \right) + \\ & (E_a^2 - B_a^2) [\rho v_3 / \rho_a]_{-}^{+} - [E_1 D_3 + H_1 B_3]_{-}^{+} v_{S1} - \\ & [E_2 D_3 + H_2 B_3]_{-}^{+} v_{S2} - \mathbf{v}_S \cdot \nabla (E_a^2 - B_a^2) / 2 - \\ & c [\mathbf{E} \times \mathbf{H}]_{-3}^{+} + [(\mathbf{P} \cdot \mathbf{E} + \mathbf{M} \cdot \mathbf{B}) v_3]_{-}^{+} - \dot{W}_{\psi a} \end{aligned} \quad [4.121]$$

4.3.4. Entropy production rate

By proceeding in the same way as we did in section 4.1.2, we can deduce the entropy production rate, which also verifies equation [4.88].

Thus, we obtain:

$$\dot{W}_{Sa} = \dot{W}_{Sa}^m + \dot{W}_{Sa}^{fld} \quad [4.122]$$

$$\begin{aligned}
\dot{W}_{Sa}^m &= \mathbf{q}_a \cdot \nabla_S \left(\frac{1}{T_S} \right) - \nabla_S \left(\frac{\mathbf{g}_{kS}}{T_S} \right) - \frac{1}{T_S} \mathbf{\Pi}_a : \nabla_S \otimes \mathbf{v}_S \\
&- \sum_k \frac{\mathbf{g}_{kS}}{T_S} \dot{W}_{ka} + \left[\left(\frac{1}{T} - \frac{1}{T_S} \right) q_3 - \sum_k \left(\frac{\mathbf{g}_k}{T} - \frac{\mathbf{g}_{kS}}{T_S} \right) j_{Dk3} - \frac{1}{T} (\mathbf{v} - \mathbf{v}_S) \cdot \mathbf{\Pi} \right. \\
&\left. + \frac{\rho}{T} \left((T_S - T) s + \sum_k (\mathbf{g}_{kS} - \mathbf{g}_k) Y_k - \frac{1}{2} (\mathbf{v} - \mathbf{v}_S)^2 \right) v_3 \right]_+^+
\end{aligned} \quad [4.123]$$

$$\begin{aligned}
\dot{W}_{Sa}^{fld} &= -\frac{1}{T_S} [\rho v_3]_+^+ \left[(\mathbf{E}'_a - \mathbf{E}'_{a,eq}) \cdot \mathbf{p}'_S + (\mathbf{B}'_a - \mathbf{B}'_{a,eq}) \cdot \mathbf{m}'_S \right] + \\
&\frac{1}{T_S} \left[\rho v_3 \left[(\mathbf{E}' - \mathbf{E}'_{eq}) \cdot \mathbf{p}' + (\mathbf{B}' - \mathbf{B}'_{eq}) \cdot \mathbf{m}' \right] \right]_+^+ + \\
&\frac{\rho_a}{T_S} \left[(\mathbf{E}'_a - \mathbf{E}'_{a,eq}) \cdot \frac{d\mathbf{p}'_S}{dt} + (\mathbf{B}'_a - \mathbf{B}'_{a,eq}) \cdot \frac{d\mathbf{m}'_S}{dt} \right] - \\
&\frac{c}{T_S} \left[(\mathbf{E} \times \mathbf{H})_3 + \frac{\mathbf{v}_S}{c} \cdot (D_3 \mathbf{E} + B_3 \mathbf{H}) \right]_+^+ - \frac{1}{T_S} \dot{W}_{\psi a}
\end{aligned} \quad [4.124]$$

where the “primes” mean that we are following the motion.

These results are obtained in the non-relativistic approximation, for which we can easily verify that:

$$\begin{cases} \mathbf{E} \cdot \mathbf{p} + \mathbf{B} \cdot \mathbf{m} = \mathbf{E}' \cdot \mathbf{p}' + \mathbf{B}' \cdot \mathbf{m}', \\ \mathbf{E} \cdot \frac{d\mathbf{p}}{dt} + \mathbf{B} \cdot \frac{d\mathbf{m}}{dt} = \mathbf{E}' \cdot \frac{d\mathbf{p}'}{dt} + \mathbf{B}' \cdot \frac{d\mathbf{m}'}{dt} \end{cases} \quad [4.125]$$

4.3.5. Remark about the momentum-energy tensor

The most general 4-dimensional balance equation is, for a property F of flux density ${}^4\mathbf{J}_F$ and production ${}^4\dot{W}_F$ (see equation [2.28]):

$${}^4\nabla \cdot {}^4\mathbf{J}_F = {}^4\dot{W}_F \quad [4.126]$$

with 1st- or 2nd-order tensors for ${}^4\mathbf{J}_F$ and 0- or 1st-order tensors for ${}^4\dot{W}_F$, in the Minkowski space.

The corresponding interfacial equation is [4.52]:

$${}^4\nabla_S \cdot {}^4\mathbf{J}_{vFa} + [{}^4\mathbf{J}_{vF\perp}]_{\perp}^+ = {}^4\dot{W}_{Fa}$$

and the condition necessary for this formalism to be coherent is given by equation [4.50]:

$${}^4\mathbf{J}_{vFa} \cdot {}^4\mathbf{N} = 0 \quad [4.127]$$

By separately applying this coherence condition to the parts ${}^4\mathcal{P}_a^{fld}$ and ${}^4\mathcal{P}_a^m$ of the pressure-momentum-energy tensor [4.31], we obtain:

$$\left\{ \begin{array}{l} \left(\rho_a \mathbf{v}_S \otimes \mathbf{v}_S + \bar{\bar{\mathbf{P}}}_a \right) \cdot \mathbf{N} - V_{S\perp} \rho_a \mathbf{v}_S = \mathbf{0} \\ \left[\mathbf{q}_a + \mathbf{v}_S \cdot \bar{\bar{\mathbf{P}}}_a + \rho_a (e_a + k_a) \mathbf{v}_S \right]_{\perp}^+ \cdot \mathbf{N} - \rho_a (e_a + k_a) V_{S\perp} = 0 \\ \bar{\bar{\mathbf{P}}}_a^{fld} \cdot \mathbf{N} - \frac{V}{c} \mathbf{E}_a \times \mathbf{H}_a = \mathbf{0} \\ \mathbf{J}_{Ea}^{fld} \cdot \mathbf{N} - V_{S\perp} E_a^{fld} = 0 \end{array} \right. \quad [4.128]$$

The equations in system [4.128] give us:

$$\left\{ \begin{array}{l} \bar{\bar{\mathbf{P}}}_a \cdot \mathbf{N} = \mathbf{0}, \bar{\bar{\mathbf{P}}}_a^{fld} \cdot \mathbf{N} = \mathbf{0} \\ \mathbf{q}_a \cdot \mathbf{N} = 0, |\mathbf{E}_a|^2 - |\mathbf{B}_a|^2 = 0 \end{array} \right. \quad [4.129]$$

in light of the Maxwell equations at the interface and the condition of coherence relative to the mass flux [4.34]:

$$\mathbf{v}_S \cdot \mathbf{N} = \mathbf{V}_S \cdot \mathbf{N} = V_{S\perp} \quad [4.130]$$

Equation [4.115] also shows that a zero value of $\mathbf{E}_a^2 - \mathbf{B}_a^2$ is a sufficient condition for $\vec{\mathbf{P}}_a^{fld} \cdot \mathbf{N} = 0$ to be automatically verified in the scenario which is of interest to us here.

We shall not make such hypotheses, although they do lead to classic interfacial behaviors (surface tension tensor $\boldsymbol{\sigma} = -\vec{\mathbf{P}}_a$ and heat flux \mathbf{q}_a tangential to the interface), but we shall, of course, suppose that the overall condition ${}^4\mathbf{J}_{vFa} \cdot {}^4\mathbf{N} = 0$ is verified. Thus, this leads us to:

$$\begin{cases} \left(\vec{\mathbf{P}}_a + \vec{\mathbf{P}}_a^{fld} \right) \cdot \mathbf{N} = 0, \\ \mathbf{q}_a \cdot \mathbf{N} + V \frac{|\mathbf{E}_a|^2 - |\mathbf{B}_a|^2}{2} = 0 \end{cases} \quad [4.131]$$

which, in the case of a flat, motionless interface, gives us:

$$P_{a13} + P_{a23} = 0, P_{a33} + \frac{|\mathbf{E}_a|^2 - |\mathbf{B}_a|^2}{2} = 0, q_{a3} = 0 \quad [4.132]$$

It should also be noted that the tensor \mathbf{P}_a^{fld} is not symmetrical, and that there remains a certain amount of uncertainty regarding its very definition. This uncertainty is added to that regarding $\vec{\mathbf{P}}_a^{fld}$, which has been noted, in particular, by de Groot [GRO 69b] and de Groot and Suttrop [GRO 67a, GRO 67b, GRO 68a, GRO 68b, GRO 68c, GRO 68d, GRO 68e] (see section 3.2).

Part 2

Introduction

This second part is devoted to the applications of the equations established in Part 1. The concrete applications discussed here often require the equations to be reformulated, and sometimes need a specific model to be used.

Chapter 5, which discusses the influence of fields on flames, is primarily an application of the equations established for homogeneous media.

Chapter 6, entitled *Applications to the Peltier Effect*, relates to the thermoelectrical effects observed with the formalism of linear thermodynamics of irreversible processes, or TIP, also known as classic irreversible thermodynamics (CIT – see [PRU 12]), in the bulk (the phenomenological relations for a metal are recapped in the Appendix), and then considering the junction as an interface.

Then, in Chapter 7, we present a macroscopic approach to the interaction between a metal and a plasma at low pressure and high temperature, where simplified hypotheses have been employed [PRU 81a, PRU 81b]. This application relates to Langmuir probes.

Chapter 8 relates to the modeling of Hall-effect plasma thrusters: more specifically, small innovative thrusters (referred to as PPIs, as an acronym for their name in French).

In this part, we shall not deal with deformable and reactive interfaces in the presence of electromagnetic fields, although, in principle, we have the means to do so with the balance equations established in Chapter 4. However, we have made the choice to limit ourselves to a few simpler applications. Let us simply cite two examples which seem, to us, to be of interest. The first relates to gravitational waves in a liquid with a film on the surface in the presence of an electrical field [DUD 80, DUD 82]. The second relates to a deformable interface between two immiscible fluids which can be influenced electromagnetically [VAN 10]. We have also chosen not to look at shockwaves in magnetohydrodynamics [JAU 71].

Influence of Fields on Flames

In the wake of Chapters 2 and 3, which were devoted to electro-hydrodynamics [JAN 63] and magneto-hydrodynamics [CAB 70, MOL 07], in this chapter we give some examples of the influence of electrical and magnetic fields on flames.

In parallel, we shall also discuss the influence of other fields such as gravity and acceleration fields. What these fields have in common with electromagnetic fields is that they are exerted on every microscopic particle of the medium in question.

Certain acceleration fields are used to compensate for the earth's gravity. Note that the gradients of magnetic fields are also used for levitation [LOR 08a, LOR 08b], e.g. of evaporating droplets, by playing on their paramagnetic or diamagnetic properties [WUN 00, PIC 09, PIC 10]. It is more difficult to sustain flames in this way, because the chemical components of which they are composed have differing magnetic properties. Chechulin, noting that magnetic fields deform the molecules, thus modifies their probabilities of collision, which affects the reaction rates where they occur [CHE 09].

5.1. Diffusion flames

Non-premixed flames can be generated in a variety of ways, as detailed in [PRU 13]. Here, we examine the influence of an acceleration field, followed by that of an electrical field, on a candle flame. Finally, we look at the effect of a magnetic field on a diffusion flame from a burner formed of two coaxial cylindrical tubes, with the central tube providing the fuel and the outer tube the oxidant.

5.1.1. *Influence of an acceleration field on a candle flame*

Candle flames are created by the combustion of mixtures of paraffin with other solid fuels. The heat from the flame liquefies the solid fuel, and the combustible liquid soaks into a wick and evaporates. The flame is non-premixed.

This is a simple diffusion flame in the absence of an acceleration field (i.e. at $0 g$ – see Figure 5.2 (c)).

In the presence of an acceleration field, the exchanges are activated by convection. Gravity, for example (see Figure 5.2(a)), causes the elongation of the flame, following the acceleration linked to the forces of floatability.

In addition, the liquid phase, which accumulates in the hollow space left in the top end of the candle's cylindrical body, is animated by Bénard–Marangoni convection. The behavior of the candle flame thus results from multiple interactions, and merits a systematic study in order to characterize it [FAR 60¹, TAK 09, SUN 11].

1 See the Websites: <http://www.fordham.edu/halsall/mod/1860Faraday-candle.asp> and <https://archive.org/details/chemicalhistoryo00faraiala>.

Let us briefly describe a few experiments conducted in parabolic flight and in a centrifuge [PRU 91], which demonstrate these phenomena.

An *acceleration field* $\gamma - g$ if it is due to the earth's gravity, which the pilot of an airplane can attenuate in a parabolic flight, or which we can accentuate in a centrifuge up to several hundred $g -$ acts on the flame of a candle.

In microgravity, the flame takes the form of a spherical cap (see Figure 5.2(c)); in the presence of gravity the rising of the hot gases by the effect of the buoyancy forces tends to elongate the flame, which therefore assumes its best-known form, as shown in Figure 2.5(a). This stretching effect continues up to around 2 g ; it is observed during parabolic flight (see Figure 5.2(b)).

In a centrifuge [PRU 91], the height of the flame decreases thereafter with the increase in acceleration. Beginning with a cylindrical-bodied candle divided by a horizontal plane, the candle becomes very greatly hollowed out, and the wick vanishes from the field of the camera. The flame becomes very bright at increasing γ values, and is extinguished at around 7-8 g (see Figure 5.1).²

The acceleration field is also the cause of external vortices stemming from the Kelvin–Helmholtz instability. In certain cases, these eddies are likely to cause flickering at the apex of the flame.

² These observations probably ought to be taken with a pinch of salt, because they are specific to the experimental conditions adopted. Indeed, as is indicated in Appendix A6 of [PRU 12], in this experiment, the combustion took place in a confined atmosphere. The behavior of the candle flame and its extinguishing are perhaps due (or at least partially) to the gradual elimination of oxygen in its environment, which is concomitant with the increase in rotation speed of the centrifuge, in which case, convection only brings in a moderate amount of oxygen. Therefore, once again, the flame has to depend on diffusion.

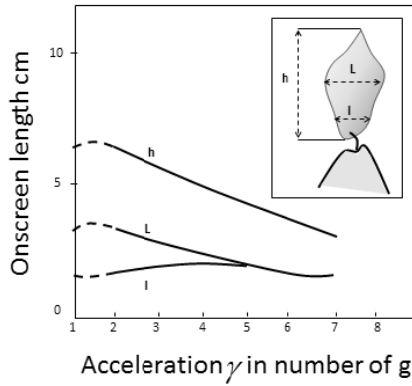


Figure 5.1. *Candle flame in a centrifuge. Dimensions of the flame as a function of the acceleration γ [PRU 91]*

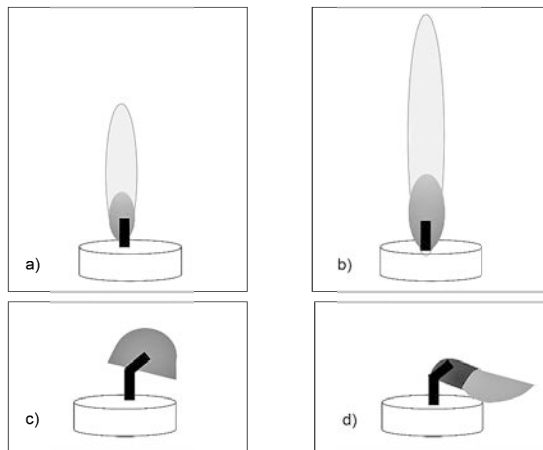


Figure 5.2. *Diagrammatic representation of candle flames in parabolic flight based on the photographs taken by Carleton and Weinberg [CAR 89]: a) at normal gravity (1 g), b) during a 0g flight (2 g), c) in microgravity (0 g), d) under the influence of a horizontal electrical field*

Ellzey and Oran [ELL 90] experimentally demonstrated that the oscillation frequencies of diffusion flames under the influence of an acceleration field are proportional to $g^{3/4}$.

5.1.2. Influence of an electric field on a candle flame

The influence of an electric field on a candle flame was studied experimentally in parabolic flight by Carleton and Weinberg in the 1980s [CAR 89]. Figure 5.2 shows a comparison of the influences of the field of gravity, acceleration fields and an electrical field on a candle flame. The main electrically-charged species are the electrons e^- and the H_3O^+ ions. Equilibrium (Saha's law) is not achieved, and the ions reach a maximum velocity $v = kE$, where k is the mobility taken to be constant. The force exerted per unit volume is $F = neE$, where ne is the charge per unit volume. The general expression is $F = (n^+ - n^-)eE$, if E is large and opposing charges coexist in the thin zone of chemical ionization.

The local density of current is $j = nekE$, so that $F = j/k$, and an "ionic wind" is created [CHA 99].

For a sufficient mean free path in cold air, we see the production of negative ions. The field becomes more unidirectional if the positive electrode is moved closer to the flame. The motion then is very intense [LAW 68].

Figure 5.2 shows the results of the exploratory experiment conducted by Carleton and Weinberg [CAR 89]. As mentioned above, in the absence of an electrical field, we see stretching of the flame at 2 g (Figure 5.2(b)), in comparison to its form at 1 g (Figure 5.2(a))³ and at 0 g (Figure 5.2(c)). The influence of an increasing electrical field has been studied in an atmosphere of 0 g. The case of deviation and stretching of the flame

³ Note that in the Plexiglass tube used in this experiment, a chimney effect is indeed observed, with a traction current $J = ANk\rho g$, where A is the cross-section of the straight part of the tube and N is the number of g units of the acceleration field.

observed for the maximum strength of the electrical field is shown by Figure 5.2(d).

5.1.3. Influence of a magnetic field on a diffusion flame

The influence of magnetic fields on flames has also been studied experimentally. A variety of authors have taken an interest in the subject [FUJ 98, GIL 07, DEL 06, CHE 97, CHA 12, KAS 12] – particularly in relation to the problems of efficiency of the combustion.

Legros *et al.* [LEG 11] recently experimented with methane diffusion flames and a co-stream mixture of nitrogen and oxygen in a magnetic field. The burner used was a coaxial burner, the level of gradient of the magnetic field and the concentration of oxygen in the flow of oxidizing agent were adjustable at will, within certain limits. The magnetic field gradient directly influences the paramagnetic oxygen, so it is possible to conduct a parametric study. According to Shinoda *et al.* [SHI 05], the force exerted per unit mass is:

$$\mathbf{f}_m = \frac{\chi_{O_2}}{2\mu_0} \nabla(B^2) \quad [5.1]$$

where $B = |\mathbf{B}|$, the magnetic permeability in a vacuum being μ_0 and the magnetic susceptibility of oxygen per unit mass being χ_{O_2} . This force plays a role in the momentum equation, written here in a steady-state flow with constant density:

$$\nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = -\nabla p + \nabla \cdot (\mu \nabla \otimes \mathbf{v}) + \rho Y_{O_2} \mathbf{f}_m + \rho \mathbf{g} \quad [5.2]$$

and is added to the force of gravity.

The experiments show the influence of the parameters on the occurrence of flickering⁴, and also on the length of the flame (see the short film on this subject at: dalembert.upmc.fr/home/legros/index.php?option=com_content&task=view&id=7&Itemid=1).

The authors then establish a plot (see Figure 5.3) in the plane (Re_T , Gr), where Gr is the Grashof number and Re_T is the total Reynolds number, equal to the sum of the viscous Reynolds number and a magnetic Reynolds number. Hence, we have the following definitions:

$$\begin{cases} Gr = g \Delta T \bar{L}_{fl} / \nu_{ox}{}^2 T_{ox}, & Re_F = V_F d_F / \nu \\ Re_m = \frac{Y_{O_2} \chi_{O_2} \nabla(B^2)}{2 \mu_0} \frac{d_F^2}{\nu_{ox} \Delta V}, & Re_T = Re_F + Re_m \end{cases} \quad [5.3]$$

with $\Delta T = T_{ad} - T_{ox}$, $\Delta V = |V_{ox} - V_F|$, where the subscript ox refers to the fresh oxidizing mixture, and ad denotes the adiabatic post-combustion temperature.

The subscript F refers to fuel, V_F the fuel injection rate, and d_F is its injection diameter. \bar{L}_{fl} is the average height of the flame above which the influence of flotation is felt, ν is the kinematic viscosity, and Y_{O_2} is the mass fraction of oxygen in the outer jet.

Gilard *et al.* [GIL 07] experimentally studied the “lift” behavior of a flame during the combustion of the air/methane mixture subjected to a magnetic field gradient. Based on

⁴ The term “flicker” describes relatively periodic oscillations of the summit of the flame. These oscillations stem from the differences in velocity between the external jet of fresh oxidant and the hotter external jet containing burned gases, which gives rise to shear instability similar to the Kelvin–Helmholtz instability and to vortex streets. The same phenomenon occurs under the influence of gravity alone [BUC 86].

experimental results obtained using non-intrusive optical techniques, they show that the reduction in lift of the flame is closely linked to the influence of the strong magnetic gradient, which induces a force acting on the paramagnetic molecules.

5.2. Premixed flames

Premixed flames are waves of combustion (for example, see [PRU 13]), whose reference velocity (that of the adiabatic planar flame) can quite easily be calculated on the basis of the thermodynamic characteristics of the constituent parts, as long as we are dealing with flames with high activation energy. Here, we shall limit ourselves to the study of the effects of gravity and of a centrifugal acceleration field on such flames, and primarily on their resulting frequency of oscillation.

Premixed flames, just like diffusion flames, often experience flickering in the presence of gravity. This is what we observe, for example, with the premixed flame of methane and air.⁵ The frequency of these quasi-periodic flickerings depends on the acceleration field, and they disappear if that

⁵ The same phenomenon occurs in the case of a premixed flame of propane and air. In this case, other instabilities, known as cellular instabilities, may arise, such as that shown in Figure A3.9 in [PRU 13]. These cells only appear spontaneously for mixtures rich in heavy hydrocarbons (propane) or which have only a small fraction of light fuels (hydrogen) – i.e. when the species, by which the reaction is limited, is lighter. The thresholds of instability and the number of cells depend not only on the equivalence ratio of the mixture, but also on the pressure [MAR 51], the circumference of the burner and the velocity of the gases ejected from it [BUC 84]. The experimental observations [DUR 87] seem to show that there is a relation which exists between the number of cells of the flame in polyhedral form and the thickness of reaction-diffusion of the premixed propane–air flame, with this thickness being a decreasing function of the pressure. Here, we shall not discuss the influence of fields on these instabilities.

field uniformly vanishes, as is shown by the experiments carried out during parabolic flight [DUR 89, DUR 90].

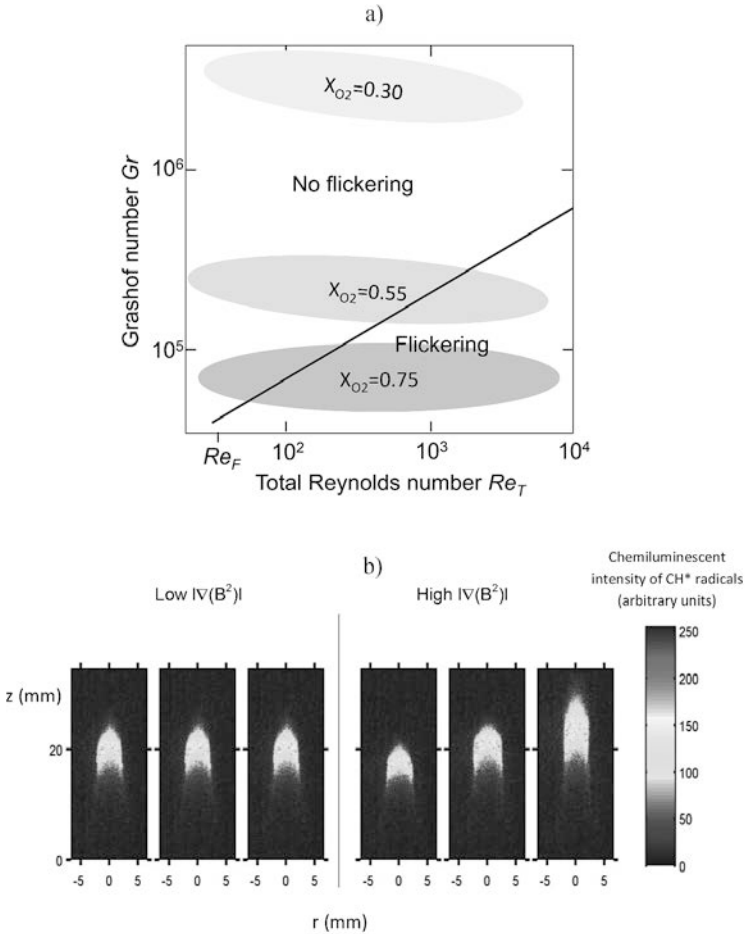


Figure 5.3. a) Flame stability plot, obtained for V_{ox} rates between 5 and 10 $cm\ s^{-1}$. The neutral line corresponds to $Gr = 8.19 \times 10^3 Re_T^{0.47}$. b) Evolution – for $X_{O_2} = 0.55$ – of a flame subjected to a magnetic field for two values of the gradient of B^2 over time, stable on the left, with periodic oscillations of the apex on the right – low, medium and high positions – (top redrawn and bottom taken from the article by Legros et al. [LEG 11] with the authors' kind permission. Data also extracted from that article). For a color version of this figure, see www.iste.co.uk/prudhomme/flows.zip

A highly simplified dimensional analysis enables us to show characteristic frequencies [PRU 92]. If we discount the forces of viscosity, the momentum equation is written thus:

$$\rho d\mathbf{v}/dt = \Delta\rho\mathbf{g} \quad [5.4]$$

where $\Delta\rho$ is the difference between the average density within the jet issuing from the burner containing the flame and the density of the outside air.

In the absence of a flame, the jet is quasi-cylindrical, and expands slightly with increasing altitude, which would tend to suggest that, at least in the particular domain under study here, the forces of viscosity do not cause destabilization.

In the presence of a flame, the average density of the jet in a horizontal plane varies with altitude. The dimensional formulation in equation [5.4], if L_c is a characteristic length, gives us: $L_c/T_c^2 = g\Delta\rho/\rho$, or indeed, with $F_c = 1/T_c$, T_c being the characteristic time, and $\Delta\rho/\rho$ an average value of the relative difference in density:

$$F_c = \sqrt{g\Delta\rho/L_c\rho} \quad [5.5]$$

This result indicates that the characteristic frequency F_c will be proportional to the square root of the acceleration, with all other values remaining equal.

However, if we take account solely of the viscous forces, equation [5.4] is replaced by:

$$\rho d\mathbf{v}/dt = \mu\Delta\mathbf{v} \quad [5.6]$$

which, by the same reasoning process as before, with the introduction of a characteristic frequency of viscous diffusion (although the phenomenon is not oscillating), gives us:

$$F_v = \nu / L_c^2 \quad [5.7]$$

The combination of the viscous effects can give us, depending on the relative strengths of the phenomena of flotation and viscosity, for example:

$$\begin{cases} F'_c = (F_c^3 / F_v)^{1/2} = (\Delta\rho / \rho)^{3/4} g^{3/4} L_c^{1/4} \nu^{-1/2} \\ F''_c = (F_c F_v)^{1/2} = (\Delta\rho / \rho)^{1/4} g^{1/4} L_c^{-5/4} \nu^{1/2} \end{cases} \quad [5.8]$$

We see the dependency on $g^{3/4}$ of diffusion flames [ELL 90], and on $\nu^{-1/2}$ and a distance to the power $1/4$.

In addition, a dependency on $g^{1/4}$ is obtained, with a thermoconvective eddy model, but the influence of the other values is then not the same.

These arguments drawn from simple dimensional analysis need to be validated by both theory and experimentation.

A physical observation is also that the accelerated jet exiting the burner must undoubtedly create shear instability by contact with the external atmosphere at rest. Thus, we would have a Kelvin–Helmholtz configuration between two flows, one of which has a velocity which increases with altitude.

The situation is also comparable to that of two superposed fluids, where the hotter of the two (and therefore the less

dense, represented by the burned gases) is under the colder one. The pulsation of the Rayleigh–Taylor instability thus created is:

$$\omega = \sqrt{gk(\rho_2 - \rho_1)/(\rho_1 + \rho_2)}$$

where the wavenumber k is the inverse of a characteristic length. Here, we can see a similarity with equation [5.5].

Applications to the Peltier Effect

The application discussed in this chapter relates to the *thermoelectrical effects* observed with the formalism of linear thermodynamics of irreversible processes, or TIP, also known as classic irreversible thermodynamics (CIT – see [PRU 12]), in volume (the phenomenological relations for a metal are recapped in Appendix A1.2), and then considering the junction as an interface.

The Peltier effect is well known. It is encountered at the joint between two metals. It is generally spoken of at the same time as the Thomson effect, because these two effects both cross-link between the thermal gradient and intensity of the current.

6.1. Introduction

De Groot and Mazur introduce the Peltier effect using the following reasoning: the conductor is composed of two pure materials, A and B , and the joint between the two is composed of an alloy of A and B . In this joint, of volume \mathcal{V} , lying between two sections Ω_A and Ω_B , the thermodynamic values vary continuously. The temperature

within the joint is supposed to be uniform (temperature T – see Figure 6.1).

The phenomenological relations enable us to write the entropy variation in the form:

$$\frac{\partial \rho s}{\partial t} = \frac{1}{T} \nabla \cdot (\lambda \nabla T) + \frac{R \mathbf{I}^2}{T} - \nabla \cdot \left(\frac{\pi \mathbf{v}}{T} \right) \quad [6.1]$$

On the right-hand side of this equation, we recognize:

the heat conduction term $\frac{1}{T} \nabla \cdot (\lambda \nabla T)$;

the Joule effect term $\frac{R \mathbf{I}^2}{T}$;

the final term shows the influence of the electrical current and of an inhomogeneity on the local variation of entropy.

By integration over a control volume \mathcal{V} (Figure 6.1), we obtain:

$$\begin{aligned} T \int_{\mathcal{V}} \frac{\partial \rho s}{\partial t} d\mathcal{V} &= \pi_A \int_{\Omega_A} \mathbf{I} \cdot d\boldsymbol{\Omega}_A + \pi_B \int_{\Omega_B} \mathbf{I} \cdot d\boldsymbol{\Omega}_B + \int_{\mathcal{V}} R \mathbf{I}^2 d\mathcal{V} \\ &= T \frac{d}{dt} \int_{\mathcal{V}} \rho s d\mathcal{V} = T \frac{dS}{dt}. \end{aligned}$$

If the volume tends toward zero, we see the influence of a discontinuity appear:

$$T \left(\frac{dS}{dt} \right)_{\mathcal{V} \rightarrow 0} = \pi_{AB} \int_{\Omega} \mathbf{I} \cdot d\boldsymbol{\Omega} \quad [6.2]$$

where π_{AB} is the Peltier heat of the joint ($\pi_{AB} = \pi_A - \pi_B$).

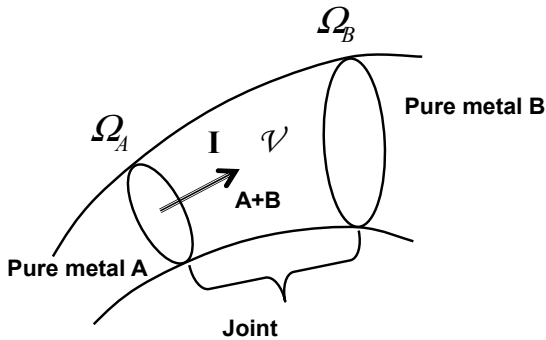


Figure 6.1. Diagram of a junction. Definition of the volume \mathcal{V}

Therefore, in conditions nearing thermodynamic equilibrium, the passage of the electrical current through the joint leads to the production of entropy proportional to the intensity of the current.

Landau and Lifchitz [LAN 69] present the Peltier effect on the basis of an energy balance. Let us first determine the entropy flux \mathbf{J}_s in order to later be able to evaluate the energy flux \mathbf{J}_E .

We have: $\mathbf{J}_s = \mathbf{j}_s + \rho \mathbf{v}_s$. The entropy balance enabled us to find the expression of the entropy flux in the barycentric motion, so that:

$$T\mathbf{j}_s = \mathbf{q} - \sum_{k=1}^N g_k \mathbf{j}_{Dk} + \rho \mathbf{v} \left(e + p/\rho - \sum_{k=1}^N g_k Y_k \right)$$

We know the expression of the heat flux \mathbf{q} as a function of the energy flux. In view of the hypothesis where we neglect

the influence of the magnetic field, we obtain (see relation [A1.10]):

$$T\mathbf{J}_S = \mathbf{J}_E - \vec{\mathbf{P}} \cdot \mathbf{v} - \varphi \mathbf{I} - \sum_{k=1}^N \mathbf{g}_k \mathcal{J}_{Dk} + \rho \mathbf{v} \left(e + p/\rho - \sum_{k=1}^N \mathbf{g}_k Y_k \right)$$

Ignoring the effect of viscosity and the kinetic energy term, the above relation is written as: $T\mathbf{J}_S = \mathbf{J}_E - \mathbf{I}(\varphi + \mathbf{g}_e/z_e)$.

It has already been mentioned that the expression of the dissipation function which appears in equation [A1.10] is still valid when we neglect the magnetic field in the Lorentz force. Hence, we have:

$$\mathbf{J}_E - \mathbf{I} \left(\varphi + \frac{\mathbf{g}_e}{z_e} \right) = -\lambda \nabla T + \pi \mathbf{I} = -L_{11} T \nabla T + L_{12} T \left(\mathbf{E} - \nabla \left(\frac{\mathbf{g}_e}{z_e} \right) \right) \quad [6.3]$$

Landau and Lifchitz consider that the left-hand side of this equation represents the total energy flux minus the energy transported by the electrons. This first term therefore no longer depends on the potential, and near thermodynamic equilibrium, it is a linear function of the field $\mathbf{E} - \nabla(\mathbf{g}_e/z_e)$ and of the temperature gradient, so:

$$\mathbf{J}_E - \mathbf{I} \left(\varphi + \frac{\mathbf{g}_e}{z_e} \right) = -\chi \nabla T + \alpha T \mathbf{I} = -\gamma \nabla T + \beta \left(\mathbf{E} - \nabla \left(\frac{\mathbf{g}_e}{z_e} \right) \right) \quad [6.4]$$

Relations [6.3] and [6.4] are therefore equivalent, if we set:

$$\lambda = \chi, \quad \alpha = \pi/T = L_{21}/L_{22}, \quad \gamma = L_{11}T, \quad \beta = L_{12}T$$

The divergence Q of the total energy flux is the quantity of heat released into the conductor:

$$Q = \partial \rho_e / \partial t = -\nabla \cdot \mathbf{J}_E = \nabla \cdot (\lambda \nabla T) + \mathbf{I} \cdot \mathbf{E} - \mathbf{I} \cdot \nabla (\alpha T) \quad [6.5]$$

This formula reveals the thermoelectric effects by way of terms similar to those in equation [6.1], showing the entropy balance.

Let us represent the joint by a surface of discontinuity (S) between the two pure materials A and B (Figure 6.2). \mathbf{N} represents the unitary normal to that surface, directed from metal A to metal B.

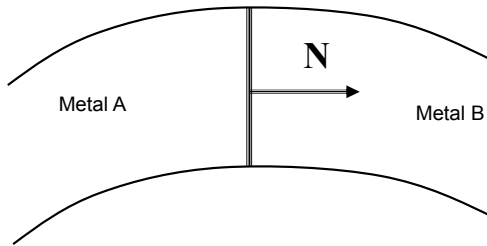


Figure 6.2. Interfacial representation of a junction

The energy balance upon crossing that interface is written as $[\mathbf{J}_E]_A^B \cdot \mathbf{N} = 0$, but: $\mathbf{J}_E = (\varphi + g_e/z_e + \alpha T)\mathbf{I} - \lambda \nabla T$. We therefore obtain:

$$\lambda \left[\frac{\partial T}{\partial N} \right]_A^B = -I(\alpha_A - \alpha_B)T \quad [6.6]$$

supposing that the potential $\varphi + g_e/z_e$ is continuous as the joint is crossed.

The left-hand term corresponds to the heat evacuated by conduction from the interface toward metals A and B. The right-hand term is the heat released at the joint.

The Peltier coefficient is: $T(\alpha_A - \alpha_B) = \pi_{AB}$, so it is identical to that introduced by de Groot and Mazur.

We can also use an energy balance involving the electromagnetic energy flux (equation [A1.5]). We obtain:

$$T \mathbf{J}_S = \mathbf{J}_E - \rho \mathbf{v} k - \mathcal{P} - \mathbf{I} g_e / z_e$$

If we neglect the kinetic energy, the energy balance becomes:

$$[\mathbf{J}_E]_A^B \cdot \mathbf{N} = -[\lambda \nabla T]_A^B \cdot \mathbf{N} - [\mathcal{P}]_A^B \cdot \mathbf{N} - \left[\mathbf{I} \frac{g_e}{z_e} \right]_A^B \cdot \mathbf{N} + [\pi \mathbf{I}]_A^B \cdot \mathbf{N} = 0$$

Using the electrical current conservation equation, we obtain:

$$\left[\lambda \frac{\partial T}{\partial N} \right]_A^B = [\mathcal{P}]_A^B + I \left[\frac{g_e}{z_e} + \pi \right]_A^B$$

where \mathcal{P} and I represent the respective projections of \mathcal{P} and \mathbf{I} on the unit vector \mathbf{N} .

If the potential g_e is continuous, the relation becomes:

$$\left[\lambda \frac{\partial T}{\partial N} \right]_A^B = [\mathcal{P}]_A^B + I [\pi]_A^B$$

We shall show in section 6.2.3 that when the surface current passing through the joint is zero, the quantity \mathcal{P} is

conserved upon crossing the interface: $[\mathcal{P}]_A^B = 0$, and

$$\text{therefore: } \left[\lambda \frac{\partial T}{\partial N} \right]_A^B = (\pi_A - \pi_B) I = \pi_{AB} I.$$

The relation obtained is then identical to that which is obtained in equation [6.6].

The introduction to the Peltier effect given by Haase [HAA 69] is made on the basis of the energy balance equation presented in the form [A1.11] – i.e.:

$$\rho c_{p,f} \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q}' - \rho c_{p,f} \mathbf{v} \cdot \nabla T - \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \rho T \frac{\partial \vartheta}{\partial t} \left(\frac{\partial p}{\partial t} + \rho T \mathbf{v} \cdot \nabla p \right) + \sum_k \mathcal{J}_{Dk} \cdot (\mathbf{F}_k - \nabla h_k)$$

Haase [HAA 69] proposes the following hypotheses:

- viscous phenomena neglected;
- $\partial p / \partial t = 0$;
- $\nabla p = 0$.

The energy balance becomes:

$$\rho c_{p,f} \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q}' - \rho c_{p,f} \mathbf{v} \cdot \nabla T + \sum_k \mathcal{J}_{Dk} \cdot (\mathbf{F}_k - \nabla h_k) \quad [6.7]$$

The hypothesis of a zero pressure gradient, associated with that of mechanical equilibrium, enables us to transform this latter term, so:

$$\rho c_{p,f} \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q}' - \rho c_{p,f} \mathbf{v} \cdot \nabla T - \sum_k \mathcal{J}_{Dk} \cdot \nabla h_k - \mathbf{I} \cdot \nabla \varphi$$

with: $\underline{\mathbf{F}}_e = z_e \underline{\mathbf{E}} = -z_e \underline{\nabla} \varphi$. Using the equality:

$$(c_{p,f}/z_e) \rho \mathbf{v} \cdot \nabla p + \sum_k \rho_k c_{p,k} \mathbf{v}_k \cdot \mathbf{J}_{Dk} = \sum_k \rho_k c_{p,k} \mathbf{v}_k \cdot \nabla T + \sum_k \rho_k \mathbf{v}_k \cdot (\nabla h_k)_{p,T}$$

where: $c_{p,k} = (\partial h_k / \partial T)_{p, Y_j(j \neq k)}$ and $\sum_k \rho_k (\nabla h_k)_{p,T} = 0$, the energy balance equation becomes:

$$\rho c_{p,f} \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q}' - \frac{\mathbf{I}}{z_e} \left[c_{p,e} \nabla T + (\nabla h_e)_{p,T} \right] - \mathbf{I} \cdot \nabla \varphi \quad [6.8]$$

Near to thermodynamic equilibrium, we can replace the fluxes \mathbf{I} and \mathbf{q}' by their expression as a function of the generalized forces (gradients of temperature and of potential):

$$\underline{\mathbf{I}} = -K \left[\nabla \varphi + \nabla \left(\frac{g_e}{z_e} \right)_T \right] - \frac{K(^*Q_e)}{z_e T} \nabla T \quad [6.9a]$$

$$\mathbf{q}' = -\frac{K(^*Q_e)}{z_e} \left[\nabla \varphi + \nabla \left(\frac{g_e}{z_e} \right)_T \right] - \lambda \nabla T \quad [6.9b]$$

where (*Q_e) is the transfer heat of the electrons.

The correspondence between the proportionality coefficients and the coefficients introduced by de Groot and Mazur is presented in the Appendix in section A1.4.

Equation [6.8] becomes:

$$\rho c_{p,f} \frac{\partial T}{\partial t} = -\nabla \cdot (\lambda_\infty \nabla T) - \frac{\mathbf{I}^2}{K} - T \frac{\mathbf{I}}{z_e} (\nabla^* s_e)_T - \tau \mathbf{I} \cdot \nabla T \quad [6.10]$$

where:

$$\lambda_\infty = \lambda_0 - \frac{K \left({}^*Q_e \right)^2}{z_e^2 T}, \left({}^*s_e \right) = s_e + \frac{\left({}^*Q_e \right)}{T}, T s_e = h_e - g_e, \tau = \left(c_{p,e} - \frac{\left({}^*Q_e \right)}{T} \right) \frac{1}{z_e}$$

An inhomogeneity in the conductor results in a variation of the quantity $\left({}^*s_e \right)$. The value characteristic of this phenomenon is therefore: $T \left({}^*s_e \right) / z_e$. A discontinuity between two materials A and B will therefore introduce the coefficient: $\frac{T}{z_e} \left[{}^*s_e \right]_A^B$. This coefficient is identical to that found previously, and we can easily verify that we have:

$$\pi_{AB} = \frac{T}{z_e} \left[\left({}^*s_e \right)_B - \left({}^*s_e \right)_A \right].$$

This presentation is less general than that of de Groot and Mazur, which involves the magnetic field. In Haase's study, the hypothesis of mechanical equilibrium ($d\mathbf{v}/dt = \mathbf{0}$) comes into play in the form of a zero pressure gradient, which is equivalent if we neglect the influence of the magnetic field in the Lorentz force and if electrical neutrality is verified.

6.2. Introduction of the Peltier effect by the general interfacial balance equations

6.2.1. Entropy production

Consider a flat interface, without internal properties, separating two pure metals. The entropy production at the interface per unit area and time is written as:

$$\left[\frac{\mathbf{q}}{T} - \sum_k \mathbf{J}_{Dk} \frac{\mathbf{g}_k}{T} + \rho s (\mathbf{v} - \mathbf{V}) \right]_A^B \cdot \mathbf{N} = \dot{W}_{Sa} \quad [6.11]$$

where \mathbf{V} is the interfacial velocity. We shall choose a frame of reference wherein the interfacial velocity is zero.

We have: $\dot{W}_{Sa} = [\mathbf{J}_S]_A^B \cdot \mathbf{N}$. If we use the phenomenological relation: $\mathbf{J}_S = -\frac{\lambda}{T} \nabla T + \frac{\pi}{T} \mathbf{I}$, the entropy production becomes:

$$\dot{W}_{Sa} = \left[-\frac{\lambda}{T} \nabla T + \frac{\pi}{T} \mathbf{I} \right]_A^B \cdot \mathbf{N} \quad [6.12]$$

This formulation enables us to directly obtain the entropy production at the interface without performing a passage to the boundary on an elementary volume surrounding the interface.

6.2.2. Influence of the magnetic field

Relations [A1.13] are written as follows, if we set $\underline{\underline{\mathbf{Z}}} = \underline{\underline{\mathbf{L}}} - \underline{\underline{\mathbf{N}}} \underline{\underline{\mathbf{M}}}^{-1} \underline{\underline{\mathbf{N}}}$ and $\underline{\underline{\mathbf{S}}} = -\underline{\underline{\mathbf{N}}} \underline{\underline{\mathbf{M}}}^{-1}$:

$$\mathbf{J}_S = -\underline{\underline{\mathbf{Z}}} \cdot \underline{\underline{\nabla}} T - \underline{\underline{\mathbf{S}}} \cdot \mathbf{I} \quad [6.13a]$$

$$\mathbf{E} - \nabla \left(\begin{array}{c} g_e \\ z_e \end{array} \right) = \mathbf{W} \cdot \nabla T - \mathbf{R} \cdot \mathbf{I} \quad [6.13b]$$

$\underline{\underline{\mathbf{Z}}}$ can be deconstructed into a symmetrical tensor $\underline{\underline{\mathbf{Z}}}^S$ and a antisymmetrical tensor $\underline{\underline{\mathbf{Z}}}^A$: $\underline{\underline{\mathbf{Z}}} = \underline{\underline{\mathbf{Z}}}^S + \underline{\underline{\mathbf{Z}}}^A$. The tensor $\underline{\underline{\mathbf{Z}}}^A$ is associated with the axial vector $\underline{\underline{\mathbf{Z}}}$. The Onsager symmetry relations are written thus, in the presence of a magnetic field: $Z_{ij}(\mathbf{H}) = Z_{ji}(-\mathbf{H})$. From this, we can deduce that $\underline{\underline{\mathbf{Z}}}(\mathbf{H})$ and $\underline{\underline{\mathbf{Z}}}^S(\mathbf{H})$ are, respectively, an odd-numbered and even-numbered function of the field \mathbf{H} .

For weak magnetic fields, a Taylor expansion can be written:

$$Z_i = \alpha_{ik} H_k + O(H^3), \quad Z_{ij}^S = Z_{ij}^{H=0} + \beta_{ijlm} H_l H_m + O(H^4)$$

If the medium is isotropic, these relations can be simplified and, if we ignore all terms whose order is greater than 1, they become: $\mathbf{Z} = z \mathbf{H}$, $\mathbf{Z}^S = Z \mathbf{1}$.

Relations [6.13] are then written as:

$$\mathbf{J}_S = -Z \nabla T - S \mathbf{I} - z(\mathbf{H} \times \nabla T) - \mathcal{S}(\mathbf{H} \times \mathbf{I}) \quad [6.14a]$$

$$\mathbf{E} - \nabla(g_e/z_e) = -W \nabla T - R \mathbf{I} - \mathcal{W}(\mathbf{H} \times \nabla T) - \mathcal{R}(\mathbf{H} \times \mathbf{I}) \quad [6.14b]$$

The entropy production at the interface becomes:

$$\dot{W}_{Sa} = \left[-\frac{\lambda}{T} \nabla T + \frac{\pi}{T} \mathbf{I} \right]_A^B \cdot \mathbf{N} - [z(\mathbf{H} \times \nabla T)]_A^B \cdot \mathbf{N} - [\mathcal{S}(\mathbf{H} \times \mathbf{I})]_A^B \cdot \mathbf{N} \quad [6.15]$$

The influence of the magnetic field on the Peltier effect is characterized by the term $[\mathcal{S}(\mathbf{H} \times \mathbf{I})]_A^B \cdot \mathbf{N}$. This is known as the *Ettingshausen effect*. The coefficient \mathcal{R} is the *Hall coefficient*.

6.2.3. Expression of heat flux

We shall now determine the expression of the discontinuity of the heat flux in the Peltier effect depending on the strength of the current passing through the junction and the discontinuity of the heat gradient. In order to do so, let us express the heat flux as a function of the entropy flux: $T \mathbf{J}_S - \mathbf{q} = -\sum_k g_k \mathcal{J}_{Dk} + \rho v_s T$. We can evaluate the right-hand side of this equation as a function of the current \mathbf{I} , noting

that the velocity of the ions in the metallic network is zero:
 $\rho \mathbf{v} = \rho_e \mathbf{v}_e + \rho_i \mathbf{v}_i = \rho_e \mathbf{v}_e = \mathbf{I}/z_e$ and:

$$g_e \mathbf{J}_{De} + g_i \mathbf{J}_{Di} = \frac{\rho_e \rho_i}{\rho} \mathbf{v}_e (g_e - g_i) \cong \frac{\mathbf{I}}{z_e} (g_e - g_i)$$

because we have: $\frac{\rho_e}{\rho_i} \ll 1$.

Relation [A1.14] enables us to evaluate \mathbf{J}_S as a function of the current \mathbf{I} and of the temperature gradient, which gives us: $\mathbf{q} = -\lambda \nabla T + \pi \mathbf{I} + \frac{\mathbf{I}}{z_e} (g_e - g_i) - \frac{\mathbf{I}}{z_e} s T$.

In the steady-state regime, the conservation of mass on passing through the joint imposes the condition: $[\rho \mathbf{v}]_A^B \cdot \mathbf{N} = 0$. Hence: $[\mathbf{I}]_A^B \cdot \mathbf{N} = [I]_A^B = 0$, and therefore, the discontinuity of the heat flux is:

$$[\mathbf{q}]_A^B \cdot \mathbf{N} = \left[-\lambda \frac{\partial T}{\partial N} \right]_A^B + \frac{I}{z_e} [\pi z_e + g_e - g_i - s T]_A^B$$

However, the energy balance at the joint imposes:

$$\left[-\lambda \frac{\partial T}{\partial N} \right]_A^B = I [\pi]_A^B$$

so that: $[\mathbf{q}]_A^B \cdot \mathbf{N} = \frac{I}{z_e} [g_e - g_i - s T]_A^B$.

The discontinuity of the heat flux is therefore proportional to the intensity of the electrical current passing through the junction.

6.3. Introduction of an average electrical field for a flat interface

We shall now introduce an average surface electromagnetic field on the basis of the momentum balance equation in the simple case of a flat, immobile interface. The general case was discussed in section 4.1.

In equation [3.104] of [PRU 12], the quantity $\sum_k \rho_k \mathbf{f}_k$ appears as a source of momentum. It is possible to transform this equation to reveal an electromagnetic momentum:

$$\frac{\partial}{\partial t} \left(\rho \mathbf{v} + \frac{1}{c} \mathbf{E} \times \mathbf{B} \right) = -\nabla \cdot \left(\rho \mathbf{v} \otimes \mathbf{v} + \vec{\vec{\mathbf{P}}} - \mathbf{T} \right) \quad [6.16]$$

We shall neglect the electrical and magnetic polarizations. The quantity $\frac{1}{c} \mathbf{E} \times \mathbf{B}$ is the electromagnetic momentum density and \mathbf{T} is the Maxwell electromagnetic stress tensor: $\mathbf{T} = \mathbf{E} \otimes \mathbf{E} + \mathbf{B} \otimes \mathbf{B} - \frac{1}{2} (|\mathbf{E}|^2 + |\mathbf{B}|^2) \mathbf{1}$.

Now consider a flat, fixed interface with no polarization (see Figure 6.3). All the phenomena are considered to be steady.

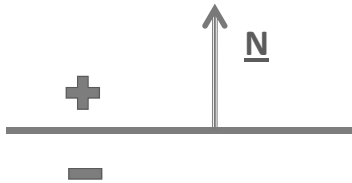


Figure 6.3. Configuration of the interface (flat, fixed and with no polarization)

The momentum balance upon crossing the interface is written:

$$\left[\rho \mathbf{v} \otimes \mathbf{v} + \vec{\mathbf{P}} - \mathbf{T} \right]_{-}^{+} \cdot \mathbf{N} = \mathbf{0} \quad [6.17]$$

so:

$$\left[\rho \mathbf{v} v_{\perp} \right]_{-}^{+} + \left[\vec{\mathbf{P}} \cdot \mathbf{N} \right]_{-}^{+} - \left[\mathbf{E} E_{\perp} \right]_{-}^{+} - \left[\mathbf{B} B_{\perp} \right]_{-}^{+} + \left[\frac{1}{2} (|\mathbf{E}|^2 + |\mathbf{B}|^2) \mathbf{N} \right]_{-}^{+} = \mathbf{0}$$

where: $v_{\perp} = \mathbf{v} \cdot \mathbf{N}$, $B_{\perp} = \mathbf{B} \cdot \mathbf{N}$, $E_{\perp} = \mathbf{E} \cdot \mathbf{N}$.

In this interfacial balance, we have neglected the source of momentum created by the forces exerted on charges and a surface current (the surface fields are null when there is no polarization). We have not taken account of the momentum associated with the displacement of the surface charges.

The mass balance across the interface is written as:
 $\dot{m} = \rho^{-} v_{\perp}^{-} = \rho^{+} v_{\perp}^{+}$.

By introducing the viscous stress tensor, we obtain:

$$\dot{m} \left[\mathbf{v} \right]_{-}^{+} + \left[p \right]_{-}^{+} \cdot \mathbf{N} + \left[\mathbf{\Pi} \cdot \mathbf{N} \right]_{-}^{+} - \left[\mathbf{E} E_{\perp} \right]_{-}^{+} - \left[\mathbf{B} B_{\perp} \right]_{-}^{+} + \left[\frac{1}{2} (|\mathbf{E}|^2 + |\mathbf{B}|^2) \mathbf{N} \right]_{-}^{+} = \mathbf{0}$$

In a projection on the normal, this relation becomes:

$$\dot{m} \left[v_{\perp} \right]_{-}^{+} + \left[p \right]_{-}^{+} + \left[\mathbf{\Pi} \cdot \mathbf{N} \right]_{-}^{+} \cdot \mathbf{N} - \left[E_{\perp}^2 \right]_{-}^{+} - \left[B_{\perp}^2 \right]_{-}^{+} + \left[\frac{1}{2} (|\mathbf{E}|^2 + |\mathbf{B}|^2) \right]_{-}^{+} = 0$$

so:

$$\dot{m} \left[v_{\perp} \right]_{-}^{+} + \left[p \right]_{-}^{+} + \left[\mathbf{\Pi} \cdot \mathbf{N} \right]_{-}^{+} \cdot \mathbf{N} - \frac{1}{2} \left[E_{\perp}^2 - |\mathbf{E}|_{//}^2 \right]_{-}^{+} - \frac{1}{2} \left[B_{\perp}^2 - |\mathbf{B}|_{//}^2 \right]_{-}^{+} = 0 \quad [6.18]$$

where $\mathbf{E}_{//}$ and $\mathbf{B}_{//}$ are the vectorial components of \mathbf{E} and \mathbf{B} in the plane of the interface. We now neglect the viscosity term. The projection in the plane of the interface is written:

$$\dot{m}[\mathbf{v}_{//}]_{-}^{+} - [\mathbf{E}_{//} E_{\perp}]_{-}^{+} - [\mathbf{B}_{//} B_{\perp}]_{-}^{+} = \mathbf{0} \quad [6.19]$$

Equations [6.18] and [6.19] can be modified in order to reveal the charge and the surface current. For this, we shall use the Maxwell equations, so that:

$$[\mathbf{E}_{//}]_{-}^{+} = \mathbf{0}, [\mathbf{E}_{\perp}]_{-}^{+} = \rho_a z_S, [\mathbf{B}_{//}]_{-}^{+} = -\frac{1}{c} \mathbf{N} \times \mathbf{I}_a, [\mathbf{B}_{\perp}]_{-}^{+} = \mathbf{0}$$

where $\rho_a z_S$ is the surface charge and \mathbf{I}_a the surface current. We then obtain the relations:

$$(E_{\perp}^{+})^2 - (E_{\perp}^{-})^2 = 2\rho_a z_S \mathcal{E}_{\perp}, (B_{\perp}^{+})^2 - (B_{\perp}^{-})^2 = -\frac{2}{c} \mathcal{B}_{//} \cdot (\mathbf{N} \times \mathbf{I})$$

with \mathcal{E} being the average electrical field: $\mathcal{E} = \frac{1}{2}(\mathbf{E}^{+} + \mathbf{E}^{-})$ and \mathcal{B} the average magnetic field $\mathcal{B} = \frac{1}{2}(\mathbf{B}^{+} + \mathbf{B}^{-})$.

With these notations, equations [6.18] and [6.19] become:

$$\begin{aligned} \dot{m}[\mathbf{v}_{\perp}]_{-}^{+} + [p]_{-}^{+} &= \rho_a z_S \mathcal{E}_{\perp} + \frac{1}{c} \mathcal{B}_{//} \cdot (\mathbf{N} \times \mathbf{I}_a), \\ \dot{m}[\mathbf{v}_{//}]_{-}^{+} &= \rho_a z_S \mathcal{E}_{//} + \frac{1}{c} \mathcal{B}_{\perp} \cdot (\mathbf{N} \times \mathbf{I}_a) \end{aligned} \quad [6.20]$$

In particular, if $[\mathbf{v}_{//}]_{-}^{+}$ is null, the final equation shows that the surface current is normal to the average electrical field. The source of momentum upon crossing the interface is

given by the quantity: $\rho_a z_s \mathcal{E} + \frac{1}{c} \mathbf{I}_a \times \mathcal{B}$, of a form equivalent to the source in a homogeneous medium where \mathcal{E} and \mathcal{B} play the role of fictitious surface fields.

The momentum balance can still be presented in the following vectorial form:

$$\dot{m} [\mathbf{v}]_{-}^{+} + [p]_{-}^{+} \mathbf{N} = \rho_a z_s \mathcal{E} + \frac{1}{c} \mathbf{I}_a \times \mathcal{B}$$

In this simplified interface model, the discontinuity $[\mathbf{v}_{//}]_{-}^{+}$ is attached to that of the Poynting vector; indeed: $[\bar{\mathcal{P}}]_{-}^{+} \cdot \mathbf{N} = (\mathbf{E}^{+} \times \mathbf{B}^{+}) \cdot \mathbf{N} - (\mathbf{E}^{-} \times \mathbf{B}^{-}) \cdot \mathbf{N}$, which becomes, using the Maxwell relations: $[\mathcal{P}]_{-}^{+} \cdot \mathbf{N} = \frac{1}{c} \mathbf{E}_{//} \cdot \mathbf{I}$. However, if the discontinuity of the tangential velocity is null, the electrical field is normal to the surface current and the flux of the Poynting vector is continuous on crossing the interface: $[\mathbf{v}_{//}]_{-}^{+} = \mathbf{0}$ leads to: $[\bar{\mathcal{P}}]_{-}^{+} \cdot \mathbf{N} = 0$, and $[\mathbf{v}_{//}]_{-}^{+} \neq \mathbf{0}$ gives us:

$$[\bar{\mathcal{P}}]_{-}^{+} \cdot \mathbf{N} = -\dot{m} \frac{\mathbf{E}_{//}}{B_{\perp}} \cdot ([\mathbf{v}_{//}]_{-}^{+} \times \mathbf{N})$$

The *flux of the Poynting vector* will thus be continuous when the discontinuity is collinear to the tangential field $\mathbf{E}_{//}$.

These different approaches to the Peltier effect have numerous points in common. In particular, the effects of viscosity are neglected; we are still operating near to thermodynamic equilibrium (in order to write the linear relations between the fluxes and the forces associated

therewith) and we suppose that the hypothesis of mechanical equilibrium is verified.

We have verified that the Peltier coefficient is identical in the different presentations.

We have shown that the entropy production at the interface, considered as a discontinuity, is easily obtained from the general formulation of the balance equations on crossing of an interface.

Interaction between Metal and Plasma with an Electrical Field (Langmuir Probe)

This section presents a macroscopic approach to the interaction between a solid and a plasma at low pressure and high temperature. The objective is to better understand what happens, for example, during the re-entry of a high-velocity body into the earth's atmosphere. In more modest terms, the aim is to be able to interpret the signal of a Langmuir probe¹ (see Figure 7.1(a)) placed in a reactive gaseous mixture in thermal disequilibrium at low pressure (Figure 7.1(b) [DUD 82, DUD 87]).

In the conditions studied here, a sheath of potential is created in the plasma surrounding an electrically-polarized metal object, which we shall attempt to characterize using the laws of TIP, thus bypassing the typical linear framework [PRU 81a, PRU 81b].

¹ Langmuir probes are commonly used in plasma physics, mainly in the non-collisional case, to determine the electronic properties (plasma density, electronic temperature, energy distribution function). The continuous case presented here is more complex, because it involves kinetics in the volume and on the surface.

The macroscopic description of a homogenous plasma in a state of thermal disequilibrium experiencing steady one-dimensional evolution is presented in section A1.5 in the Appendix and, in the case of active walls in Appendix A2 and in Chapter 8.

In this section we present that which relates more specifically to the presence of interfaces.

7.1. Structure of the medium studied here

Let us specify the hypotheses used in the problem for the different zones indicated in Figure 7.1(c). The interface is the surface of the Langmuir probe – or more specifically the extremity of the tungsten wire in Figure 7.1(b) – which is locally comparable to a plane.

The *metal phase* (see section A1.2) with uniform temperature T and *electron concentration* C_e (*number of moles per unit volume*), is characterized by a classic Ohm law (resistivity R).

At the *interface*, the surface concentration C_{at} , in terms of active sites, expressed in number of moles per unit area, is supposed to be constant. By writing the laws of classic chemical kinetics for reactions (I), (II) and (III)², we obtain the expression of the surface concentration of the electrons and an initial expression of the intensity I of the electrical current:

$$I = \mathcal{N} e C_{at} \frac{k_{des}^{III} k_{ads}^I C_e - k_{ads}^{III} k_{des}^{II} C_e^- C_+}{k_{ads}^I C_e + k_{des}^{II} C_+ + k_{des}^{III}} \quad [7.1]$$

² This is a choice. However, other reactive schemas are possible within the sheath (see section 7.4).

The k_r values denote the specific reaction rates in the direction “*ads*” (adsorption) or “*des*” (desorption); the C_j values denote the concentrations of the species in the le plasma (moles/volume); \mathcal{N} is Avogadro’s number; $(-e)$ the charge on the electron.

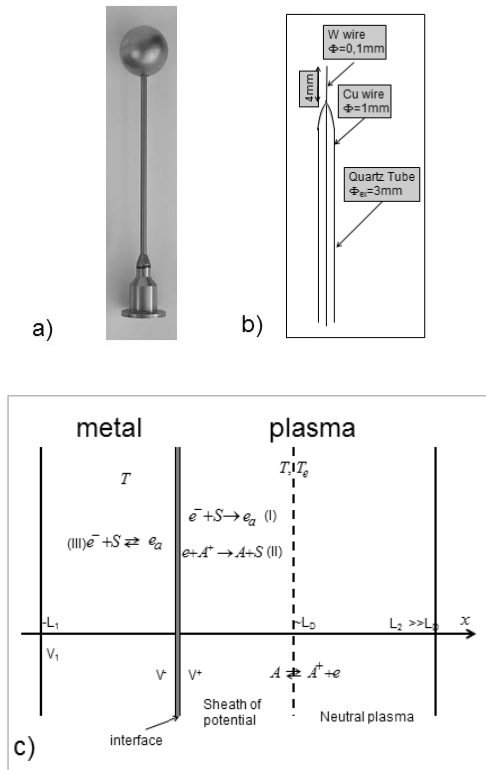


Figure 7.1. a) One of the Langmuir probes held by the Swedish Institute of Space Physics in Uppsala (reproduced from the Wikipedia site³). The spherical part of the probe, made of titanium, is 50 millimeters in diameter. b) Schema of the Langmuir probe used by Dudeck [DUD 82]. c) Diagram of the medium under study indicating the different zones and chemical reactions

3 http://en.wikipedia.org/wiki/Langmuir_probe.

The *plasma* is supposed to be at collisional chemical equilibrium, and such that the *Debye length* (equation [7.3]) is much larger than the mean free path of the charged species: $L_D \gg l$, which justifies a collisional approach to the potential sheath.⁴ It is the site of diffusion phenomena which can, in this case, be characterized by a single phenomenological coefficient R_e , similar to a resistivity value. We suppose that electrical neutrality is only assured for $x \rightarrow \infty$; everywhere else, the Maxwell equation giving the electrical charge of the gas and the diffusion law enable us to write the difference in concentrations between the charged species. We suppose, in addition, that the temperature of the heavy species is uniform and equal to T (the temperature of the metal); that of the electrons T_e is also uniform, but different to T ; and the energy exchanges are frozen between the heavy species and the electrons.

7.2. Concentration field

If we suppose a constant pressure p and a low degree of ionization, the resolution of the system leads to the differential equation giving the molar fraction of the electrons as a function of the abscissa value [PRU 81b, DUD 82]:

$$\frac{d \ln X_e}{dx} = \mathcal{N} e \varepsilon \frac{\sqrt{2p}}{RT} \sqrt{\left\{ X_e - X_{\infty} + \frac{T}{T_e} X_{\infty} \left[\left(\frac{X_{\infty}}{X_e} \right)^{T_e/T} - 1 \right] \right\}} \frac{T}{T_e} \quad [7.2]$$

where $\varepsilon = -1$ for $X_{\infty} < X_e$ and $\varepsilon = +1$ for $X_e < X_{\infty}$. From this, we derive the expression for the electrical current in the plasma.

⁴ The case of 1D non-collisional sheaths is simpler because of the strong electrical field created by the difference between the surface potential and the plasma potential.

Considerations of dimensional analysis demonstrate the order of magnitude of the *Debye length* characterizing the sheath of potential:

$$L_D = \frac{1}{\mathcal{N}e} \sqrt{\frac{RT_e}{C_{\infty}}} \quad [7.3]$$

This sheath corresponds to the domain where the concentrations and the electrical charge vary noticeably, and where electrical neutrality is no longer respected.

7.3. Characteristic curve of the potential as a function of the intensity

From the Maxwell equation relating to the surface charge, we can derive a second expression for the electrical current:

$$I = -\varepsilon \frac{\beta}{\alpha} \sqrt{\tilde{X} - 1 + \frac{T}{T_e} (\tilde{X}^{-T_e/T} - 1)} + \frac{1}{\alpha} \frac{k_{ads}^I C_{\infty} \tilde{X} + k_{ads}^{III} C_e^-}{k_{ads}^I C_{\infty} \tilde{X} + k_{des}^{II} C_{\infty} \tilde{X}^{-T_e/T} + k_{ads}^{III} C_e^- + k_{ads}^{III}} \quad [7.4]$$

where: $\alpha = \frac{R - R_e}{Ne\tilde{C}_t}$, $\beta = \frac{\sqrt{2pX_{\infty}}}{Ne\tilde{C}_t}$, $\tilde{X} = X_{e0}/X_{\infty}$.

We suppose that the specific rates of reactions II and III do not depend on T , T_e , or on the potentials, unlike the specific rate of the adsorption reaction I. Thus, we obtain two expressions giving the intensity as a function of \tilde{X} and \mathcal{V} :

$$\begin{cases} \gamma I = \frac{ae^{(1+T/T_e)\mathcal{V}} - 1}{ae^{(1+T/T_e)\mathcal{V}} + b + c\tilde{X}^{T_e/T}} \\ \alpha I = -\varepsilon\beta \sqrt{\tilde{X} - 1 + \frac{T}{T_e} (\tilde{X}^{-T_e/T} - 1)} + \frac{ae^{(1+T/T_e)\mathcal{V}} + \tilde{X}^{T_e/T}}{ae^{(1+T/T_e)\mathcal{V}} + b + c\tilde{X}^{T_e/T}} \end{cases} \quad [7.5]$$

where:

$$a = k_{des}^{II} C_{e\infty}^{III} / k_{des}^{III}, \quad b = k_{des}^{II} C_{e\infty} / k_{ads}^{III} C_e^-, \quad c = 1 + b/a, \quad \gamma = 1 / N e k_{des}^{III} \tilde{C}_i$$

The reduced potential \mathcal{V} has the expression:

$$\mathcal{V} = \frac{N e}{RT} (V_1 - V_2 - \bar{R}I - \Delta V_p) \quad [7.6]$$

where \bar{R} is the total resistance of the system: $\bar{R} = L_1 R + L_2 R_e$ and where ΔV_p is a constant, calculable on the basis of the standard molar thermodynamic potentials of the electrons [PRU 81a, PRU 81b, DUD 82]:

$$\Delta V_p = -\frac{1}{N e} \left[(\mu_{T_e}^0)_{e_2} - \mu_e^- + RT \ln \left(\frac{p T_e X_{e\infty}}{T} \right) \right] \quad [7.7]$$

The parametric equations giving I and \mathcal{V} as a function of the parameter \tilde{X} are finally deduced from the system [7.5]:

$$\left\{ \begin{array}{l} I(\tilde{X}) = a \frac{a + \tilde{X}^{T_e/T} - \varepsilon \beta \sqrt{\tilde{X} - 1 + (T/T_e)(\tilde{X}^{-T_e/T} - 1)} (a + b + c \tilde{X}^{T_e/T})}{(\alpha a + \alpha b - \gamma b)(a + \tilde{X}^{T_e/T})} \\ \mathcal{V}(\tilde{X}) = \left(1 + \frac{T}{T_e} \right)^{-1} \ln \left(\frac{\gamma^{-1} + a^{-1} (b + c \tilde{X}^{T_e/T}) I(\tilde{X})}{\gamma^{-1} - I(\tilde{X})} \right) \end{array} \right. \quad [7.8]$$

By solving system [7.8], we are able to plot the characteristic curves of current/voltage $I(\mathcal{V})$, compare their shapes to those of the curves obtained experimentally with Langmuir probes. This system enables us to evaluate the influence of the parameters $a, b, \alpha, \beta, \gamma$ on the signal, and the influence of the thermal disequilibrium.

Figure 7.2 gives some examples of resolution, and shows the effect of thermal disequilibrium. Figure 7.3 shows the characteristic curves obtained in the first two cases from

Figure 7.2 [PRU 81a]. We can see that the high number of parameters involved in $I(\psi)$ makes it difficult to determine the electronic parameters (T_e, n_e) of the plasma.

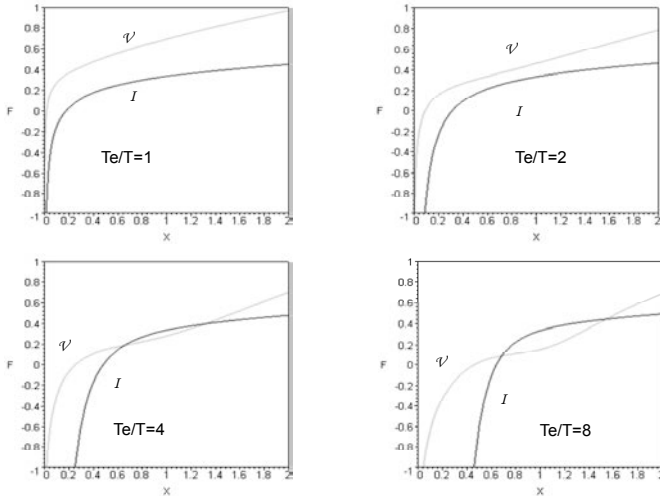


Figure 7.2. The curves $F = I$ and $F = v$ as a function of $X = \tilde{X} = X_{e0} / X_{\infty}$ for different values of the temperature ratio T_e/T in the case studied by Dudeck: $a = b = 1, \alpha = 2, \beta = 0.25, \gamma = 1$ [PRU 81a, PRU 81b, DUD 82]

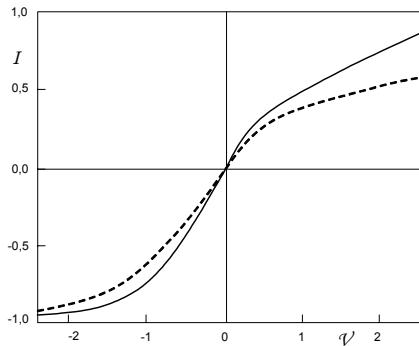


Figure 7.3. The characteristic curves $I(\psi)$ for the values 1 (solid-line curve) and 2 (dotted-line curve) of the temperature ratio T_e/T in the case studied by Dudeck: $a = b = 1, \alpha = 2, \beta = 0.25, \gamma = 1$ [PRU 81a, PRU 81b, DUD 82]

7.4. Reactive schemas on contact between metal and plasma

The reactive schema chosen in section 7.1 is not unique. If we again accept the adsorption-desorption metal-interface reaction: $e^- + S \rightleftharpoons eS$ and the reaction: $A \rightleftharpoons A^+ + e^-$ in the gaseous phase, we can also consider in the sheath of potential the other reactive schemas 2) to 4) in Table 7.1, to which, in each case, we need to add the reaction of adsorption of the electrons $e^- + S \rightarrow eS$ [PRU 81a] (see Figure 7.4).

Remember that the thickness of the sheath of potential is approximately the same as the *Debye length* of the particles in question, as we can demonstrate by studying the evolution of the concentrations in the one-dimensional flow of the plasma.

In addition, we can introduce a pre-sheath which forms the junction between the plasma and the sheath, where the disequilibrium is slight.

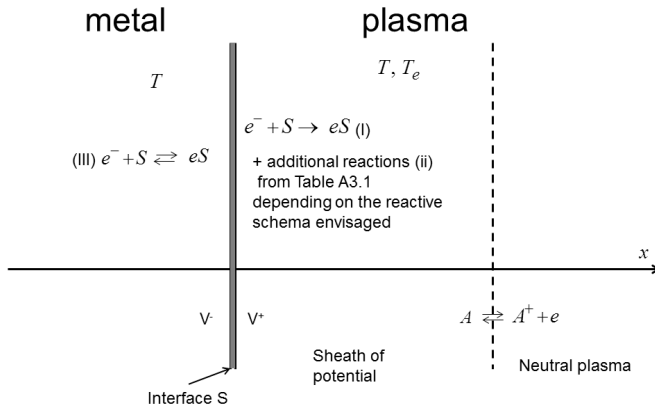


Figure 7.4. Structure and reactive processes of the medium studied here

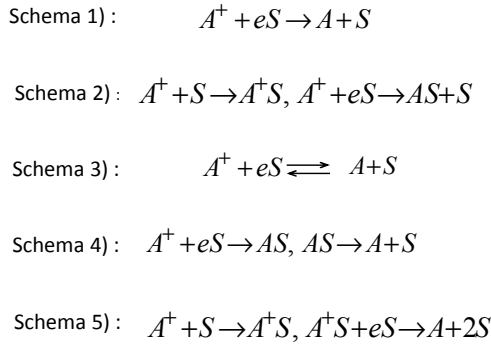


Table 7.1. *Reactive schemas envisaged by M. Dudeck in [PRU 81a]. To each schema, we need to add the reaction of adsorption of the electrons $e^- + S \rightarrow eS$. It is Schema 1) which was adopted in section 7.1*

Finally, it ought to be mentioned that this approach can also be used with an insulative medium instead of the metal, with the surface potential then being the so-called “floating” potential corresponding to a total amount of zero current collected.

Hall-Effect Space Thruster

As an example of the interaction between surface and plasma in the presence of electrical and magnetic fields, we have chosen to look at Hall-effect thrusters (HETs), the recently-released miniaturized version of them and ways of modeling them.¹

After giving a brief history of the discipline, we shall recap on some of the fundamental concepts: the Hall effect, the Debye length and the specific impulse of a rocket engine. Then we shall briefly describe how these engines work, before applying the balance equations for conductive media to plasma and examining the boundary conditions. We shall also touch on numerical modeling, looking at the CRATER code created by the IPPLM² in Warsaw.

We have made the choice here to use the microscopic notations employed by specialists in these domains, but we have shown the correspondence (see section 8.3.1) with the macroscopic notations used in previous chapters.

¹ The author would like to thank Michel Dudeck for his invaluable help in the writing of this chapter.

² Institute of Plasma Physics and Laser Microfusion, 23, ul.Hery, Warsaw, Poland.

8.1. History

8.1.1. *Hall-effect propulsion*

The mode of propulsion in which we are interested here is *Hall-effect propulsion* – electrostatic for the acceleration of the ions and electromagnetic to concentrate the electrons and create ions. This mode of propulsion was devised in the USSR in 1960 by Alexander Morozov. The weather satellite *Meteor* was the first (launched in 1971, and brought into operation in 1972) to use a Hall-effect engine. In such engines, the magnetic field is generated by an electromagnet.

8.1.2. *CubeSats*

In recent years, we have seen the increasing use of micro- and nano-satellites³ driven by the space agencies and the sectors of research and higher education. The concept of a *CubeSat* (Figure 8.1) was born in the 1990s at the University of California (in the mind of Professor Bob Twiggs), based on the idea that it was possible to put small objects into orbit (cubes with a side of 10 cm – 1 U – or parallelepipeds measuring 10 × 10 × 30 cm – 3 U), no heavier than 1 kg for the 1 U format, which costed little and had a wide variety of uses: to serve as a pedagogical tool, for the purposes of preliminary experiments for space travel, as a means of testing new technologies, or for small scale scientific experiments. Six were launched in 2003, sent into orbit by the VEGA launcher and, after a short break for observation in 2004, the number reached 14 in 2012.

CubeSats currently have an average lifespan of 3 years before they disintegrate in low atmospheric orbit. The thrust

³ The majority of these examples, unless otherwise specified, are drawn from a report by A. Mestre L3/University of Paris 11 [MES 13].

forces needed to change their orbit are not very great, so the thrusters attached to these satellites are electrical, electrostatic or electromagnetic rather than chemical, and must respect stringent constraints in terms of their size, weight, and available power.

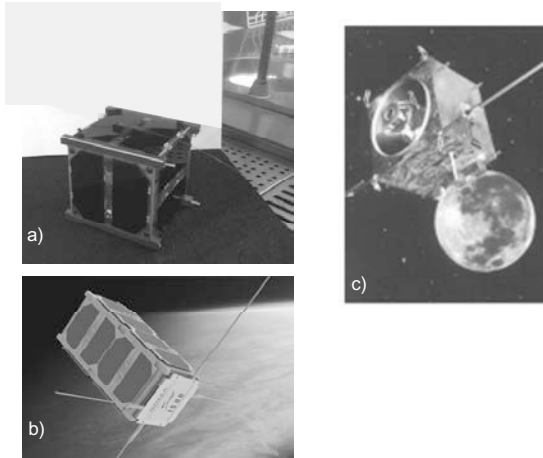


Figure 8.1. *Examples: a) the Robusta-1 nano-satellite launched by the space technology center SOLARIUM; b) Smart-1 from the ESA, which is not a CubeSat, but with a PPS1350-G made by SNECMA (images taken from [GUY 12]); c) EntrySat from the ISAE, designed to study the behavior of orbiting debris (see the ISAE Website)*

8.1.3. Miniaturization of plasma thrusters

In order to miniaturize this type of engine, make savings in terms of weight and cumbersomeness and adapt it to the constraints to which CubeSats are subject, Marcel Guyot (GEMaC⁴-CNRS/Université de Versailles Saint-Quentin) had the idea, in 2003 [GUY 08], of replacing the coils (characteristic size 3 cm) creating the magnetic field with permanent magnets (size 3 mm). A new generation of

4 GEMaC: *Groupe d'étude de la matière condensée* (Condensed Matter Study Group).

thrusters was born: *PPIs*⁵ (small innovative thrusters), of which there is also a miniature version in the μ -*PPI* [GUY 12]. Besides the advantages in terms of weight and cumbersomeness mentioned above, these smaller satellites also have lower electrical consumption and a lesser cost.

One of the major problems which arise with SPTs (*Stationary Plasma Thrusters*) is that of the *instabilities and oscillations* [CHA 61] to which the various parameters are vulnerable, and which affect the thrust and the performances of this type of thruster. The oscillations observed, which are often specific to each frequency band, have been studied experimentally by Choueiri [CHO 01] between 1 kHz and 60 MHz. The discussion relates to low-frequency waves of around ten kHz, transient oscillations propagating in an axial direction, azimuthal electronic drift waves, unstable ionization waves, and the emission of waves specific to slightly-ionized plasmas passing through electrical and magnetic fields. In order to design high-quality thrusters, it has proved necessary to make a significant effort in terms of analysis and modeling [BOE 98, BAR 03, BAR 09] and numerous problems still need to be resolved if we wish to monitor their operation [BAR 11] and employ predictive codes.

The configuration of these plasma thrusters is rather complex, so meticulous theoretical and numerical modeling is needed. One of the major benefits in terms of progression is the acquisition of a good knowledge of the interactions between the plasma and various surfaces present in the engine [BAR 03, TIA 13], whose nature (insulating or conductive) and surrounding area (sheath of potential) come into play and alter the performances.

⁵ PPI (Petits Propulseurs Innovants – small innovative thrusters) – a new design for a Hall-effect thruster, built around permanent magnets. *Patent FR 0705658 France, Dispositif d'éjection d'ions à effet Hall [Text] / M. Guyot, P. Renaudin, V. Cagan, C. Boniface. – 2007.*

8.2. Recap of the fundamental concepts

8.2.1. The Hall effect

A magnetic field acts on the moving charges. The current passing through the conductive medium is produced by charges (the free electrons) whose velocity of motion shall be represented by the symbol \mathbf{v} .

These electrons are therefore subject to a force $\mathbf{F}_m = -e \mathbf{v} \times \mathbf{B}$ (Lorentz force), where $(-e)$ corresponds to the charge on an electron. This causes the displacement of the electrons and a concentration of negative charges on one side of the material, and a deficit of negative charges on the other side. This distribution of charge gives rise to the *Hall voltage* V_{Hall} , and to an electrical field \mathbf{E}_H .

This electrical field is responsible for an electrical force which is exerted on the electrons: $\mathbf{F}_e = -e \mathbf{E}_H$ (Coulomb force). Equilibrium is reached when the sum of the two forces is zero (Newton's second law). Therefore, we can write⁶:

$$en_e (\mathbf{E}_H + \mathbf{v} \times \mathbf{B}) + \nabla p_e = \mathbf{0} \quad [8.1]$$

and the resulting flux of electrons is:

$$\mathbf{J}_e \cong -en_e \left(\frac{\mathbf{E} \times \mathbf{B}}{|\mathbf{B}|^2} + \frac{\nabla p_e \times \mathbf{B}}{en_e |\mathbf{B}|^2} \right),$$

where the first term between the parentheses is the *drift* and the second the *diamagnetic drift*. The term in $\mathbf{E} \times \mathbf{B}$ corresponds to the Hall current.

6 http://en.wikipedia.org/wiki/Hall_Effect gives the simplified formula: $\mathbf{E}_H = -\mathbf{v} \times \mathbf{B}$.

8.2.2. Debye length

The concept of the Debye length has already been touched upon in the chapter on metal/plasma interactions (Langmuir probe).

In a plasma containing neutral particles, electrons at a density n_e of charge $q_e = -e$ and positive ions with the charge $q_j = \sum_j j e$ at molar density C_{ij} , the Debye length – or Debye radius [ART 75] – has the expression:

$$L_D = \frac{1}{\mathcal{N} e} \sqrt{\frac{\epsilon_0 R}{C_e/T_e + \sum_{i,j} j^2 C_{ij}/T_i}} \quad [8.2]$$

This length becomes $\sqrt{kT/\sum_j n_j q_j^2}$ at an equilibrium temperature $T_i = T_e = T$. The quantity ϵ_0 is the *permittivity of a vacuum*, $R = \mathcal{N} k$ the universal perfect gas constant, k the Boltzmann constant and \mathcal{N} Avogadro's number, T_e the temperature of the electrons and T_i the temperature of the ions. This characteristic length was introduced in the previous chapter, by equation [7.3], where the role of the ions was discounted.

The physical meaning is as follows: in a plasma, an ion attracts electrons, which form a cloud around it and thereby act as a screen, decreasing its potential. The resulting electron sphere is the Debye sphere, and its radius is L_D .

At an observation scale smaller than L_D , there may be a separation of charge; at a scale larger than L_D , the plasma

regains its electrical neutrality in the absence of a sufficiently strong electrical field to separate the charges.

This is what happens in the vicinity of a wall, where a sheath of potential is formed, with thickness L_D (zone with electrical field, often non-collisional because L_D is much smaller than the mean free path), within which the plasma is no longer neutral (see the Chapter 7 on the interaction between plasma and metal).

8.2.3. Larmor radius

The Larmor radius [ART 75] describes the trajectory of a particle with mass M_i , charge q_i and initial velocity v_0 in a uniform magnetic field of intensity B :

$$r_L = M_j v_0 / q_j B \quad [8.3]$$

This value needs to be compared with the characteristic dimensions of the channel confining the plasma discharge in the thruster.

8.2.4. Specific impulse of a rocket

The mass flow rate of the engine being $\dot{m}S$, and with \dot{m} being the unit mass flow rate of propellant and S the cross-sectional surface area of the engine outlet, the thrust of the rocket is given by the momentum balance: $T = \dot{m}S V_s$, with the ejection velocity V_s of the propellant in relation to the body of the rocket. The specific impulse is equal to the thrust provided per unit weight of propellant consumed (and therefore ejected):

$$I_{sp} = T / \dot{m} S g_0 = V_s / g_0 \quad [8.4]$$

Konstantin Tsiolkovski⁷ showed that the mass ΔM of propellant consumed by a rocket of initial mass M_0 was equal to:

$$\Delta M = M_0 [1 - \exp(-\Delta V/V_s)] \quad [8.5]$$

where ΔV is the resulting variation in velocity. For a given rate of consumption, the increase in velocity is therefore proportional to the ejection rate of the propellant. It is also worth noting that, with an equal amount of mass consumed, the higher the gas ejection rate, the greater the velocity achieved by the rocket. Conversely, for a given operation, i.e. for a set value of ΔV , the consumption is lower when the ejection rate is higher.

One of the characteristics of the plasma thrusters presented hereinafter is that they achieved very high ejection rates by acceleration of the electrical charges, and therefore high specific impulse values, but with a low mass flow rate; hence, the variation in velocity takes a longer time than with chemical propulsion. The choice between “chemical” and “electrical” therefore depends on the intended purpose.

8.3. Hall-effect thruster

8.3.1. *Classic Hall-effect thruster*

The cross-sectional and volume diagrams given in Figure 8.2 show an HET. The cylindrical engine comprises a ring-shaped discharge channel and coils to create an external magnetic field \mathbf{B} (essentially radial), an external cathode, an anode and a gas injector (xenon gas, for example,

⁷ Konstantin Tsiolkovski formulated his equation around the end of the 19th Century. He is considered to be the father of modern astronautics [MES 13].

which is often used because of its low ionizing potential of 12.2eV), at the bottom of the channel in most thrusters.

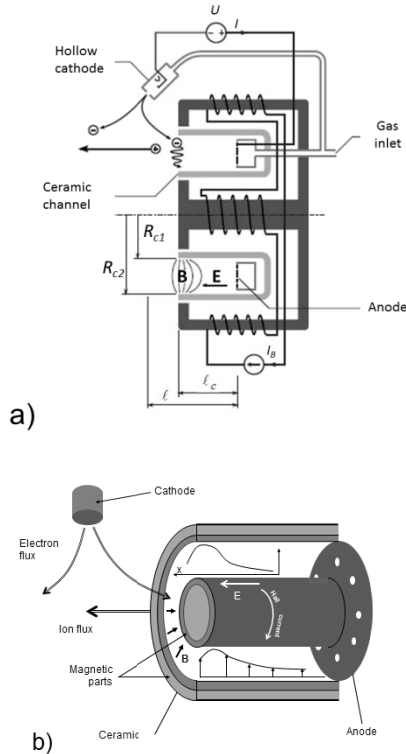


Figure 8.2. Diagrams: a) sectional view (from [BAR 11]) and b) three-dimensional representation⁸, of a classic Hall-effect thruster. The holes in the anode are generally very small indeed (around 100 μ m in diameter), and the electrical field is strongest around the outlet vent

A difference in potential of a few hundred volts is applied between the anode and the cathode. The hollow cathode emits electrons, a certain proportion of which are trapped by the external magnetic field, thereby increasing their residence time (which increases the number of ionizing

⁸ https://en.wikipedia.org/wiki/Hall_effect_thruster.

collisions) and serve to ionize the gas (essentially creating Xe^+ ions). The remaining electrons serve to electrically neutralize the plasma jet. This prevents the satellite from becoming positively charged, which would result in the divergence of the jet under the influence of the mutual repulsion of the ions with the same charge.

An electrical field \mathbf{E} is created by the difference in potential between the cathode and the anode, and facilitates the acceleration of the ions. The local value of this electrical field is not set, but results from different interactions.⁹ It is strongest in the vicinity of the outlet vent.

This configuration creates a strong azimuthal Hall current (measuring several dozen amperes). The majority of the electrical field is encountered in the vicinity of the outlet plane, where the magnetic field is strongest. In a manner of speaking, the conservation of the electrical current I (we have $I \propto E/B^n$, $v = \alpha/B^n$ with the mobility of the electrons α tending toward zero) results in a compensation of the electrical field by the plasma. We see the creation of a self-consistent electrical field without the need to generate one using electrically-polarized grids, as happens with other thrusters such as GITs (*Gridded Ion Thrusters*).

8.3.2. *PPIs and μ -PPIs*

In the case of a *PPI*, the coil is replaced by small permanent magnets placed on both sides of the thruster. The insulating walls are made of alumina or BNSiO_2 . The nominal version can generate a thrust force of between 1 and 15 mN. The gas used is a rare gas (xenon or krypton). In the

⁹ Logically, in light of the Maxwell equations, the same should be true of the magnetic field \mathbf{B} ; however, this latter field is often considered, hypothetically, to be a given, provided by the arrangement of the coils or the magnets.

case of a μ -PPI (micro-Hall Effect Thruster), the estimated thrust is nearer to 0.1 mN. In addition to atmospheric re-entry of CubeSats placed in high Earth orbit, it can be used to keep them in orbit, to perform link-ups, for distant positions or for long-distance missions.

8.4. Modeling of Hall-effect thrusters

The balance equations for homogeneous conductive media were summarized in Tables 2.1 and 3.1. Those for homogeneous plasmas at two kinetic temperatures are given in section A1.5.4. The interfacial balance equations in a conductive medium are shown in Table 4.1, and the metal/plasma interactions in the presence of an electrical field were discussed in Chapter 7.

We shall now go into greater detail with these equations in order to render them appropriate for a more in-depth study of Hall-effect thrusters.

8.4.1. *Microscopic and macroscopic values. Reminders and definitions*

Although plasma physicists generally use different notations to those used by combustion specialists, it is because they are often dealing directly with properties at the microscopic scale. However, it is possible to easily convert from one system to the other.

8.4.1.1. *Mass and density of the particles*

The particles encountered in the cold plasmas studied here (as opposed to the hot plasmas encountered in nuclear fusion) are neutral particles (atoms or molecules), ions and electrons. The ratio between the mass of a molecule-gram or mole and the mass of a molecule is equal to Avogadro's

number¹⁰ \mathcal{N} . If M is the molecular mass and \mathcal{M} the molar mass, we write: $\mathcal{M} = \mathcal{N} M$. This ratio is also valid between an electron-gram and an electron, and between an ion-gram and an ion.

The fact of considering particle-grams is linked to the macroscopic reality of the quantities of matter involved in the experiments.

With particles instead of particle-grams, the density to be considered will be $n_k = \mathcal{N} C_k$, where C_k is the number of particle-grams of species k per unit volume used in macroscopic fluid mechanics.

8.4.1.2. *Electrons, photons and universal constants*

Here, let us recap some of the fundamental constants that need to be known. Their values are listed in the following footnote.¹¹

The energy unit commonly used in plasma physics is the electronvolt. This represents the amount of energy acquired by an electron beginning in the resting state by a difference of electrical potential of 1 volt.

The mass of the electron is M_e and its charge is in Coulombs ($-e$).

The photon is a particle (a boson) with a theoretical mass of 0, and in reality, less than 10^{-54} kg, measured

¹⁰ Remember that $\mathcal{N} = 6.02214129 \times 10^{23}$ mole⁻¹.

¹¹ Electronvolt: $1\text{eV} = 1.602176487 \times 10^{-19}$ J; mass of the electron: $M_e = 9.109 \times 10^{-31}$ kg; charge on the electron in Coulombs $e = 1.602 \times 10^{-19}$ C; Planck's constant: $h = 6.62606957 \times 10^{-34}$ J.s; Boltzmann constant: $k = 1.381 \times 10^{-23}$ J.K⁻¹; universal gas constant: $R = \mathcal{N} k = 8.3144621$ J.mole⁻¹.K⁻¹; Faraday constant: $F = \mathcal{N} e = 9.648534 \times 10^4$ C. mole⁻¹.

experimentally. A photon is in perpetual motion at the speed of light. The duality between waves and corpuscles (corpuscles only manifest themselves during interactions) gives the energy carried by the photon as being equal to the product $h\nu$ of Planck's constant h by the frequency of the wave packet.

Boltzmann's constant is k . It was introduced by Boltzmann in 1873, based on the entropy of a system at macroscopic equilibrium, but free to evolve microscopically between Ω different micro-states. This system has the entropy $S = k \ln \Omega$. Boltzmann's constant also plays a role in the thermal energy of each degree of freedom of a molecule, by way of: $E = 1/2 kT$. The universal gas constant R is equal to the product of Boltzmann's constant by Avogadro's number.

Faraday's constant F is the product of the elementary charge e by Avogadro's number.

8.4.2. Unsteady mono-dimensional model for Hall-effect thrusters

Hall-effect thrusters exhibit a geometric configuration facilitating the use of a quasi-one-dimensional model, somewhat like the nozzles in chemical propulsion (often, we can even adopt the one-dimensional model with a constant straight section; on this subject, see Appendix A2).

However, in view of the interactions at the walls and the presence of the magnetic field inducing an azimuthal motion of the electrons, we need to integrate these interactions into the balance equations as a function of time t and abscissa value x . This is what we usually do in a one-dimensional flow with heat-exchange at the walls

(for example, see [PRU 81a] for a plasma and section 6.2.3 of this book for a metal).

However, there are a few differences here with regard to the interaction between the plasma and the wall. Indeed, in Chapter 7, the metal/plasma interface and the sheath of thickness L_D exhibit a prevailing direction perpendicular to the axis, whereas here, the surfaces of electromagnetic interaction are generally parallel to it.

A number of authors have established balance equations for these flows, using simplifying hypotheses. For examples, see Barral *et al.* [BAR 03] and Gascon, Dudeck and Barral [GAS 03] in the steady-state case, or Bœuf and Garrigues [BOE 98] for an initial approach to the low-frequency oscillations in plasma thrusters and, more recently, Barral and Miedzic [BAR 11] for a more elaborate model of these phenomena in the context of a closed-loop study of Hall-effect accelerators. Also see Dabiri *et al.* [DAB 13].

We refer readers to the aforementioned articles, and also to Barral and Ahedo [BAR 09], which goes into greater detail to present the system of balance equations appropriate to deal, in particular, with low-frequency oscillations¹² (~10 kHz, *breathing mode*). The species injected in this case is xenon.

8.4.2.1. *Equations of the charged species*

We shall suppose that the ions have straight-line trajectories parallel to the axis of the thruster. The velocity of the electrons has an axial component and an azimuthal component. The charge on the ion is equal to that of the electron, but of the opposite sign. The condition of neutrality $n_e = n_i$ is respected outside of the sheath of potential.

¹² On this subject, see the articles by Choueiri [CHO 01] and Bœuf and Garrigues [BOE 98] for reviews concerning the low-frequency oscillating regimes of plasma thrusters.

The system of balance equations adopted for the charged species is given in Table 8.1. In this table, the electrons have an axial velocity $v_{e,x}$ and an azimuthal velocity $v_{e,\theta}$; the electrical field has an axial component E_x and an azimuthal component E_θ (but has only the axial component E in [BAR 09], because this article does not take account of E_θ , which is possibly generated by a non-steady-state magnetic field, owing to the axisymmetrical relation $\partial E_\theta/\partial x = -\partial B/\partial t$ given in [BAR 11]); the quantities marked with a w relate to the walls.

Neutral species, electrons and ions	$\frac{\partial n_n}{\partial t} + V \frac{\partial n_n}{\partial x} = -\beta n_n n_e + v_{i,w} n_e \quad (1)$
	$\frac{\partial n_e}{\partial t} + \frac{\partial(n_e v_{e,x})}{\partial x} = \beta n_n n_e - v_{i,w} n_e \quad (2)$
	$\frac{\partial n_e}{\partial t} + \frac{\partial(n_e v_i)}{\partial x} = \beta n_n n_e - v_{i,w} n_e \quad (3)$
Momentum balance	$\frac{\partial(n_e v_{e,\theta})}{\partial t} + \frac{\partial(n_e v_{e,x} v_{e,\theta})}{\partial x} = -n_e e E_\theta / M_e + \omega_{ce} n_e v_{e,x} - v_e n_e v_{e,\theta} \quad (4)$
	$\frac{\partial(n_i v_i)}{\partial t} + \frac{\partial(n_i v_i^2)}{\partial x} = n_e e E_x / M_i + \beta n_n n_e V - v_{i,w} n_e v_i \quad (5)$
Ohm's law	$e E_x = -\frac{1}{n_e} \frac{\partial(n_e k T_e)}{\partial x} - v_e M_e v_{e,x} - \omega_{ce} M_e v_{e,x} \quad (6)$
Electron energy balance	$\left\{ \frac{\partial}{\partial t} \left[\frac{3}{2} n_e k T_e + \frac{1}{2} n_e M_e v_e^2 \right] + \frac{\partial}{\partial x} \left[\frac{5}{2} n_e v_{e,x} k T_e + \frac{1}{2} n_e v_{e,x} M_e v_e^2 \right] \right. \\ \left. = -\beta n_n n_e \gamma_i \varepsilon_i - v_{e,w} n_e \varepsilon_w - n_e v_{e,x} e E_x - n_e v_{e,\theta} e E_\theta \right. \quad (7)$

Table 8.1. Mono-dimensional balance equations for the charged species, as given by [BAR 11]. The meanings of the various terms are explained in the text

If we adopt a simplified model¹³ [BAR 03, AHE 03], the frequencies of interaction between the ions and the wall and between the electrons and the walls are written with the notations given in Figure 8.2(a):

$$v_{i,w} = \begin{cases} a \frac{\sqrt{kT_e/M_i}}{R_{c2} - R_{c1}} & \text{for } x \leq \ell_c \\ 0 & \text{for } x > \ell_c \end{cases} \quad [8.6]$$

$$v_{e,w} = v_{i,w} / (1 - \sigma)$$

In these expressions, ℓ_c is the length of the channel, $v_{i,w}$ is the Bohm velocity (acoustic velocity of the ions), σ is the rate of secondary electron emission at the wall, and we take account of a wall with floating potential. The coefficient a is equal to 2 according to Dudeck and 4/3 according to Barral and Ahedo [BAR 09].¹⁴

The loss of energy of the electrons at the wall and the radial potential of the sheath are, respectively [BAR 09]:

$$\begin{cases} \varepsilon_w = 2kT_e + 1/2 M_e v_e^2 + (1 - \sigma) e \phi_w \\ \phi_w = \frac{kT_e}{e} \ln \left[\sqrt{\frac{M_i}{2\pi M_e}} (1 - \sigma) \right] \end{cases} \quad [8.7]$$

13 We discount the electrostatic lens effect occurring in the acceleration zone of the thruster channel, causing the divergence of the jet. The ionization reaction is: $Xe + e \rightarrow Xe^+ + e + e$. The energy of the electrons creates few doubly-charged ions.

14 The second term on the right-hand side of equation (2) in Table 8.1 is equal to: $-\frac{2\pi(R_{c1} + R_{c2})}{\pi(R_{c1}^2 - R_{c2}^2)} n_e v_{e,w} = \frac{2n_e v_{e,w}}{R_{c2} - R_{c1}} = n_e v_{e,w}$, according to Dudeck

(December 2013), which gives us $a = 2$. We also need to take into account the electron emission rate σ , which gives system [8.6]. In the calculation performed by Barral and Ahedo, account is taken of the radial form of the flux between the inner and outer walls [BAR 03, AHE 02a, AHE 02b], which gives us the value $a = 4/3$.

The ionization rate is written as:

$$\beta = \beta_0 \left(\frac{\mathcal{E}}{\mathcal{E}_i} \right)^{1/4} \exp\left(-\frac{2\mathcal{E}_i}{\mathcal{E}} \right), \beta_0 = 1.8 \times 10^{-13} m^3 s^{-1},$$

$$\text{where: } \mathcal{E} = \frac{3}{2} T_e + \frac{1}{2} M_e v_e^2, v_e^2 = v_{e,x}^2 + v_{e,\theta}^2 \quad [8.8]$$

The total electron transfer rate is equal to:

$$v_e = \beta^{(m)} n_n + \alpha_B \omega_{ce} + v_{e,w} \quad [8.9]$$

where $\beta^{(m)}$ corresponds to the collisions between electrons and neutral species, α_B is Bohm's electron diffusion coefficient¹⁵ and $\omega_{ce} = eB/M_e$ is the cyclotronic frequency associated with the local magnetic field B . With regards to the magnetic field, it is assumed to have a Gaussian profile:

$$B(x) = B_{\max} \exp\left[-\left(\frac{x - \ell_c}{\ell_B} \right)^2 \right] \quad (\text{where } \ell_B = 1.25 \text{ cm and } B_{\max} =$$

22 mT in the article [BAR 09], but B_{\max} fluctuates over time in [BAR 11]).

The boundary conditions at $x = 0$ and $x = \ell$ are as follows:

$$v_i|_{x=0} = -\sqrt{\frac{5kT_e|_{x=0}}{3M_i}}, v_{e\theta}|_{x=\ell} = \frac{v_{e,x}\omega_B}{v_e + \beta n_n - v_{i,w}} \Big|_{x=\ell}, T_e|_{x=\ell} = \text{Const.} \quad [8.10]$$

The first is the *Bohm condition*, affecting the radial velocity of the ions, at the sheath of the anode; the second

¹⁵ The diffusion of plasmas in a magnetic field is assumed to obey a Bohm law [BOH 49]. This is characterized by a diffusion coefficient: $D_b = (1/16)kT/eB$, with the coefficient (1/16) being modified later on.

condition results from an approximation where the inertial terms are discounted.

For simplicity's sake, we choose a simple advection model for the *neutral species* where $V = \text{Const.}$, which gives us equation (1) from Table 8.1. The boundary condition needing to be respected is at the inlet anode:

$$n_n|_{x=0} = \frac{1}{V} \left(\frac{\dot{M}}{AM_i} - n_e v_i|_{x=0} \right) \quad [8.11]$$

where \dot{M} is the mass flow rate of the propellant injected and A the area of the straight section of the channel.

We could replace the condition of constant current I with that of constant potential U at the boundaries of the system. The boundary conditions are unchanged, and we can solve the system by taking an arbitrary distribution $n_n(t, x)$. The low-frequency solution will then be determined in terms of v_i and n .

8.4.3. Results and conclusions

The model defined above has given rise to a theoretical analysis [BAR 09] and numerical simulations. This has proved effective in terms of closed-loop control of Hall-effect accelerators [BAR 11].

8.4.3.1. Modeling of "breathing-mode oscillations"

A valid model of a Hall-effect thruster must involve the phenomena observed during normal operation and the influences of the different parameters. Many authors have attempted to construct such a model.

We adopt a simplified form of the system of equations. By subtracting equations (2) and (3), term by term, we obtain:

$$I = e A n_e (v_i - v_{e,x}) = \text{Const.} \quad [8.12]$$

The straight cross-sectional area A of the channel is taken to be constant. Relation [8.12] is equivalent to the relation $I = \dot{m} z_e = \text{Const.}$ mentioned above. This confirms the coherence of the system of equations given in Table 8.1.

In addition, we eliminate the electrical field E between equations (4) and (6).

By introducing the quantities h_j , $j = 1, \dots, 5$ defined in [BAR 09], as not being functions of the electron density n_e , and integrating Ohm's law (5), we find a new form of the system of balance equations.

Finally, a form of the charged species balance equations, steady but only with the new variables: $v_i = \frac{1}{I} \frac{dI}{dt}$ and $n = \frac{n_e}{I}$, will give us a system which is easier to solve numerically and analyze:

$$\left\{ \begin{array}{l} e A n (v_i - v_{e,x}) = I, \quad \frac{d(n v_i)}{dx} = n h_1 - n v_i, \quad \frac{d(n M_i v_i^2 + n T_e)}{dx} = n h_2 - n M_i v_i v_i, \\ \frac{d(n v_{e,x} v_{e,\theta})}{dx} = n h_3 - n v_{e,\theta} v_i, \quad v_{e,x} \frac{d(T_e^{3/2}/n)}{dx} = h_4/n + v_i T_e^{3/2}/n, \\ U = \int_{x=0}^{\ell} E dx = \int_{x=0}^{\ell} \left[-\frac{1}{en} \frac{d(n T_e)}{dx} + h_5 \right] dx \end{array} \right. \quad [8.13]$$

With an asymptotic approach based on the parameter $\varepsilon = n_{e0}/n_{n0}$, we obtain a general representation of the small disturbance breathing mode. In particular, we can show that the density of the plasma is a steady-state wave, whereas the transfer of the neutral particles involves both a steady-state

wave and a convective wave. Although the scale analysis is in close agreement with the small disturbance modes found by the simulations, it no longer works at the frequencies of the nonlinear unstable modes.

8.4.3.2. Looped control of the oscillations

The system of unsteady equations shown in Table 8.1 has been applied to the study of looped control of Hall-effect thrusters with the aim of controlling the oscillations of the plasma [BAR 11].

A classic method is the use of a *resistor-inductor-capacitor* (RIC) network.

This process stands in contrast to the PID (*Proportional Integral Derivative*) method, which has two subdivisions: magnetic PID and voltage PID. In the PID method, the error is minimized by playing on a parameter of the system, which is modified in proportion to that error, along with its integral and its derivative.

A comparison between these methods is presented in Figure 8.3.

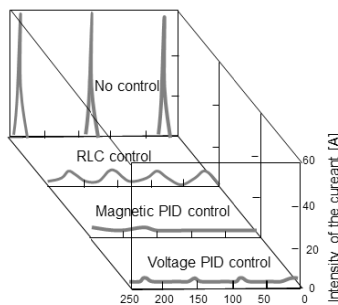


Figure 8.3. Oscillations of the discharge current, with or without a control loop, in the reference conditions (taken from Barral and Miedzik [BAR 11], with the authors' permission)

Magnetic PID requires only a low amount of power, but is underpinned by complex physical phenomena.

Voltage PID functions very well, and presents the advantage of having a simple theoretical basis.

8.4.3.3. *Other considerations*

In other articles, consideration is taken of the existence of several neutral species. In addition, the complexity of the motions of the electrons has led authors to consider two temperatures: $T_{e||}$, along the magnetic field, and $T_{e\perp}$, perpendicularly to the magnetic field [BAR 03].

After integration of kinetic equations, and accepting a bi-Maxwellian distribution with an agitation rate in the plane (x, θ) , this leads us to write two independent steady-state equations of the energy for the electrons:

$$\begin{cases} \frac{d\left[\left(\frac{1}{2}\right)n_e v_{e,x} T_{e||}\right]}{dx} = Q_{e||} \\ \frac{d\left[n_e v_{e,x} (\varepsilon_d + 2kT_{e\perp})\right]}{dx} = -n_e v_{e,x} eE + Q_{e\perp} \end{cases} \quad [8.14]$$

where $Q_{e||}$ and $Q_{e\perp}$ are defined in the article by Barral, Makowski, Peradzyski, Gascon and Dudeck [BAR 03].

Note that another very important problem, in addition to the plasma/surface interactions and the oscillations, is that of the electron transport, in a direction transversal to the magnetic field lines.

Finally, it should be mentioned that electrical fields can be used to influence fluid flows beyond the realm of combustion. Such is the case with the control of air flows by

“plasma actuators” [SOS 07, LOM 11], which is the subject of study of the research group “*Contrôle des décollements*”¹⁶ (separation control): for example, we could use a high-voltage electrical field to reattach wall boundary layers.

¹⁶ Research group bringing together 30 or so teams from the CNRS, various universities in France and ONERA. See the Website at: <http://www.univ-orleans.fr/GDR2502/GDR2502.html>.

APPENDICES

Appendix 1

Additional Points About Balance Laws in the Presence of an Electromagnetic Field

To begin with in this appendix, we shall give an overview of the case of the simplest possible fluid mixture – i.e. one which is non-reactive and non-polarized. Then we shall discuss the case of metal. Next, we shall revisit the energy equation and the phenomenological relations. Finally, we shall present the case of homogenous plasmas.

A1.1. Recap on energy and entropy production

For the purposes of our discussion here, we suppose that the medium under examination, composed of different chemical species, is isotropic, in a state of *local thermodynamic equilibrium with no polarization or chemical reaction* [PRU 76]. The flow velocity is much slower than the speed of light, so the relativistic phenomena can be discounted: $R_c = U^2/c^2 \ll 1$, where U is the velocity characterizing the medium, and c the celerity of light.

The state of the system is therefore defined locally by the electromagnetic variables of state \mathbf{E} and \mathbf{B} (the electrical

and magnetic fields) and by neutral variables of state such as the temperature, the density of the component ingredients and the pressure.

A1.1.1. *Balance equations*

The system conforms to the balance laws affecting mass, momentum and energy, the Maxwell equations (which can also be expressed on the basis of a balance) and finally, the Gibbs equation.

A1.1.1.1. *Conservation of mass of species k*

Let \mathbf{J}_{Dk} represent the diffusion flux of species k in the barycentric motion $\mathbf{J}_{Dk} = \rho_k (\mathbf{v}_k - \mathbf{v})$. The mass balance in the absence of a chemical reaction is written thus:

$$\rho \frac{dY_k}{dt} = -\nabla \cdot \mathbf{J}_{Dk} \quad [\text{A1.1}]$$

A1.1.1.2. *Conservation of overall mass*

By adding together the mass balance equations corresponding to each component, we obtain the overall balance:

$$\rho \frac{d\vartheta}{dt} = -\nabla \cdot \mathbf{v}, \text{ or: } \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \quad [\text{A1.2}]$$

A1.1.1.3. *Conservation of charge*

If we multiply equation [A1.1] by z_k , which is the charge per unit mass of species k , then after summation we obtain:

$$\rho dz/dt = -\nabla \cdot \mathbf{i}, \text{ or: } \frac{\partial(\rho z)}{\partial t} = -\nabla \cdot \mathbf{I} \quad [\text{A1.3}]$$

with z being the total charge per unit mass ($\rho z = \sum_k \rho_k z_k$) and \mathbf{i} the conduction current ($\mathbf{i} = \sum_k z_k \mathbf{J}_{Dk}$).

A1.1.1.4. Conservation of momentum

The momentum balance in a non-polarized medium is written as:

$$\frac{\partial(\rho \mathbf{v})}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v} + \bar{\bar{\mathbf{P}}}) + \rho z \left(\mathbf{E} + \frac{1}{c} \mathbf{I} \times \mathbf{B} \right) \quad [\text{A1.4}]$$

Or indeed: $\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \bar{\bar{\mathbf{P}}} = \rho z \left(\mathbf{E} + \frac{1}{c} \mathbf{I} \times \mathbf{B} \right)$, where $\bar{\bar{\mathbf{P}}}$ is the pressure tensor and \mathbf{I} the total current: $\mathbf{I} = \sum_k \rho_k z_k \mathbf{v}_k$.

We neglect the influence of the radiative pressure in the momentum balance.

A1.1.1.5. Conservation of energy

Let: $\rho e_{tot} = \rho \left(e + \frac{1}{2} v^2 \right) + \frac{1}{2} (|\mathbf{E}|^2 + |\mathbf{B}|^2)$ be the total energy per unit mass.

The energy balance equation is:

$$\frac{\partial(\rho e_{tot})}{\partial t} = -\nabla \cdot \left[\mathbf{q} + \rho \mathbf{v} \left(e + \frac{1}{2} v^2 \right) + \bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \boldsymbol{\Phi} \right] \quad [\text{A1.5}]$$

with e being the internal energy per unit mass, \mathbf{q} the heat flux and $\boldsymbol{\Phi} = c \mathbf{E} \times \mathbf{B}$ the Poynting vector.

A1.1.1.6. Entropy balance

If we employ the hypothesis of local equilibrium, it is possible to write the Gibbs equation:

$$T \frac{ds}{dt} = \frac{de}{dt} + p \frac{d\vartheta}{dt} + \sum_k g_k \frac{dY_k}{dt}$$

This relation, combined with the balance equations, leads us to express the entropy balance in the form:

$$\rho \frac{ds}{dt} = -\nabla \cdot \left(\frac{\mathbf{q} - \sum_{k=1}^N g_k \mathbf{J}_{Dk}}{T} \right) - \frac{1}{T^2} \mathbf{q} \cdot \nabla T - \frac{1}{T} \sum_k \mathbf{J}_{Dk} \cdot \left[T \nabla \frac{g_k}{T} - z_k \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) \right] - \frac{1}{T} \mathbf{\Pi} : \nabla \otimes \mathbf{v}$$

which gives us the terms of flux $\mathbf{J}_S = \left(\mathbf{q} - \sum_{k=1}^N g_k \mathbf{J}_{Dk} \right) / T$ and entropy production:

$$\dot{W}_S = -\frac{1}{T^2} \mathbf{q} \cdot \nabla T - \frac{1}{T} \sum_k \mathbf{J}_{Dk} \cdot \left[T \nabla \frac{g_k}{T} - z_k \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) \right] - \frac{1}{T} \mathbf{\Pi} : \nabla \otimes \mathbf{v}$$

The entropy production can be expressed as a function of the entropy flux \mathbf{J}_S instead of the heat flux, as follows:

$$\dot{W}_S = -\frac{1}{T} \mathbf{J}_S \cdot \nabla T - \frac{1}{T} \sum_k \mathbf{J}_{Dk} \cdot \left[T \nabla \frac{g_k}{T} - z_k \left(\mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{B} \right) \right] \quad [\text{A1.6}]$$

with the viscous effects being discounted.

Let us use the dissipation function introduced by Haase [HAA 69], i.e. $\psi = T \dot{W}_S$. This value characterizes all of the dissipative phenomena, and generalizes that proposed by

Rayleigh. The Rayleigh dissipation function represents only the effect of viscosity on the entropy production:

$$\psi = 2\eta \left(\nabla \overset{\circ}{\otimes} \mathbf{v} \right)^S : \left(\nabla \overset{\circ}{\otimes} \mathbf{v} \right)^S + \eta_v (\nabla \cdot \mathbf{v})^2$$

where η and η_v are, respectively, the shear viscosity and the volume viscosity, and $\left(\nabla \overset{\circ}{\otimes} \mathbf{v} \right)$ is the velocity gradient tensor deviator $(\nabla \otimes \mathbf{v})$. It can be deconstructed into a symmetrical part and an antisymmetrical part – i.e.:

$$\left(\nabla \overset{\circ}{\otimes} \mathbf{v} \right) = \left(\nabla \overset{\circ}{\otimes} \mathbf{v} \right)^S + \left(\nabla \overset{\circ}{\otimes} \mathbf{v} \right)^A$$

A1.1.2. Mechanical equilibrium

Mechanical equilibrium is defined by a zero barycentric acceleration: $\rho \frac{d\mathbf{v}}{dt} = -\nabla p + \sum_{k=1}^N \rho_k z_k \left(\mathbf{E} + \frac{1}{c} \mathbf{v}_k \times \mathbf{B} \right) = \mathbf{0}$. From the Gibbs relation, we can take the expression of $\rho s \nabla T$ – i.e. $\rho s \nabla T = -\sum_k \rho_k \nabla g_k + \nabla p$. On the right-hand side of this equation, we can substitute in the expression of the pressure gradient obtained by mechanical equilibrium, so: $\rho s \mathbf{v} \cdot \nabla T = -\sum_k \rho_k \mathbf{v} \cdot \left[\nabla g_k - z_k \left(\mathbf{E} + \frac{1}{c} \mathbf{v}_k \times \mathbf{B} \right) \right]$. This relation enables us to modify the expression of the entropy production, by revealing the flux values \mathbf{J}_S and \mathbf{J}_k :

$$T \dot{W}_S = -\mathbf{J}_S \cdot \nabla T - \sum_k \mathbf{J}_k \cdot \left[\nabla g_k - z_k \left(\mathbf{E} + \frac{1}{c} \mathbf{v}_k \times \mathbf{B} \right) \right] \quad [\text{A1.7}]$$

where: $\mathbf{J}_S = \mathbf{J}_S + \rho_S \mathbf{v}$.

A new form of the dissipation function can be obtained by introducing diffusion fluxes \mathbf{J}_k^a in relation to an arbitrary velocity \mathbf{v}^a : $\mathbf{J}_k^a = \rho_k (\mathbf{v}_k - \mathbf{v}^a)$. Hence, we find:

$$T \dot{W}_S = - \left[\mathbf{J}_S^a + \rho_S (\mathbf{v} - \mathbf{v}^a) \right] \cdot \nabla T - \sum_k \mathbf{J}_k^a \cdot \left[\nabla g_k - z_k \left(\mathbf{E} + \frac{1}{c} \mathbf{v}^a \times \mathbf{B} \right) \right] \quad [\text{A1.8}]$$

If \mathbf{v}^a corresponds to the velocity of a particular species in the system, the fluxes \mathbf{J}_k^a are called Hittorf fluxes. If \mathbf{v}^a represents the average velocity of some of the species, the fluxes are known as Washburn fluxes.

A1.1.3. Different formulations of the energy balance

The electromagnetic energy balance equation is written as:

$$\frac{\partial}{\partial t} \left(\frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2} \right) = -\nabla \cdot (c \mathbf{E} \times \mathbf{B}) + \mathbf{I} \cdot \mathbf{E} \quad [\text{A1.9}]$$

where $\frac{|\mathbf{E}|^2 + |\mathbf{B}|^2}{2}$ is the electromagnetic energy density, $c \mathbf{E} \times \mathbf{B}$ is the energy flux and finally $\mathbf{I} \cdot \mathbf{E}$ is the energy production per unit volume. This balance enables us to write the total energy balance in local form: $\partial(\rho e_{tot})/\partial t = -\nabla \cdot \mathbf{J}_E$.

Let us rewrite this relation to introduce the scalar potential φ and the vector potential \mathbf{A} , from which the electrical field and the magnetic field are, respectively, derived:

$$\frac{\partial}{\partial t} \left[\rho \left(e + v^2/2 + z \varphi \right) \right] = -\nabla \cdot \left[\mathbf{q} + \vec{\mathbf{P}} \cdot \mathbf{v} + \varphi \mathbf{I} + \rho \mathbf{v} (e + k) \right] + \rho z \frac{\partial \varphi}{\partial t} - \frac{1}{c} \mathbf{v} \cdot \frac{\partial \mathbf{A}}{\partial t}$$

By neglecting the variations of the scalar and vector potentials over time, we obtain the energy balance equation used by de Groot [GRO 69a], where the density and the energy flux are, respectively: $\rho e_{tot} = \rho(e + v^2/2 + z\phi)$ and $\mathbf{J}_E = \mathbf{q} + \bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \phi \mathbf{I} + \rho \mathbf{v}(e + k)$.

This result can be obtained directly by considering that the flow takes place in a field of external force $\mathbf{F}_k = -z_k \nabla \phi$ deriving from a steady-state potential ϕ :

$$\frac{\partial}{\partial t} [\rho(e + v^2/2 + z\phi)] = -\nabla \cdot [\mathbf{q} + \bar{\bar{\mathbf{P}}} \cdot \mathbf{v} + \phi \mathbf{I} + \rho \mathbf{v}(e + k)] \quad [\text{A1.10}]$$

This formulation will enable us to explain the presentation of the Peltier effect (see Chapter 6) given by Landau and Lipchitz [LAN 71]. It is often interesting to bring the temperature into play in the energy balance equation. The internal energy balance is:

$$\frac{\partial(\rho e)}{\partial t} = -\nabla \cdot (\rho e \mathbf{v} + p \mathbf{v} + \mathbf{q}) + \mathbf{v} \cdot \nabla p - \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \sum_k \rho_k z_k \left(\mathbf{E} + \frac{1}{c} \mathbf{v}_k \times \mathbf{B} \right)$$

Into this relation, let us introduce the heat flux, defined by the relation: $\mathbf{q}' = \mathbf{q} - \sum_k h_k \underline{\mathbf{j}}_k$, where h_k is the mass enthalpy of the species k , and define the average enthalpy h such that: $\rho h = \sum_k \rho_k h_k$.

Thus, by revealing the diffusion flux \mathbf{J}_{Dk} on the right-hand side of this equation, we obtain:

$$\frac{\partial(\rho e)}{\partial t} = -\nabla \cdot \mathbf{q}' - \sum_k h_k \nabla \cdot (\rho_k \mathbf{v}_k) - \sum_k \rho_k \mathbf{v}_k \cdot \nabla h_k + \mathbf{v} \cdot \nabla p - \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \sum_k \mathbf{J}_{Dk} \cdot \mathbf{f}_k$$

By expressing the left-hand side as a function of the mass enthalpy values, the above equation becomes:

$$\sum_k \rho_k \frac{\partial h_k}{\partial t} = -\nabla \cdot \mathbf{q}' + \sum_k \mathcal{J}_{Dk} \cdot (\mathbf{f}_k - \nabla h_k) + \mathbf{v} \cdot \nabla p - \mathbf{\Pi} : \nabla \otimes \mathbf{v} - \sum_k \rho_k \mathbf{v} \cdot \nabla h_k$$

which can then be expressed in the following form (see section A1.3 later on):

$$\begin{aligned} \rho c_{p,f} \frac{\partial T}{\partial t} = & -\nabla \cdot \mathbf{q}' + \rho c_{p,f} \mathbf{v} \cdot \nabla T - \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \rho T \frac{\partial \vartheta}{\partial t} \left(\frac{\partial p}{\partial t} + \rho T \mathbf{v} \cdot \nabla p \right) \\ & + \sum_k \mathcal{J}_k \cdot (\mathbf{f}_k - \nabla h_k) \end{aligned} \quad [\text{A1.11}]$$

with $c_{p,f} = (\partial h / \partial T)_{p, Y_k}$ being the specific heat of the mixture at constant pressure and frozen concentrations. In order to establish the energy balance in the form [A1.11], the medium must be isotropic with no polarization.

A1.2. Phenomenological relations in a metal

A1.2.1. Dissipation function

Schematically speaking, the metal is formed of a cloud of moving electrons and the positive ions of the metal structure, whose velocity is taken to be the reference velocity. In practical terms, this velocity \mathbf{v}^i is supposed to be zero. With these hypotheses, the dissipation function becomes:

$$\psi = T \dot{W}_S = -\mathbf{J}_S \cdot \nabla T - \mathbf{I} \cdot \left[\nabla \left(\frac{\mathcal{G}_e}{z_e} \right) - \mathbf{E} \right] \quad [\text{A1.12}]$$

Note that when we discount the influence of the magnetic field in the Lorentz force, we obtain an expression similar to equation [A1.12] for the dissipation function.

The dissipation function in the form [A1.12] serves as a starting point for the study of thermo-electrical phenomena.

To begin with, it should be remembered that for a metal at a uniform temperature, relation [A1.12] enables us to easily introduce the electrical resistance tensor and the Hall

effect. Indeed, in this case, ψ becomes:
$$\psi = -\mathbf{I} \cdot \left[\nabla \left(\begin{array}{c} \mathcal{G}_e \\ z_e \end{array} \right) - \mathbf{E} \right].$$

Thermodynamic equilibrium is characterized by a zero flux ($\mathbf{I} = \mathbf{0}$) and by a null force associated therewith:

$$\nabla \left(\begin{array}{c} \mathcal{G}_e \\ z_e \end{array} \right) - \mathbf{E} = \mathbf{0}.$$
 Near to this state of equilibrium, there is a linear relation which exists between these quantities:
$$\mathbf{E} - \nabla \left(\begin{array}{c} \mathcal{G}_e \\ z_e \end{array} \right) = -\mathbf{R} \cdot \mathbf{I}$$
 where \mathbf{R} is the electrical resistance tensor.

The relations of symmetry of the coupling tensor (Onsager's theory of microscopic fluctuations [ONS 31]) enable us to characterize the tensor \mathbf{R} and thus explain the Hall effect¹ (see section 3.4.1.1; also see [GRO 63, GRO 69a, DUD 93]). These properties, established for a metal, are still valid for a solution where the reference velocity is that of the neutral solvent.

A1.2.2. General points about thermo-electrical effects

The Peltier effect is a thermo-electrical phenomenon caused by the passage of electrical current into a non-homogeneous material. The Thomson effect, on the other

¹ An electrical current along one axis creates an electrical field along the other two axes. Similarly, a field in one direction produces a current in the other two directions. The Onsager symmetry relations give us:

$$R_{xy} = R_{yx}, R_{yz} = R_{zy}, R_{zx} = R_{xz}.$$

hand, occurs in a homogeneous material which is subject to a temperature gradient. These two effects are dependent on the direction and the modulus of the electrical current, unlike the Joule effect.

The phenomenological relations can be written in their matricial form:

$$\begin{bmatrix} \underline{\mathbf{J}}_S \\ \underline{\mathbf{I}} \end{bmatrix} = - \begin{bmatrix} \underline{\mathbf{L}} & \underline{\mathbf{N}} \\ \underline{\mathbf{M}} & \underline{\mathbf{N}} \end{bmatrix} \begin{bmatrix} \underline{\nabla} T \\ \underline{\nabla} \left(\frac{g_e}{z_e} \right) - \underline{\mathbf{E}} \end{bmatrix} \quad [\text{A1.13}]$$

When the medium is isotropic, the tensorial coefficients $\underline{\mathbf{L}}$, $\underline{\mathbf{M}}$ and $\underline{\mathbf{N}}$ are reduced to scalars; the above relations become:

$$\begin{bmatrix} \underline{\mathbf{J}}_S \\ \underline{\mathbf{E}} - \underline{\nabla} \left(\frac{g_e}{z_e} \right) \end{bmatrix} = - \begin{bmatrix} -\lambda/T & \pi/T \\ -\eta & R \end{bmatrix} \cdot \begin{bmatrix} \underline{\nabla} T \\ \underline{\mathbf{I}} \end{bmatrix} \quad [\text{A1.14}]$$

New coefficients appear: (λ , π , η and R); they are generally introduced by experience.

A detailed study of the Peltier effect is presented in Chapter 6. In section 6.1, we find a classical presentation, whilst section 6.2 shows a direct application of the interfacial balance equations established in sections 4.1 and 4.2.

A1.2.3. One-dimensional description of a metal in the presence of heat transfer and electrical conduction

The metal envisaged here is considered as a system of fixed ions within which the electrons are in motion, constituting a Fermi gas.

The chemical potential of such a gas is as follows, per unit electrical charge [GUG 49]:

$$\frac{g_e}{z_e} = -\frac{E^*}{e} + \frac{\pi^2 k^2 T^2}{12 e E^*} \quad [\text{A1.15}]$$

where $E^* = \frac{h^2}{2m} \left(\frac{3N_e}{4\pi} \right)^{2/3}$ is the Fermi level of the electron, m the mass of the electron, h Planck's constant and N_e the number of electrons per unit volume.

If we discount the second term in the development, we accept the hypothesis that g_e/z_e is constant. Further, we suppose that there is mechanical equilibrium, and that the mass of the electrons is negligible in comparison to that of the ions.

In the case of the 1D approximation, this gives us the following relations for the mass fluxes, the electrical currents, the momentum equation, the Maxwell equations, and the energy equation:

$$\begin{aligned} J_i &= \rho_i v_i = 0, \quad J_e = \rho_e v_e = \rho v = I/z_e = \dot{m} = Cte, \\ -J_{Di} &= J_{De} = \rho_e (v_e - v) = Y_i I/z_e, \\ i &= I - \rho z v = (1 - z_i/z_e) Y_i I, \\ \rho v \frac{dv}{dx} + \frac{dp}{dx} &= \frac{1}{c} (\mathbf{I} \times \mathbf{B})_x + \rho z E, \\ \frac{d}{dx} \left(\frac{I}{z_e} h + q + I v \right) &= Q_{ex} \end{aligned} \quad [\text{A1.16}]$$

where account is taken of a *heat injection* Q_{ex} from the *outside* at temperature T_{ex} .

The entropy flux and the entropy production rate are, respectively:

$$\begin{cases} J_s = \frac{1}{T} \left[q + \frac{I}{z_e} (h - g_e) \right], \\ T \dot{W}_s = I \left(E - \frac{d g_e / z_e}{dx} \right) - J_s \frac{dT}{dx} + \left(1 - \frac{T}{T_{ex}} \right) Q_{ex} \end{cases} \quad [\text{A1.17}]$$

From this, we can generally deduce the linearized phenomenological relations:

$$\begin{bmatrix} J_s \\ E - \frac{d g_e / z_e}{dx} \\ Q_{ex} \end{bmatrix} = \begin{bmatrix} -\lambda/T & \pi/T & A_{13} \\ -\eta & R & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \begin{bmatrix} dT/dx \\ I \\ 1 - T/T_{ex} \end{bmatrix} \quad [\text{A1.18}]$$

In the isothermal case: A_{33} is infinite, $T = T_{ex} = \text{Const.}$ and because g_e/z_e is constant, $-E = dV/dx = RI$.

In the adiabatic case: $Q_{ex} = 0, T \neq T_{ex}, A_{3i} = A_{i3} = 0$, and it is necessary to determine the thermal profile [PRU 79].

A1.3. Recap of the energy balance equation

The energy balance equation is:

$$\begin{aligned} \sum_k \rho_k \frac{\partial h_k}{\partial t} = & -\nabla \cdot \mathbf{q}' + \sum_k \mathcal{J}_{Dk} \cdot (\mathbf{F}_k - \nabla h_k) - \underline{\mathbf{v}} \cdot \sum_k \rho_k \nabla h_k \\ & + \mathbf{v} \cdot \nabla p - \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \frac{\partial p}{\partial t} \end{aligned} \quad [\text{A1.19}]$$

A1.3.1. General expression $\sum_k \rho_k dh_k$

The mass enthalpy, h , is, by definition: $h = \sum_k \rho_k h_k$, and is a function of the quantities T, Y_k and L_i (the L_i values being the coefficients of work, $dW = \sum_k L_i dl_i$): $h = h(T, Y_k, L_i)$.

By differentiating these two expressions of h , we obtain the relation:

$$\rho c_{p,f} dT + \rho \left(\frac{\partial h}{\partial L_i} \right)_{T, L_j, Y_k} dL_i = \sum_k \rho_k dh_k, \quad \text{where:}$$

$$c_{p,f} = \left(\frac{\partial h}{\partial T} \right)_{L_i, Y_k}$$

If we consider an isotropic region with no electrical or magnetic polarization, the only work variable is the pressure, so:

$$\rho c_{p,f} dT + \rho \left(\frac{\partial h}{\partial p} \right)_{T, Y_k} dp = \sum_k \rho_k dh_k \quad [\text{A1.20}]$$

A1.3.2. Expression of $\left(\frac{\partial h}{\partial p} \right)_{T, Y_k}$

We suppose that the Gibbs relation is satisfied:

$$de = T ds + \sum_{i=1}^n L_i dl_i + \sum_{k=1}^N g_k dY_k$$

i.e.: $dg = -s dT - \sum_{i=1}^n l_i dL_i + \sum_{k=1}^N g_k dY_k$, where g is the Gibbs function per unit mass.

In particular, the Schwartz equality gives us the relation:

$$\left(\frac{\partial s}{\partial L_i}\right)_{T, L_j, Y_k} = \left(\frac{\partial L_i}{\partial T}\right)_{L_j, Y_k}$$

This relation, in combination with the Gibbs relation, enables us to express the quantity we are looking for:

$\left(\frac{\partial h}{\partial p}\right)_{T, Y_k}$, so that:

$$\left(\frac{\partial h}{\partial p}\right)_{T, Y_k} = \frac{1}{\rho} - T \left(\frac{\partial(1/\rho)}{\partial T}\right)_{p, Y_k} \quad [\text{A1.21}]$$

A1.3.3. *New expression for the energy balance*

From the above equations, we can deduce the expression of $\sum_k \rho_k dh_k$:

$$\sum_{k=1}^N \rho_k dh_k = \rho c_{p,f} dT + \left[1 - \rho T \left(\frac{\partial(1/\rho)}{\partial T}\right)_{p, Y_k} \right] dp$$

Thus, when we look at the time-related partial derivatives:

$$\sum_{k=1}^N \rho_k \frac{\partial h_k}{\partial t} = \rho c_{p,f} \frac{\partial T}{\partial t} + \left[1 - \rho T \left(\frac{\partial(1/\rho)}{\partial T}\right)_{p, Y_k} \right] \frac{\partial p}{\partial t}$$

and if we then look at the gradient:

$$\sum_{k=1}^N \rho_k \nabla h_k = \rho c_{p,f} \nabla T + \left[1 - \rho T \left(\frac{\partial(1/\rho)}{\partial T}\right)_{p, Y_k} \right] \nabla p$$

Using these last two relations, the energy balance equation becomes:

$$\begin{aligned} \rho c_{\rho,f} \frac{\partial T}{\partial t} = & -\nabla \cdot \mathbf{q}' - \rho c_{\rho,f} \mathbf{v} \cdot \nabla T + \rho T \left(\frac{\partial p}{\partial t} + \mathbf{v} \cdot \nabla p \right) \\ & - \Pi : \underline{\nabla} \otimes \underline{\mathbf{v}} + \sum_k \mathcal{J}_{Dk} \cdot (\mathbf{F}_k - \nabla h_k) \end{aligned} \quad [\text{A1.22}]$$

For a perfect gas $\rho T \left(\frac{\partial(1/\rho)}{\partial T} \right)_{p, Y_k} = 1$.

A1.4. Comparisons of phenomenological relations

Let us express the phenomenological coefficients employed by de Groot and Mazur as a function of those introduced by Haase [HAA 69].

The total entropy flux \mathbf{J}_S is written as a function of the heat flux \mathbf{q} , thus:

$$\mathbf{J}_S = \mathcal{J}_S + \rho s \mathbf{v} = \frac{1}{T} \mathbf{q}' + \sum_{k=1}^N s_k \mathcal{J}_{Dk} + \rho s \mathbf{v} = \frac{1}{T} \mathbf{q}' + \frac{s_e}{z_e} \mathbf{I}$$

We also need to transform the gradient of the chemical potential of the electrons:

$$\nabla g_e = \frac{g_e}{T} \nabla T + T \nabla \left(\frac{g_e}{T} \right) = \frac{g_e}{T} \nabla T + (\underline{\nabla} g_e)_T - \frac{h_e}{T} \nabla T = (\nabla g_e)_T - s_e \nabla T$$

from which we derive the expression of the heat flux by substituting back into equation [A1.14]:

$$\mathbf{q}' = - \left(\lambda - \frac{\pi \eta}{R} - \frac{2\pi s_e}{R z_e} + \frac{T s_e^2}{z_e^2} \right) \nabla T - \frac{1}{R} \left(\pi - \frac{s_e T}{z_e} \right) \left[\nabla \varphi + \left(\underline{\nabla} \frac{g_e}{z_e} \right)_T \right]$$

We also obtain:

$$\mathbf{I} = \frac{1}{R} \left(\eta + \frac{s_e}{z_e} \right) \nabla T - \frac{1}{R} \left[\nabla \varphi + \left(\nabla \frac{g_e}{z_e} \right)_T \right]$$

By comparison with equations [6.9a] and [6.9b], we find:

$$\lambda_0 = \lambda - \frac{\pi \eta}{R} - 2 \frac{\pi s_e}{R z_e} + \frac{T s_e^2}{R z_e^2}, \quad K = \frac{1}{R}, \quad {}^* Q_e = z_e \left(\pi - \frac{s_e}{z_e} T \right) = -T (\eta z_e + s_e)$$

and therefore:

$$\lambda = \lambda_0 - \frac{K ({}^* Q_e)^2}{z_e^2 T} \quad [\text{A1.23}]$$

Hence, there is equality between the coefficient λ and the coefficient λ_∞ from equation [6.10], which is to say that $\lambda = \lambda_\infty$.

We also find the relations:

$$\begin{cases} ({}^* s_e) = -z_e \eta \\ \tau = \eta + \frac{1}{z_e} (c_{p,e} + s_e) \end{cases} \quad [\text{A1.24}]$$

A1.5. Plasmas

The balance equations for an electrically-conductive fluid have been established in the foregoing sections. Such equations apply to homogeneous plasmas. A one-dimensional case was discussed in [PRU 79]. The one-dimensional approximation, applied to another 1-dimensional case which is more complex because it exhibits instances of heterogeneity, will be presented in Chapter 8.

The plasmas with which we are dealing here are gases at high temperature [DEL 59], which are partially ionized.² The groundwork laid down in this section will be useful for the discussion to come – particularly for Chapter 7.

These results are supplemented here by the inclusion in the discussion of a well-known characteristic: the fact that the *one-dimensional flow of a plasma placed in an electrical field takes place at constant intensity, $I = \dot{m} z_e$* . This result still holds true in our case-study here, and is unaffected by the presence of a metal on contact with the plasma, regardless of the behavior of the metal/plasma interface, whether or not a surface reaction occurs [PRU 81b]. In addition, we shall take account of the possibility of heat exchanges with the surrounding medium, as we did in section A1.2, with regard to the evolution in a metal conductor.

A1.5.1. Balance equations for a homogeneous plasma at two temperatures

The balance equations [APP 64] enable us to establish the entropy production rate, from which we deduce the form of the phenomenological relations by way of linearized TIP. Note that with regard to the chemical reactions, there is no need to linearize the system, because the literature generally gives us nonlinear chemical kinetic laws with known coefficients (the specific reaction rates). In addition, the balance laws give us the system of equations to be solved in order to determine the fields of variables characterizing the evolution of the plasma in space and time, by means of the knowledge of the physical coefficients. Here, we shall assume steady-state one-dimensional evolution.

² This is unlike what happens with gaseous mixtures at high temperature (between 4500 and 8500K), which we examined in Chapter 1 of [PRU 13], without taking ionization into account.

A1.5.2. Energy balance for a homogeneous plasma

Let us write the energy balance for species i , following an elementary volume moving with the barycentric motion of the flow. We obtain [PRU 79]:

$$\begin{aligned} & \frac{\partial}{\partial t} \left[\rho Y_i \left(e_i + \frac{v_i^2}{2} \right) \right] + \frac{\partial}{\partial x} \left[\rho v Y_i \left(e_i + \frac{v_i^2}{2} \right) + p_i^b v + q_i \right] \\ & = \left(\rho_i g_i + \frac{dP_i}{dx} \right) E v_i + \dot{W}_{Ei}^e + \dot{W}_{Ei}^{n.e} \end{aligned} \quad [\text{A1.25}]$$

\dot{W}_{Ei}^e and $\dot{W}_{Ei}^{n.e}$ respectively represent the energy production of species i caused by elastic and non-elastic shocks, $\dot{W}_{Ei}^e + \dot{W}_{Ei}^{n.e} = \dot{W}_{Ei}^e$.

The total energy in an elementary volume is $\rho(e_i + v_i^2/2)$, where e_i represents the internal energy of species i per unit mass of that species. Because our frame of reference moves with the fluid particle in its barycentric motion, the pressure which comes into play in the above balance equation is linked to the partial pressure that plays a role in the momentum equation for species i ³:

$$p_i^b = p_i + v_i J_{Di} \quad [\text{A1.26}]$$

³ This equation: $\frac{\partial(\rho_i v_i)}{\partial t} + \frac{\partial(\rho_i v_i^2 + p_i)}{\partial x} = \left(\rho_i z_i + \frac{dP_i}{dx} \right) E + f_i^e + f_i^{n.e}$, is given by Appelton and Bray in [APP 64]; f_i^e and $f_i^{n.e}$ are the creations of momentum resulting respectively from the elastic and non-elastic shocks; P_i is the electrical polarization. The other balance equations relate to the total mass, the chemical species A, e^-, A^+ : $\frac{\partial \rho_i}{\partial t} + \frac{\partial(\rho_i v_i)}{\partial x} = \dot{W}_i = v_i \mathcal{M}_i \zeta$, with $v_A = -1, v_e = 1, v_{A^+} = 1$, and the electrical charge.

By revealing the mass enthalpy of species i of electrical polarization P_i , for a steady-state flow, we obtain:

$$\begin{aligned} & \frac{d}{dx}(\rho v Y_i h_i + q_i) + \frac{d}{dx} \left(\rho_i v \frac{v_i^2}{2} + v_i v J_{Di} \right) \\ & = \left(\rho_i z_i + \frac{dP_i}{dx} \right) E v_i + \dot{W}_{Ei}^e + \dot{W}_{Ei}^{n,e} \end{aligned} \quad [\text{A1.27}]$$

From the momentum balance, we can see that:

$$\frac{d}{dx} \left(\rho_i v \frac{v_i^2}{2} + v_i v J_{Di} \right) = v \frac{d(\rho_i v_i^2)}{dx} + \rho_i \left(v_i^2 - \frac{3}{2} v^2 \right) \frac{dv}{dx} + \rho v \frac{d(Y_i V_i^2)}{dx} - \frac{1}{2} v^3 \frac{dp_i}{dx}$$

If we accept that the barycentric acceleration is slight (i.e. the hypothesis of mechanical equilibrium), that the square of the diffusion velocity $V_i^2 = (v_i - v)^2$, is negligible, and finally that the flow is at a low velocity such that we can ignore the term involving the cube of the velocity, we obtain the following equation:

$$\frac{d}{dx}(\rho v Y_i h_i + q_i) + v \frac{d}{dx} \left(\rho_i \frac{v_i^2}{2} \right) = I_i E + \frac{dP_i}{dx} E v_i + \dot{W}_{Ei}^e + \dot{W}_{Ei}^{n,e} \quad [\text{A1.28}]$$

Hence, for the various species of the medium under study here, we have:

$$\left\{ \begin{aligned} & \frac{d}{dx}(\rho v Y_A h_A + q_A) + v \frac{d}{dx}(\rho_A v_A^2) = \frac{dP_A}{dx} E v_A + \dot{W}_{EA}^e + \dot{W}_{EA}^{n,e} \\ & \frac{d}{dx}(\rho v Y_e h_e + q_e) + v \frac{d}{dx}(\rho_e v_e^2) = I_e E + \frac{dP_e}{dx} E v_e + \dot{W}_{Ee}^e + \dot{W}_{Ee}^{n,e} \\ & \frac{d}{dx}(\rho v Y_+ h_+ + q_+) + v \frac{d}{dx}(\rho_+ v_+^2) = I_+ E + \frac{dP_+}{dx} E v_+ + \dot{W}_{E+}^e \\ & + \dot{W}_{E+}^{n,e} \end{aligned} \right. \quad [\text{A1.29}]$$

A1.5.3. Phenomenological relations for a homogeneous plasma

If we take into account the relation $I = \dot{m} z_e$ and the lateral heat exchanges Q_{jext} , the entropy production rate for the homogeneous plasma in one-dimensional evolution reveals the following five generalized fluxes [PRU 81a]:

$$\begin{aligned} J_1 &= \frac{1}{T} \sum_j (\tilde{q}_j - g_j J_j), \quad J_2 = \frac{1}{T_e} \left(E - \frac{d g_e / z_e}{dx} \right), \\ J_3 &= \frac{1}{T_e} (\tilde{q}_e - g_e J_e), \quad J_4 = -\frac{1}{\mathcal{N}_e T} \frac{dA}{dx}, \quad J_5 = Q_{ext} \end{aligned} \quad [\text{A1.30}]$$

and the corresponding generalized forces:

$$F_1 = \frac{dT}{dx}, \quad F_2 = I, \quad F_3 = T_e \frac{d\theta^{-1}}{dx}, \quad F_4 = I^+, \quad F_5 = \frac{1}{T} - \frac{1}{T_{ext}} \quad [\text{A1.31}]$$

and the matrix $\underline{\underline{A}}$ of the phenomenological coefficients A_{kl} introduced by TIP such that $J_k = \sum_l A_{kl} F_l$. By definition, we

have: $\tilde{q}_j = q_j + \rho v Y_j h_j$, $\frac{1}{\theta} = \frac{1}{T_e} - \frac{1}{T}$. Furthermore, we have:

$Q_{ext} = \sum_{i=1}^N Q_{jext}$. We know the expressions for four of the coefficients A_{kl} : $A_{11} = -\lambda/T$, $A_{12} = \pi/T$, $A_{21} = -\eta/T_e$, $A_{22} = R/T_e$.

Note that we cannot linearize the term stemming from the chemical kinetics.

A1.5.4. Chemical equilibrium in conditions of thermal disequilibrium

The “internal disequilibrium” part of the entropy production rate is written as:

$$\dot{W}_{S_{\text{int}}} = -\frac{A}{T}\dot{W} + \frac{1}{\theta}\dot{E}_e = \frac{K}{\theta^2} + (C_{12} + C_{21})\frac{1}{\theta}\frac{A}{T} + A\left(\frac{A}{T}\right)^2,$$
 and we note that it does not vanish at chemical equilibrium (chemical affinity $A=0$). Only if $K \cong 0$ also does it become negligible.

At chemical equilibrium, the relation $A = \mu_e + \mu_+ - \mu_A = 0$, in conditions of thermal disequilibrium, gives us:

$$C_+ C_e^{T_e/T} / C_A = K_C(T, T_e) \quad [\text{A1.32}]$$

where: $-RT \ln K_C(T, T_e) = (\mu_T^0)_e + (\mu_T^0)_+ - (\mu_T^0)_A - RT \ln RT_e$.

Appendix 2

One-Dimensional Approximation for a Hall-Effect Thruster

The purpose of this appendix is to give a detailed discussion of the establishment of the local balance equations presented in Chapter 8, i.e. a one-dimensional flow of plasma with active walls.¹

In a simplified one-dimensional (1D) model (see Figure A2.1), we consider an elementary volume of the thruster channel located between the neighboring positive abscissa values x and $x + dx$, which enables us to introduce the wall conditions (internal and external surfaces of the channel).

The integral balance:

$$\frac{\partial}{\partial t} \int_{\mathcal{V}} \bar{f} d\mathcal{V} = - \int_{\partial\mathcal{V}} \mathbf{J}_F \cdot \mathbf{n} dS + \int_{\mathcal{V}} \dot{W}_F d\mathcal{V}$$

where \bar{f} is the value F per unit volume, $\mathbf{J}_F \cdot \mathbf{n}$ the flux vector of F projected onto the fixed boundary $\partial\mathcal{V}$ of the volume \mathcal{V} under consideration, and \dot{W}_F the production rate (source)

¹ This appendix was written with the help of M. Dudeck [DUD 13].

per unit volume and time, needs to be expressed in local form.

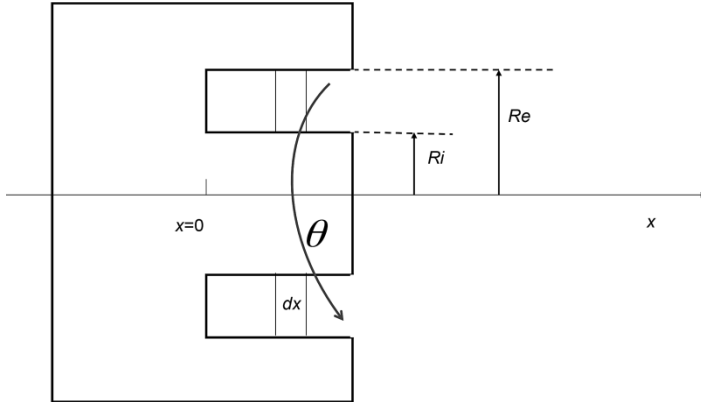


Figure A2.1. Diagrammatic representation for a 1D model.
For further detail, see the diagram of a Hall-effect thruster given by Choueiri [CHO 01], and also Figure 8.10 of this book

In this chapter, we apply the integral general balance equation to the following properties: number of electrons, number of ions, momentum of the species, of the electrons in the axial and azimuthal directions, and energy of the free electrons. We shall do so in the control volume with straight section S and thickness dx of the channel with axial symmetry, shown in Figure A2.1.

This method is comparable to that used for nozzles, with the simplification of a constant area of the cross section, but with peculiarities stemming, firstly, from the presence of active surfaces, and secondly, from the azimuthal drift of the electrons (coming from the cathode) under the influence of the magnetic field (mainly radial) and the axial electrical field. The type of flow studied here is described in detail in Choueiri's article [CHO 01].

A2.1. Balances of species

A2.1.1. Electron balance

The electron balance for this volume of plasma, with the length dx being the length of the channel (see Figure A2.1) is:

$$\frac{\partial}{\partial t} \int_{\mathcal{V}} n_e d\mathcal{V} = - \int_{\partial\mathcal{V}} \mathbf{J}_e \cdot \mathbf{n} dS + \int_{\mathcal{V}} \dot{W}_e d\mathcal{V} \quad [\text{A2.1}]$$

When writing the electron balance, we need to take account of:

- the electron velocity $v_{e,w}$ normal to the lateral surfaces of the thruster channel – a velocity which is taken to be the same on both the internal surface (at $r = R_i$) and the external surface (at $r = R_e$), and that of the electrons re-emitted by secondary electron collisions with the walls, at a rate written as σ ;

- the electrons created in the volume by ionization and by the process $Xe + e \rightarrow Xe^+ + e + e$ of formation of singly-charged xenon ions with a reaction rate $\beta(T_e)$, there are only 10% doubly-charged ions, and this production depends on the electrical potential of the discharge. Successively, we write:

$$\begin{aligned} (\partial n_e / \partial t) S dx &= (n_e v_e)_x S - (n_e v_e)_{x+dx} S - 2\pi R_i n_e v_{e,w} dx - 2\pi R_e n_e v_{e,w} dx \\ &\quad + \beta n_n n_e S dx, \\ (\partial n_e / \partial t) S dx &= -(\partial n_e v_e / \partial x) - 2\pi (R_i + R_e) n_e v_{e,w} dx + \beta n_n n_e S dx, \\ \partial n_e / \partial t &= -\partial n_e v_e / \partial x - \left[2\pi (R_i + R_e) / \pi (R_e^2 - R_i^2) \right] n_e v_{e,w} + \beta n_n n_e \end{aligned}$$

The local form of the free electron balance equation is therefore as follows:

$$\frac{\partial n_e}{\partial t} + \frac{\partial(n_e v_e)}{\partial x} = \beta n_n n_e - \frac{2(1-\sigma)v_{e,w}}{R_e - R_i} n_e \quad [\text{A2.2}]$$

with account taken of the electrons re-emitted by secondary collisions.

In a Hall-effect thruster, the wall of the discharge channel is made of insulating ceramic, and its electrical potential is therefore the floating potential obtained when we have equality (in modulus) of the wall currents of electrons and ions, which gives us the equality $(1-\sigma)n_e e v_{e,w} = n_i e v_{i,w}$. The expression of the electron velocity is therefore

$$v_{e,w} = \frac{v_{i,w}}{1-\sigma} = \frac{\sqrt{kT_e/\mathcal{M}_i}}{1-\sigma},$$

using the *Bohm velocity* for the ions and the symbol σ to represent the rate of secondary electron emission by electron bombardment. The velocity of the ions at the boundary of the sheath of potential is the ionic acoustic velocity, whose expression is given by *Bohm's relation* (condition of sheath stability stated by Bohm) $v_{i,w} = \sqrt{kT_e/\mathcal{M}_i}$. Although the ion velocity is a directed velocity due to the electrostatic lens, this Bohm velocity is a function of the electron temperature T_e . The electron balance [A2.2] becomes:

$$\frac{\partial n_e}{\partial t} + \frac{\partial(n_e v_e)}{\partial x} = \beta n_n n_e - \frac{2}{R_e - R_i} \sqrt{\frac{kT_e}{\mathcal{M}_i}} n_e \quad [\text{A2.3}]$$

The term $\frac{2}{R_e - R_i} \sqrt{\frac{kT_e}{\mathcal{M}_i}}$ corresponds to the inverse of a time – it is the frequency of electron collisions with the channel walls, and is written as $\nu_{e,w}$. Hence:

$$\frac{\partial n_e}{\partial t} + \frac{\partial(n_e v_e)}{\partial x} = \beta n_n n_e - \nu_{e,w} n_e \quad [\text{A2.4}]$$

A2.1.2. Ion balance

The singly-charged xenon ion balance is:

$$\frac{\partial n_i}{\partial t} + \frac{\partial(n_i v_i)}{\partial x} = \beta n_n n_e - \frac{2}{R_e - R_i} \sqrt{\frac{kT_e}{\mathcal{M}_i}} n_e = \beta n_n n_e - v_{i,w} n_i \quad [\text{A2.5}]$$

where v_i is the axial velocity of the ions along the x axis.

The frequency of collision between the ions and the walls is $\frac{2}{R_e - R_i} \sqrt{\frac{kT_e}{\mathcal{M}_i}}$ and, if we introduce the condition of electroneutrality $n_i = n_e$ (in volume), the above balance relation [A2.5] becomes:

$$\frac{\partial n_e}{\partial t} + \frac{\partial(n_e v_i)}{\partial x} = \beta n_n n_e - v_{i,w} n_e \quad [\text{A2.6}]$$

A2.1.3. Equation verified by the discharge current I in a cross-section

By writing the difference between equations [A2.6] and [A2.4], we obtain:

$$\partial[n_e(v_i - v_e)]/\partial x = (-v_{i,w} + v_{e,w})n_e = 0$$

The total current reaching one surface of the channel is zero (an insulating surface); the total current passing through a cross-section of the channel is conserved as a function of the abscissa value x :

$$I = eS n_e (v_i - v_e) = \text{Const.} \quad [\text{A2.7}]$$

A2.2. Momentum balances

In this section, we establish the momentum balances for the species, with a particular case study focusing on the electrons, which are animated with a motion with two components: axial and azimuthal.

A2.2.1. Momentum balance for species j

A2.2.1.1. Integral form

The momentum balance $m_j \mathbf{v}_j$ for species j for the domain in question with surface S and axial length dx is:

$$\begin{aligned} \frac{\partial}{\partial t} \int_{\mathcal{V}} n_j M_j \mathbf{v}_j d\mathcal{V} &= - \int_{\partial\mathcal{V}} \bar{\bar{\mathbf{P}}}_j \cdot \mathbf{n} dS - \int_{\partial\mathcal{V}} n_j M_j \mathbf{v}_j (\mathbf{v}_j \cdot \mathbf{n}_j) dS \\ &- \int_{\substack{\text{wall} \\ \text{channel}}} \dot{W}_{m_j \mathbf{v}_j, \text{wall}} dS + \int_{\mathcal{V}} n_j \mathbf{f}_j d\mathcal{V} + \int_{\mathcal{V}} \dot{\mathbf{W}}_{m_j \mathbf{v}_j, \text{chemistry}} d\mathcal{V} \end{aligned} \quad [\text{A2.8}]$$

A2.2.1.2. First term

The first term in equation [A2.8] can be transformed into:

$$\frac{\partial}{\partial t} \int_{\mathcal{V}} n_j M_j \mathbf{v}_j d\mathcal{V} = M_j \int_{\mathcal{V}} \frac{\partial n_j \mathbf{v}_j}{\partial t} d\mathcal{V} \cong M_j \frac{\partial n_j \mathbf{v}_j}{\partial t} S dx$$

A2.2.1.3. Pressure term

The pressure term on the right-hand side of equation [A2.8] becomes: \mathbf{e}_x

$$\begin{aligned} - \int_{\partial\mathcal{V}} \bar{\bar{\mathbf{P}}}_j \cdot \mathbf{n} dS &= - \int_{\partial\mathcal{V}} p_j \mathbf{n} dS = - \left[-p_j(x)S + p_j(x+dx)S \right] \mathbf{e}_x \\ &= - \left[-p_j(x) + p_j(x+dx) \right] S \mathbf{e}_x \cong - \partial p_j / \partial x S dx \mathbf{e}_x \end{aligned}$$

A2.2.1.4. Flow rate term

The momentum flow rate term is written as:

$$\begin{aligned}
 -\int_S n_j M_j \mathbf{v}_j (\mathbf{v}_j \cdot \mathbf{n}_j) dS &= -n_j(x) M_j v_{j,x}(x) [-v_{j,x}(x)] S \mathbf{e}_x - n_j(x+dx) M_j \\
 v_{j,x}(x+dx) [-v_{j,x}(x+dx)] S \mathbf{e}_x &- n_j(x) M_j \mathbf{v}_j (\mathbf{v}_j \cdot \mathbf{e}_r) 2\pi R_e dx \\
 -n_j(x) M_j \mathbf{v}_j (\mathbf{v}_j \cdot \mathbf{e}_r) &2\pi R_i dx
 \end{aligned}$$

On the right-hand side, the first two terms correspond to the momentum flow rates passing through the cross-section of the channel, and the latter two to the momentum flow rates over the lateral surfaces of axial length dx of the control volume examined here. Thus:

$$\begin{aligned}
 &= n_j(x) M_j v_{j,x}^2(x) S \mathbf{e}_x - n_j(x+dx) M_j v_{j,x}^2(x+dx) S \mathbf{e}_x \\
 &+ n_j(x) M_j \mathbf{v}_j v_{j,r} 2\pi R_e dx - n_j(x) M_j \mathbf{v}_j v_{i,r} 2\pi R_i dx
 \end{aligned}$$

If we suppose that the radial velocities at the surfaces are equal (i.e. that the jet is symmetrical), the above expression can be simplified to give:

$$= -\frac{\partial(n_j v_{j,x}^2)}{\partial x} M_j S dx \mathbf{e}_x - n_j(x) \mathbf{v}_j v_{j,r} M_j 2\pi (R_e - R_i) dx$$

A2.2.2. Electron momentum balance

A2.2.2.1. Momentum in direction of x axis

The electron pressure tensor is isotropic, with $\vec{\vec{P}}_e = p_e \mathbf{1}$ (no electron viscosity). By projection along the x axis, the momentum balance becomes:

$$\begin{aligned}
 \frac{\partial(n_e M_e v_{e,x})}{\partial t} &= p_e(x) S - p_e(x+dx) S \\
 -\left[(n_e M_e v_{e,x}^2)(x+dx) - (n_e M_e v_{e,x}^2)(x) \right] &S dx - n_e |e| E S dx + \dot{W}_{e,chemistry} S dx
 \end{aligned}$$

The force on the electrons due to the field $\mathbf{B} = B_r \mathbf{e}_r$ (supposed to be radial) is:

$$\begin{bmatrix} F_{e,x} \\ F_{e,\theta} \\ F_{e,r} \end{bmatrix} = \begin{bmatrix} v_{e,x} \\ v_{e,\theta} \\ v_{e,r} = 0 \end{bmatrix} \times \begin{bmatrix} 0 \\ 0 \\ B_r \end{bmatrix} = \begin{bmatrix} B_r v_{e,\theta} \\ B_r v_{e,x} \\ 0 \end{bmatrix}$$

The production of electron momentum along the x axis, per unit time and volume, is $(\beta n_e n_n)(n_e M_e v_{e,x})$. We write:

$$\begin{aligned} \frac{\partial(n_e M_e v_{e,x})}{\partial t} S dx &= -\frac{\partial(p_e + n_e M_e v_{e,x}^2)}{\partial x} S dx - n_e |e| (E + v_{e,\theta} B_r) S dx \\ &+ (\beta n_e n_n)(n_e M_e v_{e,x}) S dx \end{aligned}$$

and from this, deduce:

$$\frac{\partial(n_e M_e v_{e,x})}{\partial t} = -\frac{\partial(p_e + n_e M_e v_{e,x}^2)}{\partial x} - n_e |e| (E + v_{e,\theta} B_r) + (\beta n_e n_n)(n_e M_e v_{e,x})$$

If we neglect the terms introducing the mass M_e of the electrons, it follows that:

$$n_e |e| E = -\frac{\partial p_e}{\partial x} - n_e |e| v_{e,\theta} B_r$$

The local momentum balance equation for the electrons is therefore reduced to:

$$|e| E = -\frac{1}{n_e} \frac{\partial(n_e k T_e)}{\partial x} - |e| v_{e,\theta} B_r \quad [\text{A2.9}]$$

A2.2.2.2. Momentum in the azimuthal direction θ

The frequency ω_{ce} of cyclotronic resonance of the electrons is introduced with the relation: $\omega_{ce} = |e| B_r / M_e$, giving us the form:

$$|e|E = -\frac{1}{n_e} \frac{\partial(n_e k T_e)}{\partial x} - \omega_{ce} M_e v_{e,\theta} \quad [\text{A2.10}]$$

A2.3. Energy balance for the free electrons

A2.3.1. Integral form for the total energy

The energy balance equation is written solely for the free electrons at temperature T_e . In its integral form, the total energy balance (internal + kinetic) is written as:

$$\begin{aligned} \frac{\partial}{\partial t} \int_{\mathcal{V}} n_e (E_e + K_e) d\mathcal{V} = & - \int_{\partial\mathcal{V}} \left(\mathbf{q}_e + \bar{\bar{\mathbf{P}}}_e \cdot \mathbf{v}_e \right) \cdot \mathbf{n} dS \\ & - \int_{\substack{\text{wall} \\ \text{channel}}} \dot{W}_{E+K,\text{wall}} dS + \int_{\mathcal{V}} n_e \mathbf{v}_e \cdot \mathbf{f}_e d\mathcal{V} + \int_{\mathcal{V}} \dot{W}_{E+K,\text{chemistry}} d\mathcal{V} \end{aligned} \quad [\text{A2.11}]$$

The internal energy per unit volume is $n_e E_{e,t}$ where n_e is the number of electrons per unit volume and $E_e = E_{e,t}$ is the internal energy of an electron, which can be reduced to the energy of translational motion $E_{e,t} = 3/2 k T_e$.

A2.3.2. Internal energy

A2.3.2.1. Time derivative of the internal energy

For the control volume $S dx$, the internal energy is

$\int_{\mathcal{V}} \frac{3}{2} n_e k T_e d\mathcal{V}$, and its variation per unit time is:

$$\frac{\partial}{\partial t} \left(\int_{\mathcal{V}} \frac{3}{2} n_e k T_e d\mathcal{V} \right) = \int_{\mathcal{V}} \frac{\partial}{\partial t} \left(\frac{3}{2} n_e k T_e \right) d\mathcal{V}$$

so:

$$\frac{\partial}{\partial t} \left(\int_{\mathcal{V}} n_e E_e d\mathcal{V} \right) = \frac{\partial}{\partial t} \left(\int_{\mathcal{V}} \frac{3}{2} n_e k T_e d\mathcal{V} \right) \equiv \frac{\partial}{\partial t} \left(\frac{3}{2} n_e k T_e \right) S dx \quad [\text{A2.12}]$$

A2.3.2.2. Internal energy flux

The *internal energy flux* is $-\int_{\partial V} n_e E_e \mathbf{v}_e \cdot \mathbf{n} dS$, where the surface contains the cross sections at x and $x + dx$ and the lateral surfaces of length dx .

If, for the time being, we consider only the two cross sections at x and $x + dx$:

$$n_e E_e(x) v_e(x) S \mathbf{e}_x - n_e E_e(x + dx) v_e(x + dx) S \mathbf{e}_x = -\frac{\partial(n_e E_e v_e)}{\partial x} S dx \mathbf{e}_x$$

Hence:

$$\int_{\partial V} n_e E_e \mathbf{v}_e \cdot \mathbf{n} dS \cong -\frac{\partial}{\partial x} \left(\frac{3}{2} n_e k T_e \right) S dx \quad [\text{A2.13}]$$

A2.3.3. Kinetic energy

The *kinetic energy* of an electron is $1/2 M_e v_e^2$ if M_e is its mass.

A2.3.3.1. Temporal derivative of the kinetic energy

For the control volume, the kinetic energy of the free electrons is:

$$\int_V n_e 1/2 M_e v_e^2 dV$$

and its variation per unit time is:

$$\frac{\partial}{\partial t} \int_V \frac{1}{2} n_e M_e v_e^2 dV = \int_V \frac{\partial}{\partial t} \left(\frac{1}{2} n_e M_e v_e^2 dV \right) \cong \frac{\partial}{\partial t} \left(\frac{3}{2} n_e k T_e \right) S dx$$

and therefore, because the kinetic theory of gases (e.g. see section 2.4.3 in [PRU 12]) tells us that for monatomic particles, the average kinetic energy of the molecules is such that: $\frac{1}{2}M\bar{c}^2 = \frac{3}{2}kT$, and here the average agitation speed \bar{c} is replaced by the velocity v_e ²:

$$\frac{\partial}{\partial t} \left(\int_{\partial V} n_e K_e dS \right) = \frac{\partial}{\partial t} \left(\int_{\partial V} \frac{1}{2} n_e M_e v_e^2 dS \right) \cong - \frac{\partial}{\partial t} \left(\frac{3}{2} n_e k T_e \right) S dx \quad [\text{A2.14}]$$

A2.3.3.2. Kinetic energy flux

The *kinetic energy flux*, similarly to the internal energy, is:

$$- \frac{\partial}{\partial x} \left(\frac{1}{2} M_e n_e v_e^2 \right) S dx \quad [\text{A2.15}]$$

A2.3.3.3. Pressure term

The pressure term in the energy balance is $-\nabla \cdot (\bar{\bar{\mathbf{P}}}_e \cdot \mathbf{v}_e)$ and, in the absence of any effect of electron viscosity: $-\nabla \cdot (p_e \mathbf{1} \cdot \mathbf{v}_e) = -\nabla \cdot (p_e v_e \mathbf{e}_x) = -\partial(p_e v_e)/\partial x$, so:

$$- \int_{\partial V} \nabla \cdot (\bar{\bar{\mathbf{P}}}_e \cdot \mathbf{v}_e) dV = - \frac{\partial(p_e v_e)}{\partial x} S dx = - \frac{\partial(n_e k T_e v_e)}{\partial x} S dx, \quad \text{and}$$

therefore:

² For any given species in the mixture, we can more rigorously write the following (see [JAN 63]), if $f_j(\mathbf{v}_j, r, t)$ is the velocity distribution function for the particles of species j and if we accept the hypothesis that the species has its own temperature T_j :

$$n_j = \int f_j(\mathbf{v}_j, r, t) d\mathbf{v}_j, \quad n_j \bar{\mathbf{v}}_j = \int f_j \mathbf{v}_j d\mathbf{v}_j, \quad \frac{1}{2} n_j k T_j = \int f_j \frac{1}{2} M_j (\mathbf{v}_j - \bar{\mathbf{v}}_j)^2 d\mathbf{v}_j \cong \int f_j \frac{1}{2} M_j v_j^2 d\mathbf{v}_j$$

if the square of the agitation velocity of the species $\overline{v_j^2}$ is much greater than the square $\bar{\mathbf{v}}_j^2$ of the macroscopic velocity, which is true for the free electrons at high temperature.

$$-\int_{\mathcal{V}} \nabla \cdot (\mathbf{P}_e \cdot \mathbf{v}_e) d\mathcal{V} = -\frac{\partial(n_e k T_e v_e)}{\partial x} S dx \quad [\text{A2.16}]$$

We combine this result with the previous ones, which, for the term showing the total energy flux of the electrons, gives us:

$$\begin{aligned} \int_{\mathcal{V}} \nabla \cdot (\mathbf{q}_e + \mathbf{P}_e \cdot \mathbf{v}_e) d\mathcal{V} &= \frac{\partial(n_e E_e v_e)}{\partial x} S dx + \frac{\partial(n_e k T_e v_e)}{\partial x} S dx \\ &+ \frac{\partial(5/2 n_e k T_e v_e)}{\partial x} S dx \end{aligned} \quad [\text{A2.17}]$$

The left-hand side of the total electron energy equation can therefore be reformulated, with the unsteady term and the convection term, to give:

$$\frac{\partial}{\partial t} \left(\frac{3}{2} n_e k T_e + n_e M_e \frac{v_e^2}{2} \right) + \frac{\partial}{\partial x} \left(\frac{5}{2} n_e k T_e v_{e,x} + n_e M_e \frac{v_e^2}{2} v_{e,x} \right)$$

A2.3.4. Terms of total energy production of the electrons

A2.3.4.1. Term of work due to the external force

The *term of work due to the external force* is, per unit volume, $n_e \mathbf{f}_e \cdot \mathbf{v}_e = -n_e |e| \mathbf{E} \cdot \mathbf{v}_e = -n_e |e| E v_{e,x}$, and therefore for the elementary volume $S dx$:

$$\int_{\mathcal{V}} n_e \mathbf{f}_e \cdot \mathbf{v}_e d\mathcal{V} = -n_e |e| E v_{e,x} S dx \quad [\text{A2.18}]$$

A2.3.4.2. Loss of electron energy at the wall

The *loss of electron energy at the wall* is $-n_e v_{e,w} \mathcal{E}_{e,w}$, with $v_{e,w}$ being the frequency of collisions between the electrons and the surface and $\mathcal{E}_{e,w}$ the energy deposited (i.e. lost)

which can be deconstructed into two contributions – that containing the incident energy per electron:

$$(\mathcal{E}_{e,w})_1 = \frac{3}{2}kT_e + \frac{1}{2}M_e v_e^2 \quad [\text{A2.19}]$$

and that involving the secondary electron emission rate:

$$(\mathcal{E}_{e,w})_2 = (1-\sigma)|e|\Phi_w \quad [\text{A2.20}]$$

And with equation [A2.12], we already have some of the terms needed for equation (7) in Table 8.1:

$$\frac{\partial}{\partial t} \left(\frac{3}{2}n_e kT_e + n_e M_e \frac{v_e^2}{2} \right) + \frac{\partial}{\partial x} \left(\frac{5}{2}n_e kT_e v_{e,x} + n_e M_e \frac{v_e^2}{2} v_{e,x} \right) = -n_e |e| E v_{e,x}$$

Let us now examine the other energy sources.

A2.3.4.3. *Other sources of electron energy*

Chemical effect

The production of electrons per unit volume is $\beta n_n n_e$, and the energy of the first ionization reaction is written as ε_i (12.12eV). This initial ionization is described by $Xe + e_1 \rightarrow Xe^+ + e_1 + e_2$. The electron e_1 loses energy to the Xe atom, thereby ionizing the latter. The electron e_2 created by that ionization reaction has low energy, and the energy loss in the electron balance is written in the following form per unit volume:

$$-\beta n_n n_e \gamma_i \varepsilon_i \quad [\text{A2.21}]$$

where γ_i is a parameter representing the energy loss in comparison to the ideal loss $-\beta n_n n_e \varepsilon_i$ (energy effect of the electron e_2 created, influence of the metastable states Xe^* of xenon in the ionization process).

Electromagnetic field

The electromagnetic force exerted on an electron can have an axial component and an azimuthal component:

$$\mathbf{f}_e = -|e| \begin{bmatrix} E_x + v_{e,\theta} B_r \\ -v_{e,x} B_r \\ 0 \end{bmatrix}$$

The power associated with that force is, per unit volume:

$$n_e \mathbf{f}_e \cdot \mathbf{v}_e = -n_e |e| (E_x + v_{e,\theta} B_r) v_{e,x} + n_e |e| v_{e,x} B_r v_{e,\theta}$$

so:

$$n_e \mathbf{f}_e \cdot \mathbf{v}_e = -n_e |e| E_x v_{e,x} \quad [\text{A2.22}]$$

Walls of the channel

The interaction of electrons with the walls of the channel in the thruster involves several processes:

– an energy value per electron (internal and kinetic) in the plasma (at the edge of the sheath of potential): $3/2 k T_e + 1/2 M_e v_e^2$;

– a sheath of potential between the plasma potential and the surface potential;

– a wall of the channel at the floating electrical potential Φ_f (to give a null sum of the electronic and ionic currents);

– secondary electron emission at the wall.

The *sheath potential* a long the radius r is:

$$\phi_w = \frac{kT_e}{e} \ln \left[\sqrt{\frac{M_i}{2\pi M_e}} (1 - \sigma) \right] \text{ (a); that is:}$$

$$\exp \left(\frac{|e| \phi_w}{kT_e} \right) = \sqrt{\frac{M_i}{2\pi M_e}} (1 - \sigma)$$

– *In the absence of secondary electron emission at the wall, the total electrical current collected for a negative surface polarization is:*

$$n_e |e| \sqrt{\frac{kT_e}{2\pi M_e}} \exp\left(\frac{|e|\phi_w}{kT_e}\right) - n_i |e| \sqrt{\frac{kT_i}{2\pi M_i}} = 0$$

Hence, taking account of the condition of electroneutrality, we have $\exp\left(\frac{|e|\phi_w}{kT_e}\right) = \sqrt{\frac{T_i M_e}{T_e M_i}}$ and therefore:

$$\phi_w = \frac{kT_e}{|e|} \ln \left[\frac{T_i M_e}{T_e M_i} \right] \quad (\text{b})$$

which differs from (a) because of the Maxwellian expression of the ionic current with the kinetic temperature T_i at the edge of the sheath.

– *With a Bohm ion velocity at the wall, the condition of zero total current is written as follows, still without secondary electron emission:*

$$n_e |e| \sqrt{\frac{kT_e}{2\pi M_e}} \exp\left(\frac{|e|\phi_w}{kT_e}\right) - n_i |e| \sqrt{\frac{kT_e}{M_i}} = 0 \quad (\text{c})$$

which gives us:

$$\phi_w = \frac{kT_e}{|e|} \ln \left[\sqrt{\frac{2\pi M_e}{M_i}} \right] \quad (\text{d})$$

– *With a Bohm ion velocity [BOH 49] and a secondary electron emission rate at the wall σ , we have:*

$$(1-\sigma)n_e |e| \sqrt{\frac{kT_e}{2\pi M_e}} \exp\left(\frac{|e|\phi_w}{kT_e}\right) - n_i |e| \sqrt{\frac{kT_e}{M_i}} = 0$$

which leads to:

$$\phi_w = \frac{kT_e}{|e|} \ln \left[\sqrt{\frac{2\pi M_e}{M_i}} \frac{1}{1-\sigma} \right] \quad (\text{e})$$

which, in turn, can be expressed by equation [8.7] (i.e. the formula given in Appendix A of [BAR 09]), with the exception of the sign.

– *The electron energy deposition* on the surface (internal + external) of the channel is:

$$v_{e,w} n_e e_{e,w} \text{ where } e_{e,w} = \frac{3}{2} kT_e + \frac{1}{2} M_e v_e^2 + e\Phi_w - \sigma e\Phi_w \quad (\text{f})$$

A2.3.5. Final form for the total energy of the electrons

The electron energy balance is therefore:

$$\begin{aligned} \frac{\partial}{\partial t} \left(\frac{3}{2} n_e kT_e + \frac{1}{2} n_e M_e v_e^2 \right) + \frac{\partial}{\partial x} \left(\frac{5}{2} n_e v_{ex} kT_e + \frac{1}{2} n_e v_{ex} M_e v_e^2 \right) \\ = -\beta n_n n_e \gamma_i \varepsilon_i - v_{e,w} n_e \varepsilon_w - n_e v_{e,x} |e| E \end{aligned} \quad [\text{A2.23}]$$

This is equation (7) from Table 8.1, for: $E_x = E$, $E_\theta = 0$, which corresponds to the hypotheses adopted by Barral and Ahedo [BAR 09].

A2.3.6. Another form of the electron energy equation

Barral and Ahedo [BAR 09] manage to write, after a series of algebraic computations, the balance equations in a form which yields the system of equations [8.13].

In order to do so, they rearrange the energy balance equation for the free electrons, placing it in the form:

$$\frac{\partial (T_e^{3/2}/n_e)}{\partial t} + v_{e,x} \frac{\partial (T_e^{3/2}/n_e)}{\partial x} = h_4/n_e \quad [\text{A2.24}]$$

This result is obtained by eliminating the electrical field using Ohm's law (equation [6] in Table 8.1) and setting $E_x = E$, $E_\theta = 0$. They also express the kinetic energy carried by the electrons in the same way as in equation [A2.14], in the term: $\frac{1}{2}n_e M_e v_e^2 = \frac{3}{2}n_e k T_e$. The quantity h_4 is not a function of the electron density n_e .

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