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Multicomponent Interfacial Transport

Described by the Square
Gradient Model during
Evaporation and Condensation

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Kirill Glavatskiy

Multicomponent Interfacial Transport

Described by the Square Gradient Model
during Evaporation and Condensation

Doctoral Thesis accepted by
Norwegian University of Science and Technology,
Trondheim, Norway

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*There are more things in heaven
and earth, Horatio,
Than are dreamt of in your
philosophy.*

W. Shakespeare

О, сколько нам открытий чудных
Готовят просвещенья Дух
И Опыт, сын ошибок трудных,
И Гений, парадоксов друг,
И Случай, бог изобретатель...

A. S. Pushkin

*So many marvelous discoveries
Are due to the enlightenment Spirit,
To the Experience – a child of tough
mistakes,
The Genius – a friend of paradox,
The Incident – the Lord inventor...*

A. S. Pushkin

Parts of this thesis have been published in the following journal articles:

K. S. Glavatskiy and D. Bedeaux, Nonequilibrium properties of a two-dimensionally isotropic interface in a two-phase mixture as described by the square gradient model. *Physical Review E* 77, 061101 (2008)

K. S. Glavatskiy and D. Bedeaux, Numerical solution of the nonequilibrium square-gradient model and verification of local equilibrium for the Gibbs surface in a two-phase binary mixture. *Physical Review E* 79, 031608 (2009)

K. S. Glavatskiy and D. Bedeaux, Transport of heat and mass in a two-phase mixture: from a continuous to a discontinuous description. *Journal of Chemical Physics* 133:144709 (2010)

K. S. Glavatskiy and D. Bedeaux, Resistances for heat and mass transfer through a liquid–vapor interface in a binary mixture. *Journal of Chemical Physics* 133:234501 (2010)

Supervisor's Foreword

This is excellent work of luminescent scientific novelty. A thermodynamically consistent description of transport across interfaces in mixtures has for a long time been an open issue. In this dissertation this issue is brought a significant step further. The findings of this work will facilitate further applications of the theoretical framework to important problems. The thesis is an original and novel theoretical study. The systematic nature of the approach is also reflected in the thorough structure of the thesis.

This research addresses mass and heat transport thorough an interface, using an extension of the square gradient theory, according to van der Waals and Cahn–Hilliard, in the systematic context of non-equilibrium thermodynamics. An important achievement is the formulation of the appropriate Gibbs relation, which contains a new contribution in the interfacial region due to the difference between the parallel and the normal pressure.

An important issue clarified in this thesis is that the interface between a liquid and a vapor in a mixture is in local equilibrium during evaporation and condensation. It implies that the thermodynamic description developed for interfaces by Gibbs can be applied also away from equilibrium, which is typically the case in reality. This provides a powerful tool for addressing phase transitions and transport through the interface.

Results from non-equilibrium molecular dynamic simulations for two-phase systems support the validity of local equilibrium. The great advantage of the method developed in the thesis is its relative numerical simplicity.

A general definition of the temperature and the chemical potentials of the nonequilibrium surface is given. These are found to be independent of the choice of the so-called dividing surface for planar surfaces. A surprising consequence of this property is that density and energy differences across the surface have their equilibrium values at the temperature and chemical potential of the nonequilibrium surface.

Resistances for transport of heat and mass through the surface are calculated. Integral relations are given, which simplify the calculation of these resistances, using equilibrium enthalpy profiles.

The description of phase transitions is of great importance for the understanding of both natural and industrial processes. It is relevant for understanding the increase of the CO₂ concentration in the atmosphere and for further improvements in the efficiency of distillation columns, to name two widely differing examples. Significant progress towards solving these problems has become possible through this research.

Much of the work in the thesis has been published in the literature. The thesis gives, however, a pedagogical exposition of a difficult subject, which makes the subject more accessible than the publications. This merits publication of this work as a book.

Norway, December 2010

Dick Bedeaux

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Norway, December 2010

K. S. Glavatskiy¹

¹ The present passport name is Kyrilo Glavatskyy.

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Chapter 1

Introduction

1.1 Summary

The aim of this thesis is to build a theoretical approach which allows to describe the behavior of fluid during evaporation and condensation in multi-component systems. We consider isotropic non-polarizable mixtures. We have developed the description of the surface using continuous non-equilibrium thermodynamics [1] and established the link to the macroscopic non-equilibrium thermodynamics of surfaces [2], which uses excess densities and fluxes. The present analysis for the mixture's surface generalizes the equilibrium square gradient model and the non-equilibrium description of one-component systems.

The thesis is based on four articles [3–6]. Within this work we have addressed three major issues. First, we have established an analytical continuous description of an interfacial region between two different phases of a mixture under non-equilibrium conditions [3]. Next, we have verified numerically the possibility to describe the non-equilibrium surface as a separate phase [4]. Finally, we have investigated the connection between transport properties of a mixture inside an interfacial region and those for the whole surface, both analytically [5, 6] and numerically [5]. The work on mixtures in three-dimensional space presented in the thesis extends and generalizes the previous work on one-component systems [7–10].

Within the continuous approach we have gone through a number of steps. First, the equilibrium thermodynamic behavior in the interfacial region was established. We used the square gradient theory [11–13] as a model which describes thermodynamic phenomena in the interfacial region. It has been widely used for one-component equilibrium systems and has been extended to mixture interfaces. Next, we extended the description to non-equilibrium. The non-equilibrium Gibbs relation has been postulated and we discussed how the gradient theory motivates the chosen form of this equation. The expression for the entropy production, which gives one information about the measure of the irreversibility everywhere in the interfacial region, has been obtained. We have discussed how the gradient description breaks the three-dimensional isotropy of a mixture inside the interface.

The resulting linear laws relating the forces and the fluxes were given. Having this approach established we have gotten the complete continuous description of a two-phase mixture under non-equilibrium conditions. The theory was applied to and solved for a particular mixture of cyclohexane and *n*-hexane. The details of the numerical procedure were discussed and resulting profiles of various thermodynamic quantities were obtained.

Another focus of the thesis was to make a link to the macroscopic description of transport through a surface. Within this approach a surface in non-equilibrium is treated as a separate phase which has its own thermodynamic properties, such as the temperature or the excess density. This hypothesis is called local equilibrium of a Gibbs surface. This is a simplifying assumption about the behavior of real systems which is physically elegant. With the help of the continuous gradient description we have verified the hypothesis of local equilibrium of a surface for a binary mixture.

The macroscopic approach uses interfacial resistances to heat and mass transfer through the surface as parameters of the theory. The continuous description allowed us to obtain these coefficients directly and gave insight of the nature of these coefficients. With the help of the continuous description we obtained the excess entropy production of the whole surface and the resulting linear laws. The interfacial resistances have been evaluated both numerically and with the help of derived integral relations. By comparison with results from kinetic theory it was shown that the continuous resistivity profiles have a peak in the interfacial region. We have also shown that the interfacial resistances depend among other things on the enthalpy profile across the interface. The enthalpy of evaporation is one of the main differences between liquid and vapor phases and therefore the interface is important for the resistance to heat and mass transfer.

1.2 Motivation and Scope

Evaporation and condensation phenomena happening in mixtures are very important in many industrial applications. A distinct example is distillation. A typical distillation column consists of several stages at which separation of components happens: more volatile components turn to the gas phase, less volatile turn to the liquid phase.

Evaporation and condensation take place through the surface. In order to describe these phenomena one needs to understand processes which happen at the surface. The surface is a special thermodynamic system. It contains very few particles, so that its width is about a few molecular diameters. On the other hand this is a transition region from gas to liquid, the existence of which one may not neglect. There are clear observable effects which are only due to the existence of this region, for instance, the surface tension.

During these processes heat and mass transfer take place simultaneously. Non-equilibrium thermodynamics is a natural tool to describe these phenomena. It gives

a systematic derivation of the necessary relations between the temperature and chemical potential (pressure) differences across the surface in terms of the heat and mass fluxes through the surface. Within this framework, the transport through the surface is determined by the transfer coefficients, which are the proportionality factors in a linear relations between the forces and the fluxes. It is therefore important to investigate how evaporation and condensation depend on the values of the interfacial coefficients. There is, for instance, evidence [2, 14] that coupling of heat and mass transfer is much more important in the interfacial region than in the description of non-equilibrium processes in the bulk phase. It can be shown that neglecting these coupling effects, as is often done, is equivalent to neglecting the enthalpy differences in the two phases for the components involved [2].

There are several methods to investigate surface phenomena. They may be classified by the applied tool: theoretical, experimental or computational,—or by scale: macroscopic, microscopic and mesoscopic. Each of these methods has advantages and disadvantages.

1.2.1 Experiments

In experiments one can measure directly the thermodynamic forces which one applies to the system and the resulting thermodynamic fluxes [15–17] or the heat of transfer [14, 18].

A spatial resolution of most of the experiments is such that it is not possible to get the details about the temperature distribution in the interfacial region. For instance, the experiments of Badam et al. [17] have a resolution of about 10 μm . They are basically macroscopic.

Experiments are expensive to set up. They also require to treat *each* system at any set of various conditions. As the number of possible mixtures being used in applications is very big as well as the range of conditions they are applied to is very wide, it becomes very inconvenient to use experiments as the only source of transport data.

1.2.2 Computer Simulations

Another source of the data are computer simulations. Non-equilibrium processes are described well by non-equilibrium molecular dynamic simulations [19–22]. The motion of each molecule is determined mechanically by Newton's equation. Each particle moves in the potential field which is created by all other particles. Usually this is a kind of Lennard–Jones (LJ) potential, which is known to represent well the interactions in the fluid.

There are a few problems with molecular dynamics as well. Given the exact interaction potential between molecules one may in principle determine the motion

of all the molecules exactly. The interaction potential between molecules is long-range and in order to get correct data one may not restrict oneself by only the interaction with nearest neighbors. In principle one should take into account interaction of each molecule with all other molecules. In contrast to hard-sphere gas, molecules in which interact only during collision, effects in real fluids are described by taking into account the whole LJ-potential, including its “tail”. In order to save on computer time, one uses a cut-off LJ-potential, however. This leads to considerable error in the determination of, for instance, the surface tension [23]. Also the value of the transfer coefficients for the surface depend strongly on this cut-off [22].

Another restriction in molecular dynamics, which is limited by the computational power, is the number of molecules. Taking into account all the interactions between the molecules, not many molecules can be treated in simulations. Typically, it is 10^3 – 10^4 particles. Since the interfacial region is very thin, the typical number of particles which actually “belong” to this region might be small compared to this number. One should be careful applying thermodynamic statements to such systems.

1.2.3 Theory

For a meaningful interpretation of experiments or simulations it is important to have a theory. The experiments and simulations also verify or reject the validity of the theory. Depending on the length scales involved there are several levels of description.

1.2.3.1 Microscopic Approach

On a microscopic level one considers separate molecules. They are treated using statistical mechanical methods or using the equation of motion of separate particles [24]. If the number of particles is big enough, their behavior is determined by collective properties, which are studied by statistical mechanics. The Green–Kubo relations relate bulk transport coefficients to equilibrium correlation functions of the system. There are several difficulties when building the statistical description for surfaces. As it was said, the number of molecules in the interfacial region is not big, so it is inappropriate to apply the ordinary bulk approach there. The boundaries of the interfacial region need to be specified. Such a specification identifies the system one works with. The major problem is related to the fact that the density distribution in equilibrium interfacial region is not uniform: it varies from a low value in the gas phase to a large value in the liquid phase.

Another microscopic approach is to use kinetic theory to describe transport through the surface. Originally it was built for ideal gases of hard spheres. The results of this approach should therefore be most appropriate when the density of the gas is low and the interaction potential is short range. Simulations confirm this [22, 25].

1.2.3.2 Mesoscopic Approach

On a mesoscopic level one consider small volume elements with a nanometer size. This allows to introduce field variables, such as local density or local temperature. These variables are the averages of some microscopic properties over a small volume. They depend continuously on the position and time. An important example of the mesoscopic approach is the square gradient model, which is the subject of this thesis. It makes it possible not only to describe fluctuations near critical point in the homogeneous phases, but also to give a detailed description of the interfacial region at temperatures far from critical temperature. In [Sect. 1.4.1](#) we will give a short introduction to the square gradient model.

There are many problems for which mesoscopic non-equilibrium thermodynamics is relevant. We refer to the monograph of de Groot and Mazur [[1](#), pp. 226–234] for an introduction in this method.

1.2.3.3 Macroscopic Approach

On a macroscopic level of description of a homogeneous phase one considers the thermodynamic properties averaged over the whole system. In the thermodynamic limit (i.e. infinite volume and quasistatic processes) this gives the exact properties of a system. In non-equilibrium systems all the properties vary in space and in time. Everywhere the system may be assumed as being in local equilibrium, which makes a description using non-equilibrium thermodynamics possible.

In the description of the transport properties through the interface one may consider the interfacial region as a separate phase. The origin of this idea comes from equilibrium, where the surface can be described by the Gibbs excess densities. The coexistence between liquid and vapor implies therefore the existence of the Gibbs surface which modifies the thermodynamics of a system. This approach uses the fact that the system is in equilibrium, i.e. the temperature profile as well as the chemical potentials are constant through the homogeneous phases and the interface. This is not the case for non-equilibrium systems. One may however simplify the description assuming that it is possible to assign a temperature and a chemical potential to the surface. Thus a non-equilibrium system with an interface may be considered as three adjacent macroscopic phases: gas, interface, and liquid. The transport in such systems has been extensively studied using non-equilibrium thermodynamics in the monograph by Kjelstrup and Bedeaux [[2](#)]. In [Sect. 1.4.2](#) we give some further introductory remarks about this approach.

1.2.4 *Multi-Component Systems*

Evaporation of a single component is already a difficult problem. All the statements given above are true for such system. It becomes even more difficult when

one wants to describe multi-component evaporation and condensation. One needs to take into account effects which are present due to mixing. This is limited not only to the use of special mixing rules. The presence of special components may favor another component to accumulate in the surface, i.e. adsorption. Other components may favor the homogeneous phases.

1.3 Structure of the Thesis

1.3.1 Nomenclature

1.3.1.1 Notation Convention

In this thesis we study the interface between multi-component phases, gas and liquid, using the continuous mesoscopic approach. The continuous description uses the field variables such as the temperature $T(\mathbf{r}, t)$ of the velocity $\mathbf{v}(\mathbf{r}, t)$ at a particular position \mathbf{r} in a specified time t . We refer to Appendix A for the description of the symbols and nomenclature used in the thesis.

The field description also uses *specific* (i.e. per unit of mass or per unit of mol) quantities such as the specific internal energy. It is common in physics to make the derivation in mass specific units while chemists use molar specific units. The equilibrium properties are usually given in molar units while the dynamics is usually described in mass units. While these two descriptions are equivalent in equilibrium, it is extremely inconvenient to use molar units in non-equilibrium. The main reason for this is the equation of motion, which is essentially given for mass units. For one-component fluids the form of this equation in molar units is the same as in mass units, since the molar mass M is a constant number. The molar mass of mixtures, to be defined below, depends, in general, on position and time. The form of the equation of motion in molar units is therefore different from the one in mass units. Another reason is the use of the barycentric velocity, i.e. the velocity of the center of mass, for the description of the dynamics of the system. The use of an alternative velocity, like the molar velocity, does not eliminate these inconveniences.

In view of that, we will use mass specific units everywhere in this thesis if not specified the opposite. Thus, most of derivation is done in mass specific units. We will use the molar units when we speak about the homogeneous thermodynamics in Sect. 3.4 and in some other places where we specify it explicitly. Furthermore, we give the numerical results mostly in molar specific units. These are the numerical profiles in Sect. 4.5 and the whole Chap. 5. For a specific quantity q we will use superscript v , if it is a specific quantity per unit of mol, and superscript m , if it is a specific quantity per unit of mass. If a specific quantity q is used without any of these superscripts, it is a mass specific quantity.

Some aspects of the description require the use of *densities*, i.e. quantities per unit of volume. We will use superscript v to indicate a density per unit of volume.

Thus, for internal energy, u^m or u is the mass specific internal energy, u^v is the molar specific internal energy, and u^v is internal energy density per unit of volume.

We use common symbols for mass and molar densities. Thus, ρ is the mass density of the mixture per unit of volume and c is the molar density of the mixture per unit of volume. Furthermore, ρ_i and c_i , where $i = \overline{1, n}$ are, respectively, the mass and the molar density of the i th component. Apparently, $\rho = cM$ and $\rho_i = c_i M_i$ where M and M_i are, respectively, the molar mass of the mixture and the molar mass of component i . While the molar masses of the components are constants, the overall molar mass is not.

We will use the mass and the molar fractions which are defined, respectively, as $\xi_i \equiv \rho_i/\rho$ and $\zeta_i \equiv c_i/c$. It follows therefore that $M = \sum_{i=1}^n \zeta_i M_i$. In general, for any specific quantity like, for instance, the internal energy, $u = \sum_{i=1}^n \zeta_i u_i$, where u_i is the partial internal energy of component i .

1.3.1.2 Naming Convention

Within the thesis we will use the terms *interfacial region*, *interface*, *surface* as synonyms. We will also use the terms *bulk* and *homogeneous phase* as synonyms. The latter should not be confused with a pure one-phase fluid.

In an n -component mixture there are $n + 2$ independent thermodynamic variables, for instance, the temperature, the pressure and n masses of components. However, a continuous description implies only $n + 1$ independent thermodynamic variables, since all the extensive variables are scaled by either total mass, total number of mols, or total volume. All the variables become intensive therefore. We will nevertheless continue to call the quantities like the mass densities or the partial internal energy the *extensive* quantities to distinguish them from the quantities like the temperature or the chemical potentials, which we will continue to call *intensive*.

In this thesis we are not focused on the specific mixing conditions and other related issues. We will therefore use the terms *partial quantity*, *partial specific quantity*, and *specific quantity* of component i as synonyms. The latter should not be confused with the specific quantity of the pure component i .

Because of the identity $\sum_{i=1}^n \zeta_i = 1$, many thermodynamic relations contain combinations $q_i - q_n$ of the partial specific quantity q . For instance, as we will see further, the combination $\mu_i - \mu_n$ is very common both in equilibrium thermodynamics and in the description of the transport processes. We will therefore define $\psi_i \equiv \mu_i - \mu_n$ and call ψ_i the *reduced chemical potential* of component i or the *chemical potential difference* of component i .

All the derived equations must be Galilean invariant, i.e. independent of the *frame of reference*. Moreover all the measurable quantities must be independent of the reference state for the definition of the thermodynamic potentials. We use this observation in order to distinguish between the *measurable heat flux*, the *heat flux*, and the *total energy flux* as well as between the corresponding resistivities. We address and discuss these issues in [Chap. 3](#).

We use the term *resistivities* to describe phenomenological coefficients in local force–flux relations written on mesoscopic level, while we use the term *resistances* to describe the phenomenological coefficients in force–flux relations written for the whole surface. The former are used starting from [Chap. 3](#), while the latter appear in [Chap. 6](#) for the first time.

1.3.2 Overview of the Thesis

There have been prepared four articles [[3–6](#)] the contents of which are presented (with some modifications) in the following seven chapters. Here we give a brief review of the thesis.

In the next section we give a review of the state of the art in the description of the the surfaces using the square gradient theory and an overview of the macroscopic non-equilibrium thermodynamics for surfaces. In the subsequent chapters we focus on particular topics of our work. Each issue addressed there has a detailed introduction and conclusion with relevant references.

In [Chap. 2](#) we discuss the equilibrium interfacial thermodynamics using the square gradient theory for mixtures. The equilibrium square gradient theory of a single component has been developed over many years and we give an overview in the introduction to the chapter. Less work has been done for mixtures, however. We derive all the properties and relations required for the subsequent analysis. We give explicit expressions for the pressure tensor and other thermodynamic quantities for multi-component systems in the interfacial region. To our knowledge, many of these expressions were not given earlier for mixtures. We also focus on the Gibbs relation in the surface and discuss its difference from the one in the bulk.

In [Chap. 3](#) we build the general non-equilibrium description for the interfacial region. It requires the hydrodynamic equations, equilibrium thermodynamics, and the phenomenological force–flux relations. We use the usual hydrodynamic conservation laws. Equilibrium thermodynamics for mixtures requires, in its turn, the square gradient model and the homogeneous mixture theory. The former one, being developed in [Chap. 2](#) is extended directly to the non-equilibrium case. It requires, among other things, postulating the Gibbs relation, and we discuss this issue. A particular mixture theory of a homogeneous fluid is not a focus of this thesis, so we consider one-fluid model for mixtures as being satisfactory for most of the practical purposes. Using the non-equilibrium Gibbs relation and the balance equations we obtain expression for the entropy production for the mixture’s surface. The linear force–flux relations, which come from the expression for the entropy production, require the consideration of the surface symmetry. The three-dimensional isotropy of the fluid is broken and we discuss in detail the two-dimensional isotropy of the surface and the resulting phenomenological relations.

In [Chap. 4](#) we study a particular binary mixture, which contains cyclohexane and *n*-hexane as components. We give an extensive description of numerical procedure used to solve a system of non-linear differential equations. We choose a

particular point in the phase diagram as initial coexistence state and perturb the system out of equilibrium. We study the behavior only in the neighborhood of this state and do not go to all possible domains in the phase diagram. As a result, we give continuous profiles of various thermodynamic quantities which this mixture has in the interfacial region.

In [Chap. 5](#) we focus on the surface property which is important for macroscopic description of interfaces. We perform a numerical verification of the hypothesis of local equilibrium for the surface. The numerical analysis makes it possible to discuss in detail what local equilibrium implies for a surface.

In [Chap. 6](#) and subsequent chapters, we focus on the overall surface resistance to heat and mass transfer through the surface. This is done for stationary states as the commonly used condition in many applications. It is therefore interesting to study this case separately. We do it with no restrictions to a particular mixture. The local resistivities in the interfacial region are not measurable, so it is desired to investigate the effect of the whole surface, which is given by the overall resistances. Moreover, these coefficients are important in the macroscopic approach where one uses the hypothesis of local equilibrium for the surface and considers therefore the surface as a separate phase.

In [Chaps. 7](#) and [8](#) we derive the expressions for the overall surface resistances given the local expressions for the resistivities. In [Chap. 7](#) the surface resistances are obtained from the non-equilibrium forces and fluxes through the surface. This is done using two different methods and the results are compared to the results of kinetic theory. In [Chap. 8](#) we obtain the surface resistances directly from the local resistivity profiles using integral relations. This also requires the equilibrium coexistence profiles but not the non-equilibrium ones. We consider these methods for an arbitrary binary mixture, they can easily be generalized to multi-component systems. We then again study the numerical values of the surface resistances for the mixture of cyclohexane and *n*-hexane.

Finally, in [Chap. 9](#) we give concluding remarks to the whole thesis and possible directions for further research.

1.4 Non-Equilibrium Thermodynamics of a Surface

1.4.1 The Square Gradient Theory

The square gradient model has been used for many years to describe phenomena related to coexistence of different phases. It originates from van der Waals [12] who in 1893 introduced a nonlocal contribution to the Helmholtz free energy density of coexisting vapor and liquid (see also translation by Rowlinson [11]). In 1901 Korteweg [26] introduced a nonlocal contribution to the stress tensor to describe the dynamics of moving fluids (see also Appendix 2.B). In 1950 Ginzburg and Landau [27] introduced a nonlocal contribution to the Hamiltonian to describe

a superconductor near the critical point. Finally, Cahn and Hillard in 1958 [13] used a nonlocal contribution to the Helmholtz energy to describe a liquid–liquid interface of a binary mixture.

In contrast to the description of a surface which assumes existence of a sharp boundary between two phases, it is assumed in the square gradient theory that all the quantities vary smoothly within a very thin interfacial region. Thus, the fluid behavior at any position \mathbf{r} is determined not only by the local density $\phi(\mathbf{r})$ but also by the densities in the nearest surroundings. This is accounted by allowing the system's Hamiltonian depend on density gradients. Usually, the gradients of higher order than two are neglected, and the Helmholtz free energy of an isotropic fluid is written as

$$F(T; \phi) = F_0(T; \phi) + \frac{1}{2} \int_V d\mathbf{r} \kappa(\phi, T) |\nabla \phi(\mathbf{r})|^2 \quad (1.1)$$

where κ is some coefficient which in general depends on the density and the temperature, and F_0 is the local part of the Helmholtz energy.

The square gradient model is very fruitful since it allows to describe many different phenomena related to the surface. Among them are theory of capillarity [28, 29], critical phenomena and spinodal decomposition [30, 31], dynamic phase separation [32–34], mixture diffusion [35–38], heat transport [7, 39, 40], etc. This made the square gradient model to be also known as the *van der Waals square gradient model*, the *H-model*, *diffuse-interface model*, *phase-field model*, *fluctuations model*. It has been widely applied both to equilibrium and non-equilibrium phenomena. It has also been used for liquid–vapor, liquid–liquid, and liquid–solid interfaces. We refer to the above articles and references therein for deeper review.

Different areas of focus of the square gradient model imply different approximations. Thus, for the mixing phenomena one often assumes that fluids are incompressible or immiscible [35]. In many dynamical problems it is assumed that the temperature is constant [31] throughout the system. Both of the assumptions are not unreasonable and reflect the applications these descriptions are used for. However, this restricts the system to such conditions where there is no heat flow or fluids may mix only in the interfacial region. Many of the approaches, which take into account both the temperature and density variations in non-equilibrium, assume no coupling between heat and mass transfer [39] which is expected to be important in the interfacial region [2]. Some of the approaches perform the analysis in general but make the above simplifications for a specific application [33, 37].

Most of the extensions of the square gradient model assume only one variable to be treated as the order parameter in the interfacial region. This is either the density in a one-component fluid or the fraction of one of the components in a binary mixture. Thus, these analyses are restricted in number of components to two. This does not govern such industrial applications as distillation, where the number of components may be large.

Another issue, which is important in the thermodynamic non-equilibrium description, is the Gibbs relation. It is probable, that because of the gradient

contributions to the Helmholtz energy, the Gibbs relation would also have such contributions. Many of the descriptions use the local form of the Gibbs relation.

In this thesis we try to establish a systematic approach which is free of most simplifications. We follow the method of irreversible thermodynamics stated in [1] for homogeneous systems. It requires a consecutive coverage of the equilibrium thermodynamics and equation of state, the hydrodynamics of a fluid, the Gibbs relation, the entropy production and the phenomenological force–flux relations.

1.4.2 Macroscopic Transport

A different way to describe a surface is using the excess quantities. This approach originates from Gibbs [41], who introduced the excesses of thermodynamic densities in equilibrium. A two-phase system is then considered as two homogeneous phases separated by a surface phase. The intensive properties, such as the temperature, are constant throughout the system in equilibrium. All three phases, two bulk phases and surface, have the same values of these properties. The extensive properties of the bulk phases, such as the density, are determined by the coexistence conditions. The excess densities play the role of the extensive properties for the surface. Spatially they are described by, respectively, the constant values in either bulk phase and singular (δ -function like) excesses at the dividing surface.

During evaporation and condensation heat and mass is transported through the interface. The common description of these phenomena uses certain assumptions which are debatable. For instance, one usually assumes equilibrium conditions at the interface [42]. This is a zero approximation and it is desirable to extend it to a more accurate theory.

It is possible to describe the interface using the excess densities in non-equilibrium [43]. It is, however, more complicated since the intensive properties are no longer constant throughout such a system. One has to use the local equilibrium hypothesis, assuming that every small element of the fluid is in local equilibrium. For the surface it implies that one may speak about the temperature of the surface T^s and the chemical potentials of the surface μ_i^s , which are related by the usual thermodynamic relation

$$u^s = T^s s^s - \gamma^s + \sum_{i=1}^n \mu_i^s \Gamma_i^s \quad (1.2)$$

where u^s , s^s , Γ_i^s are the excesses of the internal energy, entropy and density per unit area, and γ^s is the surface tension. One may therefore build a non-equilibrium description of singular surfaces [44].

In the non-equilibrium description of the interfacial phenomena, one observe jumps of, for instance, the temperature between two adjacent bulk phases. Moreover, the temperature of the non-equilibrium surface may be different from either bulk values. Thus, macroscopic description of non-equilibrium surfaces is

essentially discontinuous. Given a traditional non-equilibrium approach [1] and hypothesis of local equilibrium of a surface, it was possible to build a systematic theory which describes transport through a surface using the excess densities and surface intensive properties [2]. Within this theory the expression for the entropy production of the surface was obtained

$$\sigma^s = J_q^s X_q^s + \sum_{i=1}^n J_i^s X_i^s \quad (1.3)$$

where J_q^s is the heat flux, J_i^s are the matter fluxes and X_q^s and X_i^s are corresponding interfacial forces. This implies the phenomenological force–flux relations

$$\begin{aligned} X_q^s &= R_{qq}^s J_q^s + \sum_{i=1}^n R_{qi}^s J_i^s \\ X_j^s &= R_{jq}^s J_q^s + \sum_{i=1}^n R_{ji}^s J_i^s \end{aligned} \quad (1.4)$$

Within the hypothesis of local equilibrium of a surface, the coefficients R^s are the surface resistances, which control the transport of heat and mass through the surface. In a macroscopic theory they are parameters, which determine the jumps of the intensive variables through the surface.

The common description of heat and mass transfer through the surface consider only pure heat conduction or pure diffusion and neglects the coupling effects between heat and mass [2]. Neglecting the coupling coefficients was shown to violate the second law of thermodynamics for a one-component system [45]. The coupling is important since the corresponding transfer coefficients depend on the enthalpy of vaporization. The significance of this quantity in this context is due to the large difference between the liquid and the vapor values of the enthalpy.

The situation becomes even more complicated when one consider evaporation in mixtures. These processes happen in such industrial applications as distillation and therefore the precise description is important. Depending on conditions one can get the mass fluxes of components in the same or in the opposite directions.

There has been done a number of studies of the interfacial transport for one-component systems: experiments [14, 15, 18, 46], molecular dynamic simulations [19, 20, 25, 47, 48], kinetic theory [49–51] and square gradient continuous description [9, 10]. All these works use different approaches, which allows one to investigate different aspects. Mainly one-component systems have been studied. One of the points of interest is the dependence of the overall interfacial resistances on the continuous profiles. Once we have a description which relates the resistance of the Gibbs surface [52] to the continuous profiles of, in particular, local resistivities, we can describe the surface separately from the adjacent bulk phases which is closely related to hypothesis of local equilibrium of a surface [2].

In this thesis we establish a link between the continuous description of a mixture's surface under non-equilibrium conditions using the square gradient theory

and discontinuous description which uses the assumption of local equilibrium of a surface. Using the continuous description we verify this hypothesis numerically. The square gradient theory allows us to establish the macroscopic relation (1.3) and obtain the expressions for the interfacial resistances R^s .

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Chapter 2

Equilibrium Square Gradient Model

2.1 Introduction

In order to describe the equilibrium properties of an interface between two coexisting phases, using a continuous model, it is necessary to consider contributions to the Helmholtz energy which depend on the gradients of for instance the density [1]. Van der Waals [2, 3] was in 1893 the first to introduce such a term for a one-component system. In 1958 Cahn and Hilliard [4] extended the analysis of van der Waals and introduced gradient terms of the mol fraction in binary mixtures. As the Helmholtz energy density given by van der Waals is no longer a function of the local density or local densities alone. The continuous description is in other words “not autonomous”. We refer to the monograph by Rowlinson and Widom [1] for a thorough discussion of the van der Waals model in general and of this point in particular. A lot of work on the equilibrium gradient model was done by Cornelisse [5]. We refer to his thesis for the relevant references.

The gradient model is often used for a system in which properties vary only in one direction. We do not restrict ourself in this manner and do the analysis for a three-dimensional system.

We use the standard thermodynamic variables which obey the standard thermodynamic relations for homogeneous mixtures. In Sect. 2.2 we consider an inhomogeneous mixture. We postulate the dependence of the specific Helmholtz energy on the thermodynamic variables and their gradients, using the fact, that in equilibrium the temperature is constant. Using the fact that in equilibrium the total Helmholtz energy has a minimum and that the amount of the various components is fixed, we derive the expressions for the chemical potentials of all the components, using Lagrange’s method. This is done for specific variables in Sect. 2.3 and for mass densities in Sect. 2.4. Extending a method developed by Yang et al. [6], an expression is also found for the pressure tensor. We derive the different forms of the Gibbs relations: for a variation of thermodynamic quantities at a fixed position and for their difference along spatial coordinates. Their importance is crucial for the non-equilibrium description which should be based on the

equilibrium analysis. Explicit expressions are also given for the internal energy, the enthalpy, and the Gibbs energy densities. In [Sect. 2.6](#) we give a discussion and conclusion.

2.2 The Gradient Model

In order to describe inhomogeneous systems in equilibrium, one could assume that this can be done by the usual thermodynamic variables, which depend on the spatial coordinates. All standard thermodynamic relations are then assumed to remain valid.

As van der Waals has shown for a one-component system [\[3\]](#), this, however, is not enough to describe the surface. It is necessary to assume that thermodynamic potentials, particularly the Helmholtz energy density, also depend on spatial derivatives of the density. Cahn and Hilliard have shown for a binary mixture [\[4\]](#), that the Helmholtz energy should depend on the gradients of the mole fraction of one of the components. For a multi-component non-polarizable mixture the general form of the Helmholtz energy density is

$$f^v(\mathbf{r}) = f_0^v(T; \phi_1(\mathbf{r}), \dots, \phi_n(\mathbf{r})) + \frac{1}{2} \sum_{i,j=1}^n \tilde{\kappa}_{ij}(\phi_1, \dots, \phi_n) \nabla \phi_i(\mathbf{r}) \cdot \nabla \phi_j(\mathbf{r}) \quad (2.1)$$

where f_0^v is the homogeneous Helmholtz energy density and $\phi_i, i = \overline{1, n}$, are the generalized densities. They can be either the mass density ρ_i or the molar density c_i of each of the component. They can also be either the total density ρ together with the $n - 1$ mass fractions of the components, $\{\xi_1, \dots, \xi_{n-1}\}$, or the total concentration c together with the $n - 1$ mol fractions of the components, $\{\zeta_1, \dots, \zeta_{n-1}\}$. The corresponding sets of variables are treated in [Sects. 2.3](#) and [2.4](#). The gradient coefficients $\tilde{\kappa}_{ij}$ are different for each set of the variables. They depend only on these variables, but neither on the temperature, nor on the position explicitly.

This form of the Helmholtz energy density is obtained by the following arguments (cf. also [\[2, 3, 6\]](#)). Dependence of the Helmholtz energy density on the density gradients can be represented by the Taylor series in these gradients. We describe here isotropic fluids, so any coefficient in this Taylor series may not depend on any direction and thus should be a scalar. The zeroth term, taken when all the gradients are equal to zero, is the homogeneous Helmholtz energy $f_0^v(T; \phi_1(\mathbf{r}), \dots, \phi_n(\mathbf{r}))$. In equilibrium, the total Helmholtz energy of the system has a minimum. Thus, the first order term, with the first order density gradients, $\nabla \phi_i(\mathbf{r})$, is zero. The second order term contains the terms which are quadratic in the first order density gradients $\nabla \phi_i(\mathbf{r}) \cdot \nabla \phi_j(\mathbf{r})$, and the terms which are linear in the second order density gradients $\nabla^2 \phi_i(\mathbf{r})$. The latter ones, however, contribute to the total Helmholtz energy the same way as the former ones:

$$\begin{aligned}
\int_V d\mathbf{r} \tilde{\kappa}_i \nabla^2 \phi_i(\mathbf{r}) &= - \int_V d\mathbf{r} \nabla \tilde{\kappa}_i \cdot \nabla \phi_i(\mathbf{r}) + \int_V d\mathbf{r} \nabla \cdot (\tilde{\kappa}_i \nabla \phi_i(\mathbf{r})) \\
&= - \int_V d\mathbf{r} \sum_{j=1}^n \frac{\partial \tilde{\kappa}_i}{\partial \phi_j} \nabla \phi_j(\mathbf{r}) \cdot \nabla \phi_i(\mathbf{r}) + \int_S d\mathbf{S} \tilde{\kappa}_i \cdot \nabla \phi_i(\mathbf{r})
\end{aligned} \tag{2.2}$$

The first term on the right-hand side of this equation can be combined with the quadratic term in the first order gradients. The second one can be chosen equal to zero by proper choice of the boundaries of integration. Thus, we end up with Eq. 2.1 for the specific Helmholtz energy where the coefficients $\tilde{\kappa}_{ij}$ are the combinations of those from the quadratic in the first order density gradients term and the corresponding ones from the linear in the second order density gradients term. For ease of notation we will write $\tilde{\kappa}_{ij}$ instead of $\tilde{\kappa}_{ij}(\phi_1(\mathbf{r}), \dots, \phi_n(\mathbf{r}))$, remembering their dependence on these variables.

We note the ambiguity in the definition of the specific Helmholtz energy. Different expressions for $f(\mathbf{r})$ give the same expression for the total Helmholtz energy F , due to the cancelation of the boundary contributions. This can be interpreted such that the measurable quantity is only the total Helmholtz energy, but not the specific one. To build the local description we need the local quantities, however. We will use Eq. 2.1 for the specific Helmholtz energy, remembering that a divergence of a vector field, the normal component of which is zero on the boundary, can in principal be added. We show in Appendix 2.A that the ambiguity in the Helmholtz energy density in the interfacial region does not lead to an ambiguity in the pressure and chemical potentials in the interfacial region.

We may choose the matrix $\tilde{\kappa}_{ij}$ to be symmetric with respect to the component number ($\tilde{\kappa}_{ij} = \tilde{\kappa}_{ji}$) without loss of generality (since it appears only in symmetric combinations). We shall always take $\tilde{\kappa}_{ij}$ independent of the temperature.

We note, that the square gradient model is, as it has been used here, a general approach and is not only applied to surfaces. It has, for instance, been used in the description of critical behavior using renormalization group theory [7, 8]. In this thesis we will focus on its use for the description of the surface.

In the following chapter, where we extend the analysis to non-equilibrium two-phase mixtures, we need all the thermodynamic variables. We therefore derive them and the necessary relations here for the given choice of the independent variables. This is done in Sect. 2.3. for mass specific variables. We determine how the Helmholtz energy varies with a change of the variables and with a change of position and obtain so-called Gibbs relations in Sect. 2.3.2. In Sect. 2.3.3 we determine the physical meaning of the Lagrange multipliers and other quantities, for which expressions are derived. In Sect. 2.4 we derive the results for volume specific variables following the same procedure as in Sect. 2.3.

The analysis for molar specific units or the molar densities per unit of volume is obtained from the present one in a straightforward manner by the replacing mass densities with the molar densities and the mass fractions with the molar fractions. The gradient coefficients $\tilde{\kappa}_{ij}$ should be modified appropriately.

Further we will suppress \mathbf{r} as an argument where this is not confusing. We will indicate \mathbf{r} as an argument mostly to emphasize the dependence of a quantity on position.

2.3 Gradient Model for the Mass Specific Variables

2.3.1 The Lagrange Method

We write the mass specific Helmholtz energy as

$$f(\mathbf{r}) = f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \nabla \rho, \nabla \xi) \quad (2.3)$$

where

$$\mathcal{K}(\rho, \xi, \nabla \rho, \nabla \xi) \equiv \frac{1}{2} \frac{\kappa_{\rho\rho}}{\rho} |\nabla \rho|^2 + \sum_{i=1}^{n-1} \frac{\kappa_{\rho\xi_i}}{\rho} \nabla \rho \cdot \nabla \xi_i + \frac{1}{2} \sum_{i,j=1}^{n-1} \frac{\kappa_{\xi_i \xi_j}}{\rho} \nabla \xi_i \cdot \nabla \xi_j \quad (2.4)$$

and we use ξ as short notation instead of whole set $\{\xi_1, \dots, \xi_{n-1}\}$ and $\nabla \xi$ as short notation instead of $\{\nabla \xi_1, \dots, \nabla \xi_{n-1}\}$. The mass density distributions are such that they minimize the total Helmholtz energy

$$F = \int_V d\mathbf{r} \rho(\mathbf{r}) f(\mathbf{r}) \quad (2.5)$$

Assuming that no chemical reactions occur, the total mass of each component, $m_i = \int_V d\mathbf{r} \xi_i(\mathbf{r}) \rho(\mathbf{r})$ for $i = \overline{1, n-1}$, as well as the overall total mass, $m = \int_V d\mathbf{r} \rho(\mathbf{r})$, are constant. The problem of minimizing the functional (2.5), having n constraints can be done using the Lagrange method. Thus we minimize the integral

$$\Omega = \int_V d\mathbf{r} \rho(\mathbf{r}) \left[f(\mathbf{r}) - \mu_n - \sum_{i=1}^{n-1} \psi_i \xi_i(\mathbf{r}) \right] \equiv - \int_V d\mathbf{r} p(\mathbf{r}) \quad (2.6)$$

where μ_n and ψ_i are scalar Lagrange multipliers. The densities distributions which minimize the integral (2.6) must be solutions of the corresponding Euler–Lagrange equations

$$\begin{aligned} \frac{\partial p}{\partial \rho} - \nabla \cdot \frac{\partial p}{\partial \nabla \rho} &= 0 \\ \frac{\partial p}{\partial \xi_i} - \nabla \cdot \frac{\partial p}{\partial \nabla \xi_i} &= 0, \quad i = \overline{1, n-1} \end{aligned} \quad (2.7)$$

These relations give for the introduced Lagrange multipliers:

$$\begin{aligned}\mu_n &= \frac{\partial}{\partial \rho}(\rho(f_0 + \mathcal{K})) - \sum_{i=1}^{n-1} \psi_i \xi_i - \nabla \cdot \left(\kappa_{\rho\rho} \nabla \rho + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i} \nabla \xi_i \right) \\ \psi_k &= \frac{\partial}{\partial \xi_k}(f_0 + \mathcal{K}) - \frac{1}{\rho} \nabla \cdot \left(\kappa_{\rho\xi_k} \nabla \rho + \sum_{i=1}^{n-1} \kappa_{\xi_i\xi_k} \nabla \xi_i \right), \quad k = \overline{1, n-1}\end{aligned}\quad (2.8)$$

and an expression for p :

$$p(\mathbf{r}) = \rho^2 \frac{\partial}{\partial \rho}(f_0 + \mathcal{K}) - \rho \nabla \cdot \left(\kappa_{\rho\rho} \nabla \rho + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i} \nabla \xi_i \right) \quad (2.9)$$

The ambiguity in $f(\mathbf{r})$ discussed above does not affect the expressions for μ_n , ψ_k and $p(\mathbf{r})$ (see Appendix 2.A). We will see in Sect. 2.3.3 that the Lagrange multipliers μ_n and ψ_k are the chemical potentials of the components and $p(\mathbf{r})$ is a pressure. The exact meaning of this pressure as well as the meaning of the other quantities derived in this section will be discussed in Sect. 2.3.3.

Solving Eq. 2.8 for ρ and ξ , one obtains the density profiles for the system. To do this one needs the values for the Lagrange multipliers μ_n and ψ_k .

Multiplying the first of the equations in Eq. 2.8 with $\nabla \rho(\mathbf{r})$ and the other $(n-1)$ ones with $\nabla \xi_k(\mathbf{r})$ and summing them all up¹ we obtain the following expression

$$\nabla_\alpha \sigma_{\alpha\beta}(\mathbf{r}) = 0 \quad (2.10)$$

where we use the summation convention over double Greek subscripts. The tensor

$$\sigma_{\alpha\beta}(\mathbf{r}) = p(\mathbf{r})\delta_{\alpha\beta} + \gamma_{\alpha\beta}(\mathbf{r}) \quad (2.11)$$

will be identified as the pressure tensor. Furthermore, the tensor

$$\gamma_{\alpha\beta}(\mathbf{r}) = \kappa_{\rho\rho} \frac{\partial \rho}{\partial x_\alpha} \frac{\partial \rho}{\partial x_\beta} + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i} \left(\frac{\partial \xi_i}{\partial x_\alpha} \frac{\partial \rho}{\partial x_\beta} + \frac{\partial \rho}{\partial x_\alpha} \frac{\partial \xi_i}{\partial x_\beta} \right) + \sum_{i,j=1}^{n-1} \kappa_{\xi_i\xi_j} \frac{\partial \xi_i}{\partial x_\alpha} \frac{\partial \xi_j}{\partial x_\beta} \quad (2.12)$$

will be referred to as the *tension tensor*.² We note, that both $\sigma_{\alpha\beta}(\mathbf{r})$ and $\gamma_{\alpha\beta}(\mathbf{r})$ are symmetric tensors.

From the definition (2.6) of the $p(\mathbf{r})$, we can see that the Helmholtz energy given in (2.3) and quantities which are given by the Eqs. 2.8 and 2.9 are related in the following way

¹ This method is a generalization of the one given by Yang et al. [6] for a one-component system.

² This form of the explicit expression for the pressure tensor in the square gradient model for a multi-component mixture was, to the best of our knowledge, not given before. See also the relevant discussion in Appendix 2.B.

$$f(\mathbf{r}) = \mu_n + \sum_{i=1}^{n-1} \psi_i \xi_i(\mathbf{r}) - p(\mathbf{r})v(\mathbf{r}) \quad (2.13)$$

Including a possible divergence term in $f(\mathbf{r})$ would modify this equation by adding this term also on the right hand side.

2.3.2 Gibbs Relations

Before we consider the variation of the thermodynamic quantities, let us make a comment on the notation. In this section we will come up with two different kinds of the Gibbs relation which have different meanings. It is therefore important to understand the precise meaning of the symbols used in them. We use three different symbols to indicate different types of variation of thermodynamic variables. We use symbol δ to indicate that $\delta\phi$ is an independent (total) differential of a thermodynamic quantity ϕ at a particular location \mathbf{r} . We use the notation $\nabla_\alpha\phi$ to indicate the spatial variation of ϕ with respect to coordinate x_α . We use the notation $d\phi$ to indicate the “substantial” differential of ϕ (though it is used only in the following chapters). One should not confuse the symbol δ with an arbitrary variation of a thermodynamic quantity. The meaning of δ here (wherever it is used in the Gibbs relations in this thesis) is the same as the total thermodynamic differential usually denoted by d . We use the notation $\delta\phi$ to distinguish this differential from the spatial variation of ϕ and the “substantial” differential of ϕ . We also use the word *variation* in one of the three above meanings and never in the sense of a variation which depends on a thermodynamic process.

2.3.2.1 Ordinary Gibbs Relation

Consider a variation of the total Helmholtz energy $\mathfrak{D}F[T, \rho, \xi, \nabla\rho, \nabla\xi]$ with respect to the variation of the variables, which it depends on:

$$\mathfrak{D}F[T, \rho, \xi, \nabla\rho, \nabla\xi] = \int_V d\mathbf{r} \{ f(T, \rho, \xi, \nabla\rho, \nabla\xi) \delta\rho + \rho \delta f(T, \rho, \xi, \nabla\rho, \nabla\xi) \} \quad (2.14)$$

where the variation

$$\begin{aligned} \delta f(T, \rho, \xi, \nabla\rho, \nabla\xi) &= \frac{\partial f}{\partial T} \delta T + \frac{\partial f}{\partial \rho} \delta\rho + \sum_{i=1}^{n-1} \frac{\partial f}{\partial \xi_i} \delta\xi_i \\ &+ \frac{\partial f}{\partial \nabla\rho} \cdot \delta\nabla\rho + \sum_{i=1}^{n-1} \frac{\partial f}{\partial \nabla\xi_i} \cdot \delta\nabla\xi_i \end{aligned} \quad (2.15)$$

is the total thermodynamic differential of the specific Helmholtz energy with respect to the thermodynamic variables, which it depends on.³ Given Eqs. 2.3, 2.8, and 2.9, one can show that Eq. 2.15 becomes

$$\delta f(T, \rho, \xi, \nabla \rho, \nabla \xi) = \frac{\partial f_0}{\partial T} \delta T + \frac{p}{\rho^2} \delta \rho + \sum_{i=1}^{n-1} \psi_i \delta \xi_i + \frac{1}{\rho} \nabla \cdot \delta \Theta \quad (2.16)$$

where

$$\begin{aligned} \delta \Theta(\rho, \xi, \nabla \rho, \nabla \xi) \equiv & \left(\kappa_{\rho\rho} \nabla \rho + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i} \nabla \xi_i \right) \delta \rho \\ & + \sum_{k=1}^{n-1} \left(\kappa_{\rho\xi_k} \nabla \rho + \sum_{i=1}^{n-1} \kappa_{\xi_i \xi_k} \nabla \xi_i \right) \delta \xi_k \end{aligned} \quad (2.17)$$

Upon substituting Eq. 2.16 into Eq. 2.14, the term containing $\delta \Theta$ does not contribute to the variation of the total Helmholtz energy: the boundary integral $\int_S d\mathbf{S} \cdot \delta \Theta$ disappears, because we have chosen boundaries of the system such that the density gradients are zero everywhere along the boundaries. Thus, we will interpret the following expression

$$\delta f(T, \rho, \xi, \nabla \rho, \nabla \xi) = \frac{\partial f_0}{\partial T} \delta T + \frac{p}{\rho^2} \delta \rho + \sum_{i=1}^{n-1} \psi_i \delta \xi_i \quad (2.18)$$

as the total thermodynamic differential of the specific Helmholtz energy.

We note the ambiguity in the definition of the total thermodynamic *differential* of the specific Helmholtz energy. Different expressions Eqs. 2.14 and 2.18 for δf give the same expression Eq. 2.14 for $\mathfrak{D}F$, due to the cancelation of the boundary contributions. This can be interpreted such that the measurable quantity is only the total thermodynamic differential of the total Helmholtz energy, but not the total thermodynamic differential of the specific one. This ambiguity is similar to the ambiguity in definition of the specific Helmholtz energy. We will use Eq. 2.18, remembering this ambiguity.

We write Eq. 2.18 in the form

$$\delta f(T, v, \xi_1, \dots, \xi_{n-1}) = -s \delta T - p \delta v + \sum_{i=1}^{n-1} \psi_i \delta \xi_i \quad (2.19)$$

where $v \equiv 1/\rho$ is the specific volume and

³ Within the gradient model, T, ρ , and ξ as well as $\nabla \rho$ and $\nabla \xi$ are considered to be the independent thermodynamic *variables*. The Helmholtz energy density is a function of these variables. Equation 2.15 gives therefore the total differential of f by definition.

$$s \equiv -\frac{\partial}{\partial T} f(T, v, \xi) = -\frac{\partial}{\partial T} f_0(T, v, \xi) \quad (2.20)$$

Equation 2.19 has the form of the usual Gibbs relation for a homogeneous mixture. For an inhomogeneous mixture, however, the validity of such a relation is not obvious. Equation 2.19 together with Eq. 2.13 imply that with respect to the variations of the thermodynamic variables the specific Helmholtz energy is still homogeneous of the first order. We will call Eq. 2.19 the ordinary Gibbs relation. With the help of Eqs. 2.13 and 2.19 we obtain the Gibbs–Duhem relation

$$s(\mathbf{r}) \delta T - v(\mathbf{r}) \delta p(\mathbf{r}) + \delta \mu_n + \sum_{i=1}^{n-1} \xi_i(\mathbf{r}) \delta \psi_i = 0 \quad (2.21)$$

2.3.2.2 Spatial Gibbs Relation

Using the following conditions, which are true for equilibrium

$$\begin{aligned} \nabla T(\mathbf{r}) &= 0 \\ \nabla \mu_n(\mathbf{r}) &= 0 \\ \nabla \psi_i(\mathbf{r}) &= 0, \quad \text{for } i = \overline{1, n-1} \\ \nabla_\alpha \sigma_{\alpha\beta}(\mathbf{r}) &= 0 \end{aligned} \quad (2.22)$$

and Eq. 2.13 together with Eq. 2.11, we obtain

$$\nabla_\beta f(\mathbf{r}) = -p(\mathbf{r}) \nabla_\beta v(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i \nabla_\beta \xi_i(\mathbf{r}) + v(\mathbf{r}) \nabla_\alpha \gamma_{\alpha\beta}(\mathbf{r}) \quad (2.23)$$

We will call Eq. 2.23 the spatial Gibbs relation. As the temperature is independent of position, the expected term $-s(\mathbf{r}) \nabla_\beta T$ is zero.

2.3.3 Equilibrium Surface

Away from the surface $\rho(\mathbf{r}) \rightarrow \rho$, $\xi_k(\mathbf{r}) \rightarrow \xi_k$ and $\nabla \rho(\mathbf{r}) \rightarrow 0$, $\nabla \xi_k(\mathbf{r}) \rightarrow 0$ and we have the homogeneous mixture. In that region we may use the usual thermodynamic relations for the homogeneous mixture. The specific Helmholtz energy is given by

$$f_0(T, c, \xi) = \mu_{n,0}(T, c, \xi) + \sum_{k=1}^{n-1} \psi_{k,0}(T, c, \xi) \xi_k - p_0(T, c, \xi) v \quad (2.24)$$

with the specific entropy, pressure and chemical potential differences given by

$$\begin{aligned}
s_0(T, c, \xi) &= -\frac{\partial}{\partial T} f_0(T, c, \xi) \\
p_0(T, c, \xi) &= -\frac{\partial}{\partial v} f_0(T, c, \xi) \\
\psi_{k,0}(T, c, \xi) &= \frac{\partial}{\partial \xi_k} f_0(T, c, \xi), \quad k = \overline{1, n-1}
\end{aligned} \tag{2.25}$$

such that the differential of the specific Helmholtz energy is given by

$$df_0(T, c, \xi) = -s_0(T, c, \xi) dT - p_0(T, c, \xi) dv + \sum_{k=1}^{n-1} \psi_{k,0}(T, c, \xi) d\xi_k \tag{2.26}$$

where $\psi_{k,0}(T, c, \xi) \equiv \mu_{k,0}(T, c, \xi) - \mu_{n,0}(T, c, \xi)$.

Quantities derived in [Sect. 2.3.1](#) converge in the homogeneous limit in a following way

$$\begin{aligned}
\psi_k &\rightarrow \frac{\partial}{\partial \xi_k} f_0(T, c, \xi) &&= \psi_{k,0}(T, c, \xi) \\
\mu_n &\rightarrow f_0(T, c, \xi) - \sum_{i=1}^{n-1} \psi_{i,0}(T, c, \xi) \xi_i + p_0(T, c, \xi) v = \mu_{n,0}(T, c, \xi) \\
p(\mathbf{r}) &\rightarrow \rho^2 \frac{\partial}{\partial \rho} f_0(T, c, \xi) &&= p_0(T, c, \xi) \\
\sigma_{\alpha\beta}(\mathbf{r}) &\rightarrow p_0(T, c, \xi) \delta_{\alpha\beta} &&= \sigma_{\alpha\beta,0}(T, c, \xi)
\end{aligned} \tag{2.27}$$

We use these limits to determine the meaning of the derived quantities in the interfacial region, where gradients are not negligible.

In equilibrium ψ_k and μ_n are everywhere constant. Away from the surface they represent the homogeneous chemical potentials, which in equilibrium should be constant everywhere, particularly throughout the whole interfacial region. Thus it is natural to identify μ_n and ψ_k with, respectively, the chemical potential of the n th component and the difference between the chemical potential of the k th and the n th components, also within the interfacial region.

To determine the meaning of $p(\mathbf{r})$ and $\sigma_{\alpha\beta}(\mathbf{r})$ we have to resolve an ambiguity in the definition of $\sigma_{\alpha\beta}(\mathbf{r})$. It follows from [Eq. 2.10](#) that a constant tensor can be added to $\sigma_{\alpha\beta}(\mathbf{r})$ without affecting the validity of this equation. In a homogeneous limit this tensor does not vanish, so it should be present in the homogeneous tensor $\sigma_{\alpha\beta,0}(\mathbf{r})$, which is proportional to the homogeneous pressure $p_0(T, c, \xi)$. The homogeneous pressure $p_0(T, c, \xi)$, however, is determined unambiguously by the specified equations of state. It follows then that this constant tensor has to be equal to zero and $\sigma_{\alpha\beta}(\mathbf{r})$ is given by [Eq. 2.11](#) unambiguously.

Using that $\psi_k = \mu_k - \mu_n$ and μ_n have the same meaning as in the bulk phase and [Eq. 2.13](#), it is then also natural to identify $p(\mathbf{r})$ given by [Eq. 2.9](#) with a pressure everywhere. This pressure is not constant, however. The tensor $\sigma_{\alpha\beta}(\mathbf{r})$ can be identified with the tensorial pressure. It is known that at the surface one can

speak about the “parallel” and the “perpendicular” pressure [1], so the pressure reveals tensorial behavior. For a flat surface, when all the properties change in one direction, say x , one can show that $\sigma_{xx}(\mathbf{r})$ is the “perpendicular” pressure and $p(\mathbf{r}) = \sigma_{yy}(\mathbf{r}) = \sigma_{zz}(\mathbf{r})$ is the “parallel” pressure. For curved surfaces such an identification, however, can in general not be made.

One can also conclude, that the quantity, determined by Eq. 2.20 is the specific entropy of the mixture in the interfacial region. It does not have gradient contributions. This is due to the assumption that the coefficients of the square gradient contributions are independent of temperature. We refer to van der Waals [1–3] who discussed this property.

We shall also define other thermodynamic potentials in the square gradient model for the interfacial region. Considering Eq. 2.13 and conforming to Eq. 2.27 we define interfacial specific internal energy, enthalpy and Gibbs energy densities as follows

$$\begin{aligned} u(\mathbf{r}) &\equiv f(\mathbf{r}) + s(\mathbf{r})T \\ h(\mathbf{r}) &\equiv u(\mathbf{r}) + p(\mathbf{r})v(\mathbf{r}) \\ g(\mathbf{r}) &\equiv f(\mathbf{r}) + p(\mathbf{r})v(\mathbf{r}) \end{aligned} \quad (2.28)$$

It is important to realize that these thermodynamic relations are true in the interfacial region only by definition. One can also find support for these definitions in [9] where they were considered for a simplified one-component system.

Using Eqs. 2.19 and 2.28, for the internal energy at each point in space we then get the ordinary Gibbs relation

$$\delta u(s, v, \xi_1, \dots, \xi_{n-1}) = T \delta s(\mathbf{r}) - p(\mathbf{r}) \delta v(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i \delta \xi_i(\mathbf{r}) \quad (2.29)$$

From Eqs. 2.22 and 2.28 we get the spatial Gibbs relation

$$\nabla_\beta u(\mathbf{r}) = T \nabla_\beta s(\mathbf{r}) - p(\mathbf{r}) \nabla_\beta v(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i \nabla_\beta \xi_i(\mathbf{r}) + v(\mathbf{r}) \nabla_\alpha \gamma_{\alpha\beta}(\mathbf{r}) \quad (2.30)$$

One can easily write the Gibbs relations for other thermodynamic potentials.

2.4 Gradient Model for the Densities (Per Unit of Volume)

We write the extended Helmholtz energy per unit of volume as

$$f^v(\mathbf{r}) = f_0^v(T, \rho) + \mathcal{K}^v(\rho, \nabla \rho) \quad (2.31)$$

where

$$\mathcal{K}^v(\rho, \nabla \rho) \equiv \frac{1}{2} \sum_{i,j=1}^n \kappa_{\rho_i \rho_j} \nabla \rho_i(\mathbf{r}) \cdot \nabla \rho_j(\mathbf{r}) \quad (2.32)$$

We use ρ as an argument as a short notation for the set $\{\rho_1, \dots, \rho_n\}$ and $\nabla\rho$ as a short notation for $\{\nabla\rho_1, \dots, \nabla\rho_n\}$ in Sect. 2.4. As it is used only as an argument, it should not be confused with the total density.

We will not repeat in details the procedure, given in Sect. 2.3 and give only the results here. Using the Lagrange method we obtain the expressions for the constant Lagrange multipliers, which are equal to the chemical potentials

$$\mu_k = \frac{\partial}{\partial \rho_k} (f_0^v + \mathcal{K}^v) - \sum_{i=1}^n \nabla \cdot (\kappa_{\rho_i \rho_k} \nabla \rho_i) \quad (2.33)$$

and the expression for a pressure p :

$$p(\mathbf{r}) = \sum_{i=1}^n \rho_i \frac{\partial}{\partial \rho_i} (f_0^v + \mathcal{K}^v) - (f_0^v + \mathcal{K}^v) - \sum_{i,j=1}^n \rho_j \nabla \cdot (\kappa_{\rho_i \rho_j} \nabla \rho_i) \quad (2.34)$$

which was defined by

$$f^v(\mathbf{r}) = \sum_{i=1}^n \mu_i \rho_i(\mathbf{r}) - p(\mathbf{r}) \quad (2.35)$$

One can derive the same symmetric pressure tensor $\sigma_{\alpha\beta}(\mathbf{r})$ as in Eq. 2.11, which obeys the relation Eq. 2.10, where the symmetric tension tensor $\gamma_{\alpha\beta}(\mathbf{r})$ is given by

$$\gamma_{\alpha\beta}(\mathbf{r}) = \sum_{i,j=1}^n \kappa_{\rho_i \rho_j} \frac{\partial \rho_i}{\partial x_\alpha} \frac{\partial \rho_j}{\partial x_\beta} \quad (2.36)$$

Varying the total Helmholtz energy $F[T, \rho, \nabla\rho]$ with respect to the variation of the variables, we obtain the total thermodynamic differential of the specific Helmholtz energy as

$$\delta f^v(T, \rho, \nabla\rho) = \frac{\partial f_0^v}{\partial T} \delta T + \sum_{k=1}^n \mu_k \delta \rho_k + \nabla \cdot \delta \Theta^v \quad (2.37)$$

where

$$\delta \Theta^v(\rho, \nabla\rho) \equiv \sum_{i,j=1}^n (\kappa_{\xi_i \xi_j} \nabla \rho_i) \delta \rho_j \quad (2.38)$$

The total Helmholtz energy variation becomes then

$$\mathfrak{D}F[T, \rho, \nabla\rho] = \int_V d\mathbf{r} \left(\frac{\partial f_0^v}{\partial T} \delta T + \sum_{k=1}^n \mu_k \delta \rho_k \right) \quad (2.39)$$

since the boundary integral $\int_S d\mathbf{S} \cdot \delta \Theta^v$ disappears. Thus, we will interpret the expression in parenthesis as the total thermodynamic differential of the specific Helmholtz energy:

$$\delta f^v(T, \rho, \nabla \rho) = \frac{\partial f_0^v}{\partial T} \delta T + \sum_{k=1}^n \mu_k \delta \rho_k \quad (2.40)$$

We write Eq. 2.40 in a form

$$\delta f^v(T, \rho_1, \dots, \rho_n) = -s^v \delta T + \sum_{i=1}^n \mu_i \delta \rho_i \quad (2.41)$$

which we will call Eq. 2.41 the ordinary Gibbs relation. Here

$$s^v \equiv -\frac{\partial}{\partial T} f^v(T, \rho_1, \dots, \rho_n) = -\frac{\partial}{\partial T} f_0^v(T, \rho_1, \dots, \rho_n) \quad (2.42)$$

is the specific entropy of the mixture, which has no gradient contribution. With the help of Eqs. 2.35 and 2.41 we obtain the Gibbs–Duhem relation

$$s^v(\mathbf{r}) \delta T - \delta p(\mathbf{r}) + \sum_{k=1}^n \rho_k(\mathbf{r}) \delta \mu_k = 0 \quad (2.43)$$

Using the following conditions, which are true for equilibrium

$$\begin{aligned} \nabla T(\mathbf{r}) &= 0 \\ \nabla \mu_k(\mathbf{r}) &= 0, \quad \text{for } k = \overline{1, n} \\ \nabla_\alpha \sigma_{\alpha\beta}(\mathbf{r}) &= 0 \end{aligned} \quad (2.44)$$

and Eq. 2.35 together with Eq. 2.11 we obtain the spatial Gibbs relation

$$\nabla_\beta f^v(\mathbf{r}) = \sum_{i=1}^n \mu_i \nabla_\beta \rho_i(\mathbf{r}) + \nabla_\alpha \gamma_{\alpha\beta}(\mathbf{r}) \quad (2.45)$$

The interfacial internal energy, enthalpy and Gibbs energy densities are

$$\begin{aligned} u^v(\mathbf{r}) &\equiv f^v(\mathbf{r}) + s^v(\mathbf{r})T \\ h^v(\mathbf{r}) &\equiv s^v(\mathbf{r})T + \sum_{i=1}^n \mu_i \rho_i(\mathbf{r}) \\ g^v(\mathbf{r}) &\equiv \sum_{i=1}^n \mu_i \rho_i(\mathbf{r}) \end{aligned} \quad (2.46)$$

The Gibbs relations for the internal energy are

$$\delta u^v(s, \rho_1, \dots, \rho_n) = T \delta s^v(\mathbf{r}) + \sum_{i=1}^n \mu_i \delta \rho_i(\mathbf{r}) \quad (2.47)$$

and

$$\nabla_\beta u^v(\mathbf{r}) = T \nabla_\beta s^v(\mathbf{r}) + \sum_{i=1}^n \mu_i \nabla_\beta \rho_i(\mathbf{r}) + \nabla_\alpha \gamma_{\alpha\beta}(\mathbf{r}) \quad (2.48)$$

2.5 Gradient Coefficients

2.5.1 Mass and Volume Specific Coefficients

The coefficients $\kappa_{\rho_i\rho_j}$ used in Sect. 2.4 are different from $\kappa_{\rho\rho}$, $\kappa_{\rho\xi_i}$, and $\kappa_{\xi_i\xi_j}$ used in Sect. 2.3. Comparing Eqs. 2.4 and 2.32, one can derive the following relations between them

$$\begin{aligned} \kappa_{\rho_i\rho_j} = & \kappa_{\rho\rho} + \frac{1}{\rho}(\kappa_{\rho\xi_i} + \kappa_{\rho\xi_j}) - \frac{2}{\rho^2} \sum_{k=1}^n \kappa_{\rho\xi_k} \rho_k \\ & + \frac{1}{\rho^2} \kappa_{\xi_i\xi_j} - \frac{1}{\rho^3} \sum_{k=1}^n (\kappa_{\xi_k\xi_j} + \kappa_{\xi_i\xi_k}) \rho_k + \frac{1}{\rho^4} \sum_{k,l=1}^n \kappa_{\xi_k\xi_l} \rho_k \rho_l \end{aligned} \quad (2.49)$$

and

$$\begin{aligned} \kappa_{\rho\rho} = & \sum_{i,j=1}^{n-1} \xi_i \xi_j (\kappa_{\rho_i\rho_j} + \kappa_{\rho_n\rho_n} - \kappa_{\rho_i\rho_n} - \kappa_{\rho_n\rho_j}) + 2 \sum_i^{n-1} \xi_i (\kappa_{\rho_i\rho_n} - \kappa_{\rho_n\rho_n}) + \kappa_{\rho_n\rho_n} \\ \kappa_{\rho\xi_i} = & \rho \sum_{j=1}^{n-1} \xi_j (\kappa_{\rho_i\rho_j} + \kappa_{\rho_n\rho_n} - \kappa_{\rho_i\rho_n} - \kappa_{\rho_n\rho_j}) + \rho (\kappa_{\rho_i\rho_n} - \kappa_{\rho_n\rho_n}) \\ \kappa_{\xi_i\xi_j} = & \rho^2 (\kappa_{\rho_i\rho_j} + \kappa_{\rho_n\rho_n} - \kappa_{\rho_i\rho_n} - \kappa_{\rho_n\rho_j}) \end{aligned} \quad (2.50)$$

We note, that these relations are exact.

2.5.2 Mixing Rules

All the coefficients $\kappa_{\rho\rho}$, $\kappa_{\rho\xi_i}$, and $\kappa_{\xi_i\xi_j}$, as well as $\kappa_{\rho_i\rho_j}$ are in principle known functions of the densities. In practice they are not known for mixtures. Only the values for pure components may be more or less obtained from experiments, measuring the surface tension. Thus, it is necessary to express the cross-coefficients in a form such that one can approximate them using pure-component values. From Sect. 2.4 one can see, that $\kappa_{\rho_i\rho_i}$ are simply related to the pure-component coefficients: $\kappa_{\rho_i\rho_i} \equiv \kappa_i$ is the coefficient for the pure component i .

Cross-coefficients can then be approximated by one of the so-called mixing rules for the gradient coefficients. We will assume the following mixing rule

$$\kappa_{\rho_i\rho_j} = \sqrt{\kappa_i \kappa_j} \quad (2.51)$$

For $i = j$, Eq. 2.51 is just a definition. For $i \neq j$, this relation is an approximation.

This mixing rule for the gradient coefficients is analogous to the mixing rule for the van der Waals coefficients in an equation of state (see Sect. 3.4 for details). Given these mixing rules for $\kappa_{\rho_i\rho_j}$ coefficients, one can easily deduce the corresponding mixing rules for $\kappa_{\rho\rho}$, $\kappa_{\rho\xi_i}$, and $\kappa_{\xi_i\xi_j}$, using Eq. 2.50.

We shall note here, that the choice of the particular mixing rule is based on the empirical knowledge and does not follow from any theory. We may expect, that for similar components, the mixing rule (2.51) would be adequate. However, for different components, one may probably not use it. The extensive investigation of the mixing rule for the gradient coefficient goes beyond the issues addressed in this thesis. We therefore will use only Eq. 2.51 as a mixing rule.

2.6 Discussion and Conclusions

In this chapter we have established the framework of the gradient model for the liquid–vapor (or, alternatively, liquid–liquid) interface in an isotropic non-polarizable mixture. It is necessary that the homogeneous Helmholtz energy f_0 allows solutions which imply equilibrium coexistence between different phases. Otherwise we only have the homogeneous phase. Standard mixture theories [10] give a Helmholtz energy which allows liquid–vapor coexistence.

Using the assumption that in the interfacial region the fluid can be described by the local densities and their gradients, we have extended the gradient models, used to describe one-component fluids and binary mixtures, to three-dimensional multi-component mixtures. The condition which the system should satisfy is that the total Helmholtz energy is minimal. With the help of Lagrange method it was possible to derive the equations, which the profile distribution should satisfy, given the fixed total content of the components. The Lagrange multipliers are equal to the chemical potentials of the coexisting liquid and vapor. It was also possible to determine the pressure behavior in the interfacial region. It is crucial, that the pressure has a tensorial behavior. The difference between the tensorial part of the pressure tensor and the scalar part determines the surface tension.

An important observation is the ambiguity in the determination of the local thermodynamic potentials, for instance the specific Helmholtz energy. While the total Helmholtz energy is unique and has a minimum, the specific Helmholtz energy is not unique. One can add a term which is the divergence of some vector field without affecting the total Helmholtz energy, if the normal component of this field vanishes on the system boundaries. This general observation in the context of the gradient model implies that the density gradients are taken equal to zero on the boundary. It must be emphasized, that for realistic boundaries these gradients are not zero. We refer to the wall-theorem [11] in this context. We take the freedom to set them equal to zero assuming, that the boundary layer does not affect the

properties of the interface we want to study. In the Appendix 2.A we show that this ambiguity does not affect the results.

As one can see from Eqs. 2.13 and 2.35, it is possible to relate the thermodynamic variables for an inhomogeneous fluid in the same way as it is done for a homogeneous one. However, unlike the homogeneous mixture, these variables contain gradient contributions. The local behavior of the mixture is determined not only by it's local properties but also by it's nearest surroundings.

We have given explicit expressions for each thermodynamic quantity in the interfacial region. We have also determined how the thermodynamic potentials change with the change of the variables they depend on. An important part of the thermodynamic description is the relations between the rate of change of the thermodynamic variables, the Gibbs relations. In an equilibrium interfacial region thermodynamic variables vary in space, unlike in a homogeneous system. Thus one can speak about the relation between the rates of change of thermodynamic variables for a given point in space, the ordinary Gibbs relation. One has also to speak about the rates of change of the thermodynamic variables in space, the spacial Gibbs relation. Even though the thermodynamic potentials, particularly the specific Helmholtz energy, depend on the spatial derivatives of the densities, we have shown that variation of these gradients do not contribute to the ordinary Gibbs relations. Thus, the ordinary Gibbs relations have the ordinary form of the Gibbs relations for the homogeneous mixture. The important observation here is, however, that the ordinary Gibbs relations relate the inhomogeneous thermodynamic variables, i.e. those, which contain the gradient contribution. As the spatial derivatives of the temperature, chemical potentials and pressure tensor are zero in equilibrium, we can determine the spatial Gibbs relation. The new term which appears because of the inhomogeneity is $\nabla_\alpha \gamma_{\alpha\beta}(\mathbf{r})$, which is only unequal to zero close to the surface.

For temperatures far from the critical point the surface thickness is known to be very small (in the sub-nanometer range). This imposes an upper limit to the values of the coefficients $\kappa_{\rho\rho}$, $\kappa_{\rho\xi_i}$, $\kappa_{\xi_i\xi_j}$, and $\kappa_{\rho_i\rho_j}$.

In previous sections we used different specific variables. For the mass specific quantities we used the coefficients $\kappa_{\rho\rho}$, $\kappa_{\rho\xi_i}$, and $\kappa_{\xi_i\xi_j}$ and for densities per unit of volume we used $\kappa_{\rho_i\rho_j}$. One can determine the relations between these coefficients and verify, that all the quantities, determined in Sects. 2.3 and 2.4 are the same. Thus, Eqs. 2.9 and 2.34 give the same pressure $p(\mathbf{r})$, as well as Eqs. 2.12 and 2.34 give the same tension tensor $\gamma_{\alpha\beta}(\mathbf{r})$. And $\sigma_{\alpha\beta}(\mathbf{r})$, which is given by Eq. 2.11 is the same for both sets of variables. μ_n in Eqs. 2.8 and 2.33 is the same and ψ_k taken from Eq. 2.8 are equal to $\mu_k - \mu_n$ taken from Eq. 2.33. This shows that the inhomogeneous equilibrium description is independent of the choice of independent variables. This is similar to the description of the homogeneous equilibrium phase.

The analysis in this chapter gives the basis to extend the description to non-equilibrium systems. For one-component systems, in which the properties varied only in one direction, such an extension was given by Bedeaux et al. [9].

2.A On the Ambiguity in the Specific Quantities

We show here that ambiguities present in the definition of the specific Helmholtz energy and the total thermodynamic differential of the specific Helmholtz energy do not affect the validity of all the thermodynamic relations, derived in this chapter. We do this for mass specific variables, the same arguments can be used for the densities per unit of volume.

The total Helmholtz energy of a mixture $\int_V d\mathbf{r} \rho(\mathbf{r}) f(\mathbf{r})$ can be expanded around a homogeneous state as

$$\begin{aligned}
 F = \int_V d\mathbf{r} & \left[\rho f_0(T, \rho, \xi) \right. \\
 & + \frac{1}{2} \kappa_{\rho\rho}^{(1)} |\nabla\rho|^2 + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i}^{(1)} \nabla\rho \cdot \nabla\xi_i + \frac{1}{2} \sum_{i,j=1}^{n-1} \kappa_{\xi_i\xi_j}^{(1)} \nabla\xi_i \cdot \nabla\xi_j \\
 & \left. + \kappa_{\rho\rho}^{(2)} \nabla^2\rho + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i}^{(2)} \nabla^2\xi_i + \dots \right] \quad (2.52)
 \end{aligned}$$

where the series is truncated after the second order terms. As it is shown in Eq. 2.2 this can be rearranged as following:

$$\begin{aligned}
 F = \int_V d\mathbf{r} & \left[\rho f_0(T, \rho, \xi) \right. \\
 & + \frac{1}{2} \kappa_{\rho\rho} |\nabla\rho|^2 + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i} \nabla\rho \cdot \nabla\xi_i + \frac{1}{2} \sum_{i,j=1}^{n-1} \kappa_{\xi_i\xi_j} \nabla\xi_i \cdot \nabla\xi_j \\
 & \left. + \nabla \cdot \left(\kappa_{\rho\rho}^{(2)} \nabla\rho + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i}^{(2)} \nabla\xi_i \right) + \dots \right] \quad (2.53)
 \end{aligned}$$

where

$$\begin{aligned}
 \kappa_{\rho\rho} &= \kappa_{\rho\rho}^{(1)} - 2 (\partial\kappa_{\rho\rho}^{(2)}/\partial\rho) \\
 \kappa_{\rho\xi_i} &= \kappa_{\rho\xi_i}^{(1)} - (\partial\kappa_{\rho\rho}^{(2)}/\partial\xi_i) - (\partial\kappa_{\rho\xi_i}^{(2)}/\partial\rho) \\
 \kappa_{\xi_i\xi_j} &= \kappa_{\xi_i\xi_j}^{(1)} - (\partial\kappa_{\rho\xi_i}^{(2)}/\partial\xi_j) - (\partial\kappa_{\rho\xi_j}^{(2)}/\partial\xi_i)
 \end{aligned} \quad (2.54)$$

are the coefficients used in Eq. 2.4.

Let us define

$$\begin{aligned}
 f(\mathbf{r}) &\equiv \rho f_0(T, \rho, \xi) + \frac{1}{2} \kappa_{\rho\rho} |\nabla\rho|^2 + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i} \nabla\rho \cdot \nabla\xi_i + \frac{1}{2} \sum_{i,j=1}^{n-1} \kappa_{\xi_i\xi_j} \nabla\xi_i \cdot \nabla\xi_j \\
 \tilde{f}(\mathbf{r}) &\equiv f(\mathbf{r}) + \nabla \cdot \left(\kappa_{\rho\rho}^{(2)} \nabla\rho + \sum_{i=1}^{n-1} \kappa_{\rho\xi_i}^{(2)} \nabla\xi_i \right)
 \end{aligned} \quad (2.55)$$

so that $F = \int_V d\mathbf{r} \rho(\mathbf{r}) f(\mathbf{r}) = \int_V d\mathbf{r} \rho(\mathbf{r}) \tilde{f}(\mathbf{r})$. One can also define

$$\begin{aligned} p(\mathbf{r}) &\equiv \mu_n + \sum_{i=1}^{n-1} \psi_i \zeta_i(\mathbf{r}) - f(\mathbf{r}) \\ \tilde{p}(\mathbf{r}) &\equiv \mu_n + \sum_{i=1}^{n-1} \psi_i \zeta_i(\mathbf{r}) - \tilde{f}(\mathbf{r}) = p(\mathbf{r}) - \nabla \cdot \left(\kappa_{\rho\rho}^{(2)} \nabla \rho + \sum_{i=1}^{n-1} \kappa_{\rho\zeta_i}^{(2)} \nabla \zeta_i \right) \end{aligned} \quad (2.56)$$

and follow the same procedure as in Sect. 2.3.1. (Note, that the second order terms should be added to the Euler–Lagrange equations in such case). Then, as it follows from a known theorem of variational calculus, one obtains for the chemical potentials μ_n and ψ_k

$$\begin{aligned} \mu_n &= \frac{\partial}{\partial \rho}(\rho f) - \sum_{i=1}^{n-1} \psi_i \zeta_i - \nabla \cdot \left(\kappa_{\rho\rho} \nabla \rho + \sum_{i=1}^{n-1} \kappa_{\rho\zeta_i} \nabla \zeta_i \right) \\ \psi_k &= \frac{\partial}{\partial \zeta_k}(f) - \frac{1}{\rho} \nabla \cdot \left(\kappa_{\rho\zeta_k} \nabla \rho + \sum_{i=1}^{n-1} \kappa_{\zeta_i\zeta_k} \nabla \zeta_i \right), \quad k = \overline{1, n-1} \end{aligned} \quad (2.57)$$

and for the pressure tensor $\sigma_{\alpha\beta}(\mathbf{r})$

$$\sigma_{\alpha\beta}(\mathbf{r}) = p(\mathbf{r}) \delta_{\alpha\beta} + \gamma_{\alpha\beta}(\mathbf{r}) \quad (2.58)$$

for both definitions of $p(\mathbf{r})$ and $\tilde{p}(\mathbf{r})$. As one can see, there is no ambiguity in the expressions for the chemical potentials and the pressure tensor. They are determined irrespective of the ambiguity in the definition of the specific Helmholtz energy. Technically, the reason for this is that μ_n and ψ_k are the *integral* properties of the equilibrium mixture, which minimize the Helmholtz energy of the whole mixture. Thus, they cannot depend on *local* ambiguities.

Thus, it is natural to use $f(\mathbf{r})$ as the specific Helmholtz energy and use $p(\mathbf{r})$ as a pressure. As we have seen in Sect. 2.3.3 only $p(\mathbf{r})$ has a physical meaning but not $\tilde{p}(\mathbf{r})$. With such a choice, all the thermodynamic quantities derived in this chapter do not contain any ambiguity.

2.B Interfacial Pressure

In this section we shall see how our expressions for the pressure and the tension tensors in the interfacial region Eqs. 2.9, 2.12, and 2.11, reduce to the conventional quantities such as the parallel and the perpendicular pressures for the flat interface and the Korteweg tensor. These quantities were mostly given for systems in which only one variable changes through the surface, either the density in one-component systems or the mass fraction in binary mixtures. We will therefore consider here only such systems, assuming that we speak about the density in a one-component system. The discussion for a binary mixture is analogous.

2.B.1 Korteweg Tensor

The scalar pressure in a one-component system is

$$p(\mathbf{r}) = \rho^2 \frac{\partial}{\partial \rho} \left(f_0 + \frac{\kappa}{2} |\nabla \rho|^2 \right) - \rho \nabla \cdot (\kappa \nabla \rho) \quad (2.59)$$

and the tension tensor is

$$\gamma_{\alpha\beta}(\mathbf{r}) = \kappa \frac{\partial \rho}{\partial x_\alpha} \frac{\partial \rho}{\partial x_\beta} \quad (2.60)$$

and the pressure tensor is still given by Eq. 2.11.

Taking into account that $\rho^2(\partial f_0/\partial \rho) = p_0$ is the homogeneous pressure, we obtain

$$p(\mathbf{r}) = p_0(\rho, T) - \kappa \rho \nabla^2 \rho - \frac{1}{2} \kappa |\nabla \rho|^2 - \frac{1}{2} \frac{\partial \kappa}{\partial \rho} \rho |\nabla \rho|^2 \quad (2.61)$$

so the pressure tensor (2.11) becomes

$$\sigma_{\alpha\beta} = p_0(\rho, T) \delta_{\alpha\beta} + w_{\alpha\beta} \quad (2.62)$$

where

$$w_{\alpha\beta}(\mathbf{r}) \equiv \gamma_{\alpha\beta}(\mathbf{r}) - \kappa \left(\rho \nabla^2 \rho + \frac{1}{2} \kappa |\nabla \rho|^2 \right) - \frac{1}{2} \frac{\partial \kappa}{\partial \rho} \rho |\nabla \rho|^2 \quad (2.63)$$

is the Korteweg tensor [12, 13].

In this work we use the scalar pressure $p(\mathbf{r})$ and the tension tensor $\gamma_{\alpha\beta}(\mathbf{r})$ instead of the homogeneous pressure $p_0(\rho, T)$ and the Korteweg tensor $w_{\alpha\beta}(\mathbf{r})$. The reason for this is that in the interfacial region, it is $p(\mathbf{r})$, not $p_0(\rho, T)$, which enters all the thermodynamic relations, and it is $\gamma_{\alpha\beta}(\mathbf{r})$, not $w_{\alpha\beta}(\mathbf{r})$, which determines the surface tension.

2.B.2 Parallel and Perpendicular Pressure

In the case of planar interface with cartesian coordinate x directed perpendicular to the surface, the pressure tensor takes the following form

$$\sigma_{\alpha\beta}(x) = \begin{pmatrix} p_\perp(x) & 0 & 0 \\ 0 & p_\parallel(x) & 0 \\ 0 & 0 & p_\parallel(x) \end{pmatrix} \quad (2.64)$$

where

$$\begin{aligned}
 p_{\perp}(x) &\equiv p(x) + \gamma_{xx}(x) = p_0(\rho, T) - \kappa\rho\rho'' + \frac{1}{2}\kappa\rho'^2 - \frac{1}{2}\frac{\partial\kappa}{\partial\rho}\rho\rho'^2 \\
 p_{\parallel}(x) &\equiv p(x) = p_0(\rho, T) - \kappa\rho\rho'' - \frac{1}{2}\kappa\rho'^2 - \frac{1}{2}\frac{\partial\kappa}{\partial\rho}\rho\rho'^2
 \end{aligned}
 \tag{2.65}$$

are the perpendicular and parallel pressures in the interfacial region. Here prime indicates the derivative with respect to x . The difference between them

$$\gamma_{xx}(x) \equiv p_{\perp}(x) - p_{\parallel}(x) = \kappa\rho'^2
 \tag{2.66}$$

determines the surface tension [1, 6]

$$\gamma = \int_x dx \gamma_{xx}(x)
 \tag{2.67}$$

According to Eq. 2.10, the perpendicular pressure is constant in the interfacial region

$$p'_{\perp}(x) = 0
 \tag{2.68}$$

while the parallel is not: it has a peak which is opposite to $\gamma_{xx}(x)$ in sign.

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Chapter 3

Non-Equilibrium Continuous Description

3.1 Introduction

Because of the lack of local equilibrium, the extension of non-equilibrium thermodynamics to a continuous description of an interface is not straightforward. Earlier work [1–3] has shown that such an extension is possible for one-component fluids, with all the variables dependent on the normal coordinate for a planar interface. Temperature gradients, pressure differences and the resulting heat flux and evaporation or condensation fluxes were determined through the interface. For systems away from equilibrium, square gradient models have been used before, we refer to [4–6] in this context. Very little work has been done on systems with a varying temperature [6], and on two-phase systems, however. The systematic treatment of heat and mass transport through the liquid–vapor interface, along the lines sketched in [1–3], was to our knowledge, new.¹

In the first chapter we extended the analysis of van der Waals to equilibrium multi-component systems. Explicit expression for all the thermodynamic quantities were given. In particular, we derived the expression for the pressure tensor and discussed the validity of the Gibbs relation in the interfacial region. In this chapter we will extend this approach to multi-component non-equilibrium mixtures in three-dimensions. Because of considering three-dimensional systems it is possible to derive systematically all system properties, which were postulated in the one-dimensional description.

The traditional local equilibrium hypothesis implies that in non-equilibrium a small volume of the system at each moment of time can be considered to be in equilibrium. Thus, all thermodynamic relations, valid for the whole system, remain valid for this small volume. The important assumption is that the state of each small volume is determined only by the properties of this volume, and no other ones. To describe the interface in equilibrium, one needs to introduce a

¹ Since then there have appeared some works addressing the similar issues [7–9]. See [Sect. 1.4.1](#) for a review.

dependence on the density gradients however. Such a description is not local in the traditional sense: the system behavior in a small volume depends on the properties of this volume and the properties of the nearest neighborhood. This implies that one cannot apply the usual local equilibrium hypothesis to the interfacial region.

A mixture can be described by mass densities and temperature T as independent variables. We will use ρ as the total mass density of the mixture, or $v = 1/\rho$ as the mass specific volume, and $\{\xi_1, \dots, \xi_{n-1}\}$ as the mass fractions of components. Furthermore, we will write ξ instead of the set of arguments $\{\xi_1, \dots, \xi_{n-1}\}$ and $\nabla\xi$ instead of the set $\{\nabla\xi_1, \dots, \nabla\xi_{n-1}\}$ to simplify the formulas. New variables which appear in the non-equilibrium description are the velocities of each component $\{\mathbf{v}_1(\mathbf{r}, t), \dots, \mathbf{v}_n(\mathbf{r}, t)\}$. For a one-fluid mixture it is more convenient to use the barycentric velocity of the whole mixture

$$\mathbf{v}(\mathbf{r}, t) = \frac{1}{\rho(\mathbf{r}, t)} \sum_{i=1}^n \rho_i(\mathbf{r}, t) \mathbf{v}_i(\mathbf{r}, t) \quad (3.1)$$

where $\rho_i \equiv \xi_i \rho$ is the mass density of component i , and $n - 1$ diffusion fluxes $\{\mathbf{J}_1, \dots, \mathbf{J}_{n-1}\}$ where

$$\mathbf{J}_k \equiv \rho \xi_k (\mathbf{v}_k - \mathbf{v}), \quad k = \overline{1, n} \quad (3.2)$$

as independent variables. We note that $\sum_{i=1}^n \mathbf{J}_k = 0$ so only $n - 1$ of n diffusion fluxes are independent.

We will follow the traditional procedure used in non-equilibrium thermodynamics. In [Sect. 3.2](#) we review briefly the main results of the equilibrium square gradient model for the interface. We extend all equilibrium results, derived in the first chapter to non-equilibrium. Explicit expressions for the necessary thermodynamic properties of the non-equilibrium mixture are given. To be able to derive the entropy production one needs the Gibbs relation. It was shown in the first chapter that within the interfacial region one can speak about two kinds of Gibbs relation, the ordinary Gibbs relation and the spatial Gibbs relation. We show in [Sect. 3.3](#) how these two static relations are combined into a non-equilibrium Gibbs relation. For a one-component system this non-equilibrium Gibbs relation reduces to that given in [1]. Within the framework of the one-fluid approach we discuss the expression for the homogeneous Helmholtz energy f_0 which is needed to determine thermodynamic quantities in [Sect. 3.4](#). In [Sect. 3.5](#) we give the hydrodynamic equations. We use the so-called one-fluid approach which has been shown [10, 11] to be appropriate for common mixtures. In [Sect. 3.6](#) we discuss the consequences of the special surface symmetry. After deriving the entropy production in [Sect. 3.7](#) and using the Curie principle, we give the linear relations between the thermodynamic fluxes and forces in [Sect. 3.8](#). It is found that, for instance, the resistivities for transport through and into the interfacial region will in general contain square gradient contributions. Concluding remarks and a discussion are given in [Sect. 3.9](#).

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3.2 The Square Gradient Model

Assuming that the specific Helmholtz energy can be written as

$$f(\mathbf{r}) = f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \nabla\rho, \nabla\xi) \quad (3.3)$$

where

$$\mathcal{K}(\rho, \xi, \nabla\rho, \nabla\xi) \equiv \frac{1}{2} \frac{\kappa}{\rho} |\nabla\rho|^2 + \sum_{i=1}^{n-1} \frac{\kappa_i}{\rho} \nabla\rho \cdot \nabla\xi_i + \frac{1}{2} \sum_{i,j=1}^{n-1} \frac{\kappa_{ij}}{\rho} \nabla\xi_i \cdot \nabla\xi_j \quad (3.4)$$

and where all coefficients κ , κ_i and κ_{ij} are assumed to be independent of the temperature, one can derive the chemical potential μ_n of the n th component and the reduced chemical potentials $\psi_k = \mu_k - \mu_n$, where $k = \overline{1, n-1}$ (all integers from 1 to $n-1$), which are constant through the surface in equilibrium. We refer to the first chapter for the expressions for the chemical potentials, $p(\mathbf{r})$ and other quantities. These quantities are related by the ordinary thermodynamic relation

$$f(\mathbf{r}) = \mu_n - p(\mathbf{r})v(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i \xi_i(\mathbf{r}) \quad (3.5)$$

Other thermodynamic potentials, like the specific internal energy was *defined* in the interfacial region as

$$u(\mathbf{r}) = f(\mathbf{r}) + s(\mathbf{r})T \quad (3.6)$$

The entropy and the enthalpy are also given there.

In the interfacial region, the pressure has a tensorial behavior:

$$\sigma_{\alpha\beta}(\mathbf{r}) = p(\mathbf{r})\delta_{\alpha\beta} + \gamma_{\alpha\beta}(\mathbf{r}) \quad (3.7)$$

where the tension tensor is given by

$$\gamma_{\alpha\beta} = \kappa \frac{\partial\rho}{\partial x_\alpha} \frac{\partial\rho}{\partial x_\beta} + \sum_{i=1}^{n-1} \kappa_i \left(\frac{\partial\xi_i}{\partial x_\alpha} \frac{\partial\rho}{\partial x_\beta} + \frac{\partial\rho}{\partial x_\alpha} \frac{\partial\xi_i}{\partial x_\beta} \right) + \sum_{i,j=1}^{n-1} \kappa_{ij} \frac{\partial\xi_i}{\partial x_\alpha} \frac{\partial\xi_j}{\partial x_\beta} \quad (3.8)$$

For a flat surface, $p(\mathbf{r})$ is the parallel pressure.

In order to describe non-equilibrium processes in a multi-phase mixture using thermodynamics, one must assume, that all thermodynamic quantities are defined at each point in space and at all times. This in particular holds also in the interfacial region. In non-equilibrium, the density $\rho(\mathbf{r}, t)$ and the mass fractions $\xi(\mathbf{r}, t)$ depend on the time explicitly. We do not have the restriction of a constant temperature and chemical potentials: $T(\mathbf{r}, t)$, $\mu_n(\mathbf{r}, t)$ and $\psi_i(\mathbf{r}, t)$ may therefore depend both on position and time as well.

To describe non-equilibrium inhomogeneous systems we shall assume that all the relations between thermodynamic variables valid in equilibrium, which were

discussed in more details in the second chapter, remain valid away from equilibrium. Away from the surface this is the usual assumption made in non-equilibrium thermodynamics. In the interfacial regions, it extends this assumption to places where the gradient contributions become important. As said in [13], the validity of such a hypothesis can be verified only by experiment.

3.3 The Gibbs Relation

An important part of the equilibrium description is the relation between the variation of thermodynamic potentials and the independent thermodynamic variables, in other words the Gibbs relation. In the interfacial region, properties may change with position, so we have to speak about two kinds of Gibbs relations: ordinary Gibbs relations and spatial Gibbs relations. Ordinary Gibbs relations relate the changes of thermodynamic variables at the given point in space for different states. For the internal energy the ordinary Gibbs relation was found to be

$$\delta u(s, v, \xi) = T \delta s(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i \delta \xi_i(\mathbf{r}) - p(\mathbf{r}) \delta v(\mathbf{r}) \quad (3.9)$$

Spatial Gibbs relations relate differences of thermodynamic variables for the given state at neighboring points in space. For the internal energy it was found to be

$$\nabla_{\beta} u(\mathbf{r}) = T \nabla_{\beta} s(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i \nabla_{\beta} \xi_i(\mathbf{r}) - p(\mathbf{r}) \nabla_{\beta} v(\mathbf{r}) - v(\mathbf{r}) \nabla_{\alpha} \gamma_{\alpha\beta}(\mathbf{r}) \quad (3.10)$$

Notice in particular the last contribution on the right hand side.

Similar to the description of a homogeneous fluid, we extend the equilibrium Gibbs relations to non-equilibrium in the simplest way. One needs to make an important observation before such an extension, however: equilibrium equation Eq. 3.9 describes the change of local thermodynamic variables between two different states at a fixed point in space. These two states can be separated in time. So we can say that this equation describes the change of local thermodynamic variables in time at a fixed point in space:

$$T(\mathbf{r}, t) \frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \sum_{i=1}^{n-1} \psi_i(\mathbf{r}, t) \frac{\partial \xi_i}{\partial t} + p(\mathbf{r}, t) \frac{\partial v}{\partial t} \quad (3.11)$$

We similarly use the equilibrium spatial Gibbs relation for the specific internal energy, Eq. 3.10, for the non-equilibrium case:

$$T(\mathbf{r}, t) \nabla s = \nabla u - \sum_{i=1}^{n-1} \psi_i(\mathbf{r}, t) \nabla \xi_i + p(\mathbf{r}, t) \nabla v - v \frac{\partial \gamma_{\alpha\beta}}{\partial x_{\alpha}} \quad (3.12)$$

See also relevant discussion in Appendix 3.A.

Next we combine Eqs. 3.11 and 3.12 in order to get the non-equilibrium Gibbs relation in terms of the substantial (barycentric) time derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \quad (3.13)$$

This should be done carefully, taking into account that all dynamic equations, particularly the Gibbs relation, must be Galilean invariant. Thus, a naive approach to contract Eq. 3.12 with $\mathbf{v}(\mathbf{r}, t)$ and sum with Eq. 3.11 is not appropriate here. The resulting equation would contain the term $v_\beta \nabla_\alpha \gamma_{\alpha\beta}$ which is not Galilean invariant, while the other terms containing substantial derivative are, of course, Galilean invariant. We shall *construct* the non-equilibrium Gibbs relation from Eqs. 3.11 and 3.12 in such a way that it satisfies the Galilean invariance.

We contract all the terms in Eq. 3.12, except $v \nabla_\alpha \gamma_{\alpha\beta}$, with the barycentric velocity $\mathbf{v}(\mathbf{r}, t)$, while the term $v \nabla_\alpha \gamma_{\alpha\beta}$ is contracted with a velocity $\mathbf{v}(\mathbf{r}, t) - \mathbf{v}^s(\mathbf{r}, t)$, where the exact meaning of a velocity $\mathbf{v}^s(\mathbf{r}, t)$ will be clarified later. Summing the result with Eq. 3.11 we and obtain

$$T(\mathbf{r}, t) \frac{ds}{dt} = \frac{du}{dt} - \sum_{i=1}^{n-1} \psi_i(\mathbf{r}, t) \frac{d\xi_i}{dt} + p(\mathbf{r}, t) \frac{dv}{dt} - v(v_\beta - v_\beta^s) \frac{\partial \gamma_{\alpha\beta}}{\partial x_\alpha} \quad (3.14)$$

We emphasize that one should not regard the above procedure as the *derivation* of the non-equilibrium Gibbs relation. One may not *derive* any non-equilibrium Gibbs relation. Any non-equilibrium Gibbs relation should be considered as an assumption which satisfies the following requirements: (1) it is Galilean invariant; (2) it reduces to the equilibrium Gibbs relation in the limit of quasi-static processes; (3) the conclusions derived from it are not contradictory and agree with experiments. Equation 3.14 satisfies the first requirement by construction. As in equilibrium both $\mathbf{v}(\mathbf{r}, t)$ and $\mathbf{v}^s(\mathbf{r}, t)$ are zero, Eq. 3.14 satisfies also the second requirement. The question whether it satisfies the third requirement cannot be answered here. It can only be justified by virtue of the results of, for instance, this thesis. We therefore take it as an assumption for the further analysis.

Equation 3.14 is the Gibbs relation for the non-equilibrium two-phase mixture including the interface. One can show that it reduces to the Gibbs relation used by Bedeaux et al. [1] for the case of a one-component fluid. The above analysis gives more insight in the origin of the contribution proportional to the divergence of the surface tension field. This was not clarified in the analysis of Bedeaux et al.

3.4 Homogeneous Thermodynamics of One-Fluid Mixture

In this section, we shall discuss the homogeneous expressions for the thermodynamic quantities needed for the non-equilibrium description. This analysis uses the equations of state which are usually written for the molar specific variables. We

will therefore use the molar variables in this section. The final results can be converted to the mass specific variables.

3.4.1 Equation of State

To obtain the homogeneous specific Helmholtz energy one may use the common one-fluid equations of state:

- van der Waals equation of state:

$$p_W(T, c, \zeta) = \frac{RTc}{1 - B(\zeta)c} - A(T, \zeta)c^2 \quad (3.15)$$

- Soave–Redlich–Kwong equation of state:

$$p_{SRK}(T, c, \zeta) = \frac{RTc}{1 - B(\zeta)c} - \frac{A(T, \zeta)}{1 - B(\zeta)c}c^2 \quad (3.16)$$

- Peng–Robinson equation of state:

$$p_{PR}(T, c, \zeta) = \frac{RTc}{1 - B(\zeta)c} - \frac{A(T, \zeta)}{1 + 2B(\zeta)c - B^2(\zeta)c^2}c^2 \quad (3.17)$$

where ζ is a short notation for the molar fractions $\{\zeta_1, \dots, \zeta_n\}$.

In the one-fluid approach, constants $A(T)$ and B , depend on the fractions of the species according to the mixing rules:

$$\begin{aligned} A(T, \zeta_1, \dots, \zeta_n) &= \sum_{i,k=1}^n a_{ik}(T)\zeta_i\zeta_k \\ B(\zeta_1, \dots, \zeta_n) &= \sum_{k=1}^n b_k\zeta_k \end{aligned} \quad (3.18)$$

where usually $a_{ik}(T) = \sqrt{a_i(T)a_k(T)}$, and $a_k(T)$ and b_k are the corresponding coefficients for the pure substances (see e.g. [14, 15]). For one-fluid mixtures, these mixing rules, as well as the above equations of state, are considered to be satisfactory. The matrix $a_{ik}(T)$ is symmetric in its indexes.

3.4.2 Helmholtz Energy of a Mixture of Ideal Gases

According to [16] the total Helmholtz energy of a homogeneous mixture of ideal gases is

$$F_{0,id}[T, c, \zeta] = -RT \sum_{k=1}^n v_k \ln \left[\frac{e w_k(T)}{c_k N_A \Lambda_k^3(T)} \right] \quad (3.19)$$

where v_k is the number of moles and c_k the molar density of component k . Furthermore, Λ_k is the thermal de Broglie wavelength and w_k is a characteristic sum over the internal degrees of freedom of component k

$$\Lambda_k(T) \equiv \hbar N_A \sqrt{2\pi/M_k RT}, \quad w_k(T) \equiv \sum_{\ell} \exp(-\varepsilon_k^{\ell}/k_B T) \quad (3.20)$$

where M_k is the molar mass of component k and ε_k^{ℓ} are the energy levels of the internal degree of freedom of component k . If one describes the mixture using molar specific variables the following equivalent expression is more useful

$$F_{0,id}[T, c, \zeta] = -vRT \ln \left[\frac{e w(T, \zeta)}{c N_A \Lambda^3(T, \zeta)} \right] - RT \sum_{k=1}^n v_k \ln \left[\frac{c}{c_k} \frac{\Lambda^3(T)}{\Lambda_k^3(T, \zeta)} \frac{w_k(T)}{w(T, \zeta)} \right] \quad (3.21)$$

where c is the total molar density of the mixture,

$$\Lambda(T, \zeta) \equiv \hbar N_A \sqrt{2\pi/M(\zeta)RT} \quad (3.22)$$

is the mixture's thermal de Broglie wavelength, $w(T, \zeta)$ a characteristic sum over all the internal degrees of freedom of the mixture and

$$M(\zeta) = \sum_{k=1}^n \zeta_k M_k = M_n + \sum_{k=1}^{n-1} \zeta_k (M_k - M_n) \quad (3.23)$$

is the molar mass of the mixture. The exact expression for $w(T, \zeta)$, as well as expression for $w_k(T)$, is determined by model approximation for the mixture.

The specific Helmholtz energy of a mixture of ideal gases then becomes

$$f_{0,id}^v(T, c, \zeta) = -RT \ln \left[\frac{e w(T, \zeta)}{c N_A \Lambda^3(T, \zeta)} \right] - RT \sum_{k=1}^n \zeta_k \ln \left[\frac{1}{\zeta_k} \left(\frac{M_k}{M(\zeta)} \right)^{3/2} \frac{w_k(T)}{w(T, \zeta)} \right] \quad (3.24)$$

Due to the spirit of the one-fluid approach we have to equate the second term to 0. Thus,

$$f_{0,id}^v(T, c, \zeta) = -RT \ln \left[\frac{e w(T, \zeta)}{c N_A \Lambda^3(T, \zeta)} \right] \quad (3.25)$$

where

$$w(T, \zeta) \equiv \exp \sum_{k=1}^n \zeta_k \ln \left[\frac{w_k(T)}{\zeta_k} \left(\frac{M_k}{M(\zeta)} \right)^{3/2} \right] \quad (3.26)$$

can be considered as a mixing rule for the w . We note that Eq. 3.25 together with Eq. 3.26 does not impose any assumptions: it is nothing but Eq. 3.24 written with the help of one-fluid terms.

3.4.3 Homogeneous Helmholtz Energy

To find the homogeneous specific Helmholtz energy $f_0^v(T, c, \zeta)$ we integrate the equations of state over the volume at constant temperature and molar fractions of the components. The integration constant should be chosen such that the specific Helmholtz energy of the system with a small mixture's concentration ($c \rightarrow 0$) is equal to the specific Helmholtz energy for a mixture of ideal gases (3.25).

Integrating the equations of state Eqs. 3.15–3.17 and using 3.25, we obtain the following expression for the homogeneous molar Helmholtz energy²:

$$f_0^v(T, c, \zeta) = -RT \ln \left[\frac{e}{c N_A} \frac{w(T, \zeta)}{\Lambda^3(T, \zeta)} (1 - B(\zeta) c) \right] - A(T, \zeta) c \phi(B(\zeta) c) \quad (3.27)$$

where $\phi(\omega)$ has the following expressions, respectively, corresponding to each equation of state:

$$\begin{aligned} \phi_W(\omega) &= 1 \\ \phi_{\text{SRK}}(\omega) &= \frac{1}{\omega} \ln(1 + \omega) \\ \phi_{\text{PR}}(\omega) &= \frac{1}{2\sqrt{2}} \frac{1}{\omega} \ln \left(1 + \frac{2\sqrt{2}\omega}{1 + \omega(1 - \sqrt{2})} \right) \end{aligned} \quad (3.28)$$

To obtain $w(T, \zeta)$ one has to know $w_k(T)$ defined in Eq. 3.20. The particular mixture would imply a particular expressions for $w_k(T)$. Again, as the focus of this thesis is not the homogeneous mixture theory, we neglect any particular dependence of these quantities on the temperature and the molecular structure. For the exact values we refer to the next chapter where we give the numerical values for all the parameters.

² We note, that Eq. 3.27 is the expression for the specific Helmholtz energy of a *non-ideal* mixture. This is accounted by using the equation of state of a real mixture, see Sect. 3.4.1. The reference to an ideal mixture is needed only for the determination of the integration constant.

3.5 Hydrodynamics of One-Fluid Mixture

The analysis in the above sections defines all the quantities and gives all the relations we need for the non-equilibrium description. It is a generalization of the hypothesis of local equilibrium. We will further omit the arguments (\mathbf{r}, t) to simplify the notation.

We can now derive all hydrodynamic equations, using the conservation laws of matter, momentum and energy. The laws of conservation of mass can be written as

$$\begin{aligned} \frac{d\rho}{dt} &= -\rho \nabla \cdot \mathbf{v} \\ \rho \frac{d\xi_k}{dt} &= -\nabla \cdot \mathbf{J}_k, \quad k = \overline{1, n-1} \end{aligned} \quad (3.29)$$

The momentum conservation law, i.e. the equation of motion, can be written as

$$\rho \frac{d\mathbf{v}_\beta}{dt} = -\frac{\partial(\sigma_{\alpha\beta} + \pi_{\alpha\beta})}{\partial x_\alpha} + \rho \mathbf{g}_\beta \quad (3.30)$$

where \mathbf{g} is the gravitational acceleration. $\sigma_{\alpha\beta}$ the thermodynamic pressure tensor defined by Eq. 3.7 and $\pi_{\alpha\beta}(\mathbf{r}, t)$ the viscous pressure tensor, which still is to be determined. We assume, that this tensor is symmetric. The thermodynamic pressure tensor and the viscous pressure tensor without subscripts will be indicated by $\Xi(\mathbf{r}, t)$ and $\Pi(\mathbf{r}, t)$, respectively.

The law of energy conservation is (see [13])

$$\rho \frac{de}{dt} + \nabla \cdot (\mathbf{J}_e - \rho \mathbf{v} e) = 0 \quad (3.31)$$

where \mathbf{J}_e is the total energy flux and the total specific energy e is given by

$$e(\mathbf{r}, t) = u(\mathbf{r}, t) + \tau(\mathbf{r}, t) + \varphi(\mathbf{r}) \quad (3.32)$$

φ the gravitational potential field, so that $\mathbf{g} \equiv -\nabla\varphi$. We will assume, that φ does not depend on the time.

We restrict ourself to systems, where the acceleration of the components relative to each other is small compared to the acceleration of the mixture's center of mass. This implies that the kinetic energy of the component's relative motion is small compared to the kinetic energy of the mixture's center of mass motion. This is true, when the relaxation time of the relative motion is very small. For the common mixtures which are described by one-fluid approach this is the case. Thus, the specific kinetic energy is

$$\tau(\mathbf{r}, t) = \frac{1}{2} \mathbf{v}^2(\mathbf{r}, t) \quad (3.33)$$

From momentum conservation we obtain:

$$\rho \frac{d\tau}{dt} = -v_\beta \frac{\partial(\sigma_{\alpha\beta} + \pi_{\alpha\beta})}{\partial x_\alpha} + \rho \mathbf{v} \cdot \mathbf{g} \quad (3.34)$$

For the internal energy we get

$$\rho \frac{du}{dt} = -\nabla \cdot \tilde{\mathbf{J}}_q - \pi_{\alpha\beta} v_{\beta\alpha} - \sigma_{\alpha\beta} v_{\beta\alpha} \quad (3.35)$$

where $v_{\beta\alpha} \equiv \partial v_\beta / \partial x_\alpha$ and where

$$\tilde{\mathbf{J}}_q \equiv \mathbf{J}_e - \rho \mathbf{v} e - \mathfrak{E} \cdot \mathbf{v} - \Pi \cdot \mathbf{v} \quad (3.36)$$

is called the total heat flux.

We write the Gibbs relation (3.14) in the form

$$T \rho \frac{ds}{dt} = \rho \frac{du}{dt} - \sum_{i=1}^{n-1} \rho \psi_i \frac{d\xi_i}{dt} + p \rho \frac{dv}{dt} - (v_\beta - v_\beta^s) \frac{\partial \gamma_{\alpha\beta}}{\partial x_\alpha} \quad (3.37)$$

Using previous equations and performing algebraic transformations we obtain³

$$\begin{aligned} \rho \frac{ds}{dt} = & -\nabla \cdot \left[\frac{1}{T} \left(\tilde{\mathbf{J}}_q - \sum_{k=1}^{n-1} \psi_k \mathbf{J}_k + (\mathbf{v} - \mathbf{v}^s) \cdot \Upsilon \right) \right] \\ & + \left(\tilde{\mathbf{J}}_q + (\mathbf{v} - \mathbf{v}^s) \cdot \Upsilon \right) \cdot \nabla \frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_k \cdot \nabla \frac{\psi_k}{T} - \frac{1}{T} \pi_{\alpha\beta} v_{\beta\alpha} - \frac{1}{T} \gamma_{\alpha\beta} \nabla_\alpha v_\beta^s \end{aligned} \quad (3.38)$$

where $\Upsilon \equiv \gamma_{\alpha\beta}$.

3.5.1 The Energy Fluxes

We follow [13] in the naming the fluxes of energy and heat. In general, the energy flux \mathbf{J}_e contains various contributions. It is natural to call it the *total energy flux*, as it contains all the possible energy flows by definition

$$\frac{\partial \rho e}{\partial t} = -\nabla \cdot \mathbf{J}_e \quad (3.39)$$

The total energy flux contains the following contributions. One is a co-moving energy $\rho \mathbf{v} e$, which represents a convective energy flux. Another term is the thermodynamic work performed on the system, $\mathfrak{E} \cdot \mathbf{v}$. For inhomogeneous regions

³ Note that $\sum_{k=1}^{n-1} \psi_k \mathbf{J}_k = \sum_{k=1}^n \mu_k \mathbf{J}_k$ and $\sum_{k=1}^{n-1} \mathbf{J}_k \cdot \nabla(\psi_k/T) = \sum_{k=1}^n \mathbf{J}_k \cdot \nabla(\mu_k/T)$.

like surface, thermodynamic pressure is a tensor and the corresponding work has therefore this form. For viscous mixtures there is also a dissipative work $\Pi \cdot \mathbf{v}$ which contributes to the total energy flux. The rest of the energy flow is due to a heat flow. Thus, it is natural to call the flux $\tilde{\mathbf{J}}_q$ defined by Eq. 3.36 a heat flux. Convective energy flux, thermodynamic work, and viscous work all depend on the frame of reference. After we deducted all these fluxes from the total energy flux, the remaining flux is independent on the frame of reference, i.e. Galilean invariant.

It is possible, however, to define another heat flux which would also represent the flow of a heat. A heat flux \mathbf{J}'_q is defined in the homogeneous region as

$$\mathbf{J}'_q \equiv \tilde{\mathbf{J}}_q - \sum_{i=1}^n h_i \mathbf{J}_i \quad (3.40)$$

where h_i is the partial specific enthalpy of component i . One can define it similarly in the interfacial region as well. We do not introduce this flux here, since we do not give the explicit expressions for the partial enthalpies in the interfacial region.

All the thermodynamic potentials, such as the internal energy or the chemical potentials are defined with respect to some reference state. This determines some thermodynamic state as an absolute state and all the thermodynamic potentials are measured with respect to this reference state. This is similar to choosing the particular frame of reference, which has an absolute velocity. Similarly to the Galilean invariance of the mechanical equations, the thermodynamic relations must be independent of the reference state.

Both heat fluxes $\tilde{\mathbf{J}}_q$ and \mathbf{J}'_q are Galilean invariant, i.e. independent on the particular *frame of reference*. However, the heat flux $\tilde{\mathbf{J}}_q$ depends on the choice of particular *reference state*, while the heat flux \mathbf{J}'_q does not. It means that the essential measure of the heat flow is the flux \mathbf{J}'_q . It is therefore natural to call \mathbf{J}'_q the *measurable heat flux*, while $\tilde{\mathbf{J}}_q$, by analogy with \mathbf{J}_e , the *total heat flux*.

The above definitions of energy fluxes in the interfacial region are straightforwardly reduced to the ones in the homogeneous region, and coincide with the definitions used in [13].

3.6 Two-Dimensional Isotropy of the Surface

Even though the fluid does not have any preferred direction microscopically, we cannot say that it has a three-dimensional isotropy everywhere, since there are the mesoscopic directions of the density gradients. The two-phase equilibrium state is not three-dimensionally isotropic.

A special care should be taken to determine the normal direction to the surface. With the help of the equilibrium analysis one can obtain distributions of the equilibrium densities in the interfacial region. It is possible therefore to determine the equidensity surfaces, i.e. mathematical surfaces, where either density is

constant, and which are normal to the corresponding density gradient. One may in principle use the gradients of either of the densities to define a direction normal to the surface. For the mixture we find it more convenient, however, to define a normal using the tension field $\nabla_\alpha \gamma_{\alpha\beta}(\mathbf{r})$. We call the surfaces, which are everywhere normal to this vector field, the *equitensional* surfaces. The thickness of the interfacial region will be assumed to be much smaller than the radii of curvature of these equitensional surfaces. Given this assumption the tension vector field in good approximation does not change its direction through the interface. Thus, it is possible to speak about the normal vector \mathbf{n} on the surface, which is parallel to the tension vector in this region.

This allows us to speak about the symmetry of the surface. If the surface curvature is the same in both directions, parallel to the surface, a small surrounding of the normal through the interfacial region is invariant for any rotations around and reflections with respect to this normal. Thus we can say, that such a system has a local two-dimensional isotropy. We shall refer to such a property of the interfacial region as the two-dimensional isotropy of the surface. If the two radii of curvature differ, the surface is not two-dimensionally isotropic anymore. For a surface which is thin compared to the radii of curvature one can, in a good approximation, consider it to be two-dimensionally isotropic. We assume this to be the case for the systems we will consider.

If the system has three-dimensional (3D) isotropy, then coupling occurs only between forces and fluxes of the same 3D tensorial character. For an interfacial region, which is two-dimensionally (2D) isotropic, coupling occurs only between forces and fluxes of the same 2D tensorial character. Thus, phenomenological coefficients must remain unchanged under rotations and reflections with respect to the direction normal to the surface. Below we show how one can extract 2D-isotropic quantities from 3D scalars, vectors and tensors.

We shall use the special notation for the tensorial quantities of different order and different behavior in this section. Any tensorial quantity is denoted as $Q^{(dr)}$. Here d indicates the dimensionality of the space, in which the quantity is being considered, and can be either 3 or 2 here. r indicates the rank of the tensorial quantity, and can be s for scalar, v for vectorial or t for tensorial quantities. We refer to Appendix 3.B for the details.

Consider the entropy production, which has a form

$$\sigma_s = S^{(3s)} R^{(3s)} + V^{(3v)} \cdot W^{(3v)} + T^{(3t)} : \Pi^{(3t)} \quad (3.41)$$

To be able to use the 2D Curie principle [17] one may proceed along the steps, explained in [13]. To clarify this we shall write this expression as a combination of independent 2D scalars, vectors and tensors. The details are given in Appendix 3.B, here we will give the results.

One can split the vectorial and tensorial quantities into the normal and parallel components with respect to the normal vector \mathbf{n} on the surface. We use the subscripts \perp and \parallel for this quantities. Because of 2D-isotropy of the surface, these quantities reveal the scalar, vectorial or the tensorial behavior under rotations

around and reflections with respect to this normal in a 2D space. This will be indicated by superscripts 2r as explained above.

Any 3D scalar is also 2D scalar, since it remains invariant under any kind of coordinate transformations.

$$S^{(3s)} = S^{(2s)} \equiv S^{(s)} \quad (3.42)$$

Any 3D vector $V^{(3v)}$ can be written as (cf. the notation with Eq. 3.67):

$$V^{(3v)} = \left(V_{\perp}^{(s)}, V_{\parallel}^{(2v)} \right) \quad (3.43)$$

Any 3D tensor $T^{(3v)}$ can be written as (cf. the notation with Eq. 3.70):

$$T^{(3t)} = \begin{pmatrix} T_{\perp\perp}^{(s)} & T_{\perp\parallel}^{(2v)} \\ T_{\parallel\perp}^{(2v)} & T_{\parallel\parallel}^{(2t)} \end{pmatrix} = \begin{pmatrix} T_{\perp\perp}^{(s)} & T_{\perp\parallel}^{(2v)} \\ T_{\parallel\perp}^{(2v)} & \frac{1}{2}(\text{Tr } T_{\parallel\parallel}^{(2t)})U^{(2t)} + \overset{\circ}{T}_{\parallel\parallel}^{(2t)} \end{pmatrix} \quad (3.44)$$

Combining these components we obtain for the entropy production

$$\sigma_s = \sigma_{s, \text{scal}} + \sigma_{s, \text{vect}} + \sigma_{s, \text{tens}} \quad (3.45)$$

where

$$\begin{aligned} \sigma_{s, \text{scal}} &= S^{(s)}R^{(s)} + V_{\perp}^{(s)}W_{\perp}^{(s)} + T_{\perp\perp}^{(s)}\Pi_{\perp\perp}^{(s)} + \frac{1}{2}(\text{Tr } T_{\parallel\parallel}^{(2t)})\left(\text{Tr } \Pi_{\parallel\parallel}^{(2t)}\right) \\ \sigma_{s, \text{vect}} &= V_{\parallel}^{(2v)} \cdot W_{\parallel}^{(2v)} + T_{\perp\parallel}^{(2v)} \cdot \Pi_{\parallel\perp}^{(2v)} + T_{\parallel\perp}^{(2v)} \cdot \Pi_{\perp\parallel}^{(2v)} \\ \sigma_{s, \text{tens}} &= \overset{\circ}{T}_{\parallel\parallel}^{(2t)} : \overset{\circ}{\Pi}_{\parallel\parallel}^{(2t)} \end{aligned} \quad (3.46)$$

The little circle above a 2×2 tensor like in $\overset{\circ}{T}$ indicates the symmetric traceless part of this tensor.

The 2D Curie principle tells us that coupling occurs only between quantities of the same 2D tensorial order.

3.7 The Entropy Production

Comparing Eq. 3.38 with the balance equation for the entropy

$$\rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_s \quad (3.47)$$

we conclude, that the entropy flux and the rate of entropy production in the interfacial region are given by, respectively,

$$\mathbf{J}_s = \frac{1}{T} \left(\tilde{\mathbf{J}}_q - \sum_{k=1}^{n-1} \psi_k \mathbf{J}_k + (\mathbf{v} - \mathbf{v}^s) \cdot \Upsilon \right) \quad (3.48)$$

and

$$\sigma_s = \left(\tilde{\mathbf{J}}_q + (\mathbf{v} - \mathbf{v}^s) \cdot \Upsilon \right) \cdot \nabla \frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_k \cdot \nabla \frac{\psi_k}{T} - \frac{1}{T} \pi_{\alpha\beta} v_{\beta\alpha} - \frac{1}{T} \gamma_{\alpha\beta} \nabla_\alpha v_\beta^s \quad (3.49)$$

According to the second law σ_s is non-negative.

Consider the last term in Eq. 3.49. It is the product of the tension tensor $\gamma_{\alpha\beta}$ which is nonzero only in the interfacial region and the gradient of some velocity (the factor $1/T$ is irrelevant for the upcoming arguments). The contribution to the entropy production from this term moves along with the surface in non-equilibrium processes. It is therefore natural to associate \mathbf{v}^s with a velocity of the surface.⁴

Each of the terms in Eq. 3.49, except the last one, has a form JX , where both flux J and force X vanish in equilibrium. In other words, their Taylor expansion in the powers of perturbation starts from the first order term. Their product therefore has a Taylor expansion which starts from the second order term. Since σ_s is non-negative the coefficient at this second order term must be non-negative.

Now consider the last term in Eq. 3.49. It is the product of a velocity gradient, which vanishes in equilibrium, and the tension tensor $\gamma_{\alpha\beta}$, which remains finite in equilibrium in the interfacial region. The first non-zero term in the Taylor expansion of this product therefore is proportional to the first order of perturbation. The only option for this term to be non-negative for any perturbation is to be equal to zero. \mathbf{v}^s is therefore equal to some constant. Since any velocity is determined up to the constant velocity relative to the selected frame of reference, we may conclude, that \mathbf{v}^s represents the *surface frame of reference*. With no loss in generality we may impose

$$\mathbf{v}^s = 0 \quad (3.50)$$

meaning that we choose the surface frame of reference rather than the laboratory frame of reference. All subsequent analysis is done in the surface frame of reference.

Equations 3.48 and 3.49 in the surface frame of reference become respectively

$$\mathbf{J}_s = \frac{1}{T} \left(\tilde{\mathbf{J}}_q - \sum_{k=1}^{n-1} \psi_k \mathbf{J}_k + \mathbf{v} \cdot \Upsilon \right) \quad (3.51)$$

and

$$\sigma_s = \left(\tilde{\mathbf{J}}_q + \mathbf{v} \cdot \Upsilon \right) \cdot \nabla \frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_k \cdot \nabla \frac{\psi_k}{T} - \frac{1}{T} \pi_{\alpha\beta} v_{\beta\alpha} \quad (3.52)$$

⁴ One could, in fact, do this identification immediately after the introduction of this velocity in Eq. 3.14. We consider it more convenient to do it here, however.

Note, that the expressions for \mathbf{J}_s and σ_s in the interfacial region are different from those given in [13] for homogeneous phase. They however reduce to the homogeneous expressions in homogeneous phase. The fundamental difference here is the presence of the tension tensor $\Upsilon \equiv \gamma_{\alpha\beta}$ which is only nonzero in the interfacial region. This makes the interfacial transport to be essentially different from the bulk one.

We define the *heat flux* \mathbf{J}_q in the surface frame of reference (i.e. taking into account that $\mathbf{v}^s = 0$) as

$$\mathbf{J}_q \equiv \tilde{\mathbf{J}}_q + \mathbf{v} \cdot \Upsilon = \mathbf{J}_e - \rho \mathbf{v} e - p \mathbf{v} - \Pi \cdot \mathbf{v} \quad (3.53)$$

Away from the interfacial region \mathbf{J}_q and $\tilde{\mathbf{J}}_q$ coincide. \mathbf{J}_q is also the flow of essentially a heat, which explains its name.

With this definition, the entropy flux and the entropy production become respectively

$$\mathbf{J}_s = \frac{1}{T} \left(\mathbf{J}_q - \sum_{k=1}^{n-1} \psi_k \mathbf{J}_k \right) \quad (3.54)$$

and

$$\sigma_s = \mathbf{J}_q \cdot \nabla \frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_k \cdot \nabla \frac{\psi_k}{T} - \frac{1}{T} \pi_{\alpha\beta} \nabla_{\beta\alpha} \quad (3.55)$$

which has the same form as in [13]. As we mentioned above, there is a crucial difference between homogeneous and interfacial expressions, which is hidden behind this form.

3.8 The Phenomenological Equations

3.8.1 The Force–Flux Relations

Comparing Eq. 3.55 with Eqs. 3.45 and 3.46 we can write the entropy production for a 2D-isotropic surface as the sum of two-dimensional scalar, vectorial and tensorial contributions

$$\begin{aligned} \sigma_{s, \text{scal}} &= J_{q, \perp} \nabla_{\perp} \frac{1}{T} - \sum_{k=1}^{n-1} J_{k, \perp} \nabla_{\perp} \frac{\psi_k}{T} - \pi_{\perp\perp} \frac{\nabla_{\perp} v_{\perp}}{T} - \frac{\text{Tr} \pi_{\parallel\parallel}}{2} \frac{\nabla_{\parallel} \cdot \mathbf{v}_{\parallel}}{T} \\ \sigma_{s, \text{vect}} &= \mathbf{J}_{q, \parallel} \cdot \nabla_{\parallel} \frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_{k, \parallel} \cdot \nabla_{\parallel} \frac{\psi_k}{T} - (\nabla_{\perp} \mathbf{v}_{\parallel}) \cdot \frac{1}{T} \boldsymbol{\pi}_{\parallel\perp} - (\nabla_{\parallel} v_{\perp}) \cdot \frac{1}{T} \boldsymbol{\pi}_{\perp\parallel} \\ \sigma_{s, \text{tens}} &= \overset{\circ}{\pi}_{\parallel\parallel} : \frac{(\nabla_{\parallel} \mathbf{v}_{\parallel})}{T} \end{aligned} \quad (3.56)$$

Following the common procedure in non-equilibrium thermodynamics, we shall provide the constitutive force–flux relations, based on the form of the entropy production (3.56) (and following the sign convention in [2] from Chap. 1).

We distinguish the following scalar forces and fluxes. The thermodynamic forces are $\nabla_{\perp}(1/T)$, $-\nabla_{\perp}(\psi_i/T)$, $-(\nabla_{\perp}\mathbf{v}_{\perp})/T$, and $-(\nabla_{\parallel}\cdot\mathbf{v}_{\parallel})/T$. The corresponding fluxes are $J_{q,\perp}$, $J_{k,\perp}$, $\pi_{\perp\perp}$, and $\text{Tr}\pi_{\parallel\parallel}/2$, respectively. The linear force–flux equations for the scalar force–flux pairs then are

$$\begin{aligned}
\nabla_{\perp}\frac{1}{T} &= r_{qq,\perp\perp}J_{q,\perp} + \sum_{k=1}^{n-1} r_{qk,\perp\perp}J_{k,\perp} + r_{q\pi,\perp\perp}\pi_{\perp\perp} + r_{q\pi,\perp\parallel}\frac{\text{Tr}\pi_{\parallel\parallel}}{2} \\
-\nabla_{\perp}\frac{\psi_i}{T} &= r_{iq,\perp\perp}J_{q,\perp} + \sum_{k=1}^{n-1} r_{ik,\perp\perp}J_{k,\perp} + r_{i\pi,\perp\perp}\pi_{\perp\perp} + r_{i\pi,\perp\parallel}\frac{\text{Tr}\pi_{\parallel\parallel}}{2} \\
-\frac{\nabla_{\perp}\mathbf{v}_{\perp}}{T} &= r_{\pi q,\perp\perp}J_{q,\perp} + \sum_{k=1}^{n-1} r_{\pi k,\perp\perp}J_{k,\perp} + r_{\pi\pi,\perp\perp}\pi_{\perp\perp} + r_{\pi\pi,\perp\parallel}\frac{\text{Tr}\pi_{\parallel\parallel}}{2} \\
-\frac{\nabla_{\parallel}\cdot\mathbf{v}_{\parallel}}{T} &= r_{\pi q,\parallel\perp}J_{q,\perp} + \sum_{k=1}^{n-1} r_{\pi k,\parallel\perp}J_{k,\perp} + r_{\pi\pi,\parallel\perp}\pi_{\perp\perp} + r_{\pi\pi,\parallel\parallel}\frac{\text{Tr}\pi_{\parallel\parallel}}{2}
\end{aligned} \tag{3.57}$$

We distinguish the following vectorial forces and fluxes. The thermodynamic forces are $\nabla_{\parallel}(1/T)$, $-\nabla_{\parallel}(\psi_i/T)$, $-(\nabla_{\parallel}\mathbf{v}_{\perp})/T$, and $-(\nabla_{\parallel}\mathbf{v}_{\parallel})/T$. The corresponding fluxes are $J_{q,\parallel}$, $J_{k,\parallel}$, $\pi_{\perp\parallel}$, and $\pi_{\parallel\perp}$ respectively. For the vectorial force–flux pairs we write the phenomenological equations in the following form

$$\begin{aligned}
\mathbf{J}_{q,\parallel} &= \ell_{qq,\parallel\parallel}\nabla_{\parallel}\frac{1}{T} - \sum_{k=1}^{n-1}\ell_{qk,\parallel\parallel}\nabla_{\parallel}\frac{\psi_k}{T} - \ell_{q\pi,\parallel\parallel}\frac{1}{T}\nabla_{\perp}\mathbf{v}_{\parallel} - \ell_{q\pi,\parallel\perp}\frac{1}{T}\nabla_{\parallel}\mathbf{v}_{\perp} \\
\mathbf{J}_{i,\parallel} &= \ell_{iq,\parallel\parallel}\nabla_{\parallel}\frac{1}{T} - \sum_{k=1}^{n-1}\ell_{ik,\parallel\parallel}\nabla_{\parallel}\frac{\psi_k}{T} - \ell_{i\pi,\parallel\parallel}\frac{1}{T}\nabla_{\perp}\mathbf{v}_{\parallel} - \ell_{i\pi,\parallel\perp}\frac{1}{T}\nabla_{\parallel}\mathbf{v}_{\perp} \\
\pi_{\parallel\perp} &= \ell_{\pi q,\parallel\parallel}\nabla_{\parallel}\frac{1}{T} - \sum_{k=1}^{n-1}\ell_{\pi i,\parallel\parallel}\nabla_{\parallel}\frac{\psi_k}{T} - \ell_{\pi\pi,\parallel\parallel}\frac{1}{T}\nabla_{\perp}\mathbf{v}_{\parallel} - \ell_{\pi\pi,\parallel\perp}\frac{1}{T}\nabla_{\parallel}\mathbf{v}_{\perp} \\
\pi_{\perp\parallel} &= \ell_{\pi q,\perp\parallel}\nabla_{\parallel}\frac{1}{T} - \sum_{k=1}^{n-1}\ell_{\pi i,\perp\parallel}\nabla_{\parallel}\frac{\psi_k}{T} - \ell_{\pi\pi,\perp\parallel}\frac{1}{T}\nabla_{\perp}\mathbf{v}_{\parallel} - \ell_{\pi\pi,\perp\perp}\frac{1}{T}\nabla_{\parallel}\mathbf{v}_{\perp}
\end{aligned} \tag{3.58}$$

We have one tensorial thermodynamic force $(\nabla_{\parallel}\overset{\circ}{\mathbf{v}}_{\parallel})/T$ and the corresponding flux $\overset{\circ}{\pi}_{\parallel\parallel}$. So for the tensorial force–flux pairs the constitutive relations are

$$\overset{\circ}{\pi}_{\parallel\parallel} = \ell_{\pi}\frac{(\nabla_{\parallel}\overset{\circ}{\mathbf{v}}_{\parallel})}{T} \tag{3.59}$$

All the resistivities r and conductivities ℓ are scalars. One can easily invert the resistivity matrix r and write the corresponding relations for the fluxes using the conductivities ℓ , and vice versa.

For flat surfaces it was found [18] that the resistivities are additive in the normal direction to the surface while the conductivities are additive in the parallel direction. We therefore consider it convenient to write the force–flux relations in the above form.

3.8.2 The Phenomenological Coefficients

The Onsager relations for the phenomenological coefficients are the following.

$$\begin{aligned}
 \left(r_{qk}, \perp\perp \right) &= r_{kq}, \perp\perp & \left(\ell_{qk}, \parallel\parallel \right) &= \ell_{kq}, \parallel\parallel \\
 \left(r_{q\pi}, \perp\perp \right) &= r_{\pi q}, \perp\perp & \left(\ell_{q\pi}, \parallel\parallel \right) &= \ell_{\pi q}, \parallel\parallel \\
 \left(r_{q\pi}, \perp\parallel \right) &= r_{\pi q}, \parallel\perp & \left(\ell_{q\pi}, \parallel\perp \right) &= \ell_{\pi q}, \perp\parallel \\
 \left(r_{ik}, \perp\perp \right) &= r_{ki}, \perp\perp & \left(\ell_{ik}, \parallel\parallel \right) &= \ell_{ki}, \parallel\parallel \\
 \left(r_{i\pi}, \perp\perp \right) &= r_{\pi i}, \perp\perp & \left(\ell_{i\pi}, \parallel\parallel \right) &= \ell_{\pi i}, \parallel\parallel \\
 \left(r_{i\pi}, \perp\parallel \right) &= r_{\pi i}, \parallel\perp & \left(\ell_{i\pi}, \parallel\perp \right) &= \ell_{\pi i}, \perp\parallel \\
 \left(r_{\pi\pi}, \perp\parallel \right) &= r_{\pi\pi}, \parallel\perp & \left(\ell_{\pi\pi}, \parallel\perp \right) &= \ell_{\pi\pi}, \perp\parallel
 \end{aligned} \tag{3.60}$$

As the ordinary Onsager relations, these are the consequence of the microscopic time reversal invariance.

As usual, the values of the phenomenological coefficients locally will depend on the local thermodynamic variables. These are the local concentrations, ρ , ξ , and the temperature, T . In the gradient theory the density gradients are also considered as local thermodynamic variables. In view of this, the phenomenological coefficients may also depend on the gradients of the densities. The values of the phenomenological coefficients and their functional dependence on the thermodynamic variables are not given by the mesoscopic theory. They should be either calculated from statistical mechanical considerations, or from experiments, either real or computer. While they are well investigated for homogeneous fluids and fluid mixtures, such data are not available for the surface coefficients of fluid mixtures.

We shall use the following expression for each of the resistivity coefficients

$$r = r^g + (r^\ell - r^g) \frac{\phi - \phi^g}{\phi^\ell - \phi^g} + \alpha(r^\ell + r^g) \frac{|\nabla\phi|^2}{|\nabla\phi_{\text{eq}}|_{\text{max}}^2} \tag{3.61}$$

where r^g and r^ℓ are the resistivities for the coexisting homogeneous bulk phases, gas and liquid, in the equilibrium state. Here ϕ is the order parameter, typically this is just the density ρ or the molar concentration c . ϕ_{eq} is the equilibrium profile and $|\nabla\phi_{\text{eq}}|_{\text{max}}$ is the maximum value of the gradient of this profile. The first two terms are just a smooth transition of the resistivity from the value in the one phase to the value in the other phase. This is the first natural assumption for the resistivity profile. The origin of the third term comes from the assumption that the resistivity has a peak in the interfacial region. Particularly one can observe this fact in the molecular dynamic simulations [19]. The exact form of this term may be debated. It was chosen to model a rise of the resistivity in the interfacial region. The $|\nabla\phi|^2$

factor makes this term significant only in the interfacial region. It is scaled with $|\nabla\phi_{\text{eq}}|_{\text{max}}^2$ in order to make this factor dimensionless and not far from unity. The $(r^\ell + r^g)$ factor gives the average value of the resistivity of both phases. The dimensionless factor α represents the magnitude of this effect at equilibrium. The homogeneous resistivities r^g and r^ℓ are the known functions of the mass fraction and the temperature along the plane of coexistence.

For the conductivities used in Eqs. 3.58 and 3.59 one may use expressions analogous to Eq. 3.61. The conductivities along the surface are expected to be additive [18]. Thus, it is important to use this equation for the conductivities and not for the resistivities along the surface. In this respect it is important to note that α may in principle be negative as long as the corresponding r and L remain everywhere positive. For the resistivity this would describe an interfacial region with a lower resistivity and for the conductivities it would describe an interfacial region with a lower conductivity. We will only consider positive α 's.

3.9 Discussion and Conclusions

In this chapter we have built the framework for the non-equilibrium gradient model for the surface. This requires the following important steps. With the help of the equilibrium gradient model for the mixtures, established in the previous chapter, we were able to extend the thermodynamic description of the interfacial region to the non-equilibrium case. Explicit expressions for the Gibbs relation and the pressure tensor were given. We found that compared to homogeneous systems, the Gibbs relation for the interfacial region contains an additional term, proportional to the divergence of the tension tensor. This tensor plays an important role in the surface and integration of its perpendicular component gives the surface tension. Away from the surface this tensor is equal to zero and we have the familiar Gibbs relation. For a single component system the Gibbs relation in the interfacial region reduces to the one given by [1].

For the non-equilibrium description we use the standard hydrodynamic equations for the so-called “one-fluid” model of the fluid. Together with the Gibbs relation and the balance equation for the entropy density, we were then able to obtain explicit expressions for the entropy flux and the entropy production not only in the homogeneous phases but also in the interfacial region. This identifies the conjugate thermodynamic forces and fluxes in the interfacial region. This made it possible to give the general force–flux relations in this region. The explicit form of these equations depends on the symmetry of the system. We discuss why one can consider a fluid–fluid interface to be two-dimensional isotropic. Due to the Curie principle, coupling occurs only between two-dimensionally isotropic scalars, vectors and tensors of the same rank in such a system. The resulting force–flux relations in the interfacial region are accordingly simplified and given. Interesting is that the components of the fluxes normal to the surface are scalar and couple therefore to chemical reactions in the interfacial region. This is related to active

transport, a phenomenon of great importance. We do not explicitly consider reacting system in this thesis, but may do this in future. Having all these equations, the non-equilibrium description of the surface is complete.

We conclude that the description we have given, using an extension of the square gradient model, will be a useful tool to study many details of the dynamics of evaporation and condensation in multi-component systems. Non-equilibrium molecular dynamic simulations of evaporation and condensation could obtain density, mass fraction and temperature profiles. We expect the comparison of these profiles with the present model to be very useful. In particular, this will give insight in the size and possible density, mass fraction and temperature dependence of the coefficient α . In this manner we expect the model to form a bridge between the microscopic description using non-equilibrium molecular dynamic simulations and the discrete macroscopic description using the excess densities introduced by Gibbs [20]. In Chap. 5 investigate whether the discrete description satisfies the local equilibrium assumption for an arbitrary choice of the dividing surface, a property which was verified for one-component systems [2]. This would be a rather remarkable result, given the fact that the continuous description does not obey this property. For a systematic development of the non-equilibrium thermodynamic description of surfaces this property is essential [21, 22].

3.A On the Extension of the Gibbs Relation to Non-Equilibrium

For the specific Helmholtz energy the ordinary Gibbs relation in equilibrium was found to be

$$\delta f(T, v, \xi) = -s(\mathbf{r}) \delta T + \sum_{i=1}^{n-1} \psi_i \delta \xi_i(\mathbf{r}) - p(\mathbf{r}) \delta v(\mathbf{r}) \quad (3.62)$$

Spatial Gibbs relations in equilibrium was found to be

$$\nabla f(\mathbf{r}) = \sum_{i=1}^{n-1} \psi_i \nabla \xi_i(\mathbf{r}) - p(\mathbf{r}) \nabla v(\mathbf{r}) + v(\mathbf{r}) \frac{\partial \gamma_{\alpha\beta}(\mathbf{r})}{\partial x_\alpha} \quad (3.63)$$

One may wonder why to use the Gibbs relations for the specific internal energy, not for the specific Helmholtz energy, to extend them to non-equilibrium analysis. Following the same procedure, as in Sect. 3.3, we can extend the Gibbs relations for the specific Helmholtz energy to non-equilibrium in the following way

$$\frac{\partial f(\mathbf{r}, t)}{\partial t} = -s(\mathbf{r}, t) \frac{\partial T(\mathbf{r}, t)}{\partial t} + \sum_{i=1}^{n-1} \psi_i(\mathbf{r}, t) \frac{\partial \xi_i(\mathbf{r}, t)}{\partial t} - p(\mathbf{r}, t) \frac{\partial v(\mathbf{r}, t)}{\partial t} \quad (3.64)$$

$$\nabla f(\mathbf{r}, t) = \sum_{i=1}^{n-1} \psi_i(\mathbf{r}, t) \nabla \zeta_i(\mathbf{r}, t) - p(\mathbf{r}, t) \nabla v(\mathbf{r}, t) + v(\mathbf{r}, t) \frac{\partial \gamma_{\alpha\beta}(\mathbf{r}, t)}{\partial x_\alpha} \quad (3.65)$$

For the ordinary Gibbs relations, like in homogeneous description, there is no preference in the thermodynamic potential. Provided Eq. 3.6, equilibrium ordinary Gibbs relations Eqs. 3.9 and 3.62 are equivalent. The non-equilibrium relation between these potentials

$$u(\mathbf{r}, t) = f(\mathbf{r}, t) + s(\mathbf{r}, t)T(\mathbf{r}, t) \quad (3.66)$$

makes non-equilibrium ordinary Gibbs relations (3.11) and (3.64) to be equivalent as well.

The situation is different for the spatial Gibbs relations, however. Provided Eq. 3.6, equilibrium spatial Gibbs relations Eqs. 3.10 and 3.63 are equivalent. The non-equilibrium relation Eq. 3.66 between these potentials makes, however, non-equilibrium spatial Gibbs relations (3.12) and (3.65) to be *not* equivalent. The reason for that is that the equilibrium spatial Gibbs relation for the specific Helmholtz energy, as given in Eq. 3.63, does not contain the term, proportional to ∇T , since $\nabla T = 0$ in equilibrium. In non-equilibrium $\nabla T(\mathbf{r}, t) \neq 0$ and, as one can see from Eqs. 3.12 and 3.66, $\nabla f(\mathbf{r}, t)$ contains such a term.

We see, that the Gibbs relations for the specific internal energy describe the system more adequately since they do not suffer from the unaccounted effect of possible temperature changes. Because of this reason we should use the Gibbs relations for the specific internal energy, not the specific Helmholtz energy, to extend them to non-equilibrium. Of course, this does not make the internal energy to be somehow preferred thermodynamic potential in non-equilibrium. If one does not disregard terms with ∇T or others which are zero in equilibrium, one will see the fully equivalence between all the thermodynamic potentials, as it should be.

3.B Two-Dimensional Isotropic Components in the 3D Tensorial Quantities

As in Sect. 3.6 we shall use the special notation for the tensorial quantities of different order and different behavior in this section. Any tensorial quantity is denoted as $Q^{(d,r)}$. Here d indicates the dimensionality of the space, in which the quantity is being considered, and can be either 3 or 2 here. r indicates the rank of the tensorial quantity, and can be s for scalar, v for vectorial or t for tensorial quantities. For example, $Q^{(2,t)}$ indicates the two-dimensional tensor, i.e. the quantity $\begin{pmatrix} q_{11} & q_{12} \\ q_{21} & q_{22} \end{pmatrix}$, where q_{ij} are numbers, and $Q^{(3,v)}$ indicates the three-dimensional vector, i.e. the quantity (q_1, q_2, q_3) , where q_i are numbers. Scalars are

the numbers irrespectively of the dimensionality of the space, so they will be denoted simply by $Q^{(s)}$.

Some quantities reveal the tensorial behavior of a some rank in d -dimensional space only under some specified transformations, while in general they do not. In this section we are interested only in rotations around and reflections with respect to some constant vector $N^{(3v)}$ in three-dimensional space. We will denote quantities which reveal the tensorial behavior of rank r under these transformations by $Q^{(dr_N)}$.

We show how in presence of the constant vector $N^{(3v)}$ one can split the tensorial quantity $Q^{(3r)}$ into a combination of the tensorial quantities $Q^{(2r_N)}$. Without loss of generality we will assume that $N^{(3v)} = (1, 0, 0)$.

From 3D vector $V^{(3v)}$ one can construct the following quantities, which are linear in $V^{(3v)}$: one scalar quantity

$$V^{(s_N)} \equiv V^{(3v)} \cdot N^{(3v)} = V_1^{(3v)}$$

and one vectorial quantity

$$V^{(3v_N)} \equiv V^{(3v)} - V^{(s_N)}N^{(3v)} = \left(0, V_2^{(3v)}, V_3^{(3v)}\right)$$

which is perpendicular to the $N^{(3v)}$. Denoting $V^{(2v_N)} \equiv (V_2^{(3v)}, V_3^{(3v)})$ we can write that $V^{(3v_N)} = (0, V^{(2v_N)})$. Thus,

$$V^{(3v)} = V^{(s_N)}N^{(3v)} + V^{(3v_N)} = (V^{(s_N)}, V^{(2v_N)}) \quad (3.67)$$

From 3D tensor $T^{(3t)}$ one can construct the following quantities, which are linear in $T^{(3t)}$: 2 scalar quantity,

$$T_0^{(s)} \equiv \text{Tr } T^{(3t)} = T_{11}^{(3t)} + T_{22}^{(3t)} + T_{33}^{(3t)}$$

and

$$T_1^{(s_N)} \equiv N^{(3v)} \cdot T^{(3t)} \cdot N^{(3v)} = T_{11}^{(3t)}$$

two vectorial quantities

$$T_l^{(3v_N)} \equiv N^{(3v)} \cdot T^{(3t)} - T_1^{(s_N)}N^{(3v)} = \left(0, T_{12}^{(3t)}, T_{13}^{(3t)}\right)$$

and

$$T_r^{(3v_N)} \equiv T^{(3t)} \cdot N^{(3v)} - T_1^{(s_N)}N^{(3v)} = \left(0, T_{21}^{(3t)}, T_{31}^{(3t)}\right)$$

(which are equal, if $T^{(3t)}$ is symmetric); and tensorial quantity

$$\begin{aligned}
T^{(3t_N)} &\equiv T^{(3t)} - T_1^{(s_N)} N^{(3v)} N^{(3v)} - T_l^{(3v_N)} N^{(3v)} - N^{(3v)} T_r^{(3v_N)} \\
&= \begin{pmatrix} 0 & 0 & 0 \\ 0 & T_{22}^{(3t)} & T_{23}^{(3t)} \\ 0 & T_{32}^{(3t)} & T_{33}^{(3t)} \end{pmatrix}
\end{aligned}$$

Denoting

$$\begin{aligned}
T_l^{(2v_N)} &\equiv (T_{12}^{(3t)}, T_{13}^{(3t)}) & T^{(2t_N)} &\equiv \begin{pmatrix} T_{22}^{(3t)} & T_{23}^{(3t)} \\ T_{32}^{(3t)} & T_{33}^{(3t)} \end{pmatrix} \\
T_r^{(2v_N)} &\equiv (T_{21}^{(3t)}, T_{31}^{(3t)})
\end{aligned}$$

we can write that

$$\begin{aligned}
T_l^{(3v_N)} &= (0, T_l^{(2v_N)}) & T^{(3t_N)} &= \begin{pmatrix} 0 & 0 \\ 0 & T^{(2t_N)} \end{pmatrix} \\
T_r^{(3v_N)} &= (0, T_r^{(2v_N)})
\end{aligned}$$

Thus⁵

$$\begin{aligned}
T^{(3t)} &= T_1^{(s_N)} N^{(3v)} N^{(3v)} + T_l^{(3v_N)} N^{(3v)} + N^{(3v)} T_r^{(3v_N)} + T^{(3t_N)} \\
&= \begin{pmatrix} T_1^{(s_N)} & T_l^{(2v_N)} \\ T_r^{(2v_N)} & T^{(2t_N)} \end{pmatrix} \tag{3.68}
\end{aligned}$$

Tensor $T^{(2t_N)}$ still contains the scalar part

$$T_2^{(s_N)} \equiv \text{Tr} T^{(2t_N)} = T_{22}^{(3t)} + T_{33}^{(3t)}$$

which obeys the relation

$$T_0^{(s)} = T_1^{(s_N)} + T_2^{(s_N)} \tag{3.69}$$

Two of these three scalar quantities are linearly independent, and one can use any pair. Since we want to reduce all the quantities to the form $Q^{(2r_N)}$ we will use $T_1^{(s_N)}$ and $T_2^{(s_N)}$ as independent pair. Introducing the traceless tensor

$$\overset{\circ}{T}^{(2t_N)} \equiv T^{(2t_N)} - \frac{1}{2} T_2^{(s_N)} U^{(2t)} = \begin{pmatrix} T_{22}^{(3t)} - \frac{1}{2} T_2^{(s_N)} & T_{23}^{(3t)} \\ T_{32}^{(3t)} & T_{33}^{(3t)} - \frac{1}{2} T_2^{(s_N)} \end{pmatrix}$$

and

⁵ Note, that if the product of two tensorial quantities of rank $r > 0$ is written without \cdot , it means that this is the product, not the internal product.

$$\overset{\circ}{T}^{(3t_N)} \equiv T^{(3t_N)} - \frac{1}{2}T_2^{(s_N)}U^{(3t_N)} = \begin{pmatrix} 0 & \mathbf{0} \\ 0 & \overset{\circ}{T}^{(2t_N)} \end{pmatrix}$$

where

$$U^{(2t)} \equiv \begin{pmatrix} 1 & \mathbf{0} \\ 0 & 1 \end{pmatrix} \quad U^{(3t_N)} \equiv \begin{pmatrix} 0 & \mathbf{0} \\ 0 & U^{(2t)} \end{pmatrix}$$

we can write a 3D tensor as

$$\begin{aligned} T^{(3t)} &= T_1^{(s_N)}N^{(3v)}N^{(3v)} + \frac{1}{2}T_2^{(s_N)}U^{(3t_N)} + \overset{\circ}{T}^{(3t_N)} \\ &\quad + T_l^{(3v_N)}N^{(3v)} + N^{(3v)}T_r^{(3v_N)} \\ &= \begin{pmatrix} T_1^{(s_N)} & T_l^{(2v_N)} \\ T_r^{(2v_N)} & \frac{1}{2}T_2^{(s_N)}U^{(2t)} + \overset{\circ}{T}^{(2t_N)} \end{pmatrix} \end{aligned} \quad (3.70)$$

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Chapter 4

Numerical Solution for the Binary Mixture

4.1 Introduction

In previous chapters, we have established the square gradient description of the interface between two phases in non-equilibrium mixtures. We considered temperature, density and mass fraction gradients; heat and diffusion fluxes as well as evaporation or condensation fluxes through the interface. In this chapter we apply this analysis to a particular binary mixture. We then solve the derived equations numerically. In this chapter we give the description of the numerical procedure and the profiles of various thermodynamic quantities.

To obtain the numerical solution we have to imply a number of assumptions about the system's behavior, geometry and conditions. The system is considered to be in a stationary state. The numerical analysis of stationary states is a natural first step, as the numerical analysis of non-stationary states is much more involved. We consider a flat interface between a binary liquid and its vapor with the normal $\mathbf{n} = (1, 0, 0)$ pointing from the vapor to the liquid. We choose all fluxes and gradients to be in the x -direction. Due to this, all variables depend only on the x -coordinate. We choose the system such that the gas is on the left hand side and the liquid is on the right hand side. The x -axis is directed from left to right and the gravitational acceleration \mathbf{g} is directed towards the liquid. To simplify the analysis we assume the fluid to be non-viscous, so that the viscous pressure tensor $\pi_{\alpha\beta} = 0$. Neither the parallel nor the normal hydrostatic pressure are assumed to be constant.

For all the quantities except the measurable heat flux J'_q , the prime $'$ symbol indicates the derivative with respect to position x .

In Sect. 4.2 we give the complete set of equations, which are required for the determination of the various profiles in stationary states of the system. We shall give the various thermodynamic densities which follow from the van der Waals equation of state and the gradient terms to be added in the interfacial region. In Sect. 4.3 we describe the numerical procedure which has been used to solve these equations. The numerical solution is calculated between two points where

boundary conditions are given. The region between these two points we refer to as the box. In Sect. 4.4 we specify the input data for the chosen mixture. We use cyclohexane and *n*-hexane as components. We give the profiles of different thermodynamic quantities under various conditions in Sect. 4.5.

Parts of this chapter have been published in [1, 2]: © The American Physical Society.

4.2 Complete Set of Equations

4.2.1 Conservation Equations

In a stationary state the conservation equations take the following form. The law of mass conservation for the components gives

$$\begin{aligned} \frac{d}{dx}(\rho v) &= 0 \\ \frac{d}{dx}(J_1 + \rho \xi v) &= 0 \end{aligned} \quad (4.1)$$

where $\rho = \rho_1 + \rho_2$ and $v = (\rho_1 v_1 + \rho_2 v_2)/\rho$ are the mass density and the barycentric (center of mass) velocity. Furthermore, $\xi = \rho_1/\rho$ is the mass fraction of the first component and $J_1 = \rho_1(v_1 - v) = \rho \xi(v_1 - v)$ is the diffusion flux of the first component relative to the barycentric frame of reference. The diffusion flux of the second component is $J_2 = \rho_2(v_2 - v) = -J_1$. Momentum conservation is given by

$$\frac{d}{dx}(\rho v^2 + p + \gamma_{xx}) = \rho g \quad (4.2)$$

where γ_{xx} is the normal component of the thermodynamic tension tensor, which will be given below. Furthermore, p and $p + \gamma_{xx}$ are the pressures parallel and perpendicular to the interface, for the planar interface under consideration. Energy conservation is given by

$$\frac{d}{dx} J_e = 0 \quad (4.3)$$

where $J_e \equiv J_q + \rho e v + p v$ is the total energy flux, J_q the heat flux, and $e = u + v^2/2 - g x$ the total specific energy and u the specific internal energy.

4.2.2 Thermodynamic Equations

The square gradient model, discussed in the previous chapters, gives the following expressions for the specific Helmholtz energy f , the specific internal energy u , the

parallel pressure p , the chemical potential difference $\psi \equiv \mu_1 - \mu_2$, the chemical potential of the second component $\mu \equiv \mu_2$ and the xx -element of the tension tensor γ_{xx} :

$$\begin{aligned}
 f(x) &= f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi') \\
 u(x) &= f_0(T, \rho, \xi) - T \frac{\partial}{\partial T} f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi') \\
 p(x) &= \rho^2 \frac{\partial}{\partial \rho} (f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi')) - \rho \frac{d}{dx} \left(\rho \frac{\partial}{\partial \rho'} \mathcal{K}(\rho, \xi, \rho', \xi') \right) \\
 \psi(x) &= \frac{\partial}{\partial \xi} (f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi')) - \frac{1}{\rho} \frac{d}{dx} \left(\rho \frac{\partial}{\partial \xi'} \mathcal{K}(\rho, \xi, \rho', \xi') \right) \\
 \mu(x) &= \frac{\partial}{\partial \rho} (\rho (f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi'))) - \frac{d}{dx} \left(\rho \frac{\partial}{\partial \rho'} \mathcal{K}(\rho, \xi, \rho', \xi') \right) - \psi(x) \xi \\
 s(x) &= -\frac{\partial}{\partial T} f_0(T, \rho, \xi) \\
 \gamma_{xx}(x) &= 2 \rho \mathcal{K}(\rho, \xi, \rho', \xi')
 \end{aligned} \tag{4.4}$$

Here $f_0(T, \rho, \xi) = f_0^v(T, c, \zeta)/M(\zeta)$ is the specific Helmholtz energy of the homogeneous phase (see Sect. 4.2.3), which can for instance be derived from the equation of state. Furthermore, $\mathcal{K}(\rho, \xi, \rho', \xi')$ is the gradient contribution (see Sect. 4.2.4). Since the equation of state is usually given in molar quantities, it is convenient to use them here as well. Thus, $c = \rho/M$ is the molar concentration, $\zeta = \xi M/M_1$ is the molar fraction of the first component, where $M = M_1 M_2 / (M_1 + \xi(M_2 - M_1)) = M_2 + \zeta(M_1 - M_2)$ is the molar mass of the mixture, and M_1 and M_2 are molar masses of each component.

4.2.3 The Helmholtz Energy of a Homogeneous System

This energy is given by the following equation

$$f_0^v(T, c, \zeta) = -RT \ln \left(\frac{e}{c N_A \Lambda^3(T, \zeta)} (1 - B(\zeta) c) \right) - A(T, \zeta) c \tag{4.5}$$

where the de Broglie wavelength Λ and the characteristic sum over internal degrees of freedom w are respectively:

$$\begin{aligned}
 \Lambda(T, \zeta) &= \hbar N_A \left(\frac{2\pi}{M R T} \right)^{1/2} \\
 w(T, \zeta) &= \left(\frac{w_1}{\zeta} \left(\frac{M_1}{M} \right)^{3/2} \right)^\zeta \left(\frac{w_2}{1-\zeta} \left(\frac{M_2}{M} \right)^{3/2} \right)^{1-\zeta}
 \end{aligned} \tag{4.6}$$

Expressions for the characteristic sums over internal degrees of freedom for each component, w_1 and w_2 , are given in Chap. 3. In this thesis they are assumed to be independent of the temperature and the molar fractions as well as the particular internal molecular structure, i.e. just constant numbers. Equation 4.5 together with Eq. 4.6 follow from the van der Waals equation of state.

The mixing rules for A and B are

$$\begin{aligned} A(T, \zeta) &= a_{11}\zeta^2 + 2a_{12}\zeta(1 - \zeta) + a_{22}(1 - \zeta)^2 \\ B(\zeta) &= b_1\zeta + b_2(1 - \zeta) \end{aligned} \quad (4.7)$$

with $a_{ij} = \sqrt{a_i a_j}$, where a_i as well as b_i is a coefficient of a pure component i . We will assume in this thesis that all a_{ij} and b_i are independent of temperature.

4.2.4 The Gradient Contribution

This contribution is given by the following general expression for a binary mixture

$$\mathcal{K}(\rho, \xi, \rho', \xi') \equiv \frac{1}{2\rho} \left(\kappa_{\rho\rho}(\rho, \xi)\rho'^2 + 2\kappa_{\rho\xi}(\rho, \xi)\rho'\xi' + \mathcal{K}_{\xi\xi}(\rho, \xi)\xi'^2 \right) \quad (4.8)$$

The coefficients $\kappa_{\rho\rho}$, $\kappa_{\rho\xi}$ and $\mathcal{K}_{\xi\xi}$ can be expressed in the gradient coefficients $\kappa_{\rho_1\rho_1}$ and $\kappa_{\rho_2\rho_2}$ for components 1 and 2 in the following way (see Sect. 2.5 for details)

$$\begin{aligned} \kappa_{\rho\rho}(\rho, \xi) &= (\kappa_{\rho_1\rho_1} - 2\kappa_{\rho_1\rho_2} + \kappa_{\rho_2\rho_2})\xi^2 + 2(\kappa_{\rho_1\rho_2} - \kappa_{\rho_2\rho_2})\xi + \kappa_{\rho_2\rho_2} \\ \kappa_{\rho\xi}(\rho, \xi) &= (\kappa_{\rho_1\rho_1} - 2\kappa_{\rho_1\rho_2} + \kappa_{\rho_2\rho_2})\rho\xi + (\kappa_{\rho_1\rho_2} - \kappa_{\rho_2\rho_2})\rho \\ \mathcal{K}_{\xi\xi}(\rho, \xi) &= (\kappa_{\rho_1\rho_1} - 2\kappa_{\rho_1\rho_2} + \kappa_{\rho_2\rho_2})\rho^2 \end{aligned} \quad (4.9)$$

where for the cross coefficient we use the mixing rule $\kappa_{\rho_1\rho_2} = \sqrt{\kappa_{\rho_1\rho_1}\kappa_{\rho_2\rho_2}}$ similar to the one for coefficients a_{ij} . We will further assume $\kappa_{\rho_i\rho_j}$ to be independent of the densities.

With the above mixing rules the gradient contribution can be written in the form

$$\mathcal{K}(\rho, \xi, \rho', \xi') \equiv \frac{\kappa q'^2}{2\rho} \quad (4.10)$$

where

$$\begin{aligned} \kappa &\equiv \kappa_{\rho_2\rho_2} \\ q &\equiv \rho(1 + \varepsilon_\kappa^m \xi) \\ \varepsilon_\kappa^m &\equiv \varepsilon_\kappa \equiv \sqrt{\frac{\kappa_{\rho_1\rho_1}}{\kappa_{\rho_2\rho_2}}} - 1 \end{aligned} \quad (4.11)$$

Some of the quantities from Eq. 4.4 can be rewritten as

$$\begin{aligned}
p(x) &= p_0 - \kappa \left(\frac{1}{2} q'^2 + q q'' \right) \\
\mu(x) &= \mu_0 - \kappa q'' \\
\psi(x) &= \psi_0 - \varepsilon_\kappa \kappa q''
\end{aligned} \tag{4.12}$$

where p_0, μ_0 and ψ_0 are values of the corresponding quantities in the homogeneous phase, which are found from Eq. 4.4 by setting $\mathcal{K} = 0$. For a one-component fluid q equals the density. For the two-component mixture q plays a similar role as the density for the one-component fluid. We shall therefore refer to q as the order parameter.

For the surface tension of the flat interface one may show, using Eqs. 4.10 and 4.4, that in equilibrium

$$\gamma_{\text{eq}} \equiv \int dx \gamma_{xx, \text{eq}}(x) = \kappa \int dx q'_{\text{eq}}{}^2 \tag{4.13}$$

It follows that κ_{ρ_i, ρ_i} is proportional to the surface tension $\gamma_{\text{eq}, i}$ of the pure component i . It follows therefore that as estimate for ε_κ one may use the relation

$$\varepsilon_\kappa \simeq \sqrt{\frac{\gamma_1}{\gamma_2}} - 1 \tag{4.14}$$

In an organic mixture like cyclohexane and n -hexane, a mixture we will study in more detail in this thesis, the components are very similar and as a consequence $|\varepsilon_\kappa|$ is small, as one can see from Eq. 4.14. The order parameter is then in good approximation equal to the density. When the components are very different $|\varepsilon_\kappa|$ may be large and q may become in good approximation equal to the density of one of the components.

4.2.5 Phenomenological Equations

In the previous chapter we derived the general expression for the entropy production of a mixture in the interfacial region. For a binary mixture which has only gradients and fluxes in the x -direction, it takes, neglecting the viscous contribution, the following form

$$\sigma_s = J_q \frac{d}{dx} \frac{1}{T} - J_1 \frac{d}{dx} \frac{\psi}{T} \tag{4.15}$$

where we used that $J_2 = -J_1$. The resulting linear force–flux relations are:

$$\begin{aligned}
\frac{d}{dx} \frac{1}{T} &= r_{qq} J_q + r_{q1} J_1 \\
-\frac{d}{dx} \frac{\psi}{T} &= r_{1q} J_q + r_{11} J_1
\end{aligned} \tag{4.16}$$

The resistivity coefficients r_{qq}, r_{11} and $r_{q1} = r_{1q}$ will in general depend on the densities, their gradients as well as on the temperature, so they vary through the interface. Expressions for the resistivity profiles in the interfacial region are not available. We model them, using the bulk values as the limiting value away from the surface and the order parameter profile as a modulatory curve

$$\begin{aligned} r_{qq}(x) &= r_{qq}^g + (r_{qq}^\ell - r_{qq}^g) q_0(x) + \alpha_{qq}(r_{qq}^\ell + r_{qq}^g) q_1(x) \\ r_{q1}(x) &= r_{q1}^g + (r_{q1}^\ell - r_{q1}^g) q_0(x) + \alpha_{q1}(r_{q1}^\ell + r_{q1}^g) q_1(x) \\ r_{11}(x) &= r_{11}^g + (r_{11}^\ell - r_{11}^g) q_0(x) + \alpha_{11}(r_{11}^\ell + r_{11}^g) q_1(x) \end{aligned} \quad (4.17)$$

where

$$q_0(x) \equiv \frac{q(x) - q_{\text{eq}}^g}{q_{\text{eq}}^\ell - q_{\text{eq}}^g}, \quad q_1(x) \equiv \frac{|q'(x)|^2}{|q'_{\text{eq}}(x)|_{\text{max}}^2} \quad (4.18)$$

are modulatory curves for resistivity profiles. Here q_{eq}^g and q_{eq}^ℓ are the equilibrium coexistence values of the order parameter of the gas and liquid, respectively. Furthermore, $|q'_{\text{eq}}(x)|_{\text{max}}^2$ is the maximum value of the squared equilibrium order parameter gradient. For each resistivity profile r^g and r^ℓ are the equilibrium coexistence resistivities of the gas and liquid phase, respectively. Coefficients $\alpha_{qq}, \alpha_{q1}, \alpha_{11}$ control the size of the gradient term, which gives peaks in the resistivity profiles in the interfacial region. Such a peak is observed in molecular dynamic simulations of one-component fluids [3].

Limiting coefficients r^b (where b is either g or ℓ) are related to measurable transport coefficients in the bulk phases: thermal conductivity λ^b , diffusion coefficient D^b and Soret coefficient s_T^b . In the description of transport in the *homogeneous* phases it is convenient to use measurable heat fluxes

$$J_q^b = J_q^b - J_1^b (h_1^b - h_2^b) \quad (4.19)$$

where h_i^b is a partial specific enthalpy of component i in phase b (cf. Eq. 3.40). Furthermore, we used that $J_2^b = -J_1^b$. In the homogeneous phases the entropy production then takes the following form:

$$\sigma_s = J_q' \frac{d}{dx} \frac{1}{T} - J_1 \frac{1}{T} \frac{d\psi_T}{dx} \quad (4.20)$$

where we have suppressed the superscript b for now. The subscript T of ψ indicates that the gradient is calculated keeping the temperature constant. Using the Gibbs–Duhem relation in a homogeneous phase at a constant pressure one can show that

$$\frac{d\psi_T}{dx} = \frac{\partial\mu_1}{\partial\xi} \frac{1}{(1-\xi)} \frac{d\xi}{dx} \quad (4.21)$$

After introducing measurable transport coefficients, the force–flux relations derived from Eq. 4.20 can be written in a form used in [1, p. 276]:

$$\begin{aligned} J'_q &= -\lambda \frac{dT}{dx} - \rho \xi \frac{\partial\mu_1}{\partial\xi} T D s_T \frac{d\xi}{dx} \\ J_1 &= -\rho \xi (1-\xi) D s_T \frac{dT}{dx} - \rho D \frac{d\xi}{dx} \end{aligned} \quad (4.22)$$

Comparing Eqs. 4.16 and 4.22 in the homogeneous region we find the values of resistivity coefficients in the bulk phase

$$\begin{aligned} r_{qq} &= \frac{1}{L T^2} \frac{D\rho}{\psi_\xi} \\ r_{q1} = r_{1q} &= -\frac{1}{L T^2} \left(\frac{D\rho}{\psi_\xi} (h_1 - h_2) + D s_T \rho \xi (1-\xi) T \right) \\ r_{11} &= \frac{1}{L T^2} \left(\frac{D\rho}{\psi_\xi} (h_1 - h_2)^2 + D s_T \rho \xi (1-\xi) T (h_1 - h_2) + \lambda T \right) \end{aligned} \quad (4.23)$$

where $\psi_\xi \equiv (\partial\psi/\partial\xi)$, $L \equiv (\lambda D\rho/\psi_\xi) - (D s_T \rho \xi (1-\xi))^2 T$. All the quantities in Eq. 4.23 are taken in the specified bulk phase, either gas or liquid.

4.3 Solution Procedure

The numerical procedure is similar to the one, described in [4], however it has some differences. We will describe the special features below. We use the Matlab procedure `bvp4c` [5] to solve the stationary boundary value problem. This requires a reasonable initial guess as well as boundary conditions. First, we obtain the equilibrium profile, and then we use it as the initial guess for the non-equilibrium problem. We use a box of width 80 nm with the grid containing of 81 equidistant points.

4.3.1 Equilibrium Profile

It is easier to describe equilibrium properties of the mixture using molar quantities. Everywhere in this section we will do this. The superscript v indicates a molar quantity. The total molar concentration and molar fraction of the first component are denoted by c and ζ , respectively.

Equilibrium coexistence is determined by the following system of equations

$$\begin{aligned}\mu_{\text{eq}}^v &= \mu_0^v(T_{\text{eq}}, c_{\text{eq}}^g, \zeta_{\text{eq}}^g) = \mu_0^v(T_{\text{eq}}, c_{\text{eq}}^\ell, \zeta_{\text{eq}}^\ell) \\ \psi_{\text{eq}}^v &= \psi_0^v(T_{\text{eq}}, c_{\text{eq}}^g, \zeta_{\text{eq}}^g) = \psi_0^v(T_{\text{eq}}, c_{\text{eq}}^\ell, \zeta_{\text{eq}}^\ell) \\ p_{\text{eq}} &= p_0(T_{\text{eq}}, c_{\text{eq}}^g, \zeta_{\text{eq}}^g) = p_0(T_{\text{eq}}, c_{\text{eq}}^\ell, \zeta_{\text{eq}}^\ell)\end{aligned}\quad (4.24)$$

where $\psi_0^v = (\partial f_0^v / \partial \zeta)$, $\mu_0^v = f_0^v + c(\partial f_0^v / \partial c) - \psi_0^v \zeta$ and $p_0 = c^2(\partial f_0^v / \partial c)$ are chemical potentials and pressure of the homogeneous phases. $c_{\text{eq}}^g, \zeta_{\text{eq}}^g$ and $c_{\text{eq}}^\ell, \zeta_{\text{eq}}^\ell$ are the coexistence concentration and molar fraction of the gas and the liquid phase, respectively.

Having six equations (4.24) and eight unknowns $c_{\text{eq}}^g, \zeta_{\text{eq}}^g, c_{\text{eq}}^\ell, \zeta_{\text{eq}}^\ell, \psi_{\text{eq}}^v, \mu_{\text{eq}}^v, p_{\text{eq}}, T_{\text{eq}}$, two of the unknowns are free parameters. Indeed, the phase rule says that for a two component binary mixture two parameters need to be specified. The temperature and the pressure are experimentally a convenient choice. We have found, however, that it is more convenient to control T_{eq} and ψ_{eq}^v in the calculations. This is because ψ_{eq}^v changes monotonically with ζ_{eq}^g or ζ_{eq}^ℓ , and it is therefore a good measure of the composition. Since $\psi^v = \mu_1^v - \mu_2^v$, the value of ψ^v also reflects the difference in the composition of the mixture.

To obtain the equilibrium profiles $c_{\text{eq}}(x)$ and $\zeta_{\text{eq}}(x)$ one needs to solve a system of two differential equations

$$\begin{aligned}\mu_{\text{eq}}^v &= \mu_0^v(c, \zeta) - \kappa^v (q^v)'' \\ \psi_{\text{eq}}^v &= \psi_0^v(c, \zeta) - \varepsilon_\kappa^v \kappa^v (q^v)''\end{aligned}\quad (4.25)$$

which follow from Eq. 4.12 in equilibrium. Here

$$\begin{aligned}q^v &= c(1 + \varepsilon_\kappa^v \zeta) = q M_2 \\ \kappa^v &= \kappa M_2^2 \\ \varepsilon_\kappa^v &= (1 + \varepsilon_\kappa)(M_1/M_2) - 1\end{aligned}\quad (4.26)$$

where M_1 and M_2 are the molar masses of the components. The system of equations (4.25) is, in fact, singular, since coefficients of the higher derivatives differ by a constant factor. Thus, we can deduce one algebraic equation instead of a differential one

$$\psi_0^v(c, \zeta) - \varepsilon_\kappa^v \mu_0^v(c, \zeta) = \psi_{\text{eq}}^v - \varepsilon_\kappa^v \mu_{\text{eq}}^v \quad (4.27)$$

The `bvp4c` procedure takes only differential equations, so we have to transform Eq. 4.27 to a differential one. This can be done easily by taking the derivative of both sides. After some transformations, we get the following equation set

$$\begin{aligned}(q^v)'' &= \frac{1}{\kappa^v} (\mu_0^v(c, \zeta) - \mu^v) \\ \zeta' &= -(q^v)' \left((1 + \varepsilon_\kappa^v \zeta) \frac{\psi_{0\zeta}^v - \varepsilon_\kappa^v \mu_{0\zeta}^v}{\psi_{0c}^v - \varepsilon_\kappa^v \mu_{0c}^v} - \frac{\varepsilon_\kappa^v q}{1 + \varepsilon_\kappa^v \zeta} \right)^{-1}\end{aligned}\quad (4.28)$$

where subscripts ζ or c mean partial derivative of the corresponding quantity with respect to ζ or c . This is a system of three first order differential equations for three variables ζ , q^v and $(q^v)'$, which requires three boundary conditions. One of them is Eq. 4.27 taken on one of the boundaries, which simply determines the integration constant for the second differential equation. The other two are $(q^v)'(x^g) = 0$ and $(q^v)'(x^\ell) = 0$, which indicates the fact, that box boundaries, x^g and x^ℓ , are in the homogeneous region.

The numerical procedure allows the variables to take any value. However, not all the values are allowed physically. For instance, the mole fraction ζ is bounded in the interval $(0; 1)$ and the molar concentration is bounded in the interval $(0; B^{-1})$, where B is given in Eq. 4.7. In order to avoid out-of-range problems, we use the function which safely maps a unit interval to real axes:

$$\begin{aligned} u2r(u) &\equiv \arcsin(2u - 1) \\ u2r'(u, u') &\equiv \frac{d}{dx} u2r(u) = \frac{u'}{\sqrt{u - u^2}} \end{aligned} \quad (4.29)$$

In order to translate real values back to the unit interval we use the inverse functions

$$\begin{aligned} r2u(r) &\equiv \frac{\sin(r) + 1}{2} \\ r2u'(r, r') &\equiv \frac{d}{dx} r2u(r) = \frac{r' \cos(r)}{2} \end{aligned} \quad (4.30)$$

Particularly, the actual variables, which we provide to the `bvp4c` procedure are

$$\begin{aligned} Y_1 &= u2r(\zeta) \\ Y_2 &= u2r(q^v/q_\infty^v) \\ Y_3 &= u2r'(q^v/q_\infty^v, (q^v)'/q_\infty^v) \end{aligned} \quad (4.31)$$

where $q_\infty^v \equiv \min(1/b_1, 1/b_2) \max(1, |e_k^v|)$ is the limiting value for q^v .

4.3.2 Non-Equilibrium Profile

In this section we continue to use mass specific quantities. The equilibrium solution found in previous section is translated from molar to mass specific units and is fed as an initial guess to the non-equilibrium solver.

Non-equilibrium conditions are implemented by changing temperature or pressure from their equilibrium values. This results in mass and heat fluxes through the interface. The amount of matter will then change in the gas and liquid phase. We will put the system in such conditions, that the total contents of the box is constant and equal to the equilibrium contents. It means, that if some amount of

liquid has been evaporated, the same amount of gas is condensed externally and put back into the liquid phase.

We introduce the overall mass $m(x) \equiv \int_{x^g}^x dy \rho(y)$ and the mass of the first component $m_\xi(x) \equiv \int_{x^g}^x dy \rho(y) \xi(y)$, which obey the following equations by definition

$$\begin{aligned} m'(x) &= \rho(x) \\ m'_\xi(x) &= \rho(x) \xi(x) \end{aligned} \quad (4.32)$$

We introduce the overall mass flux J_m , the mass flux of the first component J_ξ , the energy flux J_e and the “pressure“ flux J_p :

$$\begin{aligned} J_m &\equiv \rho v \\ J_\xi &\equiv J_1 + \xi J_m \\ J_e &\equiv J_q + J_m \left(u_0 + \frac{1}{2} \left(\frac{J_m}{\rho} \right)^2 + \frac{1}{\rho} \left(p_\perp - \frac{1}{2} \kappa q'^2 \right) - g x \right) \\ J_p &\equiv p_\perp + \frac{J_m^2}{\rho} - m g \end{aligned} \quad (4.33)$$

where $p_\perp(x) \equiv p(x) + \kappa q'^2$. From Sect. 4.2.1 one can see, that all these fluxes are constant.

From Eq. 4.12 we obtain

$$\begin{aligned} \kappa q'' &= \frac{1}{q} \left(p_0 - p_\perp + \frac{1}{2} q'^2 \right) \\ \kappa q'' &= \frac{1}{\varepsilon_\kappa} (\psi_0 - \psi) \end{aligned} \quad (4.34)$$

As in Eq. 4.25 we have a singular set which leads to the algebraic equation

$$\psi_0 - \psi - \frac{\varepsilon_\kappa}{q} \left(p_0 - p_\perp + \frac{1}{2} q'^2 \right) = 0 \quad (4.35)$$

Taking derivative of this equation with respect to the coordinate we obtain the expression for the first derivative of the fraction

$$\xi' = \frac{\psi' - (\psi_0|'_\xi - (p_0 - p_\perp)|'_\xi (\varepsilon_\kappa/q))}{\psi_{0\xi} - (p_0 - p_\perp)_\xi (\varepsilon_\kappa/q)} \quad (4.36)$$

where $\phi_\xi \equiv (\partial\phi/\partial\xi)$ and $\phi|'_\xi \equiv \phi' - \phi_\xi \xi' = \phi_q q' + \phi_T T'$ for any ϕ . The expressions for ψ' , T' and q' are taken from Eqs. 4.16 and 4.34. The expressions for p_0 , ψ_0 , as well as ψ_{0T} , ψ_{0q} and $\psi_{0\xi}$ can be derived from Eq. 4.5 using standard formulas. Furthermore, $p_{\perp\xi} = -J_m^2 \varepsilon_\kappa/q$ and $p_\perp|'_\xi = (g q + q' J_m^2/q^2)/(1 + \varepsilon_\kappa \xi)$.

As a consequence we have 7 unknown variables, q , q' , m , m_ξ , ζ , T , ψ and 4 unknown fluxes J_m , J_ξ , J_e , J_p . This requires 7 first order differential equations and 11 boundary conditions (7 of them determine integration constants of differential equations and 4 of them determine constant fluxes). As differential equations we use Eqs. 4.32, 4.16 (together with Eqs. 4.17 and 4.23), one of Eqs. 4.34, and 4.36. As boundary conditions we use the following.

The first boundary condition is Eq. 4.35 taken on one of the boundaries, which simply determine the integration constant for Eq. 4.36. The four other conditions control the overall content of the box (particularly, it is the same as in equilibrium)

$$\begin{aligned} m(x^g) &= 0 \\ m_\xi(x^g) &= 0 \\ m(x^\ell) &= m_{\text{eq}} \\ m_\xi(x^\ell) &= m_{\xi,\text{eq}} \end{aligned} \tag{4.37}$$

Here m_{eq} and $m_{\xi,\text{eq}}$ are the equilibrium values of the total overall mass and the total mass of the first component in the whole box.

The two more conditions are

$$\begin{aligned} q'(x^g) &= 0 \\ q'(x^\ell) &= 0 \end{aligned} \tag{4.38}$$

which indicate the fact, that box boundaries are in the homogeneous region. In contrast to the equilibrium case, the density in the non-equilibrium homogeneous region may vary with coordinate. q' may therefore differ from zero on the boundaries, and, in fact, it does. The value of the q' in the homogeneous region is, however, small, comparing to the value in the interfacial region, so we may neglect it and use such approximation. This will lead to the wrong profile behavior only in the small vicinity on the boundary, which we will exclude from the further analysis.

The choice of the four last boundary conditions should preferably reflect the conditions of a possible experiment. For instance, we may control the temperatures on both sides of the box, the pressure on the vapor side and the fraction on the liquid side.

$$\begin{aligned} T(x^g) &= T^g \\ T(x^\ell) &= T^\ell \\ p_\perp(x^g) &= p^g \\ \zeta(x^\ell) &= \zeta^\ell \end{aligned} \tag{4.39}$$

To solve these equations numerically we use the same techniques as in the equilibrium case. All the variables should be properly scaled in order to make them to be the same order of magnitude. This balances the numerical residual and gives better solution result. We use the following variables

Table 4.1 The molar mass and the van der Waals coefficients of cyclohexane (1) and *n*-hexane (2)

Component	$M (\times 10^{-3} \text{ kg/mol})$	$a (\text{Jm}^3/\text{mol}^2)$	$b (\times 10^{-5} \text{ m}^3/\text{mol})$
1	84.162	2.195	14.13
2	86.178	2.495	17.52

$$\begin{aligned}
 Y_1 &= \text{u2r}(\xi) \\
 Y_2 &= \text{u2r}(q/q_\infty) \\
 Y_3 &= \text{u2r}'(q/q_\infty, q'/q_\infty) \\
 Y_4 &= m/(x^* q^*) \\
 Y_5 &= m_\xi/(x^* q^*) \\
 Y_6 &= T^*/T \\
 Y_7 &= (\psi/T)(T^*/\psi^*)
 \end{aligned} \tag{4.40}$$

where u2r is defined in Eq. 4.29, $q_\infty \equiv q_\infty^v/M_2$ and scaling parameters $x^* \equiv x^l - x^g$, $T^* \equiv T_{\text{eq}}$, $\psi^* \equiv \psi_{\text{eq}}$, $q^* \equiv p_{\text{eq}}/\psi_{\text{eq}}$.

4.4 Data Input

We choose a mixture of cyclohexane (component 1) and *n*-hexane (component 2) and give below some of their properties relevant for our calculation. We note, that among them only the molar masses have been measured exactly. There are number of problems to obtain the values of other material properties. We determined, for instance, the two van der Waals coefficients of the pure components using critical temperatures and pressures¹ of these components. As a consequence the critical volume of each of the components in our description differs substantially from the experimental value. For the mixture, the van der Waals coefficients were then found using the mixing rules Eq. 4.7. We use the values of the molar mass and the van der Waals coefficients given in Table 4.1.

As we mentioned in Chap. 3 we do not focus on the particular internal structure of the molecules. We therefore choose the w_k to be equal $1\text{E}+4$ for each of the component. The particular value is not important as it appears under \ln operation, and being the same for both components, basically scales the Universal gas constant R .

As the basis for the numerical study we consider the liquid–vapor coexistence at $T_{\text{eq}} = 330 \text{ K}$ and $\psi_{\text{eq}}^v = 700 \text{ J/mol}$. The equilibrium state is calculated at this

¹ In this we follow the example of the Handbook of Chemistry and Physics [6] rather than Refs. [4, 7] where T_c and v_c were used.

Table 4.2 Transport coefficients

Phase/component	λ [W/(m K)]		D (m ² /s)	s_T (1/K)
	1	2		
Gas	0.0140	0.0157	3.876×10^{-5}	10^{-4}
Liquid	0.1130	0.1090	3.876×10^{-9}	10^{-4}

condition. Non-equilibrium states are created by perturbing the system from this equilibrium state.

Transport coefficients of homogeneous fluids depend on temperature and densities, while these dependencies are not always available. We use typical constant values of these coefficients at the conditions, close to the the equilibrium conditions specified above. The values of the thermal conductivity λ are well-tabulated and we take them from [8]. We take a typical value of the diffusion coefficient D for the liquid mixture in the barycentric frame of reference from [9] and estimate a typical value of the diffusion coefficient for the gas mixture as being four orders of magnitude larger (cf. [1, p. 279]). A typical value of the Soret coefficient s_T is estimated to be of the order of 10^{-5} to 10^{-3} reciprocal degrees, both in gaseous and liquid mixtures [1, p. 279]. We use an average value from that range. The values of the coefficients we use are given in Table 4.2 together with the “mixing” rules for the heat conductivity

$$\begin{aligned}\lambda^g &= \zeta_{\text{eq}}^g \lambda_1^g + (1 - \zeta_{\text{eq}}^g) \lambda_2^g \\ \lambda^\ell &= \zeta_{\text{eq}}^\ell \lambda_1^\ell + (1 - \zeta_{\text{eq}}^\ell) \lambda_2^\ell\end{aligned}\tag{4.41}$$

The values of the gradient coefficients are not available at all. One can determine them comparing the actual value of the surface tension of a pure fluid with the one, calculated with a given κ_{ρ_i, ρ_j} . For given conditions the value of the surface tension of the mixture is about 0.027 N/m. We therefore choose κ^v to be equal 12×10^{-18} J m⁵/mol² and $\varepsilon_\kappa^v = 0.01$. This gives $\kappa \simeq 16 \times 10^{-16}$ J m⁵/kg² and $\varepsilon_\kappa \simeq 0.03$ according to Eq. 4.26. This also gives values of the surface tension around 0.03 N/m.

All the profiles and the equilibrium properties were calculated with an accuracy 10^{-6} .

4.5 Results

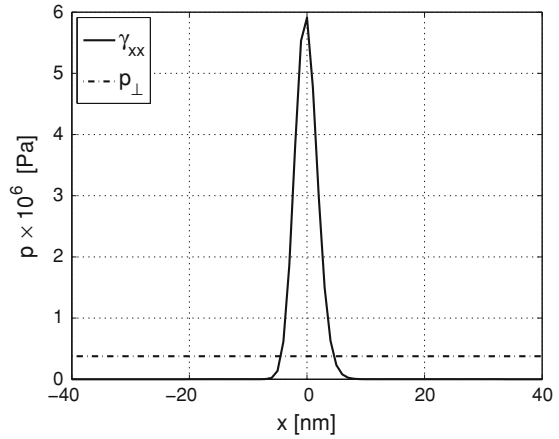
We give all the results in molar specific units.

The above parameters and conditions give the coexistence data listed in Table 4.3.

The resulting profiles for the equilibrium molar concentration, the equilibrium mole fraction of the first component and the equilibrium tension tensor component γ_{xx} , the integral of which gives the surface tension, are given in Figs. 4.1 and 4.2.

Table 4.3 Coexistence data

$T_{\text{eq}} = 330$ (K)
$\psi_{\text{eq}}^v = 700$ (J/mol)
$\mu_{\text{eq}}^v = -57,098$ (J/mol)
$p_{\text{eq}} = 3,76,095$ (Pa)
$c_{\text{eq}}^g = 153.23$ (mol/m ³)
$c_{\text{eq}}^\ell = 4898.26$ (mol/m ³)
$\zeta_{\text{eq}}^g = 0.5519$
$\zeta_{\text{eq}}^\ell = 0.5934$

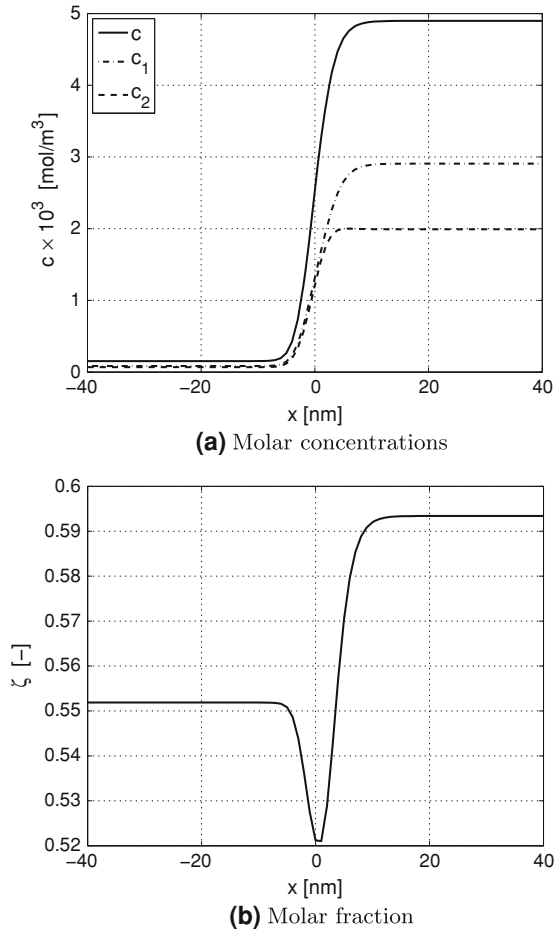
Fig. 4.1 Equilibrium tension γ_{xx} and perpendicular pressure p_\perp profiles

4.5.1 Non-Equilibrium

Here we investigate different aspects of the non-equilibrium solution. We first consider the typical profiles of various thermodynamic quantities. We give them for a rather extreme perturbation in which the temperature of the liquid boundary is 5% higher than the equilibrium value and the corresponding value at the gas boundary. In absolute units this is about 15°K. Figure 4.3a gives the profiles of the molar concentrations. Under non-equilibrium conditions the bulk values of the concentrations are no longer constant. Figure 4.3b gives the profiles of the chemical potentials of both components. In non-equilibrium they are not constant as well. In Fig. 4.4 we give the profiles of the thermodynamic potentials. Figure 4.4a gives the specific quantities per unit of mol, while Fig. 4.4b gives the densities per unit of volume.

Furthermore, we consider the entropy production profile in the interfacial region. Varying the temperature at the liquid boundary T^ℓ , the pressure at the gas boundary p^g , and the mole fraction at the liquid boundary ζ^ℓ , as well as resistivity amplitudes α_{qq} and α_{11} , we give the profiles of the entropy production in Fig. 4.5.

Fig. 4.2 Equilibrium molar concentration and fraction profiles



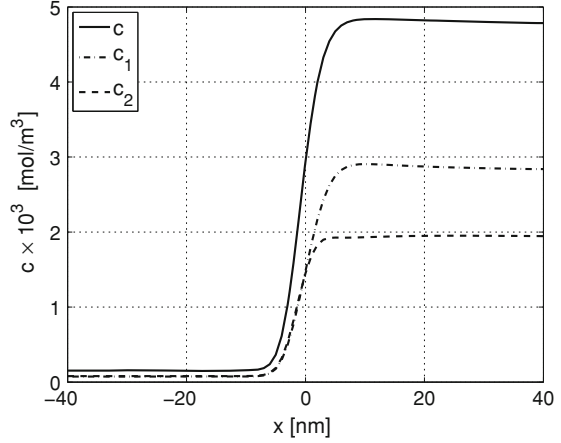
One can see, that the entropy production has a clear peak in the interfacial region. The magnitude of this peak depends on the resistivity amplitude.

Next we consider the effect of modifying different parameters of the system: resistivity amplitudes and boundary conditions.

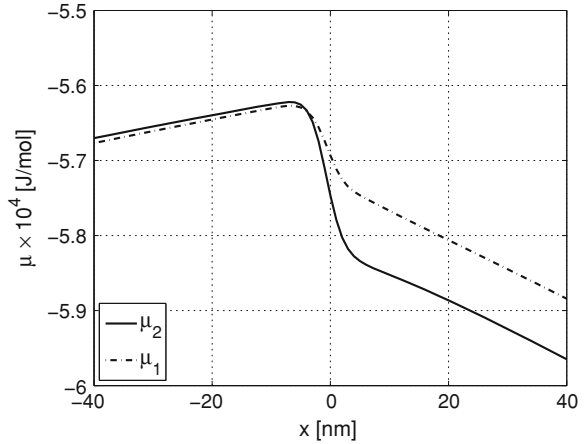
4.5.1.1 Effect of Resistivities

The first aspect we will try to clarify is the influence of the square gradient amplitude of the resistivity to transport, see Eq. 4.17. We consider in particular three cases. In the first, only α_{qq} , the square gradient amplitude for the heat resistivity coefficient r_{qq} , is unequal to zero. In the second, only α_{11} , the square gradient amplitude for the diffusion resistivity coefficient r_{11} , is

Fig. 4.3 Thermodynamic quantities for $\alpha_{qq} = \alpha_{11} = 1$ at $T^\ell = 1.05 T_{\text{eq}}$



(a) Molar concentrations

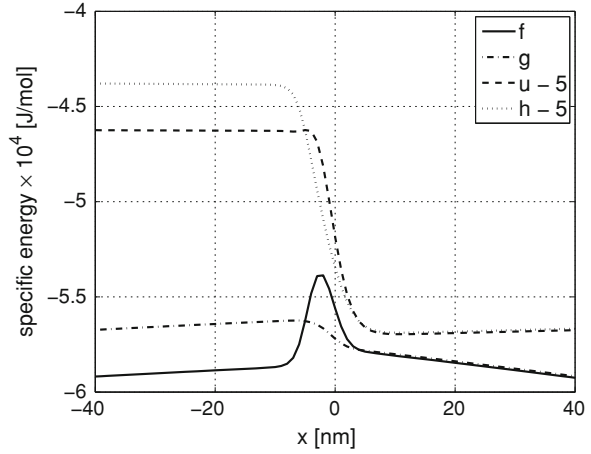


(b) Chemical potentials

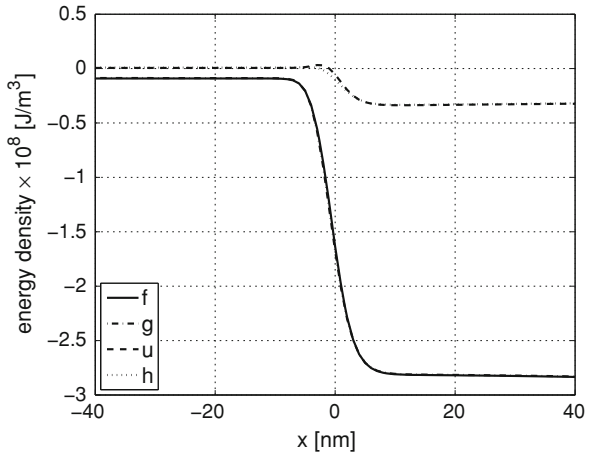
unequal to zero. In the last case, only α_{q1} , the square gradient amplitude for the diffusion resistivity coefficient r_{q1} , is unequal to zero. We do it for different perturbation conditions. We plot the temperature and the mole fraction for these cases.

In Fig. 4.6 the system is brought out of equilibrium by reducing the pressure on the vapor side to $0.95 p_{\text{eq}}$, where p_{eq} is the equilibrium pressure. The temperatures on both ends of the box are kept equal to equilibrium temperature T_{eq} , as well as the mole fraction at the liquid boundary is kept equal to the equilibrium value ζ_{eq}^ℓ . In Figs. 4.6a, b only $\alpha_{qq} \neq 0$. The mole fraction increases about 2% on the vapor side when α_{qq} increases from 0 to 10. The temperature decreases due to the evaporation. In all cases the extrapolated temperature in the liquid is higher than the value in the vapor, where we extrapolate to the inflection

Fig. 4.4 Thermodynamic potentials for $\alpha_{qq} = \alpha_{11} = 1$ at $T^\ell = 1.05 T_{\text{eq}}$



(a) Specific energies



(b) Energy densities

point of the total molar concentration. For $\alpha_{qq} = 10$ the minimum of the temperature is below both extrapolations. In that case the temperature “jump” in the extrapolated profiles has increased to about 3 K. In Figs. 4.6c, d only $\alpha_{11} \neq 0$. The modification of the mole fraction is now more dramatic. In the vapor it decreases up to 27%. The temperature increases for larger values of α_{11} . This is related to a decrease of the evaporation. The temperature jump in the extrapolated profiles is in all cases not more than 0.5 K. In Figs. 4.6e, f only $\alpha_{q1} \neq 0$. We see, that the variation of α_{q1} does not affect much the non-equilibrium profiles.

In Fig. 4.7 we consider the case when the vapor pressure and temperature are kept equal to the equilibrium values and the liquid temperature is 5% higher then

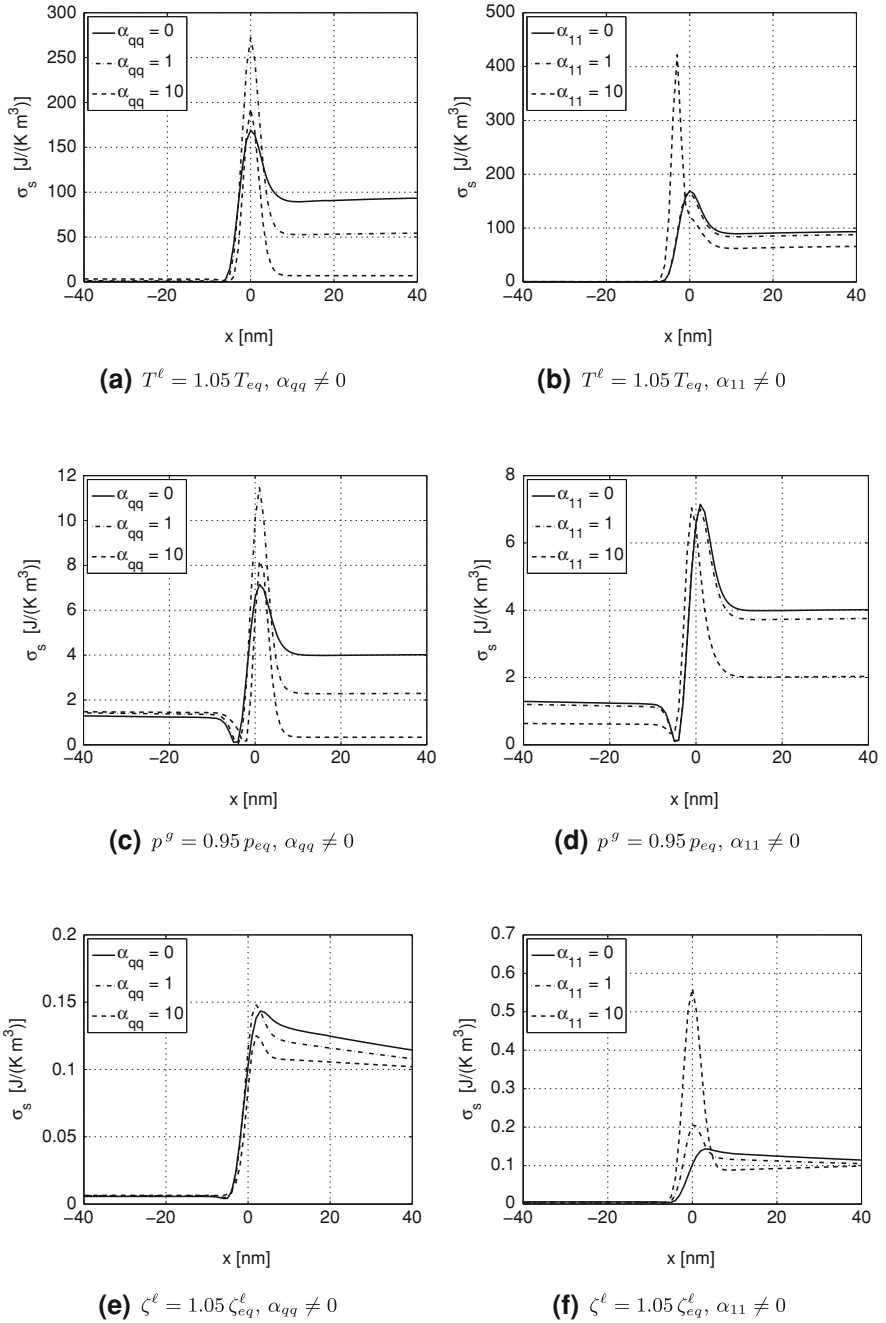


Fig. 4.5 Entropy production profiles for different α_{qq} and α_{11} at different perturbation conditions

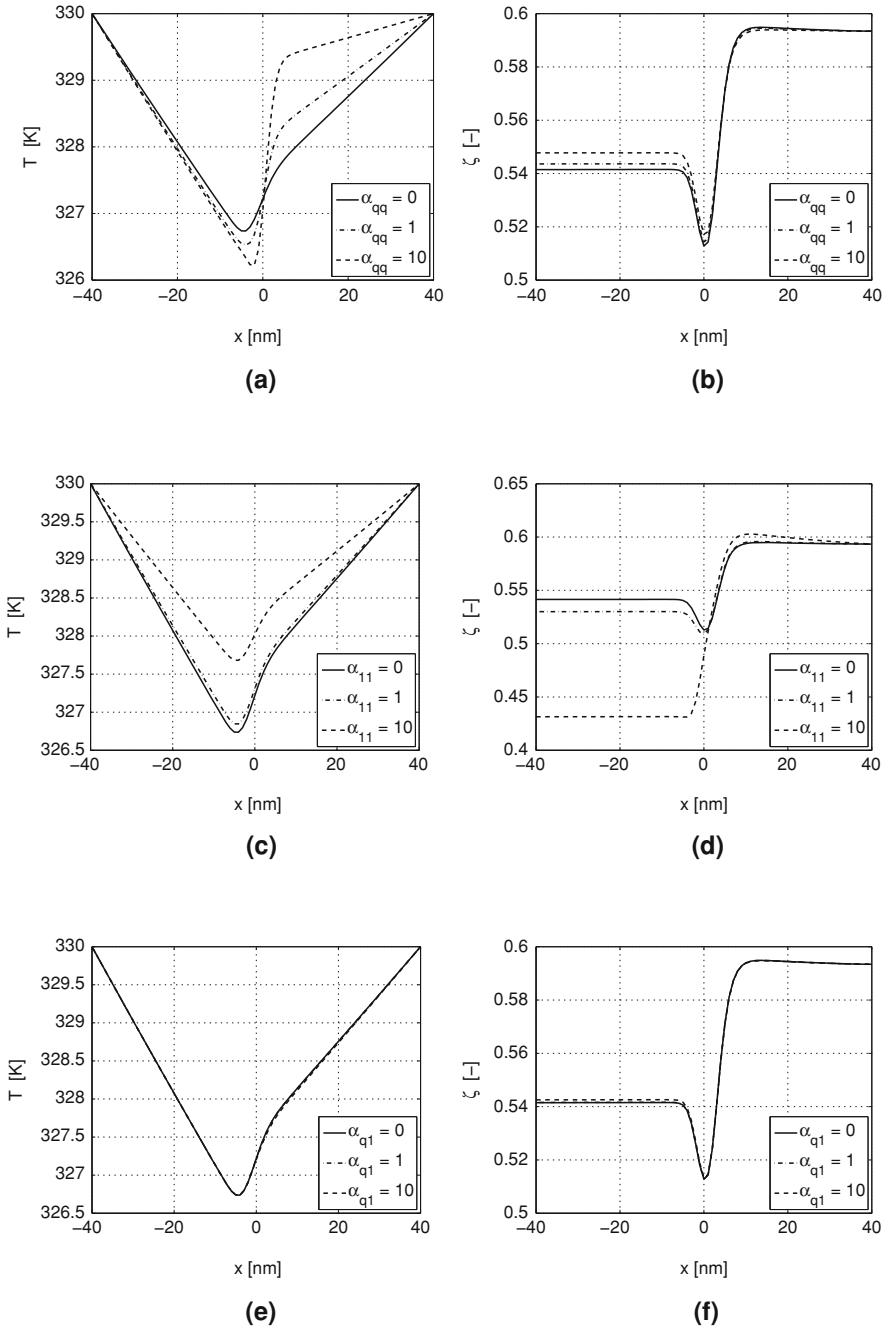


Fig. 4.6 Temperature and molar fraction profiles for different α_{qq} , α_{11} and α_{q1} at $p^s = 0.95 p_{eq}$

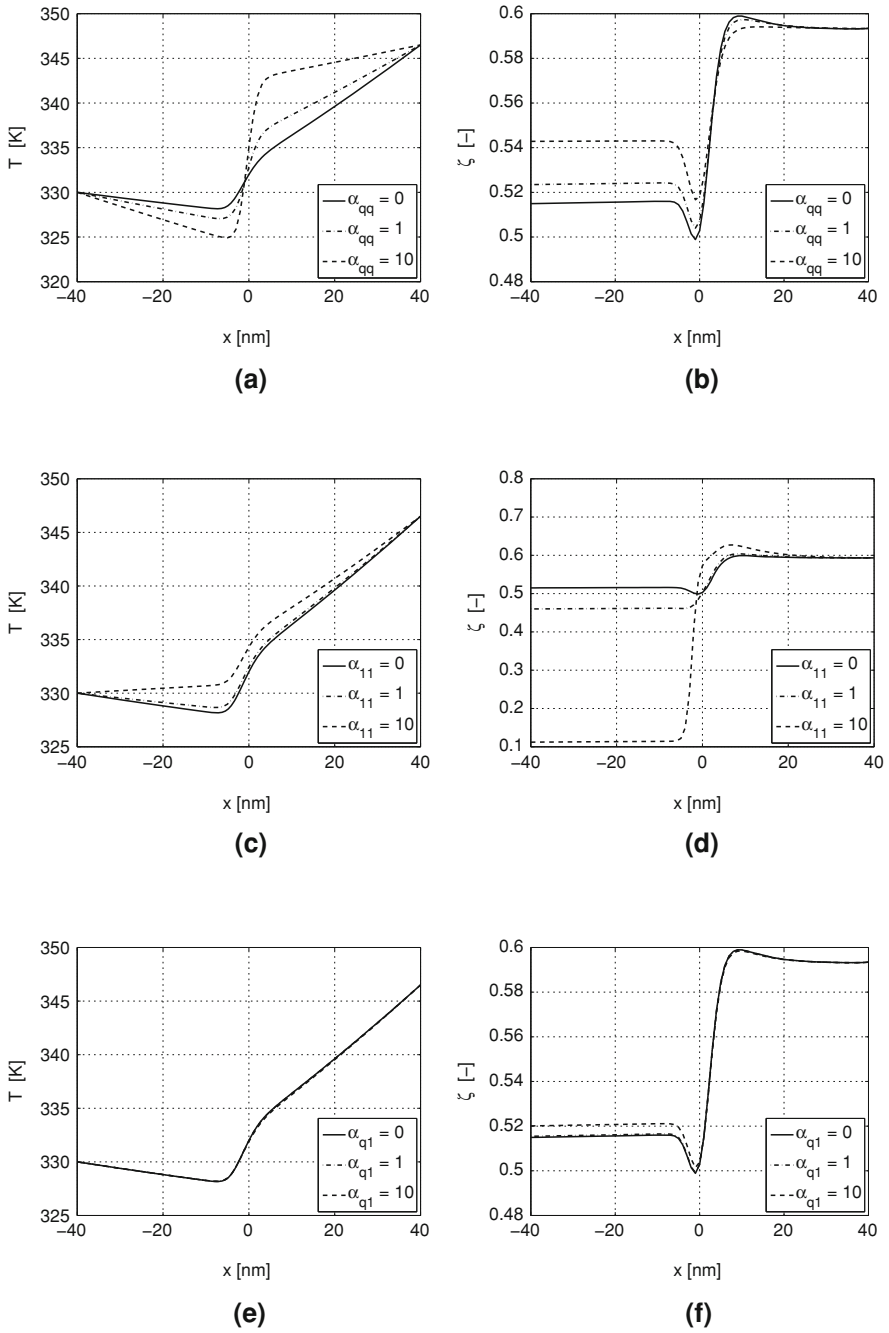


Fig. 4.7 Temperature and molar fraction profiles for different α_{qq} , α_{11} and α_{q1} at $T^\ell = 1.05T_{\text{eq}}$

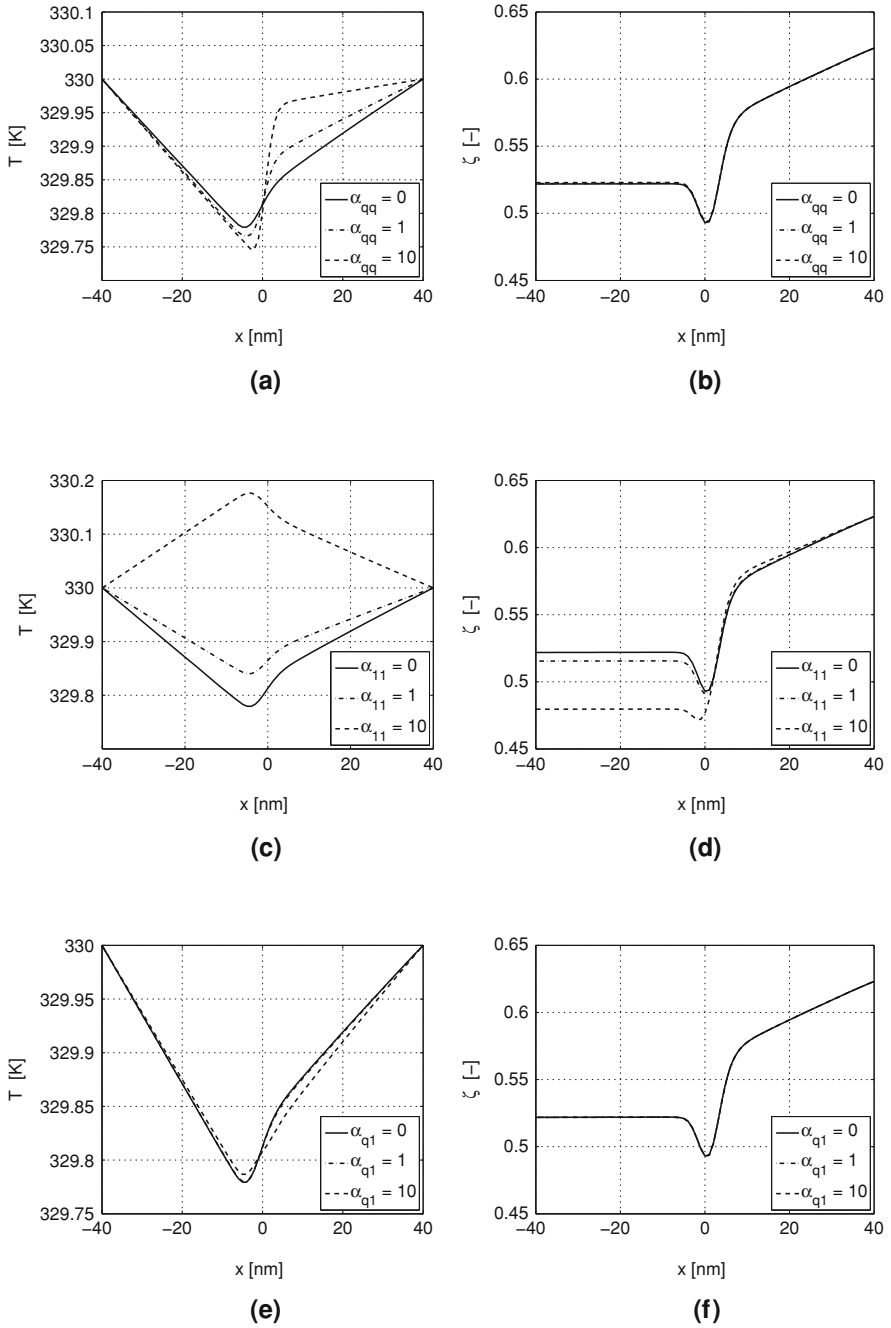


Fig. 4.8 Temperature and molar fraction profiles for different α_{qq} , α_{11} and α_{q1} at $\zeta^{\ell} = 1.05 \zeta_{eq}$

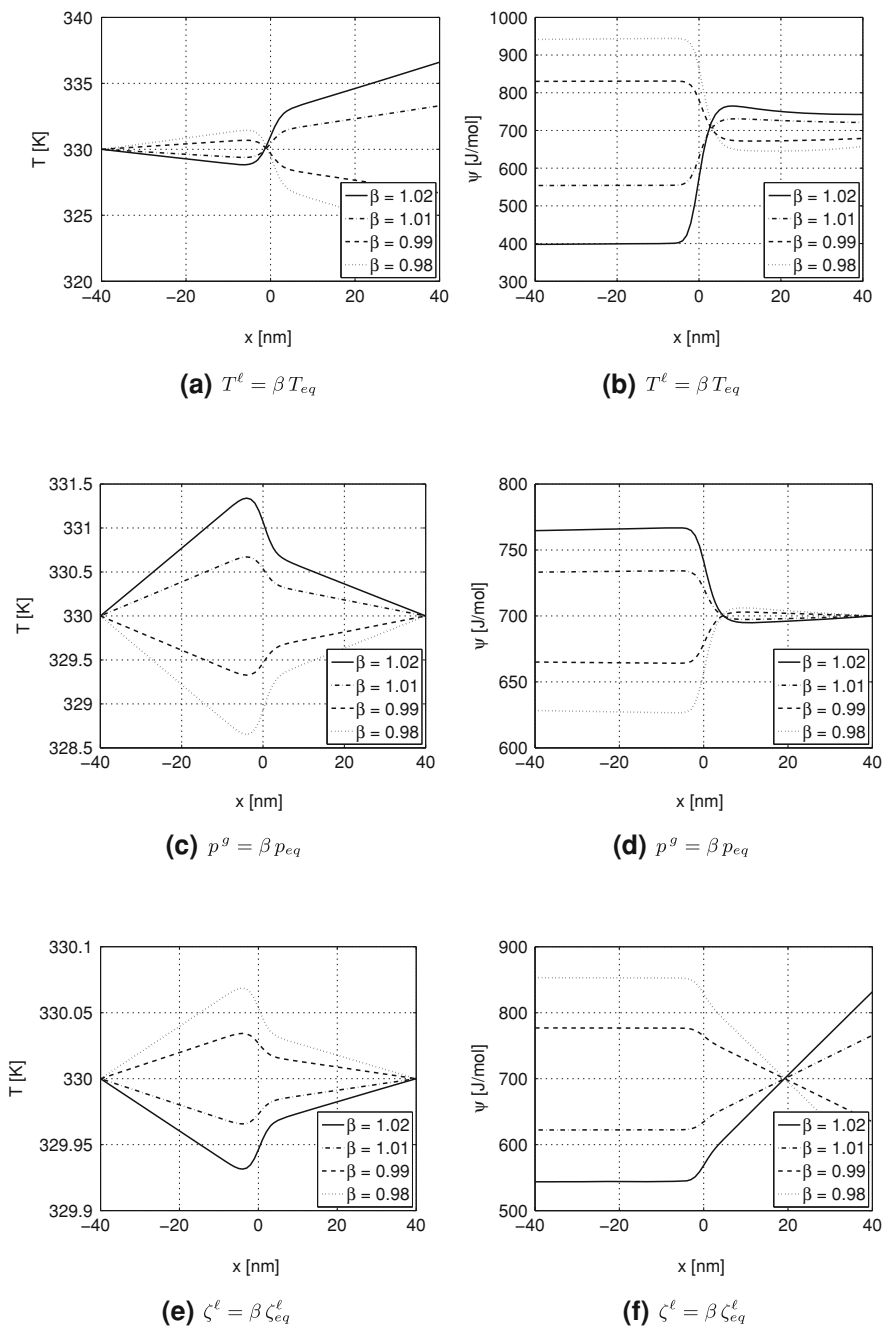


Fig. 4.9 Temperature and chemical potential difference profiles for $\alpha_{qq} = \alpha_{11} = 1$ and $\alpha_{q1} = 0$ at different perturbation conditions

the equilibrium value. The mole fraction at the liquid boundary is again kept equal to the equilibrium value ζ_{eq}^ℓ . Figure 4.7a, b consider the $\alpha_{qq} \neq 0$. The change in the mole fraction went up to 12%. The temperature jump goes up to about 20 K. In Fig. 4.7c, d we consider the $\alpha_{11} \neq 0$. One can notice again the more dramatic behavior of the mole fraction and temperature profiles for big values of α_{11} . The variation of α_{q1} considered in Fig. 4.7e, f again does not affect much the resulting profiles.

Finally, in Fig. 4.8 we consider the case when the mole fraction at the liquid boundary is 5% higher than the equilibrium value, while the vapor pressure and boundary temperatures are kept equal to the equilibrium values.

4.5.1.2 Effect of Boundary Conditions

We now fix the values of the square gradient amplitudes of the resistivity coefficients in Eq. 4.17 as $\alpha_{qq} = 1$, $\alpha_{q1} = 0$ and $\alpha_{11} = 1$. We consider the corresponding profiles in Fig. 4.9.

The mixture is then perturbed from equilibrium for the following three cases:

1. Setting T^ℓ equal to 0.98, 0.99, 1.01, 1.02 of T_{eq} and keeping T^g , p^g and ζ^ℓ equal to their equilibrium values, see Figs. 4.9a, b;
2. Setting p^g equal to 0.98, 0.99, 1.01, 1.02 of p_{eq} and keeping T^g , T^ℓ and ζ^ℓ equal to their equilibrium values, see Figs. 4.9c, d;
3. Setting ζ^ℓ equal to 0.98, 0.99, 1.01, 1.02 of ζ_{eq}^ℓ and keeping T^g , T^ℓ and p^g equal to their equilibrium values, see Figs. 4.9e, f.

Lowering (raising) T^ℓ gives evaporation (condensation). This lowers (raises) the temperature on the vapor side as expected. The temperature profile goes down for evaporation and up for condensation.

4.6 Conclusions

We considered a binary mixture of cyclohexane and *n*-hexane and described in detail how to implement the general analysis presented in the previous chapter to stationary states. We gave a numerical procedure to solve the resulting system of differential equations. The profiles of continuous variables obtained are presented in Appendix 4.A. We see, in particular, that a two-component mixture develops a temperature profile in the surface region which is similar to the temperature profile obtained for a one-component system [4]. Another characteristic of a binary mixture is the difference $\psi = \mu_1 - \mu_2$ between the chemical potentials of the components. The behavior of the profile of ψ in non-equilibrium steady-states shows that it has different values in the two bulk phases and we observe a transition from one value to the other in the surface region.

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Chapter 5

Local Equilibrium of the Gibbs Surface for the Two-Phase Binary Mixture

5.1 Introduction

In the general description of the interface one uses contributions to the Helmholtz free energy density proportional to the square of the density and mass fraction gradients. These contributions imply that it is not possible to use continuous *local* equilibrium thermodynamics in the interfacial region, i.e. to calculate the local values of the various thermodynamic parameters in terms of the local density, mass fractions and temperature only. Rowlinson and Widom (see [1, p. 43]) use the name *point thermodynamics* for this, to distinguish it from other *quasi-* or *local thermodynamic* treatments. Given the non-autonomous nature of the square gradient model, it is sensible to question whether a description in terms of excess variables along the lines given by Gibbs [2], can be autonomous. Gibbs' treatment, though only given for equilibrium systems, suggests such an assumption. This would imply that the surface is a separate thermodynamic phase. Bakker [3] and Guggenheim [4, p. 45] made this assumption, the validity of which was subsequently disputed by Defay and Prigogine [5]. We refer to Rowlinson and Widom [1, p. 33] for a discussion of this point. In the theory of non-equilibrium thermodynamics of surfaces [6–9] Gibbs' description in terms of excess variables has been used. It is then assumed that Gibbs' description of the surface in terms of excess variables is autonomous, or in other words that one can use this property, which we will call *local equilibrium of the surface*, to describe the surface. In earlier work [10], this property was verified for a one-component square gradient system. It is the main objective of this chapter to verify this property for binary mixtures. For details about the extension of the square gradient model to non-equilibrium mixtures we refer to Chaps. 3 and 4. In this chapter we focus on the properties of the excess variables.

The validity of local equilibrium for a surface in a non-equilibrium mixture is a great simplification. Without this simplification the surface excess densities depend also on the values of the temperature and chemical potentials of the

adjacent phases. This complicates the description to a level that is difficult to manage. Also the possibility to introduce and define a temperature and chemical potentials for the surface, which are independent of the location of the dividing surface chosen, is an important simplification. For the one-component system, local equilibrium has been verified on the basis of both molecular dynamics simulations [11–13] and the non-equilibrium square gradient model [10]. For binary mixtures a limited number of molecular dynamics simulations of evaporation and condensation have been done [14–17]. None are available which verify the property of local equilibrium, however. Establishing this property using the square gradient model is therefore the only available option. For a proper understanding of an important industrial process like distillation, the validity of local equilibrium for the interface would be a great help. In this chapter we succeed to prove this for a binary mixture. Given the validity for one- and two-component systems we feel confident to formulate the hypothesis that local equilibrium is valid for surfaces in non-equilibrium multi-component mixtures.

In this chapter we use molar specific units. We therefore omit superscript v , which indicates the molar specific quantity, to simplify the notation. The verification is performed numerically and we use therefore the same system as in Chap. 4. Namely, we consider a planar interface between vapor and liquid in stationary non-equilibrium states. All the perturbations are performed in the direction perpendicular to the surface, coordinate along which we denote by x . The particular numerical values are obtained for the mixture of cyclohexane and n -hexane.

In Sect. 5.2 we speak about the Gibbs surface in equilibrium and how we want to establish local equilibrium property of a surface for non-equilibrium conditions. We then introduce excesses for the Gibbs surface in Sect. 5.3. Furthermore, we will in Sect. 5.4 develop a method to obtain T^s and ψ^s which are independent of the choice of the dividing surface and introduce other thermodynamic quantities. We then define local equilibrium in Sect. 5.5. In Sect. 5.6 we give the results of the verification procedure. Finally, in Sect. 5.7 we give concluding remarks.

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5.2 Equilibrium Gibbs Surface

In equilibrium it is possible to describe the surface in terms of Gibbs excess quantities [2]. One can treat a system of coexisting liquid and vapor as a three-phase system: liquid and vapor bulk phases and the surface. The surface has thermodynamic properties. The temperature and chemical potentials have the same equilibrium value as in the rest of the system. Furthermore, the thermodynamic

state of the surface is given by excess concentrations and thermodynamic potentials. Following Gibbs we have for the surface

$$\begin{aligned}
 h_{\text{eq}}^s &= \mu_{1,\text{eq}} c_{1,\text{eq}}^s + \mu_{2,\text{eq}} c_{2,\text{eq}}^s + T_{\text{eq}} s_{\text{eq}}^s \\
 u_{\text{eq}}^s &= \mu_{1,\text{eq}} c_{1,\text{eq}}^s + \mu_{2,\text{eq}} c_{2,\text{eq}}^s + \gamma_{\text{eq}}^s + T_{\text{eq}} s_{\text{eq}}^s \\
 f_{\text{eq}}^s &= \mu_{1,\text{eq}} c_{1,\text{eq}}^s + \mu_{2,\text{eq}} c_{2,\text{eq}}^s + \gamma_{\text{eq}}^s \\
 g_{\text{eq}}^s &= \mu_{1,\text{eq}} c_{1,\text{eq}}^s + \mu_{2,\text{eq}} c_{2,\text{eq}}^s
 \end{aligned} \tag{5.1}$$

The superscript s indicates here the surface and equal to the excess of corresponding quantities. In these relations the equilibrium temperature and chemical potentials are the same everywhere independent of the choice of the dividing surface. The excesses depend on the choice of the dividing surface, in such a way that the above relations are true for any choice of the dividing surface, see Gibbs [2].

It is our aim in this chapter to show that the surface in a non-equilibrium liquid–vapor system can also be described as a separate thermodynamic phase using the Gibbs excess quantities. We will call this property local equilibrium of the surface. The property of local equilibrium for the surface implies that it is possible to define all thermodynamic properties of a surface such that they have their equilibrium coexistence values for any choice of the dividing surface given the temperature of the surface T^s and the chemical potential difference $\psi^s \equiv \mu_1^s - \mu_2^s$ of the surface.

5.3 Calculating the Excess Densities

The definition of the excesses consists of three steps: determining the phase boundaries, defining the specified dividing surface and, in particular, defining the excesses.

To determine the phase boundaries we will use the order parameter q . We introduce a small parameter β and define the β -dependent boundary between the vapor and the surface, $x_\beta^{g,s}$, by

$$\left| \frac{q(x_\beta^{g,s}) - q_{\text{eos}}(p_\perp(x_\beta^{g,s}), \zeta(x_\beta^{g,s}), T(x_\beta^{g,s}))}{q(x_\beta^{g,s})} \right| \equiv \beta \tag{5.2}$$

where $q_{\text{eos}}(p_\perp, \zeta, T)$ is the equation of state's value (no gradient contributions) of q for pressure p_\perp , mol fraction ζ and temperature T . The β -dependent boundary between the surface and the liquid, $x_\beta^{\ell,s}$, is defined in the same way.

The numerical procedure calculates profiles only at specified grid points, which we provide to the procedure. That means that $x_\beta^{g,s}$ and $x_\beta^{\ell,s}$ can only be situated at points of the grid. We choose their position to be the last bulk point of the grid

where the left hand side of Eq. 5.2 does not exceed the right hand side. In our calculations we will choose $\beta = 10^{-3}$ and use a grid of 81 points.

We shall also choose bulk boundaries near the box boundary where, because of the finite size of the box, the behavior of the profiles might be uncharacteristic. To avoid this effect, we do not consider the first five points of each phase close to these boundaries when we calculate the properties in these phases. The sixth point is called x_g and the 76th point is called x^ℓ .

The bulk gas therefore ranges from x^g to $x_\beta^{g,s}$ and the bulk liquid ranges from $x_\beta^{\ell,s}$ to x^ℓ . The surface therefore ranges from $x_\beta^{g,s}$ to $x_\beta^{\ell,s}$. In order to define excess quantities properly, we always choose conditions such, that the widths of the vapor and the liquid phases, $x_\beta^{g,s} - x^g$ and $x^\ell - x_\beta^{\ell,s}$ are larger then the surface width $x_\beta^{\ell,s} - x_\beta^{g,s}$.

In order to determine excess densities, we need to extrapolate profiles from the vapor and the liquid phases into the interfacial region. In equilibrium, extrapolated bulk profiles are constants which are equal to the coexisting values of the corresponding quantities. Non-equilibrium bulk profiles are not constant. We fit the bulk profile with a polynomial of order $n_b = 2$ and use this polynomial to extrapolate non-equilibrium bulk profiles into the interfacial region. This is done with the help of Matlab functions `polyfit` and `polyval`. The extrapolation of the bulk profiles introduces a certain error depending on the choice of β and n_b in particular for non-equilibrium systems. This error is the main source of inaccuracy in the determination of the surface quantities. We will come back to this later.

The distances between commonly used dividing surfaces, such as for instance the equimolar surface and the surface of tension, are very small [1, 10]. Thus, if there occurs an error in the determination of a dividing surface using a course grid, that would lead to inaccurate results. We therefore divide each interval of the course grid between $x_\beta^{g,s}$ and $x_\beta^{\ell,s}$ in 10^4 subintervals. This surface grid is used for all operations related to the surface. Within the interfacial region we interpolate all the profiles (which were obtained by extrapolation from the bulk to the surface region using the course grid) from the course grid to the surface grid using a polynomial of order $n_s = 3$ with the help of Matlab functions `polyfit` and `polyval`. The values $n_b = 2$ and $n_s = 3$ were chosen such that the extrapolated profiles reproduce well the original ones.

We can now define the excess $\widehat{\phi}$ of any density $\phi(x)$ as a function of a dividing surface x^s as

$$\widehat{\phi}(x^s) = \int_{x_\beta^{g,s}}^{x_\beta^{\ell,s}} dx [\phi(x) - \phi^g(x) \Theta(x^s - x) - \phi^\ell(x) \Theta(x - x^s)] \quad (5.3)$$

where ϕ^g and ϕ^ℓ are the extrapolated gas and liquid profiles and $\Theta(t)$ is the Heaviside function. The density ϕ is per unit of volume and $\widehat{\phi}$ is per unit of

surface area. In our calculations integration is performed using the trapezoidal method by Matlab function `trapz`.

We can now define different dividing surfaces. The equimolar dividing surface x^c is defined by the equation $\widehat{c}(x^c) = 0$. Analogously, we define equimolar surfaces with respect to component 1 and 2: $\widehat{c}_1(x^{c1}) = 0$ and $\widehat{c}_2(x^{c2}) = 0$, and the equidensity surface x^ρ . The surface of tension x^γ is defined from the equation¹ $x^\gamma \widehat{p}_\parallel(x^\gamma) - \bar{x} \widehat{p}_\parallel(x^\gamma) = 0$. All the profiles are given as arrays on a coordinate grid, but not as continuous functions. Thus, in order to find the solution of an equation $\phi(x) = 0$ we calculate the values $\phi_i = \phi(x_i)$ for each point x_i within the surface region and find the minimum of it's absolute value, $\min_i(|\phi_i|)$. Because of the discrete nature of the argument, this value may not be equal to zero, but it will be the closest to zero among all other coordinate points. So we will call this point the root of the equation $\phi(x) = 0$. We use the fine surface grid in this procedure.

It follows from (5.3) that

$$\frac{d\widehat{\phi}(x^s)}{dx^s} = \phi^\ell(x^s) - \phi^g(x^s) \quad (5.4)$$

which we will use later.

5.4 Surface Temperature and Chemical Potential Difference

An equilibrium two-phase two-component mixture has two free parameters, for instance, the temperature T and the chemical potential difference $\psi \equiv \mu_1 - \mu_2$. *Local equilibrium of a surface* implies, that also in non-equilibrium it should be possible to define the temperature T^s and the chemical potential difference $\psi^s \equiv \mu_1^s - \mu_2^s$ of the surface. As was found in [10], T^s for one-component system is independent of the choice of the dividing surface. We therefore expect this for both T^s and ψ^s in two-component system.

The equilibrium temperature and chemical potential difference determine all other equilibrium properties of the surface. Thus, there is a bijection from T_{eq} and ψ_{eq} to any other set of independent excess variables $X_{1,\text{eq}}$ and $X_{2,\text{eq}}$, so that one can use them equally well in order to characterize a surface. In non-equilibrium, the actual temperature and chemical potential difference vary through the interfacial region, but $X_{1,\text{ne}}$ and $X_{2,\text{ne}}$ characterize the whole surface, since they are excesses. If a non-equilibrium surface is in local equilibrium, the same bijection should exist. This implies that given two independent non-equilibrium excesses $X_{1,\text{ne}}$ and $X_{2,\text{ne}}$ one can determine the temperature T^s and the chemical

¹ $\widehat{p}_\parallel(x)$ gives the surface tension for the dividing surface x . This can be expanded in the curvatures with the coefficient $x\widehat{p}_\parallel(x) - \bar{x}\widehat{p}_\parallel(x)$ for the linear term. Zero of this expression defines the position of the surface of tension x^γ .

potential ψ^s of the whole surface. Thus one can calculate equilibrium tables of $X_{1,\text{eq}}(T_{\text{eq}}, \psi_{\text{eq}})$ and $X_{2,\text{eq}}(T_{\text{eq}}, \psi_{\text{eq}})$ for different values of T_{eq} and ψ_{eq} and then determine temperature and chemical potential of a surface as $T^s = T_{\text{eq}}(X_{1,\text{ne}}, X_{2,\text{ne}})$ and $\psi^s = \psi_{\text{eq}}(X_{1,\text{ne}}, X_{2,\text{ne}})$.

As we want the temperature and chemical potential difference to be independent of the position of the dividing surface, we shall use excesses which are also independent of the position of a dividing surface in equilibrium for X_1 and X_2 . For two component mixtures these independent variables are the surface tension γ and the relative adsorption Γ_{12} . If the number of components is more than 2, additional relative adsorptions should be used.

These quantities are well defined for equilibrium, but not for non-equilibrium. So we will define them first. In equilibrium, the surface tension is defined as minus the excess of the parallel pressure $\gamma_{\text{eq}} = -\widehat{p}_{\parallel}$. Alternatively one often uses the integral of $p_{\perp} - p_{\parallel}(x) \equiv \gamma_{xx}(x)$ across the interface: $\gamma_{\text{eq}} = \int dx \gamma_{xx}(x)$. Both definitions are equivalent in equilibrium, since p_{\perp} is constant through the interface and $\gamma_{xx}(x)$ is identically zero in the bulk phases. In non-equilibrium, $\gamma_{xx}(x)$ may differ from zero in the bulk regions, however, and this makes the second definition inappropriate. We will therefore define the non-equilibrium surface tension using the standard definition (cf. also [10])

$$\gamma(x^s) = -\widehat{p}_{\parallel}(x^s) \quad (5.5)$$

This quantity differs from $\widehat{\gamma}_{xx}$ by the term equal to \widehat{p}_{\perp} , which is usually small compared to \widehat{p}_{\parallel} .

The relative adsorption is defined as

$$\Gamma_{12,\text{eq}} = \widehat{c}_{1,\text{eq}} - \widehat{c}_{2,\text{eq}} \frac{c_{1,\text{eq}}^{\ell} - c_{1,\text{eq}}^g}{c_{2,\text{eq}}^{\ell} - c_{2,\text{eq}}^g} \quad (5.6)$$

in equilibrium [5], where $c_{i,\text{eq}}^{\ell}$ and $c_{i,\text{eq}}^g$ are coexistence concentrations of the corresponding components. Since concentration profiles are not constant in non-equilibrium, we cannot use this definition directly. One can however see from Eq. 5.4, that both, in equilibrium and non-equilibrium $\widehat{c}_i'(x^s) = c_i^{\ell}(x^s) - c_i^g(x^s)$, where the prime indicates a derivative with respect to x^s . Since in equilibrium $c_i^{\ell}(x^s) - c_i^g(x^s) = c_{i,\text{eq}}^{\ell} - c_{i,\text{eq}}^g$ we can use the following definition

$$\Gamma_{12}(x^s) = \widehat{c}_1(x^s) - \widehat{c}_2(x^s) \frac{c_1^{\ell}(x^s) - c_1^g(x^s)}{c_2^{\ell}(x^s) - c_2^g(x^s)} \quad (5.7)$$

both in equilibrium and non-equilibrium.

If the system is in local equilibrium we may write:

$$\gamma(x^s) = \gamma_{\text{eq}}(T^s, \psi^s) \quad (5.8)$$

$$\Gamma_{12}(x^s) = \widehat{c}_1(x^s) - \widehat{c}_2(x^s) \frac{c_{1,\text{eq}}^{\ell}(T^s, \psi^s) - c_{1,\text{eq}}^g(T^s, \psi^s)}{c_{2,\text{eq}}^{\ell}(T^s, \psi^s) - c_{2,\text{eq}}^g(T^s, \psi^s)}$$

Substituting the expressions for $\gamma(x^s)$ and $\Gamma_{12}(x^s)$ from Eq. 5.5 and Eq. 5.7 into Eq. 5.8 we obtain the following relations

$$\begin{aligned} \widehat{P}_{\parallel}(x^s) &= \widehat{P}_{\parallel,\text{eq}}(T^s, \psi^s) \\ \frac{c_1^{\ell}(x^s) - c_1^g(x^s)}{c_2^{\ell}(x^s) - c_2^g(x^s)} &= \frac{c_{1,\text{eq}}^{\ell}(T^s, \psi^s) - c_{1,\text{eq}}^g(T^s, \psi^s)}{c_{2,\text{eq}}^{\ell}(T^s, \psi^s) - c_{2,\text{eq}}^g(T^s, \psi^s)} \end{aligned} \quad (5.9)$$

This gives the bijection equations to determine T^s and ψ^s from the actual non-equilibrium variables. As the left hand sides in Eq. 5.9 are in good approximation independent of the position of the dividing surface, T^s and ψ^s are similarly independent on this position.

5.4.1 Other Surface Quantities

The other quantities required for the Gibbs description of the non-equilibrium surfaces we define in the following way. The surface chemical potentials are the equilibrium coexistence values determined via the procedure discussed in Sect. 4.3.1

$$\begin{aligned} \mu_1^s &\equiv \mu_{1,\text{eq}}(T^s, \psi^s) \\ \mu_2^s &\equiv \mu_{2,\text{eq}}(T^s, \psi^s) \end{aligned} \quad (5.10)$$

We define the surface extensive properties as²

$$\phi^s(x^s) \equiv \widehat{\phi}(x^s) \quad (5.11)$$

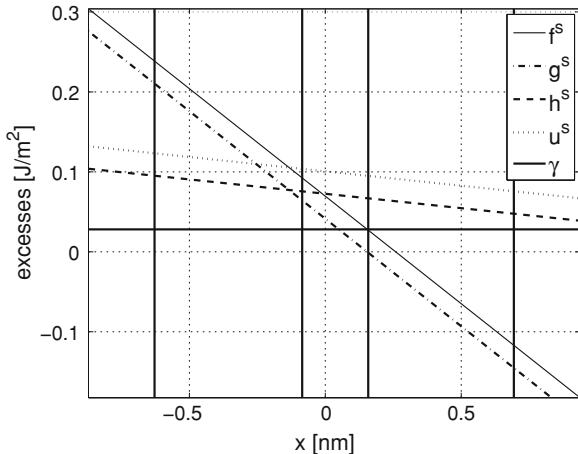
5.5 Defining Local Equilibrium of a Surface

The local equilibrium of a surface should be established for any choice of a dividing surface. The results of the calculations for any particular choice of a dividing surface may not be representative since they may be different for another choice of a dividing surface. Thus, the property of local equilibrium should be established for all dividing surfaces together.

Consider the profile of an excess $\widehat{\phi}(x^s)$ as a function of position of a dividing surface x^s . It follows from Eq. 5.4 that the slope of the excess profile at x^s is equal to the difference between the extrapolated bulk values of this profile at x^s .

² Note, that for some quantities this definition differs from the one, used in [10]. We will come back to this point later.

Fig. 5.1 Equilibrium excesses at $T = 330$ K and $\psi = 700$ J/mol as functions of the position of the dividing surface. The vertical lines indicate the $x^{c_2}, x^{\gamma}, x^c, x^{c_1}$ dividing surfaces from left to right



In equilibrium these values are constant and equal to the coexistence values. Thus, equilibrium excess densities are linear functions of the position of the dividing surface, as one can see on Fig. 5.1. Non-equilibrium profiles in the bulk phases are not constant. We construct the extrapolated profiles using n_b th order polynomials with $n_b = 2$. Resulting non-equilibrium excesses are therefore polynomials of the order $n_b + 1 = 3$, according to Eq. 5.4. These excesses, for rather extreme case of non-equilibrium perturbation $T^\ell = 1.02 T_{\text{eq}}$, are shown in Fig. 5.2. Even though these excesses are polynomials of the third order they are very close to straight lines. As one can see from Fig. 5.3, the variation in the slope is about 1% through the whole surface.³ It indicates that this non-equilibrium “state” is very close to an equilibrium one.

We therefore develop the procedure to relate the non-equilibrium state to an equilibrium one by comparing thermodynamic quantities in equilibrium and in non-equilibrium for the whole surface. The comparison performed in one particular point of the surface may not be sufficient because it may suffer from artifacts peculiar to this particular dividing surface. Moreover, any comparison performed in a particular point does not speak for the whole. We therefore compare the non-equilibrium surface with an equilibrium one for all dividing surfaces together.

To compare quantities for all dividing surfaces, we basically need to compare function profiles in the surface. We therefore need some kind of a measure of a function. We use a modified Euclidian norm defined in a following way.

Consider a non-equilibrium thermodynamic excess $\phi^s(x^s)$ and a quantity $\tilde{\phi}^s(x^s; T, \psi)$ which is a combination of excesses and may depend on (T, ψ) as parameters. We introduce the following measures of the difference between ϕ^s and $\tilde{\phi}^s$

$$\delta_{\{\phi, \tilde{\phi}\}}(x^s; T, \psi) \equiv |\phi^s(x^s) - \tilde{\phi}^s(x^s; T, \psi)| \quad (5.12)$$

³ Note, that the scale on Fig. 5.3, is different from the one on Fig. 5.2.

Fig. 5.2 Non-equilibrium excesses for the case of perturbing $T^\ell = 1.02 T_{\text{eq}}$ as functions of the position of the dividing surface. The vertical lines indicate the $x^{c_2}, x^\gamma, x^c, x^{c_1}$ dividing surfaces from left to right

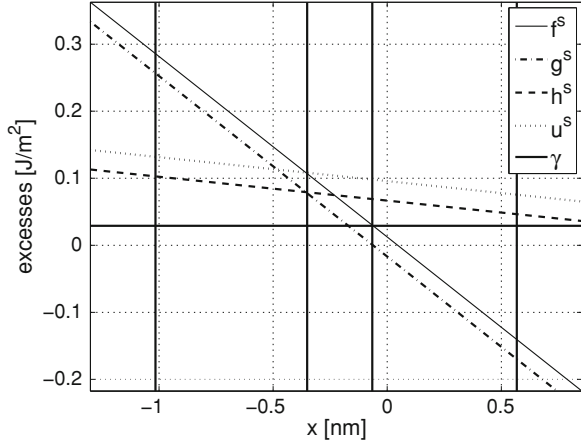
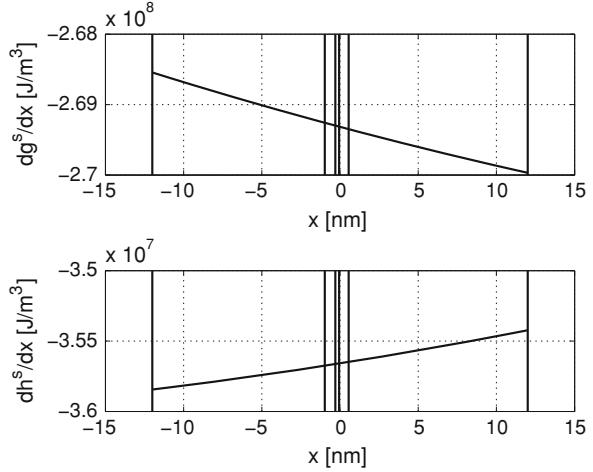


Fig. 5.3 Slopes of non-equilibrium excesses for the case of perturbing $T^\ell = 1.02 T_{\text{eq}}$ as functions of the position of the dividing surface. The vertical lines indicate the surface boundaries and $x^{c_2}, x^\gamma, x^c, x^{c_1}$ dividing surfaces



and

$$S_{\{\phi, \tilde{\phi}\}}(T, \psi) \equiv \sum_{x^s \in \text{surface}} \left[\phi^s(x^s) - \tilde{\phi}^s(x^s; T, \psi) \right]^2 \quad (5.13)$$

$$\sigma_{\{\phi, \tilde{\phi}\}}(T, \psi) \equiv \frac{1}{N} \sqrt{S_{\{\phi, \tilde{\phi}\}}(T, \psi)}$$

where N is the number of surface points.

We define ϕ^s and $\tilde{\phi}^s$ to be *equivalent* in the surface if the value of $\sigma_{\{\phi, \tilde{\phi}\}}$ is negligible compared to the typical value of either $|\phi^s(x^s)|$ or $|\tilde{\phi}^s(x^s; T, \psi)|$. Thus, $\sigma_{\{\phi, \tilde{\phi}\}}$ or $S_{\{\phi, \tilde{\phi}\}}$ represents a measure of equivalence of the functions ϕ^s and $\tilde{\phi}^s$.

Parameters T and ψ determine a whole family of functions $\tilde{\phi}^s(x^s; T, \psi)$. All of them are equivalent in the above sense, if $\tilde{\phi}^s$ is a continuous function of T and ψ . Moreover, all of them are equivalent to the function $\tilde{\phi}^s$.

Among all the values of parameters T and ψ , we want to find those $T = T_{\{x^s\}}$ and $\psi = \psi_{\{x^s\}}$, which make the function $\tilde{\phi}^s$ to correspond best to the equivalent function ϕ^s . Their measure of equivalence $S_{\{\phi, \tilde{\phi}\}}(T, \psi)$ is a function of T and ψ , which reaches minimum for certain values of these parameters. We say, that $T_{\{x^s\}}$ and $\psi_{\{x^s\}}$ *characterize* the interface in a non-equilibrium state, if

$$S_{\{\phi, \tilde{\phi}\}}(T_{\{x^s\}}, \psi_{\{x^s\}}) = \min_{T, \psi} S_{\{\phi, \tilde{\phi}\}}(T, \psi) \quad (5.14)$$

One may recall that this definition is based on the least square sum method. These definitions are easy to illustrate in equilibrium. If we define

$$h_{\text{eq, gibbs}}^s(x^s; T, \psi) \equiv \mu_{1, \text{eq}}(T, \psi) c_{1, \text{eq}}^s + \mu_{2, \text{eq}}(T, \psi) c_{2, \text{eq}}^s + T s_{\text{eq}}^s$$

which is the right hand side of Eq. 5.1 for the enthalpy, it follows from Eq. 5.1, that

$$h_{\text{eq}}^s(x^s; T_{\text{eq}}, \psi_{\text{eq}}) = h_{\text{eq, gibbs}}^s(x^s; T_{\text{eq}}, \psi_{\text{eq}})$$

Furthermore,

$$g_{\text{eq}}^s(x^s; T_{\text{eq}}, \psi_{\text{eq}}) \neq h_{\text{eq, gibbs}}^s(x^s; T_{\text{eq}}, \psi_{\text{eq}})$$

Thus

$$\delta_{\{h_{\text{eq}}, h_{\text{eq, gibbs}}\}}(x^s; T_{\text{eq}}, \psi_{\text{eq}}) = 0$$

and

$$\delta_{\{g_{\text{eq}}, h_{\text{eq, gibbs}}\}}(x^s; T_{\text{eq}}, \psi_{\text{eq}}) \neq 0$$

It is also true that

$$\min_{T, \psi} S_{\{h_{\text{eq}}, h_{\text{eq, gibbs}}\}}(T, \psi) = 0 = S_{\{h_{\text{eq}}, h_{\text{eq, gibbs}}\}}(T_{\text{eq}}, \psi_{\text{eq}})$$

and

$$\sigma_{\{h_{\text{eq}}, h_{\text{eq, gibbs}}\}}(T, \psi) \ll \sigma_{\{g_{\text{eq}}, h_{\text{eq, gibbs}}\}}(T, \psi)$$

According to the above definitions: (1) $h_{\text{eq, gibbs}}^s(x^s)$ and $h_{\text{eq}}^s(x^s)$ are *equivalent* functions, but $h_{\text{eq, gibbs}}^s(x^s)$ and $g_{\text{eq}}^s(x^s)$ are *not equivalent*; (2) the equilibrium state of the surface is *characterized* by T_{eq} and ψ_{eq} ; as it should be.

This analysis gives nothing new in equilibrium. In non-equilibrium, where we are going to implement this, it allows us to introduce properties of the interfacial

region, which (1) characterize the whole surface in a non-contradictory manner and (2) reduce to the common nomenclature in equilibrium.

Note, that while in equilibrium the conditions

$$\delta_{\{\phi, \bar{\phi}\}}(x^s; T_{\text{eq}}, \psi_{\text{eq}}) = 0 \quad \Leftrightarrow \quad S_{\{\phi, \bar{\phi}\}}(T_{\text{eq}}, \psi_{\text{eq}}) = \min S_{\{\phi, \phi\}}(T, \psi)$$

are equivalent, this is not the case in non-equilibrium. In general it does not follow in non-equilibrium from Eq. 5.14 that

$$\delta_{\{\phi, \bar{\phi}\}}(x^s; T, \psi) = 0 \quad \forall x^s \quad (5.15)$$

Thus Eq. 5.15 is not a good measure of the equality of the quantities and states in non-equilibrium. We may therefore speak about the equality of thermodynamic quantities as well as about the state $T_{\{x^s\}}$ and $\psi_{\{x^s\}}$ of the surface in non-equilibrium only in the least square sense, as it is given in Eq. 5.14.

Within establishing the local equilibrium property of a non-equilibrium surface, we would like to verify the following properties: (1) the existence of the unique temperature T^s and chemical potential difference ψ^s which characterize a non-equilibrium surface; (2) the validity of the Eq. 5.1 in non-equilibrium at the surface's T^s and ψ^s ; (3) the possibility to determine all the properties of a non-equilibrium surface from equilibrium tables at the surface's T^s and ψ^s . We do this in the following section.

5.6 Verification of Local Equilibrium

We calculate the equilibrium properties (coexistence data, such as the pressure or bulk densities, as well as various excesses) of the system for the range of temperatures $T = \{325, 326, \dots, 340\}$ K and the range of chemical potential differences $\psi = \mu_1 - \mu_2 = \{400, 450, \dots, 1,000\}$ J/mol. The value of a thermodynamic quantity at any point (T, ψ) which is between these, is interpolated using the Matlab procedures `interp2` and `griddata`.

The temperature range was chosen to be well above the triple point of both components (279.5 and 177.9 K for cyclohexane and *n*-hexane respectively) and below the critical temperature of both components (553.5 and 507.5 K, respectively). As discussed in Sect. 4.5.1 the equilibrium mole fractions of cyclohexane in the vapor and in the liquid were 0.55 and 0.59 respectively, when the temperature was 330 K and the chemical potential difference was 700 J/mol. As one can see in Fig. 4.9 it was enough to consider the range of temperatures of 15 K and the range of chemical potential differences of 600 J/mol, for the stationary state conditions considered in this paper. A larger range would be necessary to consider for unrealistically extreme non-equilibrium conditions across the system.

In the calculations in this chapter we took the square gradient amplitudes of the resistivity coefficients in Eq. 4.17 equal to zero, $\alpha_{qq} = 0$, $\alpha_{q1} = 0$ and $\alpha_{11} = 0$. As one can see in the figures in the previous chapter, the choice of $\alpha_{qq} = 1$ of $\alpha_{11} = 1$

leads to a relatively minor change in the continuous profiles. In view of the complexity of the analysis, we therefore restricted ourselves to zero α 's. We do not expect finite values of α 's (which are more realistic) will modify our results regarding the validity of local equilibrium for the surface.

5.6.1 Surface Temperature and Chemical Potential Difference

As was mentioned, in equilibrium both γ and Γ_{12} are independent of the location of the dividing surface x^s . Given the above definitions, Eqs. 5.5 and 5.7, we can calculate these quantities for non-equilibrium states. Calculations show, that even though γ and Γ_{12} are not exactly independent on x^s away from equilibrium, the relative deviation is so small (about 0.004% for γ and 4% for Γ_{12} in the worst case), that one can consider these quantities to be independent of the position of the dividing surface. Thus one may use them in order to find the temperature, T^s , and the chemical potential difference, ψ^s , of the surface in non-equilibrium states, which will be independent of the position of the dividing surface.

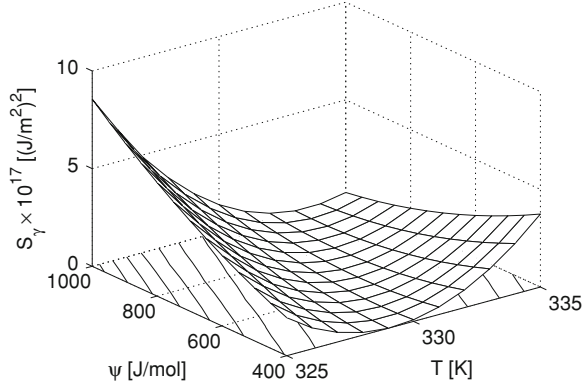
Using Eqs. 5.13 and 5.9 together with Eq. 5.4 we construct the following expressions

$$\begin{aligned} S_\gamma(T, \psi) &= \sum_{x^s} \left[\widehat{p}_\parallel(x^s) - \widehat{p}_{\parallel, \text{eq}}(T, \psi) \right]^2 \\ S_{\Gamma_{12}}(T, \psi) &= \sum_{x^s} \left[\frac{\widehat{c}'_{1, \text{eq}}(x^s; T, \psi)}{\widehat{c}'_1(x^s)} - \frac{\widehat{c}'_{2, \text{eq}}(x^s; T, \psi)}{\widehat{c}'_2(x^s)} \right]^2 \end{aligned} \quad (5.16)$$

where the prime indicates the derivative with respect to x^s .

$S_i(T, \psi)$ (where i is either γ or Γ_{12}) should reach the minimum at $T^s_{\{x^s\}}$ and $\psi^s_{\{x^s\}}$. We note however, that neither $S_i(T, \psi)$ have a minimum at a single point (T^s, ψ^s) . There is a whole generatrix curve of minima $C_i(T, \psi) = 0$ so the plot of $S_i(T, \psi)$ is a valley. One can see it on Fig. 5.4. Every point of the generatrix curve is the minimum point of $S_i(T, \psi)$ along the direction “perpendicular” to this generatrix. If $\widehat{p}_\parallel(x^s)$ or $\widehat{c}'_1(x^s)$ and $\widehat{c}'_2(x^s)$ represent the corresponding profiles for some equilibrium state $(T_{\text{eq}}, \psi_{\text{eq}})$, then $S_i(T_{\text{eq}}, \psi_{\text{eq}}) = 0$ and the generatrix is constant. Since these profiles are non-equilibrium profiles, the generatrix is not exactly constant but very close to it. Thus $C_i(T, \psi) = \partial S_i(T, \psi) / \partial w$, where w is a direction in $T-\psi$ plane which is perpendicular to generatrix. In fact, one should be careful speaking about directions, since no metric is defined in the $T-\psi$ plane. Thus we cannot introduce $\nabla_{T\psi}$ so that $C_i(T, \psi) = |\nabla_{T\psi} S_i(T, \psi)|$. In fact, w can be any direction which does not coincide or does not almost coincide with the direction of generatrix. In practice we find that we can use $w = T$, while using $w = \psi$ gives less accurate results. Thus we determine the minimum curve from the Eq. 5.17

Fig. 5.4 The plot of $S_\gamma(T, \psi)$ for the case of perturbing $T^\ell = 1.02 T_{\text{eq}}$. The lines in the $T - \psi$ plane are lines of constant value of $S_\gamma(T, \psi)$



$$\frac{\partial S_i(T, \psi)}{\partial T} = 0 \quad (5.17)$$

One needs two quantities, S_γ and $S_{\Gamma_{12}}$, in order to determine $T_{\{x^s\}}^s$ and $\psi_{\{x^s\}}^s$ uniquely. The surface temperature and chemical potential difference, $T_{\{x^s\}}^s$ and $\psi_{\{x^s\}}^s$, are determined from the intersection of two minimum curves of S_γ and S_Γ

$$\begin{aligned} \left. \frac{\partial S_\gamma(T, \psi)}{\partial T} \right|_{T_{\{x^s\}}^s, \psi_{\{x^s\}}^s} &= 0 \\ \left. \frac{\partial S_{\Gamma_{12}}(T, \psi)}{\partial T} \right|_{T_{\{x^s\}}^s, \psi_{\{x^s\}}^s} &= 0 \end{aligned} \quad (5.18)$$

Here superscript s indicates that we speak about surface quantities only (as everywhere in this chapter) and subscript $\{x^s\}$ indicates that $T_{\{x^s\}}^s$ and $\psi_{\{x^s\}}^s$ are the properties of all dividing surfaces together (in contrast to the values $T^s(x^s)$ and $\psi^s(x^s)$ determined from Eq. 5.9 for each particular dividing surface x^s).

We calculate the temperatures and the chemical potential differences for different non-equilibrium conditions. They are outlined in Tables 5.1, 5.2 and 5.3. The first row of each table, corresponding to $\{x^s\}$, gives T^s and ψ^s calculated from Eq. 5.18. The following rows give, corresponding to different particular dividing surfaces, the values of T^s and ψ^s calculated from Eq. 5.9. The equilibrium parameters around which the system is perturbed are given in Table 4.3: $T_{\text{eq}} = 330 \text{ K}$ and $\psi_{\text{eq}} = 700 \text{ J/K}$.

Note, that T^s and ψ^s are different from the actual values of T and ψ in the interfacial region.

Table 5.1 Surface temperatures (K) and chemical potential differences (J/mol) for the case of perturbing T^ℓ around $T_{\text{eq}} = 330$ K

Surface	$T^\ell = 1.02 T_{\text{eq}}$		$T^\ell = 0.98 T_{\text{eq}}$	
	T^s	ψ^s	T^s	ψ^s
$\{x^s\}$	331.831	770.53	328.129	650.92
x^c	331.823	769.51	328.124	650.29
x^γ	331.828	770.22	328.123	650.21
x^{c1}	331.814	767.97	328.127	650.43
x^{c2}	331.838	771.86	328.121	650.1

Table 5.2 Surface temperatures (K) and chemical potential differences (J/mol) for the case of perturbing p^g around $p_{\text{eq}} = 376,095$ Pa

Surface	$p^g = 1.02 p_{\text{eq}}$		$p^g = 0.98 p_{\text{eq}}$	
	T^s	ψ^s	T^s	ψ^s
$\{x^s\}$	330.796	683.87	329.059	696.52
x^c	330.8	684.68	329.063	697.22
x^γ	330.799	684.44	329.063	697.12
x^{c1}	330.804	685.19	329.065	697.46
x^{c2}	330.795	683.93	329.061	696.87

Table 5.3 Surface temperatures (K) and chemical potential differences (J/mol) for the case of perturbing ζ^ℓ around $\zeta_{\text{eq}}^\ell = 0.5934$

Surface	$\zeta^\ell = 1.02 \zeta_{\text{eq}}^\ell$		$\zeta^\ell = 0.98 \zeta_{\text{eq}}^\ell$	
	T^s	ψ^s	T^s	ψ^s
$\{x^s\}$	329.577	559.32	330.24	812.86
x^c	329.598	562.44	330.242	813.16
x^γ	329.584	560.5	330.253	814.67
x^{c1}	329.63	566.83	330.219	809.99
x^{c2}	329.554	556.3	330.278	817.99

5.6.2 The Non-Equilibrium Gibbs Surface

In this section, we would like to verify that the surface quantities defined by Eq. 5.11 satisfy Eq. 5.19 with T^s and $\psi^s = \mu_1^s - \mu_2^s$ determined by Eqs. 5.9 and 5.18.

$$\phi^s = \phi_{\text{gibbs}}^s(T^s, \psi^s) \quad (5.19)$$

Namely, we want to verify that with the definition Eq. 5.19 the following is true

$$\begin{aligned} h^s &= \mu_1^s c_1^s + \mu_2^s c_2^s + T^s s^s \\ u^s &= \mu_1^s c_1^s + \mu_2^s c_2^s + \gamma^s + T^s s^s \\ f^s &= \mu_1^s c_1^s + \mu_2^s c_2^s + \gamma^s \\ g^s &= \mu_1^s c_1^s + \mu_2^s c_2^s \end{aligned} \quad (5.20)$$

where the right hand side will also be denoted by $\phi_{\text{gibbs}}^s(T^s, \psi^s)$ for the corresponding quantity ϕ . Equation 5.20 is the non-equilibrium analog of equilibrium Eq. 5.1.

In order to analyze the measure of validity of Eq. 5.19 we construct the quantities

$$\begin{aligned} \mathcal{E}_{\phi_{\text{gibbs}}}(T, \psi) &= \sum_{x^s \in \text{surface}} \left[\frac{\phi^s(x^s) - \phi_{\text{gibbs}}^s(x^s; T, \psi)}{\phi^s(x^s)} \right]^2 \\ \epsilon_{\phi_{\text{gibbs}}}(x^s; T, \psi) &= \left| \frac{\phi^s(x^s) - \phi_{\text{gibbs}}^s(x^s; T, \psi)}{\phi^s(x^s)} \right| \end{aligned} \quad (5.21)$$

for each thermodynamic potential h, u, f, g . $\mathcal{E}_{\phi_{\text{gibbs}}}$ gives the relative error of the determination of the surface quantity ϕ^s using the Gibbs excesses relations (5.20) for all dividing surfaces together, while $\epsilon_{\phi_{\text{gibbs}}}$ gives this error for a particular dividing surface. We build $\epsilon_{\phi_{\text{gibbs}}}(T, \psi)$ both for $T = T_{\{x^s\}}^s, \psi = \psi_{\{x^s\}}^s$ determined from Eq. 5.18 for the whole surface, and for $T = T^s(x^s), \psi = \psi^s(x^s)$ determined from Eq. 5.9 for particular dividing surface. We build $\mathcal{E}_{\phi_{\text{gibbs}}}(T, \psi)$ for $T = T_{\{x^s\}}^s, \psi = \psi_{\{x^s\}}^s$ determined only for the whole surface. The values of the corresponding errors are listed in Tables 5.4, 5.5 and 5.6 in Sect. 5.8.1, and are found to be small.

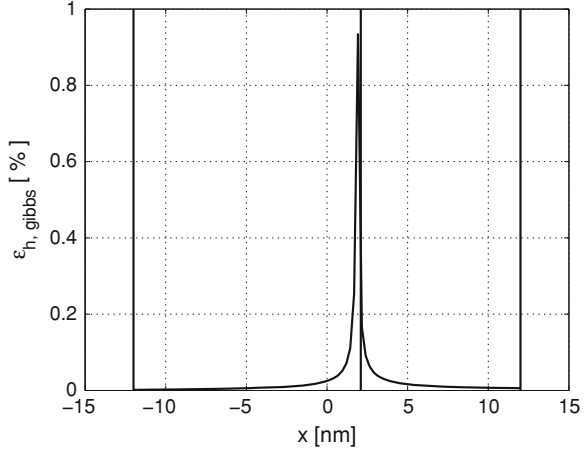
As one can see, there is a variation in the value of the error for the different dividing surfaces. This has two reasons. One reason is the slight variation in T^s and ψ^s from Tables 5.1, 5.2 and 5.3 for different dividing surfaces. The variation of each excess potential reflects the variation of T^s and ψ^s through these surfaces. So do the relative errors.

Another factor which influences the value of these errors is the actual value of an excess at a given dividing surface. If it is close to zero, then in the expression for ϵ , the value of denominator is small, which gives a large value for the error. Particularly, $g^s(x^c) \approx 0$ both in equilibrium and in non-equilibrium which makes the row corresponding to g at x^c be uninformative. One should not take into account these data.

There are such dividing surfaces for any potential ϕ . If the particular dividing surface is far from zero point of ϕ^s , then $\epsilon_{\phi_{\text{gibbs}}}$ gives a good measure of the error. But $\epsilon_{\phi_{\text{gibbs}}}$ fails to measure the error, if the particular dividing surface is close to zero point of ϕ^s . One can see from Fig 5.5 that the relative error $\epsilon_{\phi_{\text{gibbs}}}$ indeed rises enormously at x^ϕ . Particularly because of this fact, the definition of the excess quantities in [10] was different from Eq. 5.11.

We emphasize however, that the overall error $\mathcal{E}_{\phi_{\text{gibbs}}}$ represents the whole surface and does not suffer from this problem. The contribution from the dividing surfaces, which make ϕ^s be very small, is negligible, since the amount of such points is much less than the total amount of grid points in the surface. We conclude that $\mathcal{E}_{\phi_{\text{gibbs}}}$ is the appropriate measure of the deviation of local equilibrium for the surface. From Tables 5.4, 5.5 and 5.6 in Sect. 5.8.1 it then follows that even for

Fig. 5.5 The relative error $\epsilon_{h_{\text{gibbs}}}(x^s; T_{\{x^s\}}^s, \psi_{\{x^s\}}^s)$ for the case of perturbing $T^\ell = 1.02 T_{\text{eq}}$. The vertical lines indicate the surface boundaries and x^h dividing surfaces



such extreme conditions, when the temperature difference across the box is up to 10^8 K/m, the deviation is not more than a few per mill. For less extreme conditions, the deviation is correspondingly smaller. This is in agreement with the non-equilibrium surface being in local equilibrium.

Another possible test is to compare the absolute error $|\phi^s(x^s) - \phi_{\text{gibbs}}^s(x^s; T, \psi^s)|$ with the deviation $\sigma_{\phi_{\text{gibbs}}}(T, \psi)$ defined in Eq. 5.13. The calculations show that for the particular dividing surfaces the former quantity does not exceed the latter, which indicates that the absolute error is actually within the trust region.

5.6.3 Equilibrium Tables

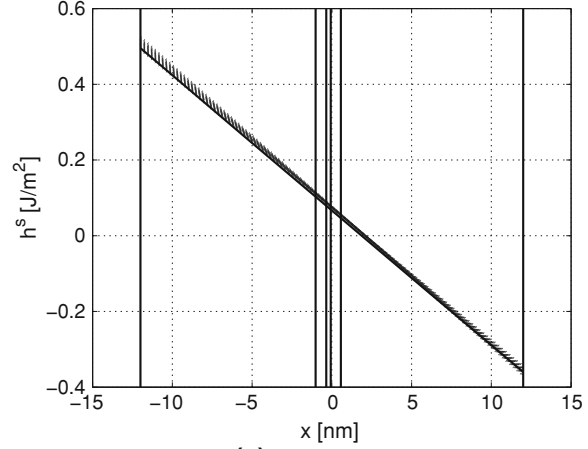
In this section we verify the possibility to determine all properties of a non-equilibrium surface from equilibrium tables at the surface's T^s and ψ^s . The surface chemical potentials μ_1^s and μ_2^s are already constructed as their equilibrium values in Eq. 5.10. So in this section we will verify the relation

$$\phi^s = \phi_{\text{eq}}^s(T^s, \psi^s) \quad (5.22)$$

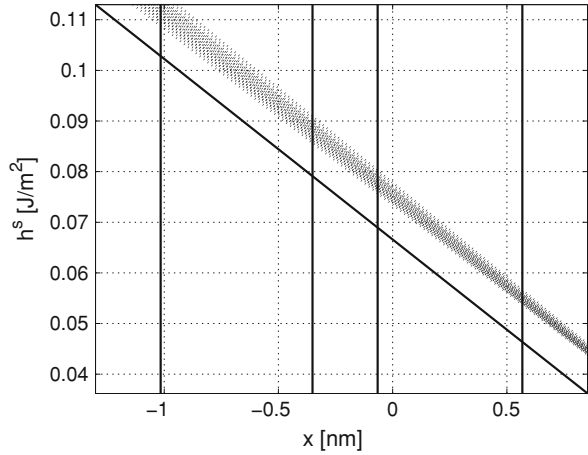
As in Sect. 5.6.2 we compare the actual excess of a thermodynamic potential with the corresponding equilibrium value at given temperature and chemical potential of the surface. Before we do this a note has to be made.

Under non-equilibrium conditions the profile of a quantity ϕ^s is shifted with respect to the equilibrium one. One can see this in Fig. 5.6 for ϕ being the enthalpy h . The reason for this is the flux of matter caused by the non-equilibrium perturbation. The whole interface is therefore shifted. One can clearly see this, comparing the positions of the particular dividing surfaces on Figs. 5.1 and 5.2. It follows therefore that the direct comparison of the profiles

Fig. 5.6 Non-equilibrium profile of h^s for the case of perturbing $T^\ell = 1.02 T_{\text{eq}}$ (solid line) compared to the profiles of h_{eq}^s calculated from the equilibrium tables for different T_{eq} and ψ_{eq} (dotted lines). The vertical lines indicate the surface boundaries and dividing surfaces for non-equilibrium case



(a) Whole surface



(b) Subregion

should be done not in the observer's frame of reference (OFO, which is used in all other calculations), but in the *surface's frame of reference* (SFO). The SFO is simply shifted with respect to the OFO, depending on the rate of non-equilibrium perturbations. Zero of the SFO is chosen at the reference surface, which can be either the equimolar surface, or any other physically sensible surface. If x^\ominus is the position of this surface in OFO and $\phi_{\text{OFO}}^s(x_{\text{OFO}}^s)$ is the profile of ϕ^s in OFO, then $\phi_{\text{SFO}}^s(x_{\text{SFO}}^s) \equiv \phi_{\text{OFO}}^s(x_{\text{OFO}}^s) = \phi_{\text{OFO}}^s(x_{\text{SFO}}^s + x^\ominus)$ is the profile of ϕ^s in SFO.

We can now determine the equilibrium state, which the non-equilibrium one should correspond to. Consider the following definitions of $\mathcal{E}_{\phi_{\text{table}}}$ and $\epsilon_{\phi_{\text{table}}}$ which have the same meaning as in Eq. 5.21:

$$\mathcal{E}_{\phi_{\text{table}}}(T, \psi) = \sum_{x_i^s \in \text{surface}} \left[\frac{\phi^s(x_i^s) - \phi_{\text{eq}}^s(x_i^s + x_{\text{eq}}^{\ominus} - x^{\ominus}; T, \psi)}{\phi^s(x_i^s)} \right]^2 \quad (5.23)$$

$$\epsilon_{\phi_{\text{table}}}(x^s; T, \psi) = \left| \frac{\phi^s(x^s) - \phi_{\text{eq}}^s(x^s; T, \psi)}{\phi^s(x^s)} \right|$$

for each thermodynamic potential h, u, f, g . Furthermore, x^{\ominus} and x_{eq}^{\ominus} are the non-equilibrium and equilibrium positions of the reference surface in OFO. The set $\{x_i^s\}$ is the non-equilibrium surface grid and is used for both profiles. Since the width of an equilibrium surface may not be the same as the non-equilibrium one, the summation may exceed the formal boundaries of the equilibrium surface. This is not a problem however, since the equilibrium profile ψ_{eq}^s is the line with constant slope everywhere, as well as beyond the formal boundaries. We do not shift the surface grid in the definition of $\epsilon_{\phi_{\text{table}}}(x^s; T, \psi)$ because here x^s means the particular dividing surface (e.g. equimolar surface), while x_i^s means the point of the surface grid.

The values of the corresponding errors are listed in Tables 5.7, 5.8 and 5.9 in Sect. 5.8.2, and, though somewhat larger than those in Sect. 5.6.2, are still small. As in Sect. 5.6.2 we see, that for the equimolar surface the relative error in g is huge. There is the same reason for this, namely that $g^s(x_c) \approx 0$ both in equilibrium and in non-equilibrium. This again makes the row corresponding to g at x^c be uninformative and one should not take into account these data.

As discussed in Sect. 5.6.2, $\mathcal{E}_{\phi_{\text{table}}}(T, \psi)$ is now the appropriate measure of the validity of local equilibrium. In view of the small size of this quantity we similarly conclude that Eq. 5.22 is satisfied in good approximation. This again supports that the non-equilibrium surface as described by Gibbs excess densities is in local equilibrium.

5.7 Discussion and Conclusions

This work continued the verification of the validity of local equilibrium for the Gibbs surface started in [10]. This property means that a surface under non-equilibrium steady-state conditions can be described as an equilibrium one in terms of Gibbs excess densities. We have discussed the meaning of the surface quantities in non-equilibrium and established the systematic procedure to obtain them. We were in particular focused on (1) the existence of the surface temperature and chemical potentials which are independent of the choice of the dividing surface; (2) the validity of the thermodynamic relations between Gibbs excesses for a non-equilibrium surface; (3) the correspondence between the non-equilibrium and equilibrium properties of the surface. It was possible to verify that these properties are valid for all choices of the dividing surface with a good accuracy. Similar results were obtained for the one-component system in [10].

The solution procedure is numerical, and contains therefore a certain error. We may not expect this error to be negligible, not only because of numerical inaccuracy, but in particular also because of the non-equilibrium nature of the system. All these errors contribute to the overall measure of the deviation ε_ϕ . As this quantity is not more than a few per mill for very extreme boundary conditions, we consider this a satisfactory verification of local equilibrium.

An important part of the analysis in the interfacial region is the introduction of the excesses of thermodynamic densities, which are constructed with the help of extrapolated bulk profiles. In contrast to equilibrium, non-equilibrium bulk profiles are not constants, and therefore their extrapolation to the surface region is not always accurate. The accuracy of extrapolation lowers when the surface width increases. Apparent small deviations from local equilibrium are therefore to some extent an artifact of the inaccuracy of the extrapolation.

In the description of the surface excess densities it may happen that for a particular choice of the dividing surface not one but several of the excesses are negligible. This increases the relative error enormously while the absolute error remains finite and more or less constant. In order to avoid this problem we consider the excesses for all dividing surfaces together, rather than for a particular dividing surface. Particularly, in [10] the definition of the excess Gibbs energy was chosen differently because this excess was very small for the equimolar surface. We have shown in this chapter why this is not needed.

One can see from these data, that within different ways of perturbing a mixture from equilibrium, the biggest error comes when one perturbs the temperature on the liquid side. This is the most extreme condition for the mixture being in non-equilibrium. While the relative temperature perturbation is only 2%, the resulting temperature gradient is about 10^8 K/m which is very far beyond ordinary non-equilibrium conditions. The other perturbations make the validity of local equilibrium for the surface more precise. Similarly smaller perturbations make the validity of local equilibrium also more precise.

We therefore conclude that the local equilibrium of the surface is valid with a reasonable accuracy also under extreme temperature gradients for binary mixtures. For the description of transport through and into surfaces this verifies that the use of non-equilibrium thermodynamics as done in, for instance [6–9] is appropriate. For the application to industrial processes this is an important simplification, which is of great importance.

5.8 Excesses' Errors

To recall, each table in this section gives the values of different errors in percent. Each line gives the relative error in the determination the corresponding surface quantity ϕ^s . A line with \mathcal{E}_ϕ gives the error over all surfaces together, while a line with ε_ϕ gives this error for a particular dividing surface.

Two major columns give the corresponding values for different perturbations. For each perturbation, two finer columns give errors from different procedures to determine surface temperature and chemical potential difference. A column with $\{x^s\}$ gives the values of corresponding errors for $T = T_{\{x^s\}}^s$, $\psi = \psi_{\{x^s\}}^s$ determined from Eq. 5.18 for the whole surface. A column with x^s gives the values of corresponding errors for $T = T^s(x^s)$, $\psi = \psi^s(x^s)$ determined from Eq. 5.9 for a particular dividing surface.

5.8.1 Gibbs Excesses' Relative Errors

See Tables 5.4, 5.5 and 5.6.

5.8.2 Equilibrium Table Excesses' Relative Errors

See Tables 5.7, 5.8 and 5.9.

Table 5.4 Gibbs excesses relative error for the case of perturbing T^ℓ in percent

ϕ	Error	$T^\ell = 1.02 T_{\text{eq}}$		$T^\ell = 0.98 T_{\text{eq}}$	
		for $\{x^s\}$	for x^s	for $\{x^s\}$	for x^s
h	\mathcal{E}_ϕ	0.01328	–	0.033276	–
	$\epsilon_\phi(x^c)$	0.023799	0.023419	0.064597	0.065002
	$\epsilon_\phi(x^\gamma)$	0.020605	0.020737	0.056585	0.057148
	$\epsilon_\phi(x^{c1})$	0.035878	0.033571	0.085212	0.085204
	$\epsilon_\phi(x^{c2})$	0.015606	0.016541	0.047847	0.048578
u	\mathcal{E}_ϕ	0.0071257	–	0.026714	–
	$\epsilon_\phi(x^c)$	0.016729	0.016462	0.045109	0.045392
	$\epsilon_\phi(x^\gamma)$	0.015059	0.015156	0.041048	0.041457
	$\epsilon_\phi(x^{c1})$	0.022033	0.020616	0.054286	0.05428
	$\epsilon_\phi(x^{c2})$	0.012161	0.012889	0.036244	0.036797
f	\mathcal{E}_ϕ	0.20039	–	0.12983	–
	$\epsilon_\phi(x^c)$	7.3727	7.3666	8.7959	8.799
	$\epsilon_\phi(x^\gamma)$	1.9809	1.981	2.2605	2.2602
	$\epsilon_\phi(x^{c1})$	1.6966	1.6881	2.5586	2.5602
	$\epsilon_\phi(x^{c2})$	0.65429	0.65354	1.0109	1.0095
g	\mathcal{E}_ϕ	0.36323	–	0.15487	–
	$\epsilon_\phi(x^c)$	272.37	272.15	73.468	73.494
	$\epsilon_\phi(x^\gamma)$	2.7241	2.7242	3.2313	3.2309
	$\epsilon_\phi(x^{c1})$	1.4054	1.3983	1.9592	1.9605
	$\epsilon_\phi(x^{c2})$	0.72857	0.72773	1.1818	1.1802

Table 5.5 Gibbs excesses relative error for the case of perturbing p^s in percent

ϕ	Error	$p^s = 1.02 p_{\text{eq}}$		$p^s = 0.98 p_{\text{eq}}$	
		for $\{x^s\}$	for x^s	for $\{x^s\}$	for x^s
h	\mathcal{E}_ϕ	0.0013703	–	0.0019532	–
	$\epsilon_\phi(x^c)$	0.0018964	0.0022352	0.0011722	0.00088793
	$\epsilon_\phi(x^\gamma)$	0.0017063	0.0019978	0.0010683	0.00083823
	$\epsilon_\phi(x^{c1})$	0.0025175	0.0030049	0.0015513	0.0010756
	$\epsilon_\phi(x^{c2})$	0.0014259	0.0016451	0.00090372	0.00076269
u	\mathcal{E}_ϕ	0.00041867	–	0.00033213	–
	$\epsilon_\phi(x^c)$	0.0013316	0.0015695	0.00081921	0.00062057
	$\epsilon_\phi(x^\gamma)$	0.00124	0.001452	0.00077388	0.00060722
	$\epsilon_\phi(x^{c1})$	0.0015926	0.001901	0.00096161	0.00066669
	$\epsilon_\phi(x^{c2})$	0.001093	0.001261	0.00069529	0.00058679
f	\mathcal{E}_ϕ	0.043422	–	0.033692	–
	$\epsilon_\phi(x^c)$	1.4194	1.4152	1.2845	1.2884
	$\epsilon_\phi(x^\gamma)$	0.3884	0.38805	0.37919	0.3795
	$\epsilon_\phi(x^{c1})$	0.40171	0.39739	0.30303	0.30621
	$\epsilon_\phi(x^{c2})$	0.13128	0.1311	0.13976	0.13952
g	\mathcal{E}_ϕ	0.08442	–	0.021892	–
	$\epsilon_\phi(x^c)$	28.236	28.152	48.786	48.935
	$\epsilon_\phi(x^\gamma)$	0.56258	0.56208	0.54645	0.5469
	$\epsilon_\phi(x^{c1})$	0.3187	0.31528	0.24447	0.24704
	$\epsilon_\phi(x^{c2})$	0.15021	0.15001	0.1583	0.15802

Table 5.6 Gibbs excesses relative error for the case of perturbing ζ^ℓ in percent

ϕ	Error	$\zeta^\ell = 1.02 \zeta_{\text{eq}}^\ell$		$\zeta^\ell = 0.98 \zeta_{\text{eq}}^\ell$	
		for $\{x^s\}$	for x^s	for $\{x^s\}$	for x^s
h	\mathcal{E}_ϕ	0.00035435	–	0.0011482	–
	$\epsilon_\phi(x^c)$	0.0023134	0.0028072	0.0042669	0.0042419
	$\epsilon_\phi(x^\gamma)$	0.0021873	0.0026065	0.0039043	0.0039484
	$\epsilon_\phi(x^{c1})$	0.0028054	0.0035457	0.0054811	0.0052479
	$\epsilon_\phi(x^{c2})$	0.0020102	0.0023063	0.0033597	0.0035215
u	\mathcal{E}_ϕ	0.00040969	–	0.0015073	–
	$\epsilon_\phi(x^c)$	0.0016206	0.0019665	0.0029893	0.0029717
	$\epsilon_\phi(x^\gamma)$	0.0015861	0.0018901	0.0028345	0.0028665
	$\epsilon_\phi(x^{c1})$	0.0017517	0.0022139	0.0034446	0.003298
	$\epsilon_\phi(x^{c2})$	0.0015408	0.0017677	0.0025842	0.0027086
f	\mathcal{E}_ϕ	0.0063873	–	0.0026805	–
	$\epsilon_\phi(x^c)$	0.17101	0.15419	0.033343	0.034999
	$\epsilon_\phi(x^\gamma)$	0.014471	0.015093	0.023261	0.022844
	$\epsilon_\phi(x^{c1})$	0.15718	0.13049	0.066572	0.055875
	$\epsilon_\phi(x^{c2})$	0.062407	0.065842	0.037405	0.042978
g	\mathcal{E}_ϕ	0.013595	–	0.0004864	–
	$\epsilon_\phi(x^c)$	5.3413	4.816	0.77321	0.8116
	$\epsilon_\phi(x^\gamma)$	0.021	0.021903	0.033471	0.032872
	$\epsilon_\phi(x^{c1})$	0.12645	0.10498	0.052965	0.044454
	$\epsilon_\phi(x^{c2})$	0.071253	0.075175	0.042467	0.048795

Table 5.7 Equilibrium table excesses relative error for the case of perturbing T^ℓ in percent

ϕ	Error	$T^\ell = 1.02 T_{\text{eq}}$		$T^\ell = 0.98 T_{\text{eq}}$	
		for $\{x^s\}$	for x^s	for $\{x^s\}$	for x^s
h	\mathcal{E}_ϕ	0.67514	–	0.21243	–
	$\epsilon_\phi(x^c)$	1.1052	1.1012	0.51202	0.50951
	$\epsilon_\phi(x^\gamma)$	0.0062189	0.0050111	0.074177	0.071345
	$\epsilon_\phi(x^{c1})$	8.5087	8.4753	6.4524	6.4581
	$\epsilon_\phi(x^{c2})$	3.9073	3.8963	6.1946	6.1882
u	\mathcal{E}_ϕ	0.32181	–	0.23381	–
	$\epsilon_\phi(x^c)$	0.77685	0.77406	0.35744	0.3558
	$\epsilon_\phi(x^\gamma)$	0.0043659	0.00366	0.053575	0.051756
	$\epsilon_\phi(x^{c1})$	5.2257	5.2046	4.1104	4.1143
	$\epsilon_\phi(x^{c2})$	3.0451	3.0361	4.692	4.6875
f	\mathcal{E}_ϕ	0.0046133	–	0.0035049	–
	$\epsilon_\phi(x^c)$	6.6737	6.67	8.0558	8.0599
	$\epsilon_\phi(x^\gamma)$	7.242	7.2428	0.37022	0.37236
	$\epsilon_\phi(x^{c1})$	15.74	15.7	25.631	25.642
	$\epsilon_\phi(x^{c2})$	13.328	13.306	20.092	20.077
g	\mathcal{E}_ϕ	0.0017615	–	0.001069	–
	$\epsilon_\phi(x^c)$	246.55	246.41	67.29	67.32
	$\epsilon_\phi(x^\gamma)$	9.9591	9.9604	0.52885	0.53228
	$\epsilon_\phi(x^{c1})$	13.038	13.006	19.627	19.635
	$\epsilon_\phi(x^{c2})$	14.84	14.817	23.49	23.472

Table 5.8 Equilibrium table excesses relative error for the case of perturbing p^s in percent

ϕ	Error	$p^s = 1.02 p_{\text{eq}}$		$p^s = 0.98 p_{\text{eq}}$	
		for $\{x^s\}$	for x^s	for $\{x^s\}$	for x^s
h	\mathcal{E}_ϕ	0.26501	–	1.3628	–
	$\epsilon_\phi(x^c)$	0.79783	0.80083	0.90685	0.90956
	$\epsilon_\phi(x^\gamma)$	1.4549	1.457	1.2481	1.2505
	$\epsilon_\phi(x^{c1})$	1.3056	1.2901	2.0582	2.0702
	$\epsilon_\phi(x^{c2})$	2.3955	2.3962	0.069749	0.072757
u	\mathcal{E}_ϕ	0.047434	–	0.20486	–
	$\epsilon_\phi(x^c)$	0.5599	0.56232	0.63362	0.63569
	$\epsilon_\phi(x^\gamma)$	1.0571	1.0589	0.90402	0.90589
	$\epsilon_\phi(x^{c1})$	0.82642	0.81614	1.2756	1.2832
	$\epsilon_\phi(x^{c2})$	1.836	1.8368	0.053565	0.055977
f	\mathcal{E}_ϕ	0.003912	–	0.0035128	–
	$\epsilon_\phi(x^c)$	1.218	1.2144	1.1886	1.1919
	$\epsilon_\phi(x^\gamma)$	4.7735	4.775	2.1767	2.1788
	$\epsilon_\phi(x^{c1})$	7.4201	7.3951	2.2105	2.2271
	$\epsilon_\phi(x^{c2})$	5.5423	5.5439	1.9531	1.9467
g	\mathcal{E}_ϕ	0.0013182	–	0.00041813	–
	$\epsilon_\phi(x^c)$	24.251	24.157	45.122	45.27
	$\epsilon_\phi(x^\gamma)$	6.9147	6.9164	3.1371	3.1398
	$\epsilon_\phi(x^{c1})$	5.8866	5.8671	1.7835	1.7967
	$\epsilon_\phi(x^{c2})$	6.3419	6.3437	2.212	2.2049

Table 5.9 Equilibrium table excesses relative error for the case of perturbing ζ^ℓ in percent

ϕ	Error	$\zeta^\ell = 1.02 \zeta_{\text{eq}}^\ell$		$\zeta^\ell = 0.98 \zeta_{\text{eq}}^\ell$	
		for $\{x^s\}$	for x^s	for $\{x^s\}$	for x^s
h	\mathcal{E}_ϕ	0.093953	–	0.20248	–
	$\epsilon_\phi(x^c)$	0.85205	0.86417	0.83511	0.8363
	$\epsilon_\phi(x^v)$	1.5557	1.5598	1.1532	1.1601
	$\epsilon_\phi(x^{c1})$	0.24334	0.33902	0.26902	0.23261
	$\epsilon_\phi(x^{c2})$	1.265	1.2405	1.2654	1.3065
u	\mathcal{E}_ϕ	0.068203	–	0.24097	–
	$\epsilon_\phi(x^c)$	0.59647	0.60537	0.585	0.58586
	$\epsilon_\phi(x^v)$	1.1278	1.1311	0.8372	0.84222
	$\epsilon_\phi(x^{c1})$	0.15127	0.21168	0.169	0.14618
	$\epsilon_\phi(x^{c2})$	0.96943	0.95081	0.97333	1.0049
f	\mathcal{E}_ϕ	0.0026249	–	0.0035651	–
	$\epsilon_\phi(x^c)$	0.095422	0.080499	0.18152	0.18276
	$\epsilon_\phi(x^v)$	4.6443	4.6454	2.382	2.3867
	$\epsilon_\phi(x^{c1})$	2.3591	2.2252	2.7907	2.8466
	$\epsilon_\phi(x^{c2})$	1.6382	1.5842	1.897	1.9858
g	\mathcal{E}_ϕ	0.00098739	–	0.0010871	–
	$\epsilon_\phi(x^c)$	3.025	2.5143	4.2062	4.237
	$\epsilon_\phi(x^v)$	6.7404	6.7414	3.4276	3.4343
	$\epsilon_\phi(x^{c1})$	1.8975	1.7901	2.2203	2.2648
	$\epsilon_\phi(x^{c2})$	1.8705	1.8088	2.1538	2.2546

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Chapter 6

From Continuous to Discontinuous Description

6.1 Introduction

In earlier chapters we developed the general approach for the square gradient description of an interface between two phases in non-equilibrium n -component mixtures. Using that approach it is possible to determine the continuous profiles of all variables through the interface during, for instance, evaporation and condensation. In this chapter we will use these results to obtain the transfer coefficients for heat and mass transfer through the liquid vapor interface. The values of these transfer coefficients, or even their order of magnitude, is extremely important for industrial processes which involve evaporation and/or condensation of mixtures. Among these processes is, for instance, distillation, when one needs to separate components with different volatilities. As this involves evaporation and/or condensation repeatedly many times, it is very important to know the exact effect of the surface. Some values of the interfacial transfer coefficients may favor transport of one component, while others may favor adsorption of a component at the surface. Of particular interest are the values of the cross coefficients, which contribute to irreversible transport, and which are in most descriptions neglected [1].

For the resistances in the relations expressing the differences of the temperature and chemical potentials across the surface we will use the word *transfer coefficients* as they describe the resistance to the transfer of heat and mass and across the surface.

A number of different methods have been used to obtain the surface transfer coefficients for one-component systems: experiments [2–5], molecular dynamic simulations [6–10], kinetic theory [11–13]. In a paper [14] the interfacial transfer coefficients obtained from the square gradient theory for a one-component system were calculated and compared to the data in the above references. Even for one-component systems the database of interfacial transfer coefficients is poor and these data are pretty scattered. The situation is even worse for mixtures. There are only few experiments available for several systems [2, 4] in very restricted ranges of conditions, i.e. for instance, at infinite dilution. No molecular dynamic

simulations are available yet. The only source of the values of interfacial coefficients is kinetic theory [12, 13]. This theory is most appropriate for short range potentials and low density gases. There is evidence from molecular dynamic simulations for longer range potentials [10] that the coupling transfer resistances for liquid–vapor interfaces of real fluids are substantially larger than those predicted by kinetic theory.

In the previous chapters we discussed the balance equations and the Gibbs relation for the square gradient model of mixtures. The Gibbs relation enabled us to derive the entropy production. It followed that if one uses as thermodynamic forces the gradient of the inverse temperature, $\nabla(1/T)$, – the gradients of the chemical potential differences divided by the temperature, $-\nabla[(\mu_i - \mu_n)/T]$, for $i = \overline{1, n-1}$, and – the gradient of the velocity divided by the temperature, $-(\nabla\mathbf{v})/T$, then the conjugate fluxes are the heat flux, \mathbf{J}_q , the diffusion fluxes of the first $n-1$ components relative to the barycentric frame of reference, \mathbf{J}_i , and the viscous pressure tensor. Linear laws relating these forces and fluxes were given. Together with the balance equations it was then possible to calculate the profiles of all the variables.

Given the validity of local equilibrium for the description in terms of the Gibbs excess densities, it is possible to develop a description using non-equilibrium thermodynamics as explained in the monograph by Kjelstrup and Bedeaux [1]. This is much easier than the continuous description. As we will verify in this chapter the expression for the excess entropy production of a surface has the general form

$$\hat{\sigma}_s = \sum_i J_i X_i \quad (6.1)$$

In this expression J_i are the heat and mass fluxes through the surface and X_i are the jumps in the intensive variables across the interface. In non-equilibrium, one uses the finite jumps of the temperature and chemical potentials across the surface, which leads to a non-zero entropy productions in the interfacial region. These jumps become the driving forces for the heat and mass transport through the interface. Following the traditional approach of non-equilibrium thermodynamics we then write the linear force–flux relations. These expressions use the interfacial resistances or transfer coefficients which are the key interest of the rest of the thesis.

Having the continuous profiles of thermodynamic quantities obtained from the non-equilibrium gradient model we are able to calculate these resistances independently. This gives a way to determine the coefficients and therefore a possible source for comparison for future experiments and simulations.

In this chapter we establish the general link between the continuous analysis described in the previous chapters and the discontinuous approach given in [1]. The analysis is done for stationary states, when all the quantities have no explicit dependence on time. In the next two chapters we focus on the methods to obtain the interfacial resistances. There we also apply them to the binary mixture of cyclohexane and n -hexane.

In Sect. 6.2 we derive the expression for the local entropy production for stationary states in the continuous description. In Sect. 6.3 we discuss the properties of the excess quantities in three-dimensional space. We consider how the stationary state condition simplifies the non-equilibrium description. In Sect. 6.4 we obtain the expression for the excess entropy production in an interfacial region. In Sect. 6.5 we give the force–flux relations and discuss the interfacial resistance coefficients. We consider different sets of coefficients which are associated with different variables: gas- and liquid-side coefficients, as well as mass and molar coefficients. Any coefficient of one set is determined by the coefficients of the other set and equilibrium properties of pure bulk components. These sets are therefore equivalent.

6.2 Local Entropy Production

6.2.1 Gibbs–Duhem Equation

Consider a two phase n -component mixture. Let T be the temperature field in this region, $\psi_i \equiv \mu_i - \mu_n$ be the chemical potential differences and p be the scalar pressure, which in case of a planar interface coincides with the parallel pressure p_{\parallel} . Furthermore, let u, s, v be the mass specific internal energy, entropy and volume respectively, $\rho \equiv 1/v$ be the overall mass density and $\zeta_i \equiv \rho_i/\rho$ be the mass fraction of the i th component. It was found that the Gibbs equation for such a two phase system is given by:

$$T(\mathbf{r}, t) \frac{ds}{dt} = \frac{du}{dt} - \sum_{i=1}^{n-1} \psi_i(\mathbf{r}, t) \frac{d\zeta_i}{dt} + p(\mathbf{r}, t) \frac{dv}{dt} - v \nabla_{\beta} \frac{\partial \gamma_{\alpha\beta}}{\partial x_{\alpha}} \quad (6.2)$$

where \mathbf{v} is the barycentric velocity, d/dt a substantial time derivative and we use the summation convention over double Greek indices. $\gamma_{\alpha\beta}$ the tension tensor, which is given by

$$\gamma_{\alpha\beta} = \kappa \frac{\partial \rho}{\partial x_{\alpha}} \frac{\partial \rho}{\partial x_{\beta}} + \sum_{i=1}^{n-1} \kappa_i \left(\frac{\partial \zeta_i}{\partial x_{\alpha}} \frac{\partial \rho}{\partial x_{\beta}} + \frac{\partial \rho}{\partial x_{\alpha}} \frac{\partial \zeta_i}{\partial x_{\beta}} \right) + \sum_{i,j=1}^{n-1} \kappa_{ij} \frac{\partial \zeta_i}{\partial x_{\alpha}} \frac{\partial \zeta_j}{\partial x_{\beta}} \quad (6.3)$$

It is non-zero in particular in the interfacial region, where the gradient variables $\nabla \rho$ and $\nabla \zeta_i$ are significant. All thermodynamic densities (except the entropy) have gradient contributions. For explicit expressions we refer to Chap. 2. These densities are related by the ordinary relation

$$u = \mu_n + \sum_{i=1}^{n-1} \psi_i \zeta_i - p v + T s \quad (6.4)$$

Substituting Eq. 6.4 into Eq. 6.2 we obtain

$$s \frac{dT}{dt} + \frac{d\mu_n}{dt} + \sum_{i=1}^{n-1} \zeta_i \frac{d\psi_i}{dt} - v \frac{dp}{dt} - v v_\beta \frac{\partial \gamma_{\alpha\beta}}{\partial x_\alpha} = 0 \quad (6.5)$$

This is the Gibbs–Duhem equation for a two-phase multi-component mixture.

For a stationary state the derivative $\partial/\partial t = 0$ and Eq. 6.5 takes the following form

$$\rho v_\beta \left(s \frac{\partial T}{\partial x_\beta} + \frac{\partial \mu_n}{\partial x_\beta} + \sum_{i=1}^{n-1} \zeta_i \frac{\partial \psi_i}{\partial x_\beta} - v \frac{\partial \sigma_{\alpha\beta}}{\partial x_\alpha} \right) = 0 \quad (6.6)$$

where $\sigma_{\alpha\beta} = p \delta_{\alpha\beta} + \gamma_{\alpha\beta}$ is the thermodynamic pressure tensor. Note that since $\psi_i \equiv \mu_i - \mu_n$, we have

$$\frac{\partial \mu_n}{\partial x_\beta} + \sum_{i=1}^{n-1} \zeta_i \frac{\partial \psi_i}{\partial x_\beta} = \sum_{i=1}^n \zeta_i \frac{\partial \mu_i}{\partial x_\beta} \quad (6.7)$$

which is the usual contribution to the Gibbs–Duhem equation associated with the chemical potentials.

6.2.2 Entropy Balance

The entropy balance equation is

$$\rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_s \quad (6.8)$$

with the entropy flux $\mathbf{J}_s \equiv \mathbf{J}_{s,\text{tot}} - \rho s \mathbf{v}$ and the entropy production σ_s . These were found to be

$$\mathbf{J}_s = \frac{1}{T} \left(\mathbf{J}_q - \sum_{i=1}^{n-1} \psi_i \mathbf{J}_i \right) \quad (6.9a)$$

$$\sigma_s = \mathbf{J}_q \cdot \nabla \frac{1}{T} - \sum_{i=1}^{n-1} \mathbf{J}_i \cdot \nabla \frac{\psi_i}{T} - \pi_{\alpha\beta} \frac{1}{T} \frac{\partial v_\alpha}{\partial x_\beta} \quad (6.9b)$$

where \mathbf{J}_q and \mathbf{J}_i are the heat and diffusion fluxes

$$\begin{aligned} \mathbf{J}_q &\equiv \mathbf{J}_e - \rho \mathbf{v} e - p \mathbf{v} - \pi \cdot \mathbf{v} = \mathbf{J}_e - \mathbf{J}_m (e + p v) - \Pi \cdot \mathbf{v} \\ \mathbf{J}_i &\equiv \rho_i (\mathbf{v}_i - \mathbf{v}) = \mathbf{J}_{\zeta_i} - \zeta_i \mathbf{J}_m \end{aligned} \quad (6.10)$$

where $\Pi \equiv \pi_{\alpha\beta}$ is the viscous pressure tensor. The energy flux \mathbf{J}_e and the mass fluxes $\mathbf{J}_{\xi_i} \equiv \rho_i \mathbf{v}_i$ and $\mathbf{J}_m \equiv \rho \mathbf{v}$ are convenient quantities, since in stationary states

$$\nabla \cdot \mathbf{J}_e = 0, \quad \nabla \cdot \mathbf{J}_{\xi_i} = 0, \quad \nabla \cdot \mathbf{J}_m = 0 \quad (6.11)$$

Furthermore, it follows from Eq. 6.8 that in stationary states

$$\sigma_s = \nabla \cdot \mathbf{J}_s + \rho \mathbf{v} \cdot \nabla s = \nabla \cdot \mathbf{J}_{s,\text{tot}} \quad (6.12)$$

Using (6.6) and the conservation laws under stationary conditions, it is possible to show that

$$\sigma_s = \mathbf{J}_e \cdot \nabla \frac{1}{T} - \sum_{i=1}^n \mathbf{J}_{\xi_i} \cdot \nabla \frac{\mu_i}{T} - \mathbf{J}_m \cdot \nabla \frac{v^2/2 - \mathbf{g} \cdot \mathbf{r}}{T} - \frac{\partial}{\partial x_\alpha} \frac{\pi_{\alpha\beta} v_\beta}{T} \quad (6.13)$$

The expression for the entropy production, used in Eq. 6.13 contains dependent fluxes \mathbf{J}_{ξ_i} and \mathbf{J}_m and thus force–flux relations cannot be obtained from it directly.

6.3 Excesses in Three-Dimensional Space

6.3.1 Definition of an Excess

The definition of an excess requires the normal direction \mathbf{n} to be defined in the interfacial region. The surface may be curved and we may introduce curvilinear orthogonal coordinates (x_1, x_2, x_3) with $\mathbf{r}_\perp \equiv x_1$ being the normal coordinate and $\mathbf{r}_\parallel \equiv (x_2, x_3)$ being the tangential coordinates.

Let $x^{g,s}$ and $x^{\ell,s}$ be the boundaries of the interfacial region¹ at the gas and liquid side, respectively. Let ϕ be a function defined in the surface region. Furthermore, let ϕ^b , where superscript b stands either for ℓ or for g , be the function ϕ extrapolated from the bulk to the surface region. The extrapolation is done using the description in homogeneous phases which does not contain gradient contributions. Outside of the interfacial region ϕ^b and ϕ are identical but inside the surface, ϕ^b in general differs from ϕ . We note the following identity for the extrapolated functions

$$\phi^b(x^{b,s}, \mathbf{r}_\parallel) = \phi(x^{b,s}, \mathbf{r}_\parallel) \quad (6.14)$$

Furthermore, for any function Φ the following relation is true by definition

$$\Phi^b(\dots, \phi, \dots) = \Phi(\dots, \phi^b, \dots) \quad (6.15)$$

¹ The exact location of these boundaries depends on particular method we use to distinguish the bulk region from the interfacial region. In Chap. 4 we discussed this issue. Here we only need to know that these boundaries exist and satisfy Eq. 6.14.

in the interfacial region. We note however, that even though Eqs. 6.14 and 6.15 are exact, any numerical procedure will break these equalities. This happens because the extrapolation procedure usually involves polynomials in order to fit an actual curve, which introduces a non-zero error in the extrapolated curve.

We then can define the excess $\widehat{\phi}(x^s, \mathbf{r}_{\parallel})$ of a density $\phi(\mathbf{r})$ per unit of volume in the three-dimensional space as² [15]

$$\widehat{\phi}(x^s, \mathbf{r}_{\parallel}) \equiv \frac{1}{h_2^s h_3^s} \int_{x^{g,s}}^{x^{\ell,s}} dx_1 h_1 h_2 h_3 \phi^{\text{ex}}(\mathbf{r}; x^s) \quad (6.16)$$

where

$$\phi^{\text{ex}}(\mathbf{r}; x^s) \equiv \phi(\mathbf{r}) - \phi^g(\mathbf{r}) \Theta(x^s - x_1) - \phi^{\ell}(\mathbf{r}) \Theta(x_1 - x^s) \quad (6.17)$$

Furthermore, $h_i \equiv h_i(x_1, \mathbf{r}_{\parallel})$ are Lamé coefficients for curvilinear coordinates and $h_i^s \equiv h_i(x^s, \mathbf{r}_{\parallel})$. Given that $\phi(\mathbf{r})$ is a density per unit of volume, excess $\widehat{\phi}(x^s, \mathbf{r}_{\parallel})$ is a density per unit of surface area. The excess depends on the position of the dividing surface x^s , which is the coordinate of the surface in the normal direction, and the position \mathbf{r}_{\parallel} along the surface.

6.3.2 Stationary State of a Surface

Consider the entropy production given in Eq. 6.13. All the terms except the last one have the form $\mathbf{J} \cdot \nabla \phi$, where according to Eq. 6.11 $\nabla \cdot \mathbf{J} = 0$ and ϕ is some scalar function. Thus, $\mathbf{J} \cdot \nabla \phi = \nabla \cdot (\mathbf{J} \phi)$. We show in Appendix 6.B that

$$\widehat{\mathbf{J} \cdot \nabla \phi} = (J_{\perp} \phi)^{\ell} - (J_{\perp} \phi)^g + \widehat{\nabla_{\parallel} \cdot (\mathbf{J}_{\parallel} \phi)} \quad (6.18)$$

where all the functions on the right hand side are evaluated at \mathbf{r}^s .

For each flux in Eq. 6.11 we can write $\nabla_{\perp} J_{\perp} + \nabla_{\parallel} \cdot \mathbf{J}_{\parallel} = 0$. This gives an approximate relation for the order of magnitude

$$\frac{|\Delta_{\perp} J_{\perp}|}{\Delta x_{\perp}} \simeq \frac{|\Delta_{\parallel} J_{\parallel}|}{\Delta x_{\parallel}} \quad (6.19)$$

As was discussed in Chap. 3, the interfacial region breaks the three-dimensional isotropy of the system. In addition to a typical macroscopic size of the problem ℓ , there exists the microscopic size δ , the surface width, which is of the order of few nanometers. There are quantities which change drastically on the distances of the

² In the literature one also uses an alternative definition, which however has a meaning only for non-highly curved surfaces, see Appendix 6.A.

order δ in the direction perpendicular to the surface. However, the significant change of any quantity along the surface may happen only on a length scale ℓ , which is of the order of either radii of surface curvature or the system size. Because of this property of a surface, we may not expect the change of the parallel component of a flux on a macroscopic scale along the surface to be much larger than the change of the perpendicular component of that flux on a microscopic scale through the surface. For the fluxes for which changes $|\Delta_{\perp} J_{\perp}|$ and $|\Delta_{\parallel} J_{\parallel}|$ are of the same order of magnitude, Eq. 6.19 takes the form $\Delta J/\delta \approx \Delta J/\ell$, which can hold only if $\Delta J = 0$, since $\delta \ll \ell$. This means that both $\Delta_{\perp} J_{\perp} = 0$ and $\Delta_{\parallel} J_{\parallel} = 0$. If $|\Delta_{\perp} J_{\perp}| \gg |\Delta_{\parallel} J_{\parallel}|$ this statement becomes even stronger. We then may require that for a thin surface³

$$\nabla_{\perp} J_{\perp}(\mathbf{r}) = 0 \quad (6.20a)$$

$$\nabla_{\parallel} \cdot \mathbf{J}_{\parallel}(\mathbf{r}) = 0 \quad (6.20b)$$

Thus, a stationary state condition $\nabla \cdot \mathbf{J} = 0$ has a form of Eq. 6.20 in an interfacial region. The extrapolated fluxes \mathbf{J}^b satisfy the same equation

$$\nabla_{\perp} J_{\perp}^b(\mathbf{r}) = 0 \quad (6.21a)$$

$$\nabla_{\parallel} \cdot \mathbf{J}_{\parallel}^b(\mathbf{r}) = 0 \quad (6.21b)$$

since the extrapolated flux fields also satisfy $\nabla \cdot \mathbf{J}^b = 0$.

Both Eqs. 6.20a and 6.21a are first order ordinary differential equations which depend on a constant. These constants must be the same, since according to Eq. 6.14 $J_{\perp}^b(\mathbf{r}^{b,s}) = J_{\perp}(\mathbf{r}^{b,s})$ at boundary points. It means that J_{\perp}^b and J_{\perp} are the same functions⁴:

$$J_{\perp}^g(\mathbf{r}) = J_{\perp}^{\ell}(\mathbf{r}) = J_{\perp}(\mathbf{r}) \quad (6.22)$$

Consider the last term in Eq. 6.18. Since parallel divergences of both \mathbf{J}_{\parallel} and \mathbf{J}_{\parallel}^b are zero,

$$\widehat{\nabla_{\parallel} \cdot (\mathbf{J}_{\parallel} \phi)} = \widehat{\mathbf{J}_{\parallel} \cdot \nabla_{\parallel} \phi} \quad (6.23)$$

where we used that $\nabla_{\parallel} \Theta(x_1) = 0$ (cf. Appendix 6.B).

³ For the special case of a system with planar surface in cartesian coordinates with all the fluxes directed perpendicular to the surface, which is the case studied in this chapter, these equations follow straightforwardly.

⁴ Note that Eq. 6.22 does not lead to the relation $J_{\perp}(x^{g,s}, \mathbf{r}_{\parallel}) = J_{\perp}(x^{\ell,s}, \mathbf{r}_{\parallel})$. Equation 6.22 is the relation between values of different functions at the same point but not the relation between values of the same function at different points. However, it follows from Eq. 6.20a that in curvilinear coordinates $\partial(\mathfrak{h}_2 \mathfrak{h}_3 J_{\perp})/(\partial x_{\perp}) = 0$ and therefore $\mathfrak{h}_2 \mathfrak{h}_3 J_{\perp} = \text{const}$ but not $J_{\perp} = \text{const}$.

Substituting Eqs. 6.22 and 6.23 into Eq. 6.18 we obtain

$$\widehat{\mathbf{J} \cdot \nabla \phi} = J_{\perp}(\phi^{\ell} - \phi^g) + \widehat{\mathbf{J}_{\parallel} \cdot \nabla_{\parallel} \phi} \quad (6.24)$$

where all the functions on the right hand side are evaluated at \mathbf{r}^s .

6.4 Excess Entropy Production

Applying Eq. 6.24 to each term in Eq. 6.13 for the entropy production we obtain the general form of the excess entropy production for a surface in stationary state

$$\begin{aligned} \widehat{\sigma}_s &= J_{s,\text{tot}\perp}^{\ell} - J_{s,\text{tot}\perp}^g + \nabla_{\parallel} \cdot \widehat{\mathbf{J}}_{s,\text{tot}\parallel} \\ &= J_{e,\perp} \left(\frac{1}{T^{\ell}} - \frac{1}{T^g} \right) - \sum_{i=1}^n J_{\xi_i,\perp} \left(\frac{\tilde{\mu}_i^{\ell}}{T^{\ell}} - \frac{\tilde{\mu}_i^g}{T^g} \right) - \left(\frac{\pi_{\perp\beta}^{\ell} v_{\beta}^{\ell}}{T^{\ell}} - \frac{\pi_{\perp\beta}^g v_{\beta}^g}{T^g} \right) \\ &\quad + \left(\widehat{\mathbf{J}_{e,\parallel} \cdot \nabla_{\parallel} \frac{1}{T}} \right) - \sum_{i=1}^n \left(\widehat{\mathbf{J}_{\xi_i,\parallel} \cdot \nabla_{\parallel} \frac{\tilde{\mu}_i}{T}} \right) - \left(\nabla_{\parallel} \cdot \widehat{\frac{\pi_{\parallel\beta} v_{\beta}}{T}} \right) \end{aligned} \quad (6.25)$$

where $\tilde{\mu}_i \equiv \mu_i + v^2/2 - \mathbf{g} \cdot \mathbf{r}^s$.

The next step of the analysis is to provide constitutive relations in order to relate thermodynamic forces X_k to thermodynamic fluxes J_k for the whole surface. This requires that the excess entropy production has a form $\widehat{\sigma}_s = \sum J_k X_k$. However, as one can see from Eq. 6.25, the terms related to fluxes along the surface do not have this form. One has to make further assumptions on the nature of these terms to write them in this form. As our work is focused on transport into and through the surface we will not consider non-equilibrium perturbations which are applied along the surface. This guarantees that all the terms along the surface are equal to zero. The only nonzero component of any flux \mathbf{J} is therefore J_{\perp} , which we will denote simply as J . We will furthermore restrict ourself to non-viscous fluids. The expression for the excess entropy production simplifies to the following

$$\widehat{\sigma}_s = J_e \left(\frac{1}{T^{\ell}} - \frac{1}{T^g} \right) - \sum_{i=1}^n J_{\xi_i} \left(\frac{\tilde{\mu}_i^{\ell}}{T^{\ell}} - \frac{\tilde{\mu}_i^g}{T^g} \right) \quad (6.26)$$

It is convenient to write the excess entropy production in terms of the measurable heat flux \mathbf{J}'_q of either bulk phase, which is defined as

$$\mathbf{J}'_q{}^{a,b} \equiv \mathbf{J}_q^b - \sum_{i=1}^n h_i^b \mathbf{J}_i^b = \mathbf{J}_e - \sum_{i=1}^n \tilde{h}_i^b \mathbf{J}_{\xi_i} \quad (6.27)$$

where we used Eq. 6.10 and $\tilde{h}_i \equiv h_i + v^2/2 - \mathbf{g} \cdot \mathbf{r}^s = \tilde{\mu}_i + Ts_i$, where s_i is the partial entropy and h_i is the partial enthalpy. While Eq. 6.22 is valid for \mathbf{J}_e and \mathbf{J}_{ξ_i} it is not valid for \mathbf{J}'_q : the difference between the measurable heat fluxes on the gas and the liquid side is

$$J'^{',g}_q - J'^{',\ell}_q = \sum_{i=1}^n J_{\xi_i} (\tilde{h}_i^{\ell} - \tilde{h}_i^g) \quad (6.28)$$

Note, that in non-equilibrium $\tilde{h}_i^{\ell} - \tilde{h}_i^g$ is not equal to $h_i^{\ell} - h_i^g$ since the velocities of the gas and liquid are substantially different. In practice, however, the magnitude of either velocity is small, so the corresponding kinetic energy term does not affect much the value of the enthalpy. Moreover, as we will see below, one should use equilibrium values of the corresponding enthalpies, which makes the expression with tilde to be identical to the expression without tilde.

In terms of measurable heat fluxes, the expression for the entropy production becomes

$$\hat{\sigma}_s = J'^{',g}_q \left(\frac{1}{T^{\ell}} - \frac{1}{T^g} \right) - \sum_{i=1}^n J_{\xi_i} \frac{1}{T^{\ell}} (\tilde{\mu}_i^{\ell} - \tilde{\mu}_i^g + s_i^g (T^{\ell} - T^g)) \quad (6.29a)$$

$$\hat{\sigma}_s = J'^{',\ell}_q \left(\frac{1}{T^{\ell}} - \frac{1}{T^g} \right) - \sum_{i=1}^n J_{\xi_i} \frac{1}{T^g} (\tilde{\mu}_i^{\ell} - \tilde{\mu}_i^g + s_i^{\ell} (T^{\ell} - T^g)) \quad (6.29b)$$

It is important to realize that Eq. 6.29 are exactly equivalent to Eq. 6.26. It is common to do these transformations neglecting third and higher order contributions in the deviation from equilibrium. Such approximations were not needed here.

Equation 6.29 has the form of the entropy production for the surface used in [1]. It was obtained there using the local equilibrium hypothesis, which we have proven to be valid in Chap. 5. Here we have derived Eq. 6.29 independently, by calculating the excess of the continuous entropy production in the square gradient model.

6.5 Surface Transfer Coefficients

Consider Eq. 6.29 for the excess entropy production which has the form

$$\hat{\sigma}_s = J'_q X_q + \sum_{i=1}^n J_{\xi_i} X_i \quad (6.30)$$

We will use the form (6.30) further, specifying the explicit expressions for fluxes and forces where needed. Following the common procedure, we write the linear force–flux relations for a given entropy production:

$$\begin{aligned}
 X_q &= R_{qq}(T_{\text{eq}}, \psi_{\text{eq}}) J'_q + \sum_{i=1}^n R_{qi}(T_{\text{eq}}, \psi_{\text{eq}}) J_{\xi_i} \\
 X_j &= R_{jq}(T_{\text{eq}}, \psi_{\text{eq}}) J'_q + \sum_{i=1}^n R_{ji}(T_{\text{eq}}, \psi_{\text{eq}}) J_{\xi_i}
 \end{aligned}
 \tag{6.31}$$

As these relations are true only to the linear order in perturbations, we must keep only linear contributions in all terms. It means that all the resistances in Eq. 6.31 are functions of only equilibrium temperature T_{eq} and equilibrium chemical potential difference ψ_{eq} around which a particular perturbation is performed. They do not depend on the nature of the perturbation.

Consider the following matrix notation of the above quantities

$$\mathbf{X} \equiv \begin{pmatrix} X_q \\ X_1 \\ \vdots \\ X_n \end{pmatrix}, \quad \mathbf{R} \equiv \begin{pmatrix} R_{qq} & R_{q1} & \dots & R_{qn} \\ R_{1q} & R_{11} & \dots & R_{1n} \\ \vdots & \vdots & \ddots & \vdots \\ R_{nq} & R_{n1} & \dots & R_{nn} \end{pmatrix}, \quad \mathbf{J} \equiv \begin{pmatrix} J'_q \\ J_{\xi_1} \\ \vdots \\ J_{\xi_n} \end{pmatrix}
 \tag{6.32}$$

Let β indicate a measure of a non-equilibrium perturbation,⁵ so that $\mathbf{X} = \mathbf{X}(\beta)$ and $\mathbf{J} = \mathbf{J}(\beta)$. Then Eq. 6.31 can be written in a matrix form as

$$\mathbf{X}(\beta) = \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \cdot \mathbf{J}(\beta)
 \tag{6.33}$$

For large values of β , Eq. 6.33 is not correct, since large perturbations are not described by the linear theory. As we decrease β , the accuracy of Eq. 6.33 increases and in the limit $\beta \rightarrow 0$ becomes exact. It means that Eq. 6.33 should be understood as

$$\lim_{\beta \rightarrow 0} \mathbf{X}(\beta) = \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \cdot \lim_{\beta \rightarrow 0} \mathbf{J}(\beta)
 \tag{6.34}$$

One should not write Eq. 6.34 in the form $\mathbf{X}(0) = \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \cdot \mathbf{J}(0)$ however, as both $\mathbf{X}(0)$ and $\mathbf{J}(0)$ contain only zeroes and such an expression makes no sense. Even though $\mathbf{X}(\beta)$ and $\mathbf{J}(\beta)$ are continuous functions of β , one should write $\lim_{\beta \rightarrow 0} \mathbf{X}(\beta)$ and $\lim_{\beta \rightarrow 0} \mathbf{J}(\beta)$ instead of $\mathbf{X}(0)$ and $\mathbf{J}(0)$ respectively. In practice there exists a particular measure β_{eq} of a perturbation, such that for all $\beta < \beta_{\text{eq}}$ Eq. 6.33 is satisfied with a satisfactory accuracy.

One should also note that the accuracy of a particular numerical procedure may limit the validity of Eq. 6.34 as well. All the non-equilibrium profiles and therefore forces and fluxes are calculated by solving the system of differential equations numerically with some particular accuracy. If a perturbation rate is lower then

⁵ Note, that a non-equilibrium state can be achieved by perturbing several independent quantities simultaneously. In this case we have several perturbation parameters β_1, \dots, β_p . A measure β is a norm of this p -dimensional vector of perturbations. The exact expression for this norm is irrelevant, as soon as it goes to zero if and only if all β_1, \dots, β_p go to zero.

this accuracy, say β_{num} , the data obtained from the numerical procedure are not reliable. Performing a numerical analysis we must therefore replace the limiting value 0 by β_{num} in Eq. 6.33.

As shown by Onsager [16], the cross coefficients must be the same. We therefore have

$$\begin{aligned} R_{qi} &= R_{iq} \\ R_{ji} &= R_{ij} \end{aligned} \quad (6.35)$$

6.5.1 Gas- and Liquid-Side Transport Coefficients

For each of Eq. 6.29 one might associate the forces with

$$\begin{aligned} X_q^g &= X_q^\ell \equiv \frac{1}{T^\ell} - \frac{1}{T^g} \\ X_j^g &\equiv -\frac{1}{T^\ell} \left(\tilde{\mu}_j^\ell - \tilde{\mu}_j^g + s_j^g (T^\ell - T^g) \right) \\ X_j^\ell &\equiv -\frac{1}{T^g} \left(\tilde{\mu}_j^\ell - \tilde{\mu}_j^g + s_j^\ell (T^\ell - T^g) \right) \end{aligned} \quad (6.36)$$

As we are in the context of the linear theory, however, we must linearize these forces with respect to the perturbation and discard all higher order terms. Leaving them would not increase accuracy but may affect the consistency of the linear theory. We therefore get the following phenomenological relations up to the linear order⁶

$$\begin{aligned} \frac{1}{T^\ell} - \frac{1}{T^g} &= R_{qq}^g J_q'^{g} + \sum_{i=1}^n R_{qi}^g J_{\xi_i} \\ -\frac{1}{T_{\text{eq}}} \left(\tilde{\mu}_j^\ell - \tilde{\mu}_j^g + s_{j,\text{eq}}^g (T^\ell - T^g) \right) &= R_{jq}^g J_q'^{g} + \sum_{i=1}^n R_{ji}^g J_{\xi_i} \end{aligned} \quad (6.37)$$

⁶ Given a small perturbation around equilibrium values, we can write $T^b = T_{\text{eq}} + \delta T^b$, $\mu^b = \mu_{\text{eq}} + \delta \mu^b$, and $s^b = s_{\text{eq}} + \delta s^b$ up to the first order. Thus, $1/T^\ell - 1/T^g = (\delta T^g - \delta T^\ell)/T_{\text{eq}}^2$ is linear in perturbations and we may keep this term as it is. Furthermore,

$$\frac{1}{T^\ell} \left[\tilde{\mu}_j^\ell - \tilde{\mu}_j^g + s_j^g (T^\ell - T^g) \right] = \left\{ \frac{1}{T_{\text{eq}}} - \frac{\delta T^\ell}{T_{\text{eq}}^2} \right\} \left[\delta \tilde{\mu}_j^\ell - \delta \tilde{\mu}_j^g + (s_{j,\text{eq}}^g + \delta s_j^g) (\delta T^\ell - \delta T^g) \right]$$

The term $\delta T^\ell/T_{\text{eq}}^2$ is already linear in perturbations, so multiplying it with the expression in parenthesis, which has also no zero order term, we get an expression which is at least quadratic in perturbations and should therefore be neglected. Similarly the term $\delta s_j^g (\delta T^\ell - \delta T^g)$ should also be neglected. The remaining expression is exactly the one, which is used in Eq. 6.37. Analogously we get Eq. 6.38.

and

$$\begin{aligned} \frac{1}{T^\ell} - \frac{1}{T^g} &= R_{qq}^\ell J_q'^{\ell} + \sum_{i=1}^n R_{qi}^\ell J_{\xi_i} \\ -\frac{1}{T_{\text{eq}}} \left(\tilde{\mu}_j^\ell - \tilde{\mu}_j^g + s_{j,\text{eq}}^\ell (T^\ell - T^g) \right) &= R_{jq}^\ell J_q'^{\ell} + \sum_{i=1}^n R_{ji}^\ell J_{\xi_i} \end{aligned} \quad (6.38)$$

Here and after we omit arguments $(T_{\text{eq}}, \psi_{\text{eq}})$ as long as it does not lead to confusion.

The measurable heat fluxes are related by Eq. 6.28 which after linearization takes the following form

$$J_q'^{g} - J_q'^{\ell} = \sum_{i=1}^n J_{\xi_i} \left(\tilde{h}_{i,\text{eq}}^\ell - \tilde{h}_{i,\text{eq}}^g \right) \quad (6.39)$$

Comparing Eqs. 6.37 and 6.38 and using Eq. 6.39 we get the following relations between the coefficients associated with the gas and liquid measurable heat fluxes to linear order

$$\begin{aligned} R_{qq}^\ell &= R_{qq}^g \\ R_{qi}^\ell - h_{i,\text{eq}}^\ell R_{qq}^\ell &= R_{qi}^g - h_{i,\text{eq}}^g R_{qq}^g \\ R_{iq}^\ell - h_{i,\text{eq}}^\ell R_{qq}^\ell &= R_{iq}^g - h_{i,\text{eq}}^g R_{qq}^g \\ R_{ji}^\ell - h_{i,\text{eq}}^\ell R_{jq}^\ell - h_{j,\text{eq}}^\ell R_{qi}^\ell + h_{i,\text{eq}}^\ell h_{j,\text{eq}}^\ell R_{qq}^\ell &= R_{ji}^g - h_{i,\text{eq}}^g R_{jq}^g - h_{j,\text{eq}}^g R_{qi}^g + h_{i,\text{eq}}^g h_{j,\text{eq}}^g R_{qq}^g \end{aligned} \quad (6.40)$$

where we took into account that $\tilde{\mu}_{i,\text{eq}}^g = \tilde{\mu}_{i,\text{eq}}^\ell$ and $\tilde{h}_{i,\text{eq}}^g - \tilde{h}_{i,\text{eq}}^\ell = h_{i,\text{eq}}^g - h_{i,\text{eq}}^\ell$.

The coefficients on the one side determine uniquely the coefficients on the other side, having the values of jumps across the surface of the extrapolated enthalpies. It follows from Eq. 6.40 that

$$\begin{aligned} R_{qq}^\ell &= R_{qq}^g \\ R_{qi}^\ell &= R_{qi}^g - (h_{i,\text{eq}}^g - h_{i,\text{eq}}^\ell) R_{qq}^g \\ R_{iq}^\ell &= R_{iq}^g - (h_{i,\text{eq}}^g - h_{i,\text{eq}}^\ell) R_{qq}^g \\ R_{ji}^\ell &= R_{ji}^g - (h_{i,\text{eq}}^g - h_{i,\text{eq}}^\ell) R_{jq}^g - (h_{j,\text{eq}}^g - h_{j,\text{eq}}^\ell) R_{iq}^g + (h_{i,\text{eq}}^g - h_{i,\text{eq}}^\ell)(h_{j,\text{eq}}^g - h_{j,\text{eq}}^\ell) R_{qq}^g \end{aligned} \quad (6.41)$$

One can notice, that symmetry of R^g coefficients implies the same symmetry of R^ℓ coefficients and vice versa.

To avoid confusion we recall that for the temperature T , chemical potential μ_j and the partial entropy s_j the superscript g or ℓ means the value of the corresponding function extrapolated from either gas or liquid to the interfacial region and evaluated at a particular dividing surface x^s . We do not indicate which dividing surface

is used, as it is irrelevant for the present analysis. In contrast, $J'_q{}^g \equiv J_e - \sum_{i=1}^n \tilde{h}_i(x^{g,s}) J_{\xi_i}$ where the partial enthalpy is evaluated at the gas-surface boundary $x^{g,s}$. To the linear order however $\tilde{h}_i(x^{g,s}) = \tilde{h}_{i,\text{eq}}(x^{g,s}) = \tilde{h}_{i,\text{eq}}^g(x^s) \equiv \tilde{h}_{i,\text{eq}}^g$. For planar interface, J_e and J_{ξ_i} are constants, and $J'_q{}^g$ may be considered as the flux, evaluated at a dividing surface x^s . Furthermore, superscript g or ℓ for the resistance R^g or R^ℓ neither indicates any position nor the extrapolated resistance coefficient. It indicates the measurable heat flux which the given resistance coefficient is associated with, either $J'_q{}^g$ or $J'_q{}^\ell$ respectively.

6.5.2 Mass and Molar Transport Coefficients

In applications, it is common to use the mass flux of the components and the partial molar thermodynamic quantities, like, for instance, partial molar entropy. The above equations should use either molar fluxes and partial molar thermodynamic quantities or mass fluxes and partial mass thermodynamic quantities. The transport coefficients are different for different choices. Consider Eq. 6.30 for excess entropy production. The thermodynamic forces X_i depend on partial thermodynamic quantities. We introduce therefore X_i^m as a force which uses partial mass quantities and X_i^v as a force which uses partial molar quantity. Furthermore, let $J_{\xi_i} \equiv \rho_i v_i$ and $J_{\zeta_i} \equiv c_i v_i$ be the mass and molar flux respectively of the i th component. As $X_i^m = X_i^v/M_i$ and $J_{\xi_i} = J_{\zeta_i} M_i$, where M_i is the molar mass of the i th component, the excess entropy production becomes

$$\hat{\sigma}_s = J'_q X_q + \sum_{i=1}^n J_{\xi_i} X_i^m = J'_q X_q + \sum_{i=1}^n J_{\zeta_i} X_i^v \quad (6.42)$$

The force–flux relations become

$$X_q = R_{qq}^m J'_q + \sum_{i=1}^n R_{qi}^m J_{\xi_i} \quad (6.43a)$$

$$X_j^m = R_{jq}^m J'_q + \sum_{i=1}^n R_{ji}^m J_{\xi_i}$$

and

$$X_q = R_{qq}^v J'_q + \sum_{i=1}^n R_{qi}^v J_{\zeta_i} \quad (6.43b)$$

$$X_j^v = R_{jq}^v J'_q + \sum_{i=1}^n R_{ji}^v J_{\zeta_i}$$

where the corresponding superscript for the resistance coefficient indicates the association with the mass or molar quantities. These transport coefficients are related in the following way

$$\begin{aligned}
R_{qq}^v &= R_{qq}^m \\
R_{qi}^v &= R_{qi}^m M_i \\
R_{iq}^v &= R_{iq}^m M_i \\
R_{ji}^v &= R_{ji}^m M_j M_i
\end{aligned} \tag{6.44}$$

6.6 Conclusions

In this chapter we have studied stationary transport of heat and mass through the liquid–vapor interface in a mixture, using the square gradient theory. We derived an expression for the excess entropy production of a surface from the continuous description, which is identical to the one derived directly for the discrete description using the property of local equilibrium [1]. This makes it possible to give the linear force–flux relations for this case. These relations involve the interfacial resistances or transfer coefficients, which were the main focus of interest in this chapter.

6.A On the Definition of an Excess Quantity

One may think of an alternative definition of an excess quantity

$$\widehat{\phi}_a(x^s, x_2, x_3) \equiv \int_{x^{g,s}}^{x^{\ell,s}} dx_1 h_1 \phi^{\text{ex}}(\mathbf{r}; x^s) \tag{6.45}$$

We note however, that $\widehat{\phi}_a$ has no physical meaning, while $\widehat{\phi}$ has. The reason for this is that

$$\Phi \equiv \int_S \int dx_2 dx_3 h_2^s h_3^s \widehat{\phi}(x^s, x_2, x_3) = \int_S \int_{x^{g,s}}^{x^{\ell,s}} dx_1 dx_2 dx_3 h_1 h_2 h_3 \phi^{\text{ex}}(\mathbf{r}; x^s) \tag{6.46}$$

is the total amount of some physical quantity in the volume which is limited by the surfaces S at $x^{g,s}$ and $x^{\ell,s}$, while

$$\Phi_a \equiv \int_S \int dx_2 dx_3 h_2^s h_3^s \widehat{\phi}_a(x^s, x_2, x_3) = \int_S \int_{x^{g,s}}^{x^{\ell,s}} dx_1 dx_2 dx_3 h_1 h_2^s h_3^s \phi^{\text{ex}}(\mathbf{r}; x^s) \tag{6.47}$$

is not. If the interfacial thickness is small compared to the radii of curvature, the difference between $\widehat{\phi}$ and $\widehat{\phi}_a$ is small and vanishes for planar interface considered under cartesian coordinates. However, it is Φ but not Φ_a which is a physical amount, and thus $\widehat{\phi}$ is the surface density.

6.B Excess of a Gradient Function in Curvilinear Coordinates

Consider a function ϕ being the divergence of a vector function: $\phi = \nabla \cdot \mathbf{q}(\mathbf{r})$. Its excess

$$\widehat{\nabla \cdot \mathbf{q}}(x^s, \mathbf{r}_{\parallel}) = \frac{1}{h_2^s h_3^s} \int_{x^{g,s}}^{x^{\ell,s}} dx_1 h_1 h_2 h_3 (\nabla \cdot \mathbf{q})^{ex}(\mathbf{r}; x^s) \quad (6.48)$$

Furthermore,

$$\begin{aligned} (\nabla \cdot \mathbf{q})^{ex}(\mathbf{r}; x^s) &\equiv \nabla \cdot \mathbf{q}(\mathbf{r}) - \{\nabla \cdot \mathbf{q}^g(\mathbf{r})\} \Theta(x^s - x_1) - \{\nabla \cdot \mathbf{q}^{\ell}(\mathbf{r})\} \Theta(x_1 - x^s) \\ &= \nabla \cdot (\mathbf{q}^{ex})(\mathbf{r}; x^s) + \mathbf{q}^g(\mathbf{r}) \cdot \nabla \Theta(x^s - x_1) + \mathbf{q}^{\ell}(\mathbf{r}) \cdot \nabla \Theta(x_1 - x^s) \end{aligned} \quad (6.49)$$

where

$$\mathbf{q}^{ex}(\mathbf{r}; x^s) \equiv \mathbf{q}(\mathbf{r}) - \mathbf{q}^g(\mathbf{r}) \Theta(x^s - x_1) - \mathbf{q}^{\ell}(\mathbf{r}) \Theta(x_1 - x^s) \quad (6.50)$$

and \mathbf{q}^g and \mathbf{q}^{ℓ} are defined similarly to ϕ^g and ϕ^{ℓ} .

Using the standard formula for the divergence of a vectorial function in curvilinear coordinates

$$\nabla \cdot \mathbf{q} = \frac{1}{h_1 h_2 h_3} \left(\frac{\partial}{\partial x_1} (h_2 h_3 q_1) + \frac{\partial}{\partial x_2} (h_1 h_3 q_2) + \frac{\partial}{\partial x_3} (h_1 h_2 q_3) \right) \quad (6.51)$$

one can show that

$$\begin{aligned} &\int_{x^{g,s}}^{x^{\ell,s}} dx_1 h_1 h_2 h_3 \nabla \cdot (\mathbf{q}^{ex})(\mathbf{r}; x^s) \\ &= h_2 h_3 q_{\perp}^{ex} \Big|_{x^{g,s}}^{x^{\ell,s}} + \int_{x^{g,s}}^{x^{\ell,s}} dx_1 \left(\frac{\partial}{\partial x_2} (h_1 h_3 q_2^{ex}) + \frac{\partial}{\partial x_3} (h_1 h_2 q_3^{ex}) \right) \end{aligned} \quad (6.52)$$

Using the standard formula for the gradient of a scalar function in curvilinear coordinates

$$\nabla\theta = \frac{1}{h_1} \frac{\partial\theta}{\partial x_1} \mathbf{i}_1 + \frac{1}{h_2} \frac{\partial\theta}{\partial x_2} \mathbf{i}_2 + \frac{1}{h_3} \frac{\partial\theta}{\partial x_3} \mathbf{i}_3 \quad (6.53)$$

one can show that for Heaviside step function Θ

$$\frac{1}{h_2^s h_3^s} \int_{x^{g,s}}^{x^{\ell,s}} dx_1 h_1 h_2 h_3 \mathbf{q}^b(\mathbf{r}) \cdot \nabla\Theta(x_1 - x^s) = \mathbf{q}^b(x^s, \mathbf{r}_{\parallel}) \cdot \mathbf{i}_1 \equiv q_{\perp}^b(x^s, \mathbf{r}_{\parallel}) \quad (6.54)$$

Substituting Eq. 6.49 into Eq. 6.48 and using Eqs. 6.52 and 6.54 we obtain

$$\widehat{\nabla} \cdot \mathbf{q}(x^s, \mathbf{r}_{\parallel}) = q_{\perp}^{\ell}(x^s, \mathbf{r}_{\parallel}) - q_{\perp}^g(x^s, \mathbf{r}_{\parallel}) + \widehat{\nabla}_{\parallel} \cdot \mathbf{q}_{\parallel}(x^s, \mathbf{r}_{\parallel}) \quad (6.55)$$

where

$$\widehat{\nabla}_{\parallel} \cdot \mathbf{q}_{\parallel} \equiv \frac{1}{h_2^s h_3^s} \int_{x^{g,s}}^{x^{\ell,s}} dx_1 \left(\frac{\partial}{\partial x_2} (h_1 h_3 q_2^{\text{ex}}) + \frac{\partial}{\partial x_3} (h_1 h_2 q_3^{\text{ex}}) \right) \quad (6.56)$$

and we took into account that according to Eq. 6.14 $q_{\perp}^{\text{ex}}(x^{g,s}) = q_{\perp}^{\text{ex}}(x^{\ell,s}) = 0$.

Consider a special form of a vector \mathbf{q} for which $\mathbf{q}_{\parallel} = \mathbf{J}_{\parallel} \phi$ where $\nabla_{\parallel} \cdot \mathbf{J}_{\parallel} = 0$. Here ∇_{\parallel} is a parallel component of three-dimensional nabla-operator so that

$$\begin{aligned} \nabla_{\parallel} \cdot \mathbf{q}_{\parallel} &= \frac{1}{h_1 h_2 h_3} \left(\frac{\partial}{\partial x_2} (h_1 h_3 q_2) + \frac{\partial}{\partial x_3} (h_1 h_2 q_3) \right) \\ \nabla_{\parallel} \theta &= \frac{1}{h_2} \frac{\partial\theta}{\partial x_2} \mathbf{i}_2 + \frac{1}{h_3} \frac{\partial\theta}{\partial x_3} \mathbf{i}_3 \end{aligned} \quad (6.57)$$

$$\nabla_{\parallel} \cdot (\mathbf{J}_{\parallel} \phi) = \mathbf{J}_{\parallel} \cdot (\nabla_{\parallel} \phi) + (\nabla_{\parallel} \cdot \mathbf{J}_{\parallel}) \phi = \mathbf{J}_{\parallel} \cdot (\nabla_{\parallel} \phi) \quad (6.58)$$

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Chapter 7

Surface Transfer Coefficients for the Binary Mixture

7.1 Introduction

In this chapter we describe how to obtain surface resistances given the non-equilibrium solution of the system. For the sake of convenience we do it for a binary mixture, however the procedure is applicable for a multi-component mixture. In Sect. 7.2 we specify the general expressions for two-component mixture. In Sect. 7.3 we discuss the different methods to obtain the resistances from a non-equilibrium continuous solution. We give the results of our analysis in Sect. 7.4. We analyze extensively different aspects of the problem and find the values of parameters, which make the interfacial resistances obtained from the continuous solution of the square gradient model to match kinetic theory. We give the discussion and concluding remarks in Sect. 7.5.

7.2 Two Component Mixture

We have the following expression for the excess entropy production

$$\hat{\sigma}_s = J'_q X_q + J_{\xi_1} X_1 + J_{\xi_2} X_2 \quad (7.1)$$

and force–flux relations (6.33) with

$$\mathbf{X} \equiv \begin{pmatrix} X_q \\ X_1 \\ X_2 \end{pmatrix}, \quad \mathbf{R} \equiv \begin{pmatrix} R_{qq} & R_{q1} & R_{q2} \\ R_{1q} & R_{11} & R_{12} \\ R_{2q} & R_{21} & R_{22} \end{pmatrix}, \quad \mathbf{J} \equiv \begin{pmatrix} J'_q \\ J_{\xi_1} \\ J_{\xi_2} \end{pmatrix} \quad (7.2)$$

We will also use an alternative expression for the excess entropy production, which uses the total mass flux $J_m = J_{\xi_1} + J_{\xi_2}$ and the flux of one of the components, say $J_{\xi_1} \equiv J_{\xi}$:

$$\hat{\sigma}_s = J'_q X_q + J_{\xi} X_{\xi} + J_m X_m \quad (7.3)$$

where $X_\xi \equiv X_1 - X_2$ and $X_m \equiv X_2$. The resulting force–flux relations (6.33)

$$\mathbf{X}(\beta) = \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}})\mathbf{J}(\beta) \quad (7.4)$$

have the following terms

$$\mathbf{X} \equiv \begin{pmatrix} X_q \\ X_\xi \\ X_m \end{pmatrix}, \quad \mathbf{R} \equiv \begin{pmatrix} R_{qq} & R_{q\xi} & R_{qm} \\ R_{\xi q} & R_{\xi\xi} & R_{\xi m} \\ R_{mq} & R_{m\xi} & R_{mm} \end{pmatrix}, \quad \mathbf{J} \equiv \begin{pmatrix} J'_q \\ J_\xi \\ J_m \end{pmatrix} \quad (7.5)$$

where the coefficients from Eq. 7.2 are related to the coefficients from Eq. 7.5 as

$$\begin{aligned} R_{q1} &= R_{q\xi} + R_{qm} & R_{11} &= R_{m\xi} + R_{\xi m} + R_{mm} + R_{\xi\xi} \\ R_{1q} &= R_{\xi q} + R_{mq} & R_{22} &= R_{mm} \\ R_{q2} &= R_{qm} & R_{12} &= R_{mm} + R_{\xi m} \\ R_{2q} &= R_{mq} & R_{21} &= R_{mm} + R_{m\xi} \end{aligned} \quad (7.6)$$

Having the numerical solution for a particular non-equilibrium stationary state, we know all the fluxes \mathbf{J} and forces \mathbf{X} used in Eq. 7.4: the constant fluxes are obtained directly from the non-equilibrium solution and the extrapolated bulk profiles are obtained using the procedure described in Chap. 4. On the other hand we know only the local resistivities but not the resistances \mathbf{R} of the whole surface.

We now consider the inverse problem: to determine the transport coefficients for the whole surface having the non-equilibrium solution. As one can see, Eq. 7.4 has nine unknown resistances¹ and only three equations. It is therefore not possible to determine all the transport coefficients uniquely having only one stationary state solution. In order to incorporate more equations we need to consider other non-equilibrium stationary solutions which are independent of the previous. As the transport coefficients depend only on equilibrium unperturbed state but not on non-equilibrium perturbations, considering different perturbations around the same equilibrium state we will give missing data. We must ensure however, that a given perturbation is small enough to be described by linear-order equations. This would require for instance Eqs. 6.35 and 6.40 to be true. There are more constraints to be fulfilled which will be discussed in Sect. 7.4.

The non-equilibrium solution uses the following profiles for local resistivities (see Chap. 4 for details)

$$\begin{aligned} r_{qq}(x) &= r_{qq}^g + (r_{qq}^\ell - r_{qq}^g) q_0(x) + \alpha_{qq} (r_{qq}^\ell + r_{qq}^g) q_1(x) \\ r_{q1}(x) &= r_{q1}^g + (r_{q1}^\ell - r_{q1}^g) q_0(x) + \alpha_{q1} (r_{q1}^\ell + r_{q1}^g) q_1(x) \\ r_{11}(x) &= r_{11}^g + (r_{11}^\ell - r_{11}^g) q_0(x) + \alpha_{11} (r_{11}^\ell + r_{11}^g) q_1(x) \end{aligned} \quad (7.7)$$

¹ In solving the inverse problem, we have to prove the Onsager reciprocal relations, rather than impose them. So we have nine unknown resistances, not six.

where $q_0(x)$ and $q_1(x)$ are modulatory curves for resistivity profiles which depend only on density profiles and their first derivatives. For each resistivity profile, r^g and r^ℓ are the equilibrium coexistence resistivities of the gas and liquid phase, respectively. Coefficients α_{qq} , α_{q1} , α_{11} control the size of the peak in the resistivity profiles in the interfacial region. The non-equilibrium stationary state depends on the values of these coefficients. The surface resistance coefficients \mathbf{R} will therefore depend on these coefficients as parameters, $\mathbf{R} = \mathbf{R}(\alpha_{qq}, \alpha_{q1}, \alpha_{11})$, which we will investigate.

7.3 Methods to Obtain Resistances

We determine the transport coefficients from three different methods: from a ‘‘perturbation cell’’ method,² from an experimental-like procedure and from kinetic theory.

7.3.1 Perturbation Cell

Consider a stationary state which is perturbed from equilibrium by setting the temperature of the liquid³ $T(x^\ell) = (1 + \beta_T)T_{\text{eq}}$, the pressure of the gas $p(x^g) = (1 + \beta_p)p_{\text{eq}}$ and the mole fraction of the liquid $\zeta^\ell(x^\ell) = (1 + \beta_\zeta)\zeta_{\text{eq}}^\ell$ independently. The resulting non-equilibrium state is therefore a function of parameters β :

$$\mathbf{X}(\beta_T, \beta_p, \beta_\zeta) = \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}})\mathbf{J}(\beta_T, \beta_p, \beta_\zeta) \quad (7.8)$$

where \mathbf{X} , \mathbf{J} and \mathbf{R} are given by Eq. 7.2. Consider the following set of eight independent non-equilibrium perturbations:

$$\begin{aligned} \mathbf{X}(\beta, \beta, \beta) &= \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \cdot \mathbf{J}(\beta, \beta, \beta) \\ \mathbf{X}(\beta, -\beta, \beta) &= \mathbf{R}(T_{\text{eq}}, \psi) \cdot \mathbf{J}(\beta, -\beta, \beta) \\ \mathbf{X}(-\beta, \beta, \beta) &= \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \cdot \mathbf{J}(-\beta, \beta, \beta) \\ \mathbf{X}(-\beta, -\beta, \beta) &= \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \cdot \mathbf{J}(-\beta, -\beta, \beta) \\ \mathbf{X}(\beta, \beta, -\beta) &= \mathbf{R}(T_{\text{eq}}, \psi) \cdot \mathbf{J}(\beta, \beta, -\beta) \\ \mathbf{X}(\beta, -\beta, -\beta) &= \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \cdot \mathbf{J}(\beta, -\beta, -\beta) \\ \mathbf{X}(-\beta, \beta, -\beta) &= \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \cdot \mathbf{J}(-\beta, \beta, -\beta) \\ \mathbf{X}(-\beta, -\beta, -\beta) &= \mathbf{R}(T_{\text{eq}}, \psi) \cdot \mathbf{J}(-\beta, -\beta, -\beta) \end{aligned} \quad (7.9)$$

² This method was first used by Johannessen et al. in [1] for one-component system. Here we discuss the grounds for the legitimacy of this procedure and generalize it to mixtures.

³ One should not confuse $T(x^\ell)$ with T^ℓ . The former is the actual temperature at $x = x^\ell$, i.e. at the box boundary on the liquid side. The latter is the temperature extrapolated from the liquid phase to the interfacial region and taken at $x = x^s$, i.e. at the dividing surface.

Consider now the 3×8 matrices \mathfrak{X} and \mathfrak{J} which contain eight column vectors X and J respectively for each non-equilibrium perturbation specified above. For these perturbations, $\mathfrak{X} = \mathfrak{X}(\beta)$ and $\mathfrak{J} = \mathfrak{J}(\beta)$ are the functions only on one parameter β . Equation 7.9 may be written as

$$\mathfrak{X}(\beta) = \mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}) \mathfrak{J}(\beta) \quad (7.10)$$

As it was discussed in Sect. 6.5, for practical purposes the values of corresponding matrices should be calculated at very small but finite value of β . $\mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}})$ depends therefore on β and we will keep it as an argument. From Eq. 7.10 we obtain

$$\mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}}; \beta) = (\mathfrak{X}(\beta) \cdot \mathfrak{J}^T(\beta)) \cdot (\mathfrak{J}(\beta) \mathfrak{J}^T(\beta))^{-1} \quad (7.11)$$

where superscript T means the matrix transpose and $^{-1}$ means the inverted matrix.

We note, that in order to obtain the resistance matrix \mathbf{R} uniquely, it is sufficient in principle to impose any three non-equilibrium perturbations which have sufficiently small perturbation parameters β_T, β_p and β_ζ . As *each* of β_T, β_p and β_ζ goes to zero, the resistance matrix will go to $\mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}})$ as fast as *all* β_T, β_p and β_ζ go to zero. The method presented above makes the resistance matrix converge to $\mathbf{R}(T_{\text{eq}}, \psi_{\text{eq}})$ as fast as β^2 goes to zero, however. This is achieved by using eight perturbations at the ‘‘corners’’ of a three-dimensional ‘‘perturbation cell’’, so changing β to $-\beta$ would not change the ‘‘perturbation cell’’ and the resulting \mathbf{R} .

Because of using eight perturbations instead of three, there are five superfluous perturbations which make the system of equations 7.10 overdetermined. Contracting both sides of Eq. 7.10 with \mathfrak{J}^T , we actually average all the perturbations which are spread around T_{eq} and ψ_{eq} in the least square sense. As the components of \mathfrak{J} matrix are linearly independent, this guarantees the matrix $\mathfrak{J} \cdot \mathfrak{J}^T$ to be invertible. Thus, the inverse matrix $(\mathfrak{J} \cdot \mathfrak{J}^T)^{-1}$ exists and Eq. 7.11 is mathematically legitimate. In the numerical procedure the expression on the right hand side of Eq. 7.11 is obtained using Matlab matrix division $\mathfrak{X}/\mathfrak{J}$.

7.3.2 Experiment-Like Procedure

In experiments it is convenient to measure the corresponding coefficients by keeping zero mass fluxes through the system. It is also convenient to work with the total mass flux J_m and the flux of one of the components J_ξ , rather than with fluxes of each component separately,⁴ J_{ξ_1} and J_{ξ_2} .

⁴ One of the reasons for this is that it is hard to make only $J_{\xi_1} = 0$, keeping J_{ξ_2} finite.

Consider a stationary state which is perturbed from equilibrium by setting the temperature of the liquid $T(x^\ell) = (1 + \beta_T)T_{\text{eq}}$. The second perturbation condition is either $J_\xi = 0$ or $\zeta^\ell(x^\ell) = \zeta_{\text{eq}}^\ell$ and we introduce the perturbation parameter β_ξ which is 0 in the former case and one in the latter one. The third perturbation condition is either $J_m = 0$ or $p(x^g) = p_{\text{eq}}$ and the corresponding perturbation parameter β_m is 0 or 1, respectively. The resulting non-equilibrium state is therefore a function of three parameters:

$$X(\beta_T, \beta_\xi, \beta_m) = R(T_{\text{eq}}, \psi_{\text{eq}}) \cdot J(\beta_T, \beta_\xi, \beta_m) \quad (7.12)$$

where X, J and R are given by Eq. 7.5. Consider the following set of three independent non-equilibrium perturbations:

$$\begin{aligned} X(\beta, 0, 0) &= R(T_{\text{eq}}, \psi_{\text{eq}}) \cdot J(\beta, 0, 0) \\ X(\beta, 1, 0) &= R(T_{\text{eq}}, \psi_{\text{eq}}) \cdot J(\beta, 1, 0) \\ X(\beta, 1, 1) &= R(T_{\text{eq}}, \psi_{\text{eq}}) \cdot J(\beta, 1, 1) \end{aligned} \quad (7.13)$$

From the first of Eq. 7.13 we find

$$\begin{aligned} R_{qq}(T_{\text{eq}}, \psi_{\text{eq}}) &= X_{q,00} / J'_{q,00} \\ R_{\xi q}(T_{\text{eq}}, \psi_{\text{eq}}) &= X_{\xi,00} / J'_{q,00} \\ R_{mq}(T_{\text{eq}}, \psi_{\text{eq}}) &= X_{m,00} / J'_{q,00} \end{aligned} \quad (7.14a)$$

where we use subscripts $\beta_\xi \beta_m$ instead the functional dependence $(\beta_T, \beta_\xi, \beta_m)$ for simplicity of notation. From the second of Eq. 7.13 we find

$$\begin{aligned} R_{q\xi}(T_{\text{eq}}, \psi_{\text{eq}}) &= (X_{q,10} - R_{qq}(T_{\text{eq}}, \psi) J'_{q,10}) / J_{\xi,10} \\ R_{\xi\xi}(T_{\text{eq}}, \psi_{\text{eq}}) &= (X_{\xi,10} - R(T_{\text{eq}}, \psi_{\text{eq}}) J'_{q,10}) / J_{\xi,10} \\ R_{m\xi}(T_{\text{eq}}, \psi_{\text{eq}}) &= (X_{m,10} - R_{mq}(T_{\text{eq}}, \psi_{\text{eq}}) J'_{q,10}) / J_{\xi,10} \end{aligned} \quad (7.14b)$$

The values X_{10} and J_{10} are found directly from the calculations and the values of $R_{qq}(T_{\text{eq}}, \psi_{\text{eq}})$, $R_{\xi q}(T_{\text{eq}}, \psi_{\text{eq}})$ and $R_{mq}(T_{\text{eq}}, \psi_{\text{eq}})$ are those which are found in Eq. 7.14a, given the perturbation rate β_T is small enough. From the third of Eq. 7.13 we find

$$\begin{aligned} R_{qm}(T_{\text{eq}}, \psi_{\text{eq}}) &= (X_{q,11} - R_{qq}(T_{\text{eq}}, \psi_{\text{eq}}) J'_{q,11} - R_{q\xi}(T_{\text{eq}}, \psi_{\text{eq}}) J_{\xi,11}) / J_{m,11} \\ R_{\xi m}(T_{\text{eq}}, \psi_{\text{eq}}) &= (X_{\xi,11} - R_{\xi q}(T_{\text{eq}}, \psi_{\text{eq}}) J'_{q,11} - R_{\xi\xi}(T_{\text{eq}}, \psi_{\text{eq}}) J_{\xi,11}) / J_{m,11} \\ R_{mm}(T_{\text{eq}}, \psi_{\text{eq}}) &= (X_{m,11} - R_{mq}(T_{\text{eq}}, \psi_{\text{eq}}) J'_{q,11} - R_{m\xi}(T_{\text{eq}}, \psi_{\text{eq}}) J_{\xi,11}) / J_{m,11} \end{aligned} \quad (7.14c)$$

Again, all the quantities on the right hand side of Eq. 7.14c are known and we therefore can find the remaining resistances.

7.3.3 Comparison to Kinetic Theory

According to [2. p. 180] kinetic theory gives the following expressions for the surface transport coefficients for a two component mixture

$$\begin{aligned}
 R_{qq}^{g,y}(T, \psi) &= 4 R_O(T, \psi) \left\{ 1 + \frac{104}{25\pi} \left(\frac{w_1^2}{\varsigma_1} + \frac{w_2^2}{\varsigma_2} \right) \right\} \\
 R_{qi}^{g,y}(T, \psi) &= R_{iq}^{g,y}(T, \psi) = 2RT R_O(T, \psi) \left\{ 1 + \frac{16 w_i}{5\pi \varsigma_i} \right\} \\
 R_{ij}^{g,y}(T, \psi) &= (RT)^2 R_O(T, \psi) \left\{ 1 + 32 \delta_{ij} \frac{1}{\varsigma_i} \left(\frac{1}{\sigma_i} + \frac{1}{\pi} - \frac{3}{4} \right) \right\}
 \end{aligned} \tag{7.15}$$

where

$$\begin{aligned}
 R_O(T, \psi) &\equiv 2^{-9/2} \sqrt{\pi} R (RT)^{-5/2} (c_1^g/\sqrt{M_1} + c_2^g/\sqrt{M_2})^{-1} \\
 \varsigma_i(T, \psi) &\equiv (c_i^g/\sqrt[4]{M_i}) / (c_1^g/\sqrt[4]{M_1} + c_2^g/\sqrt[4]{M_2}) \\
 w_i(T, \psi) &\equiv \lambda_i / (\lambda_1 + \lambda_2)
 \end{aligned} \tag{7.16}$$

where R is universal gas constant, λ_i and $c_{i,eq}^g$ are the thermal conductivity and the gas coexistence concentration of i th component, respectively. σ_i is the condensation coefficient, which is parameter in this theory and δ_{ij} is the Kroneker symbol.

7.4 Results

We consider the mixture of cyclohexane (first component) and n -hexane (second component) in a box with gravity directed along axes x from left to right. The gas phase is therefore in the left part of the box and the liquid is in the right part of the box. The surface is planar.

Using the procedures described above we obtain different sets of transport coefficients $R(T, \psi)$, each of them as a function of equilibrium temperature and chemical potential difference. Let us use subscript pc for the resistance matrix obtained from the ‘‘perturbation cell’’ method and ex for the resistance matrix obtained from the ‘‘experiment-like’’ method. In each method we calculate the resistances associated with the gas- and liquid- side measurable heat fluxes using Eqs. 6.37 and 6.38. Furthermore, we will use subscript kin for the resistance matrix obtained from kinetic theory, for which only the gas-side resistances are available.

We calculate the transport coefficients associated only with mass properties. The corresponding molar coefficients may be calculated using Eq. 6.44. As a result we obtain the following sets of resistances: $R_{pc}^g, R_{pc}^\ell, R_{ex}^g, R_{ex}^\ell$, all of which depend on temperature and chemical potential difference as well as on parameters $\alpha_{qq}, \alpha_{1q}, \alpha_{11}$. In addition we obtain R_{kin}^g which depends on temperature and chemical potential difference as well as on condensation coefficients σ_1 and σ_2 . We have the following constraints, which they must obey for each T and ψ :

1. the second law consistency;
2. the cross coefficients of each R matrix must satisfy Onsager relations (6.35);
3. the corresponding components of R_{pc}^g and R_{pc}^ℓ as well as R_{ex}^g and R_{ex}^ℓ must satisfy Eq. 6.40;
4. the corresponding components of R_{pc}^g, R_{ex}^g and R_{kin}^g as well as R_{pc}^ℓ and R_{ex}^ℓ obtained at the same T and ψ must be equal.

We study the dependence of the different resistance coefficients on α_{qq}, α_{1q} and α_{11} and on T and ψ and their convergence for small β . We determine the values of the parameters for which the above constraints are fulfilled.

7.4.1 Onsager Reciprocal Relations

In this section we investigate the values of parameters $\alpha_{qq}, \alpha_{1q}, \alpha_{11}$ for which the Onsager relations are fulfilled. This is done for a particular values of equilibrium temperature and chemical potential difference $T_{eq} = 330$ K and $\psi_{eq} = 700$ J/mol. In Tables 7.1 and 7.2 we give the relative error in percent for the gas-side cross coefficients $|(R_{ij}^g - R_{ji}^g)/R_{ij}^g| \cdot 100\%$ as a function of β for $\alpha_{qq} = 0, \alpha_{1q} = 0, \alpha_{11} = 0$ obtained by different methods.

As one can see, $\beta = 0.02$ is really an extreme perturbation and the difference is rather large. When we decrease β to $2e-4$, the differences become small. As we further decrease β to $2e-6$ the inaccuracy of the numerical solution become comparable to the size of the perturbation. We conclude that the values for β to $2e-4$ are closest to the converged values and use them as such.

Table 7.1 Relative error in percent for gas-side cross-coefficients obtained by “perturbation cell” method at $T_{eq} = 330$ and $\psi_{eq} = 700$ for different β and for $\alpha_{qq} = 0, \alpha_{1q} = 0, \alpha_{11} = 0$

β	R_{q1}	R_{q2}	R_{12}
2.0e-002	8.963066	35.863259	34.908631
2.0e-003	0.273286	0.369082	19.683274
2.0e-004	0.011726	0.007231	1.909391
2.0e-005	0.066375	0.071266	2.336652
2.0e-006	4.963895	8.128243	5.843913

Table 7.2 Relative error in percent for gas-side cross-coefficients obtained by “experiment like” method at $T_{\text{eq}} = 330$ and $\psi_{\text{eq}} = 700$ for different β and for $\alpha_{qq} = 0, \alpha_{1q} = 0, \alpha_{11} = 0$

β	R_{q1}	R_{q2}	R_{12}
2.0e-002	1.275105	0.828600	754.982200
2.0e-003	0.038759	0.363715	38.708981
2.0e-004	0.131868	0.238584	6.247648
2.0e-005	1.301483	2.056102	20.984734
2.0e-006	13.282959	20.788752	632.124504

Table 7.3 Relative error in percent for gas-side cross-coefficients obtained by “perturbation cell” method at $T_{\text{eq}} = 330$ and $\psi_{\text{eq}} = 700$ for different β and for $\alpha_{qq} = 10, \alpha_{1q} = 10, \alpha_{11} = 10$

β	R_{q1}	R_{q2}	R_{12}
2.0e-002	71.515410	78.166809	23.572836
2.0e-003	0.745604	0.896547	0.317348
2.0e-004	0.012358	0.012650	0.001919
2.0e-005	0.012078	0.007485	0.005290
2.0e-006	0.713969	1.124994	0.022121

Table 7.4 Relative error in percent for gas-side cross-coefficients obtained by “experiment like” method at $T_{\text{eq}} = 330$ and $\psi_{\text{eq}} = 700$ for different β and for $\alpha_{qq} = 10, \alpha_{1q} = 10, \alpha_{11} = 10$

β	R_{q1}	R_{q2}	R_{12}
2.0e-002	4.225362	2.559393	12.259260
2.0e-003	0.443944	0.256804	1.091842
2.0e-004	0.068621	0.019788	0.093041
2.0e-005	0.269764	0.407090	0.008844
2.0e-006	2.717575	4.149484	2.025054

In Tables 7.3 and 7.4 we give the same data for the higher continuous resistivities with rather substantial peak, when $\alpha_{qq} = 10, \alpha_{1q} = 10$ and $\alpha_{11} = 10$. As one can see, the Onsager relations are fulfilled there again best for $\beta = 2e-4$.

The similar picture is observed for the liquid-side resistances and we do not give those data here.

We may notice that the behavior of the resistances with respect to β is independent on the behavior of the resistances with respect to α_{qq}, α_{1q} and α_{11} . This is natural, as these parameters control the different aspects of the system: β controls the perturbation rate, while α 's are adjustable parameters, which control the size of the peak in the continuous resistivities.

7.4.2 Second Law Consistency

In this section we investigate the values of parameters $\alpha_{qq}, \alpha_{1q}, \alpha_{11}$ for which the second law of thermodynamics are fulfilled. That is that the excess entropy

production is positive and therefore the matrix of the resistance coefficients is positive definite. This requires that the diagonal coefficients are positive, and for each pair $q1, q2$ and 12 of the cross coefficients the expression

$$DR_{ik} \equiv R_{ii}R_{kk} - \frac{1}{4}(R_{ik} + R_{ki})^2 \tag{7.17}$$

must be positive.

In Table 7.5 we give the diagonal coefficients and expression (7.17) for each pair of the cross coefficients as a function of α_{qq} for $\alpha_{1q} = 0, \alpha_{11} = 0$ and $\beta = 2e-4$ obtained by the ‘‘perturbation cell’’ method. In Tables 7.6 and 7.7 we give the same quantities for other choices of α .

We see, that the required quantities become positive for rather big values of α_{qq} . They almost do not depend on the value of α_{1q} and they are positive for moderate values of parameter α_{11} . It is clear that finite values of α_{qq} and α_{11} are needed to have a positive excess entropy production.

All these quantities almost do not depend on the value of β in the range [1e-5, 1e-3]. The ‘‘experimental-like’’ procedure leads to almost the same values of all the quantities. The liquid-side coefficients reveal a similar behavior.

Table 7.5 Second law consistency for gas-side coefficients

α_{qq}	R_{qq}	R_{11}	R_{22}	DR_{q1}	DR_{q2}	DR_{12}
0	7.06e-015	0.075	-0.092	2.13e-015	-2.59e-015	-0.028
1	3.36e-012	0.094	-0.074	1.26e-012	-9.97e-013	-0.028
10	3.35e-011	0.260	0.085	3.48e-011	1.14e-011	0.087

Data are obtained by ‘‘perturbation cell’’ method at $T_{eq} = 330$ and $\psi_{eq} = 700$ for different α_{qq} and for $\beta = 0.0002, \alpha_{1q} = 0, \alpha_{11} = 0$

Table 7.6 Second law consistency for gas-side coefficients

α_{1q}	R_{qq}	R_{11}	R_{22}	DR_{q1}	DR_{q2}	DR_{12}
0	7.06e-015	0.075	-0.092	2.13e-015	-2.59e-015	-0.028
1	7.06e-015	0.074	-0.091	2.10e-015	-2.57e-015	-0.027
10	7.05e-015	0.067	-0.083	1.89e-015	-2.34e-015	-0.022

Data are obtained by ‘‘perturbation cell’’ method at $T_{eq} = 330$ and $\psi_{eq} = 700$ for different α_{1q} and for $\beta = 0.0002, \alpha_{qq} = 0, \alpha_{11} = 0$

Table 7.7 Second law consistency for gas-side coefficients

α_{11}	R_{qq}	R_{11}	R_{22}	DR_{q1}	DR_{q2}	DR_{12}
0	7.05e-015	0.075	-0.092	2.13e-015	-2.59e-015	-0.028
1	7.06e-015	0.370	0.266	1.04e-014	7.50e-015	0.381
10	7.10e-015	3.021	3.483	8.58e-014	9.90e-014	-69.285

Data are obtained by ‘‘perturbation cell’’ method at $T_{eq} = 330$ and $\psi_{eq} = 700$ for different α_{11} and for $\beta = 0.0002, \alpha_{qq} = 0, \alpha_{1q} = 0$

Table 7.8 Relative error in percent for invariant expressions in Eq. 6.39 obtained by “perturbation cell” method at $T_{\text{eq}} = 330$ and $\psi_{\text{eq}} = 700$ for $\beta = 0.0002$ and $\alpha_{qq} = 1$, $\alpha_{1q} = 1$, $\alpha_{11} = 1$

R_{qq}	R_{11}	R_{22}
0.000000	0.000002	0.000085
R_{q1}	R_{q2}	R_{12}
0.000001	0.000001	0.000060
R_{1q}	R_{2q}	R_{21}
0.000389	0.000389	0.000003

7.4.3 Gas- and Liquid-Coefficients

In this section we investigate the validity of Eq. 6.40. In Table 7.8 we give the relative error in percent between the left hand side and the right hand side of Eq. 6.39.

These errors almost do not depend neither on the value of β in the range [1e-5, 1e-3] nor on the values of α_{qq} , α_{1q} , α_{11} . The “experimental-like” procedure leads to almost the same results.

7.4.4 Comparison to Kinetic Theory

In this section we investigate the values of parameters α_{qq} , α_{1q} , α_{11} which make the coefficients agree with the kinetic theory coefficients. We do it for $\beta = 2e-4$ as this perturbation rate gives the most accurate results. We again do this for temperature $T_{\text{eq}} = 330$ K and chemical potential difference $\psi_{\text{eq}} = 700$ J/mol. The values of parameters, used for kinetic theory are the same, as we use in our calculations. Particularly, the heat conductivities are $\lambda_1 = 0.0140$ W/(m K) and $\lambda_2 = 0.0157$ W/(m K), $M_1 = 84.162$ g/mol and $M_2 = 86.178$ g/mol. We compare here only the “perturbation cell” method with kinetic theory.

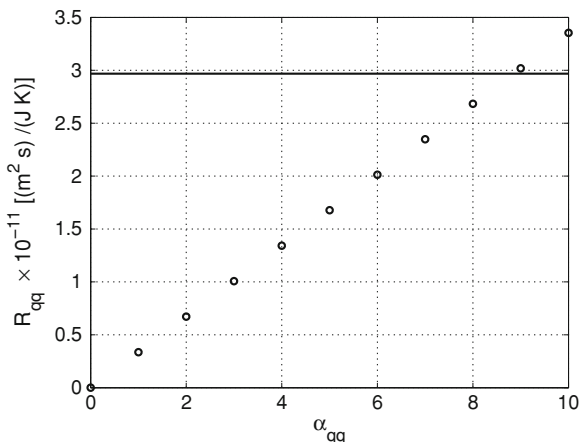
We found that the variation of α_{1q} from 0 to 10 makes the diagonal coefficients vary about 1% and the cross coefficients vary not more than 5%. As the variation of α_{1q} is quite substantial, the variation in the coefficients which it induce is negligible. We therefore take $\alpha_{1q} = 0$ in all further analysis.

For the above parameters $R_{qq, \text{kin}} = 2.96792 \times 10^{-11}$. We found that $R_{qq, \text{pc}}$ is practically independent on α_{11} while it depends linearly on α_{qq} , see Fig. 7.1. One can see from the plot, that $R_{qq, \text{kin}} = R_{qq, \text{pc}}$ for $\alpha_{qq} \approx 9$.

The diagonal coefficients $R_{11, \text{pc}}$ and $R_{22, \text{pc}}$ depend both on α_{qq} and α_{11} . Since we have found the corresponding to kinetic theory value of α_{qq} by mapping the R_{qq} coefficient, we will further investigate the dependence of $R_{11, \text{pc}}$ and $R_{22, \text{pc}}$ using this value of α_{qq} and varying only α_{11} . The diagonal coefficients $R_{11, \text{kin}}$ and $R_{22, \text{kin}}$ depend, in their turn, on the condensation coefficients σ_1 and σ_2 , respectively. We plot this dependence in the same plot with the dependency of $R_{11, \text{pc}}$ and $R_{22, \text{pc}}$ on α_{11} , see Fig. 7.2.

Consider a particular value $R_{ii, 0}$ of the diagonal coefficient R_{ii} , where i is either 1 or 2, which is indicated by a *horizontal dashed line* on a figure. To find the value

Fig. 7.1 Dependence of R_{qq} on α_{qq} obtained by “perturbation cell” method at $T_{\text{eq}} = 330$ and $\psi_{\text{eq}} = 700$ for $\alpha_{1q} = 0$ and $\alpha_{11} = 1$. $R_{qq, \text{kin}}$ is drawn as a constant line



of α_{11} for which $R_{ii, \text{pc}} = R_{ii, 0}$ we draw a perpendicular from the point where it crosses the *dotted line* to the bottom x -axes. To find the value of σ_i for which $R_{ii, \text{kin}} = R_{ii, 0}$ we draw a perpendicular from the point where the horizontal dashed line crosses the solid line to the top x -axes. For instance, the value $R_{22, 0} = 1.1$ corresponds to $\alpha_{11} = 3$ and $\sigma_2 = 0.62$. The value $\alpha_{11} = 3$, in its turn, gives $R_{11, 0} = 1.1$ which corresponds to $\sigma_1 = 0.54$.

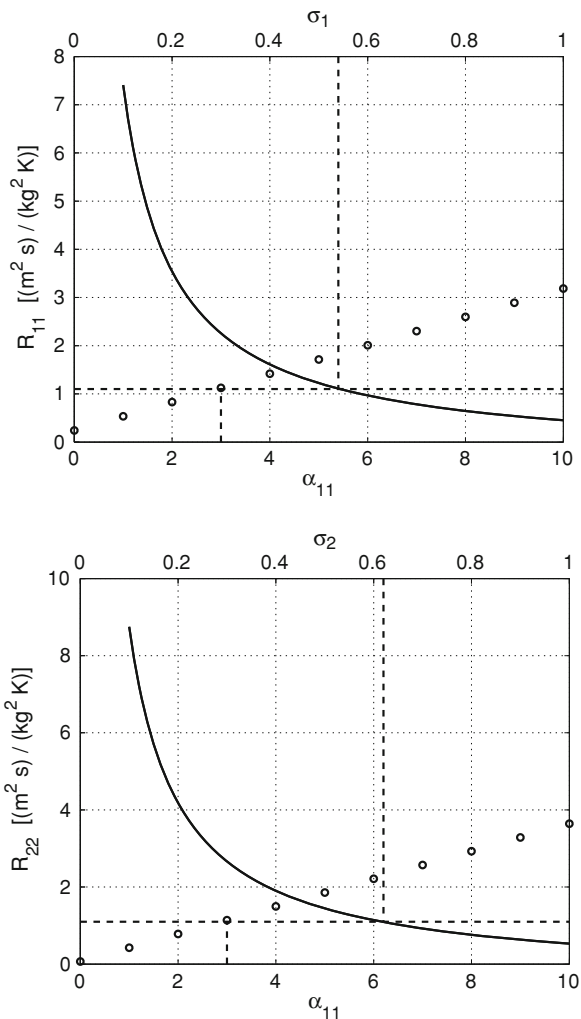
One may start by specifying α_{11} , rather than $R_{ii, 0}$, to find σ_1 and σ_2 . Then we draw a perpendicular from the bottom axes until it crosses the *dotted line*, which gives the value $R_{ii, 0}$ of $R_{ii, \text{pc}}$. Given the value of $R_{ii, \text{kin}}$ to be the same, we find the value of σ_i as described above. For the above example $\alpha_{11} = 3$ corresponds to $\sigma_1 = 0.54$ and $\sigma_2 = 0.62$. We see, that we may not specify both σ_1 and σ_2 independently: they must have the values which both correspond to the same α_{11} . For similar components, like those we are interested in, σ_1 and σ_2 should not differ much from each other, and therefore α_{11} , a coefficient which is related to the diffusion of one component through the other, should reflect this difference.

Having the diagonal coefficient mapped, we have the parameters α_{qq} and α_{11} defined uniquely (and taking into account that α_{1q} has negligible effect), as well as σ_1 and σ_2 for kinetic theory. We now compare the values of the cross coefficients given by “perturbation cell” method and kinetic theory.

One can see from Table 7.9 that while the diagonal coefficients are the same,⁵ the cross coefficients we find are between 1 and 2 orders of magnitude larger than those found by kinetic theory. R_{12} even has a different sign.

⁵ One should not expect exact compatibility between kinetic theory, which is most appropriate for gases with short range potentials, and the gradient theory, which is most appropriate for fluids with long range potentials. The purpose of this comparison is not to determine the exact values of adjustable parameters, but to show that it is possible to match coefficients in the two theories and to show the typical values of the parameters. One should not regard therefore on the difference in the values of diagonal coefficients in Table 7.9 for given parameters.

Fig. 7.2 Dependence of $R_{11,pc}$ and $R_{22,pc}$ on α_{11} (dots, bottom axes) and $R_{11,kin}$ and $R_{22,kin}$ on σ_1 and σ_2 respectively (curve, top axes). Data are obtained at $T_{eq} = 330$ and $\psi_{eq} = 700$ for $\alpha_{qq} = 9$ and $\alpha_{1q} = 0$



7.4.5 Temperature and Chemical Potential Difference Dependence

In this section we investigate the dependence of the resistance coefficients on the temperature and the chemical potential difference. In Figs. 7.3, 7.4 and 7.5 we plot these dependencies for the R_{qq} , R_{q1} and R_{11} coefficients obtained from kinetic theory and the “perturbation cell” method for the range of temperatures $[325, \dots, 335]$ and for the range of chemical potential differences $[400, \dots, 1,000]$.

The domain of T and ψ is not big, so, as we see in these figures, the dependence on them is linear, as expected.

Table 7.9 Gas-side transport coefficients obtained from kinetic theory and by “perturbation cell” method at $T_{eq} = 330$ and $\psi_{eq} = 700$ for $\beta = 0.0002$

Parameters	R_{qq}	R_{11}	R_{22}	R_{q1}	R_{q2}	R_{12}
$\sigma_1 = 0.54$	2.97e-011	1.11	1.09	-3.83e-007	-4.41e-007	0.013
$\sigma_2 = 0.62$						
$\alpha_{qq} = 9$						
$\alpha_{1q} = 0$	3.02e-011	1.12	1.14	-2.31e-006	-2.27e-006	-0.817
$\alpha_{11} = 3$						

Fig. 7.3 Dependence of R_{qq} on T and ψ obtained from kinetic theory for $\sigma_1 = 0.54$ and $\sigma_2 = 0.62$ (plane) and by “perturbation cell” method for $\alpha_{qq} = 9$, $\alpha_{1q} = 0$ and $\alpha_{11} = 3$ (points)

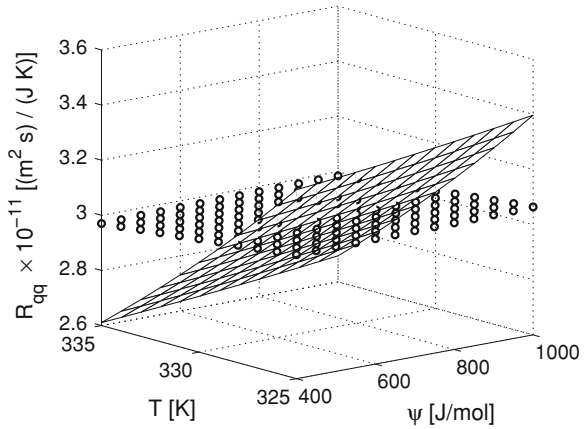


Fig. 7.4 Dependence of R_{q1} on T and ψ obtained from kinetic theory for $\sigma_1 = 0.54$ and $\sigma_2 = 0.62$ (plane) and by “perturbation cell” method for $\alpha_{qq} = 9$, $\alpha_{1q} = 0$ and $\alpha_{11} = 3$ (points)

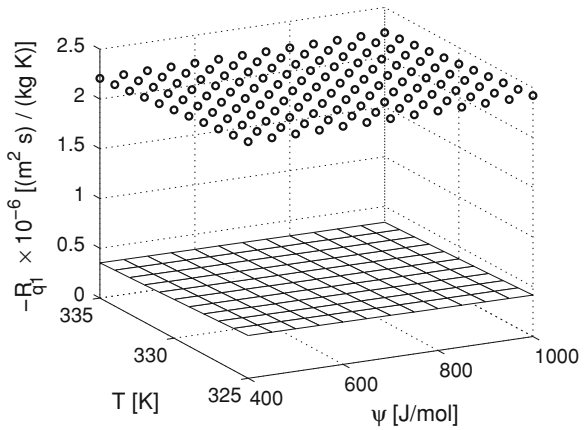
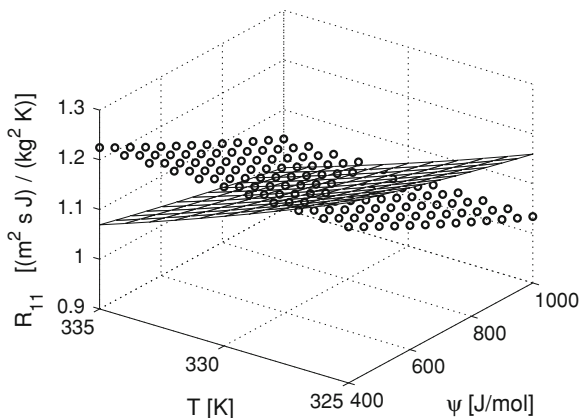


Fig. 7.5 Dependence of R_{11} on T and ψ obtained from kinetic theory for $\sigma_1 = 0.54$ and $\sigma_2 = 0.62$ (*plane*) and by “perturbation cell” method for $\alpha_{qq} = 9$, $\alpha_{1q} = 0$ and $\alpha_{11} = 3$ (*points*)



7.5 Discussion and Conclusions

In this chapter we have studied stationary transport of heat and mass through the liquid–vapor interface in a two-component mixture, using the square gradient theory. We have applied the general relations derived in Chap. 6 to the mixture of cyclohexane and *n*-hexane. Given the numerical solutions of the non-equilibrium gradient model we were able to calculate these coefficients directly. This gives an independent way to determine the interfacial resistances.

The main input parameters of the model are the local resistivity profiles used to calculate the continuous solution. There is not much theoretical information about the numerical value of these resistivities. In the vapor phase one can use kinetic theory. In the bulk phases it is most appropriate to use experimental values. There is no experimental information about the local resistivities in the interfacial region. As the local resistivities change in the surface from one bulk value to the other, it is natural to assume that they contain a contribution similar to the profile of the order parameter. There is also evidence from molecular dynamics simulations for one-component systems [2] that there is a peak in the local resistivities in the surface. As we are in the framework of the gradient theory, it is natural to assume that this peak is caused by a square gradient term, which is similar to the gradient contribution, which the Helmholtz energy density has in the interfacial region, namely $|\nabla\rho|^2$. The amplitude of this peak is not given by any theory and is used as a parameter. We therefore get that each of three local resistivities for a two-component mixture has the form given in Eq. 7.7. Thus we get three adjustable amplitudes, α_{qq} , α_{1q} and α_{11} , two of which are found to contribute significantly to the value of the transfer coefficients.

In order to determine the typical values of the α 's, we need to compare our results with independently obtained resistances. Unfortunately, not much experimental data are available for multi-component resistances and, to the best of our knowledge, no data are available for our system. Furthermore, no molecular

dynamic simulations are available for mixtures. The only reasonable source of comparison is kinetic theory, which gives the expressions for the interfacial resistances or transfer coefficients [3, 4]. We therefore compare our results to kinetic theory. Having three adjustable parameters in the gradient theory, α_{qq} , α_{1q} and α_{11} , and two adjustable parameters in kinetic theory, the condensation parameters σ_1 and σ_2 , we are able to match three diagonal coefficients R_{qq} , R_{11} and R_{22} . We found that R_{qq} does not really depend on α_{1q} and α_{11} . This makes it possible to fit α_{qq} using R_{qq} alone. For the values of the temperature and chemical potentials considered this gave $\alpha_{qq} \simeq 9$. We furthermore found that the interfacial resistances did not really depend on α_{1q} . We therefore took this amplitude equal to zero. In kinetic theory R_{11} and R_{22} depend on the condensation coefficients σ_1 and σ_2 , respectively. Choosing $\alpha_{11} = 3$ gives values for the condensation coefficients of 0.54 and 0.62. As the components are very similar, it is to be expected that these coefficients are close to each other. The values of α 's obtained from the matching are such that the excess entropy production of the surface is positive, the second law is obeyed and the Onsager relations are valid. Having found the values of the α 's from the diagonal transfer coefficients the value of the cross coefficients follows uniquely. We found that the values of the cross coefficients, obtained by our method are about one order of magnitude larger than those found from kinetic theory. This confirms results from molecular dynamics simulations [5], where it was found that increasing the range of the attractive potential increased in particular the cross coefficients substantially above the values predicted by kinetic theory. This is an interesting result, indicating that kinetic theory underestimates the transfer coefficients for real fluids. This also indicates, that the effect of coupling will be important in an interfacial region. Experiments confirm the importance of the cross coefficients [6]. We did the comparison for one value of the temperature and chemical potential only. If one extends the analysis to a larger domain, one finds that the α 's depend on the temperature and the chemical potential difference; we refer to [1] in this context. The results of kinetic theory [3, 4, 7] and molecular dynamics [8] both support the existence of a peak in the diagonal local resistivities and therefore the use of finite values for α_{qq} and α_{11} .

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Chapter 8

Integral Relations for the Surface Transfer Coefficients

8.1 Introduction

In this chapter we extend the analysis done in [1] for one-component system. Here we do the analysis for mixtures. Using the square gradient theory for the non-equilibrium interface developed in the previous chapters, we derive the general relations for the case of the transport perpendicular to the surface. We show that, as in the case of one-component systems, one can obtain the interfacial resistances using the continuous profiles obtained for equilibrium. This simplifies analysis a lot since one does not need to consider a non-equilibrium solution in order to obtain these coefficients. This is in fact a requirement, which the interfacial resistances must satisfy: as being defined within the linear force–flux relations they should depend only on unperturbed quantities, i.e. equilibrium ones.

The evaporation and condensation often take place not only through planar interfaces, but also through curved ones, like the evaporation into a bubble. We do not restrict ourselves to the planar interfaces and give the expressions for the interfacial resistances for curved surfaces.

In the previous chapter we have obtained the overall interfacial resistances R^g and R^l using three different methods: an experiment-like procedure, a perturbation cell method and kinetic theory (only R^g). Those methods were found to be in a good agreement. In this chapter we compare them with the interfacial resistances found using integral relations, which relate these quantities to the local resistivities directly. We show that the agreement is also good.

We will focus on the heat and mass transfer through the interface of a two-phase mixture. We will not consider non-equilibrium perturbation along the surface. We will also assume the fluid to be non-viscous. Furthermore, we will focus on the stationary non-equilibrium perturbation. In [Sect. 8.2](#), we recall the expressions for the local and the excess entropy production found earlier. In [Sect. 8.3](#), we derive the integral relations in general form. It is convenient to use measurable heat and mass fluxes and we therefore show how to translate general relations to the resistances associated with the measurable fluxes in [Sect. 8.4](#).

In Sect. 8.5, we give the explicit expressions for a binary mixture and apply the analysis to the particular mixture of cyclohexane and n -hexane. Concluding remarks are given in Sect. 8.6.

8.2 The Entropy Production

8.2.1 Stationary States

Consider the total energy flux \mathbf{J}_e and the mass fluxes $\mathbf{J}_{\xi_i} \equiv \rho_i \mathbf{v}_i$ and $\mathbf{J}_m \equiv \rho \mathbf{v}$, where ρ_i and ρ are the density of i th component and the overall density respectively, while \mathbf{v}_i and $\mathbf{v} \equiv \sum_{i=1}^{n-1} \xi_i \mathbf{v}_i$ are the velocity of the i th component and the barycentric velocity, respectively. Furthermore, ξ_i is the mass fraction of i th component and n is the total number of components. In the stationary states these fluxes satisfy the relations

$$\nabla \cdot \mathbf{J}_e = 0, \quad \nabla \cdot \mathbf{J}_{\xi_i} = 0, \quad \nabla \cdot \mathbf{J}_m = 0 \quad (8.1)$$

As we are interested in transport through the surface we will restrict analysis to solutions of the form $\mathbf{J}(x_1, \mathbf{r}_{\parallel}) = (J(x_1), 0, 0)$, where \mathbf{J} is one of the above fluxes. Furthermore, x_1 is the normal coordinate to the surface and $\mathbf{r}_{\parallel} \equiv (x_2, x_3)$ are the tangential coordinates. In the case of normal transport all the quantities depend only on x_1 but not on \mathbf{r}_{\parallel} . For these solutions

$$\nabla \cdot \mathbf{J} = \nabla_{\perp} J = \frac{1}{h_1 h_2 h_3} \frac{d}{dx_1} (h_2 h_3 J) = 0 \quad (8.2)$$

where $h_i \equiv h_i(x_1, \mathbf{r}_{\parallel})$ are Lamé coefficients for curvilinear coordinates. It follows from Eq. 8.2 that

$$h_2(x_1) h_3(x_1) J(x_1) = h_2(x^s) h_3(x^s) J(x^s) \equiv h_2^s h_3^s J^s \quad (8.3)$$

where x^s is the chosen dividing surface and h_2^s and h_3^s are the Lamé coefficients on that dividing surface. We will suppress the superscript s for the flux J as long as it does not lead to confusion.

8.2.2 Local Entropy Production

Consider the local entropy production for the mixture interface found earlier, written for the case of transport in the direction through the interface¹

¹ Note, that $\sum_{i=1}^{n-1} J_i \nabla_{\perp} \frac{\psi_i}{T} = \sum_{i=1}^n J_i \nabla_{\perp} \frac{u_i}{T}$.

$$\sigma_s = J_q \nabla_{\perp} \frac{1}{T} - \sum_{i=1}^{n-1} J_i \nabla_{\perp} \frac{\psi_i}{T} \quad (8.4)$$

where T is the temperature, J_q the heat flux and $J_i \equiv \rho_i (\mathbf{v}_i - \mathbf{v}) = J_{\xi_i} - \xi_i J_m$ the diffusive mass flux, which satisfies the relation $\sum_{i=1}^n J_i = 0$. Furthermore, $\psi_i = \mu_i - \mu_n$, where μ_i is the chemical potential of the i th component. The heat flux is related to the total energy flux and to the measurable heat flux J'_q as

$$J_q = J_e - J_m (h + \mathbf{v}^2/2 - \mathbf{g} \cdot \mathbf{r}) = J'_q + \sum_{i=1}^n h_i J_i \quad (8.5)$$

Here h_i and h are the partial enthalpy of the i th component and the specific enthalpy respectively, while \mathbf{g} is the gravitational acceleration.

For the stationary transport through the interface, the Gibbs–Duhem relation has the following form (see Chap. 6 for details):

$$s \frac{\partial T}{\partial x_1} + \sum_{i=1}^n \xi_i \frac{\partial \mu_i}{\partial x_1} - v \frac{\partial \sigma_{11}}{\partial x_1} = 0 \quad (8.6)$$

where σ_{11} is an element of the thermodynamic pressure tensor $\sigma_{\alpha\beta}$. Together with the equation of motion,

$$\nabla_{\perp} \sigma_{11} + \rho \nabla_{\perp} (\mathbf{v}^2/2 - \mathbf{g} \cdot \mathbf{r}) = 0 \quad (8.7)$$

it gives

$$\sum_{i=1}^n \xi_i \left(\nabla_{\perp} \frac{\tilde{\mu}_i}{T} - \tilde{h}_i \nabla_{\perp} \frac{1}{T} \right) = 0 \quad (8.8)$$

where $\tilde{\mu}_i \equiv \mu_i + \mathbf{v}^2/2 - \mathbf{g} \cdot \mathbf{r}$ and $\tilde{h}_i \equiv h_i + \mathbf{v}^2/2 - \mathbf{g} \cdot \mathbf{r}$. Substituting Eq. 8.5 and J_i into Eq. 8.4 and using Eq. 8.8, one can express the local entropy production (8.4) in terms of the total energy flux:

$$\sigma_s = J_e \nabla_{\perp} \frac{1}{T} - \sum_{i=1}^n J_{\xi_i} \nabla_{\perp} \frac{\tilde{\mu}_i}{T} \quad (8.9)$$

and in terms of the measurable heat flux:

$$\sigma_s = J'_q \nabla_{\perp} \frac{1}{T} - \sum_{i=1}^{n-1} J_i \left(\nabla_{\perp} \frac{\psi_i}{T} - \eta_i \nabla_{\perp} \frac{1}{T} \right) \quad (8.10)$$

where $\eta_i \equiv \tilde{h}_i - \tilde{h}_n = h_i - h_n$. Note that the difference between partial enthalpies with a tilde is equal to the difference without the tilde. In stationary states Eqs. 8.9, 8.10 and 8.4 are completely equivalent expressions.

8.2.3 Excess Entropy Production

We recall the definition of the excess $\widehat{\phi}(x^s)$ of a density $\phi(x^s)$ per unit of volume in curvilinear coordinates (cf. Chap. 6)

$$\widehat{\phi}(x^s) \equiv \frac{1}{h_2^s h_3^s} \int_{x^{g,s}}^{x^{\ell,s}} dx_1 h_1 h_2 h_3 \phi^{\text{ex}}(x_1; x^s) \quad (8.11)$$

where

$$\phi^{\text{ex}}(x_1; x^s) \equiv \widehat{\phi}(x_1) - \phi^g(x_1) \Theta(x^s - x_1) - \phi^\ell(x_1) \Theta(x_1 - x^s) \quad (8.12)$$

Here x^s indicates the position of the chosen dividing surface while $x^{g,s}$ and $x^{\ell,s}$ are the boundaries of the interfacial region at the gas and liquid side, respectively. These boundaries are chosen such that $\phi(x^{g,s}) = \phi^g(x^{g,s})$ and $\phi(x^{\ell,s}) = \phi^\ell(x^{\ell,s})$ with a certain accuracy. Superscripts ℓ and g indicate the function ϕ extrapolated from the liquid and gas to the surface region.

Taking the excess of the local entropy production given by Eq. 8.9, we obtain

$$\widehat{\sigma}_s = J_e \left(\frac{1}{T^\ell} - \frac{1}{T^g} \right) - \sum_{i=1}^n J_{\xi_i} \left(\frac{\widetilde{\mu}_i^\ell}{T^\ell} - \frac{\widetilde{\mu}_i^g}{T^g} \right) \quad (8.13)$$

Here $T^\ell \equiv T^\ell(x^s)$ and $T^g \equiv T^g(x^s)$ are the temperatures extrapolated from the liquid and gas to the dividing surface. The analogous meaning have $\widetilde{\mu}_i^\ell$ and $\widetilde{\mu}_i^g$. All the quantities, both the fluxes and the forces, are evaluated at the dividing surface x^s .

Using Eq. 8.5 we obtain

$$\widehat{\sigma}_s = J_q^{\prime,g} \left(\frac{1}{T^\ell} - \frac{1}{T^g} \right) - \sum_{i=1}^n J_{\xi_i} \left[\left(\frac{\widetilde{\mu}_i^\ell}{T^\ell} - \frac{\widetilde{\mu}_i^g}{T^g} \right) - \widetilde{h}_i^g \left(\frac{1}{T^\ell} - \frac{1}{T^g} \right) \right] \quad (8.14)$$

and

$$\widehat{\sigma}_s = J_q^{\prime,\ell} \left(\frac{1}{T^\ell} - \frac{1}{T^g} \right) - \sum_{i=1}^n J_{\xi_i} \left[\left(\frac{\widetilde{\mu}_i^\ell}{T^\ell} - \frac{\widetilde{\mu}_i^g}{T^g} \right) - \widetilde{h}_i^\ell \left(\frac{1}{T^\ell} - \frac{1}{T^g} \right) \right] \quad (8.15)$$

where $J_q^{\prime,\ell}$ and $J_q^{\prime,g}$ are the measurable heat fluxes on the liquid and gas side respectively. Again Eqs. 8.14, 8.15 and 8.13 are completely equivalent in stationary states.

8.3 Integral Relations

Consider the local entropy production (8.9), each term in which has a form $J \nabla_\perp \phi$. Following the common procedure in non-equilibrium thermodynamics one can write the force–flux relations for those entropy productions. Since all the terms

have the same form, it is sufficient to consider only one force–flux pair. The phenomenological relation for that pair then reads

$$\nabla_{\perp}\phi(x_1) = r(x_1) J(x_1) \quad (8.16)$$

where $\nabla_{\perp}\phi \equiv \mathfrak{h}_1^{-1}(d\phi/dx_1)$. The corresponding term in the excess entropy production in Eq. 8.13 has a form $J(\phi^{\ell} - \phi^g)$. The phenomenological relation relation for this term reads

$$\phi^{\ell}(x^s) - \phi^g(x^s) = R(x^s) J(x^s) \quad (8.17)$$

For the general case, ϕ and J must be replaced by a set, as well as R and r must be replaced by the corresponding matrix.

Let us introduce excess operators \mathfrak{E}_n and \mathfrak{E}_r which we will apply to a quantity ϕ . Let

$$\mathfrak{E}_n\{\phi\} \equiv \int_{x^{g,s}}^{x^{\ell,s}} dx_1 \mathfrak{h}_1 \phi^{\text{ex}}(\mathbf{r}; x^s) \quad (8.18)$$

and

$$\mathfrak{E}_r\{\phi\} \equiv \mathfrak{h}_2^s \mathfrak{h}_3^s \int_{x^{g,s}}^{x^{\ell,s}} dx_1 \frac{\mathfrak{h}_1}{\mathfrak{h}_2 \mathfrak{h}_3} \phi^{\text{ex}}(\mathbf{r}; x^s) \quad (8.19)$$

where ϕ^{ex} is defined by Eq. 8.12. In cartesian coordinates the excess operators \mathfrak{E}_n , \mathfrak{E}_r and the excess $\hat{\phi}$, are given by the same expression when ϕ is a density per unit of volume. One should not confuse them however, since these operators have different meanings. The excess $\hat{\phi}$ may be applied only to a volume density ϕ and means the surface density. In contrast, neither $\mathfrak{E}_n\{\phi\}$ nor $\mathfrak{E}_r\{\phi\}$ need to be applied to a volume density. In Eq. 8.9, ϕ can be the inverse temperature or a chemical potential divided by the temperature.

Applying \mathfrak{E}_n operator to the both sides of Eq. 8.16,

$$\mathfrak{E}_n\{\nabla_{\perp}\phi(x_1)\} = \mathfrak{E}_n\{r(x_1) J(x_1)\} \quad (8.20)$$

leads to

$$\phi^{\ell}(x^s) - \phi^g(x^s) = \mathfrak{E}_r\{r\} J(x^s) \quad (8.21)$$

Comparing Eq. 8.21 with Eq. 8.17 we conclude that

$$R = \mathfrak{E}_r\{r\} \quad (8.22)$$

This is the general form of the integral relation between the resistivities r and the resistances R . Equation 8.21 together with Eq. 8.22 are the most important and

fundamental results of the chapter. The generalization to a set of ϕ and J is straightforward and will be applied in the rest of the chapter.

We then proceed to the explicit expressions for the phenological equations. The local entropy production (8.9) produces the following force–flux relations

$$\begin{aligned} \nabla_{\perp} \frac{1}{T} &= r_{qq}^e J_e + \sum_{i=1}^n r_{qi}^e J_{\xi_i} \\ -\nabla_{\perp} \frac{\tilde{\mu}_j}{T} &= r_{jq}^e J_e + \sum_{i=1}^n r_{ji}^e J_{\xi_i} \end{aligned} \quad (8.23)$$

where J_e and J_{ξ_i} as well as T and μ_j are evaluated at the current position x_1 . The excess entropy production (8.13) produces

$$\begin{aligned} \frac{1}{T^{\ell}} - \frac{1}{T^g} &= R_{qq}^e J_e + \sum_{i=1}^n R_{qi}^e J_{\xi_i} \\ -\left(\frac{\tilde{\mu}_j^{\ell}}{T^{\ell}} - \frac{\tilde{\mu}_j^g}{T^g} \right) &= R_{jq}^e J_e + \sum_{i=1}^n R_{ji}^e J_{\xi_i} \end{aligned} \quad (8.24)$$

where J_e and J_{ξ_i} as well as T and μ_j are evaluated at the dividing surface x^s . The off-diagonal coefficients of both sets satisfy the Onsager reciprocal relations.

Comparing Eq. 8.23 with 8.24 and using Eq. 8.21 together with Eq. 8.22 we may conclude that

$$\begin{aligned} R_{qq}^e &= \mathfrak{E}_r \{ r_{qq}^e \} \\ R_{qi}^e &= \mathfrak{E}_r \{ r_{qi}^e \} = \mathfrak{E}_r \{ r_{iq}^e \} = R_{iq}^e \\ R_{ji}^e &= \mathfrak{E}_r \{ r_{ji}^e \} = \mathfrak{E}_r \{ r_{ij}^e \} = R_{ij}^e \end{aligned} \quad (8.25)$$

Equation 8.25 represents integral relations for the resistance coefficients associated with the total energy flux.

8.4 Measurable Heat Fluxes

It is convenient to obtain the integral relations for the interface resistances associated with the measurable heat fluxes, rather than the total energy flux. We obtain the relations between the resistivities and between the resistances for the whole surface.

First a note regarding the dependence of the resistances on the reference state of for instance the enthalpy. Both R^e and r^e coefficients depend on the reference state, as they are the coefficients associated with the absolute fluxes. The coefficients R^g and r' , which will be defined below, are associated with the measurable fluxes and therefore independent of the reference state.

8.4.1 The Whole Surface

In order to obtain the resistances for the whole surface, we consider Eq. 8.14 for the entropy production in terms of the measurable heat flux on the gas side of the surface. The analysis for the liquid side is completely equivalent to the one done for the gas side.

The entropy production (8.14) produces the following phenomenological equations

$$\begin{aligned} \frac{1}{T^\ell} - \frac{1}{T^g} &= R_{qq}^g J'_q + \sum_{i=1}^n R_{qi}^g J_{\zeta_i} \\ - \left[\left(\frac{\tilde{\mu}_i^\ell}{T^\ell} - \frac{\tilde{\mu}_i^g}{T^g} \right) - \tilde{h}_i^g \left(\frac{1}{T^\ell} - \frac{1}{T^g} \right) \right] &= R_{jq}^g J'_q + \sum_{i=1}^n R_{ji}^g J_{\zeta_i} \end{aligned} \quad (8.26)$$

The resistances from Eqs. 8.26 and 8.24 are related, using Eq. 8.5 by

$$\begin{aligned} R_{qq}^e &= R_{qq}^g \\ R_{qi}^e &= R_{qi}^g - \tilde{h}_i^g R_{qq}^g \\ R_{ji}^e &= R_{ji}^g - \tilde{h}_i^g R_{jq}^g - \tilde{h}_j^g R_{qi}^g + \tilde{h}_i^g \tilde{h}_j^g R_{qq}^g \end{aligned} \quad (8.27)$$

Equations 8.26 and 8.24 are *linear* relations between the forces and the fluxes. In Eq. 8.27 we should therefore use coexistence values of the enthalpies.

Inverting Eq. 8.27 and using the equilibrium enthalpies we obtain for the resistances associated with the measurable heat flux

$$\begin{aligned} R_{qq}^g &= R_{qq}^e \\ R_{qi}^g &= R_{qi}^e + \tilde{h}_{i,\text{eq}}^g R_{qq}^e \\ R_{ji}^g &= R_{ji}^e + \tilde{h}_{i,\text{eq}}^g R_{jq}^e + \tilde{h}_{j,\text{eq}}^g R_{qi}^e + \tilde{h}_{i,\text{eq}}^g \tilde{h}_{j,\text{eq}}^g R_{qq}^e \end{aligned} \quad (8.28)$$

where $\tilde{h}_{i,\text{eq}} \equiv h_{i,\text{eq}}(x^s) - \mathbf{g} \cdot \mathbf{r}^s$ and all the quantities are evaluated at the chosen dividing surface.

8.4.2 Local Resistivities

In order to write the linear laws for the local forces and fluxes we use Eqs. 8.10 and 8.4. The entropy production (8.10) gives

$$\begin{aligned} \nabla_\perp \frac{1}{T} &= r'_{qq} J'_q + \sum_{i=1}^{n-1} r'_{qi} J_i \\ - \left[\nabla_\perp \frac{\psi_j}{T} - \eta_j \nabla_\perp \frac{1}{T} \right] &= r'_{jq} J'_q + \sum_{i=1}^{n-1} r'_{ji} J_i \end{aligned} \quad (8.29)$$

while the entropy production (8.4) gives

$$\begin{aligned}\nabla_{\perp} \frac{1}{T} &= r_{qq} J_q + \sum_{i=1}^{n-1} r_{qi} J_i \\ -\nabla_{\perp} \frac{\psi_j}{T} &= r_{jq} J_q + \sum_{i=1}^{n-1} r_{ji} J_i\end{aligned}\tag{8.30}$$

The local resistivities r and r' are related as follows

$$\begin{aligned}r'_{qq} &= r_{qq} \\ r'_{qi} &= r_{qi} + \eta_i r_{qq} \\ r'_{ji} &= r_{ji} + \eta_i r_{jq} + \eta_j r_{qi} + \eta_i \eta_j r_{qq}\end{aligned}\tag{8.31}$$

Again, we should use the equilibrium profiles for η_i .

We now relate the local resistivities associated with the measurable heat flux to the local resistivities associated with the total energy flux, similarly² to how it was done for the overall surface resistances. Comparing Eq. 8.29 with Eq. 8.23 we obtain

$$\begin{aligned}r^e_{qq} &= r'_{qq} \\ r^e_{qi} &= -r'_{qq} \tilde{h}_i - \sum_{k=1}^{n-1} r'_{qk} \zeta_k + r'_{qi}, \quad i = \overline{1, n-1} \\ r^e_{qn} &= -r'_{qq} \tilde{h}_n - \sum_{k=1}^{n-1} r'_{qk} \zeta_k \\ r^e_{ji} &= r'_{qq} \tilde{h}_j \tilde{h}_i + \sum_{k=1}^{n-1} \zeta_k \left(r'_{kq} \tilde{h}_i + r'_{qk} \tilde{h}_j \right) - \left(r'_{jq} \tilde{h}_i + r'_{qi} \tilde{h}_j \right) \\ &\quad + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r'_{kl} \zeta_k \zeta_l - \sum_{k=1}^{n-1} \zeta_k \left(r'_{ki} + r'_{jk} \right) + r'_{ji}, \quad j, i = \overline{1, n-1} \\ r^e_{ni} &= r'_{qq} \tilde{h}_n \tilde{h}_i + \sum_{k=1}^{n-1} \zeta_k \left(r'_{kq} \tilde{h}_i + r'_{qk} \tilde{h}_n \right) - r'_{qi} \tilde{h}_n \\ &\quad + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r'_{kl} \zeta_k \zeta_l - \sum_{k=1}^{n-1} r'_{ki} \zeta_k, \quad i = \overline{1, n-1} \\ r^e_{nn} &= r'_{qq} \tilde{h}_n^2 + \tilde{h}_n \sum_{k=1}^{n-1} \zeta_k \left(r'_{kq} + r'_{qk} \right) + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r'_{kl} \zeta_k \zeta_l\end{aligned}\tag{8.32}$$

² The details of this procedure are given in Appendix 8.A.

and comparing Eq. 8.30 with Eq. 8.23 we obtain

$$\begin{aligned}
 r_{qq}^e &= r_{qq} \\
 r_{qi}^e &= -r_{qq} \tilde{h} - \sum_{k=1}^{n-1} r_{qk} \zeta_k + r_{qi}, \quad i = \overline{1, n-1, n-1} \\
 r_{qn}^e &= -r_{qq} \tilde{h} - \sum_{k=1}^{n-1} r_{qk} \zeta_k \\
 r_{ji}^e &= r_{qq} \tilde{h}^2 + \tilde{h} \sum_{k=1}^{n-1} \zeta_k (r_{kq} + r_{qk}) - \tilde{h} (r_{jq} + r_{qi}) \\
 &\quad + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl} \zeta_k \zeta_l - \sum_{k=1}^{n-1} \zeta_k (r_{ki} + r_{jk}) + r_{ji}, \quad i, j = \overline{1, n-1} \\
 r_{ni}^e &= r_{qq} \tilde{h}^2 + \tilde{h} \sum_{k=1}^{n-1} \zeta_k (r_{kq} + r_{qk}) - \tilde{h} r_{qi} \\
 &\quad + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl} \zeta_k \zeta_l - \sum_{k=1}^{n-1} r_{ki} \zeta_k, \quad i = \overline{1, n-1} \\
 r_{nn}^e &= r_{qq} \tilde{h}^2 + \tilde{h} \sum_{k=1}^{n-1} \zeta_k (r_{kq} + r_{qk}) + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl} \zeta_k \zeta_l
 \end{aligned} \tag{8.33}$$

where $\tilde{h} \equiv h + v^2/2 - \mathbf{g} \cdot \mathbf{r}$. In all the expressions i and j are in the range $\overline{1, n-1}$.

Again, as in Eq. 8.27, we should use the enthalpy and the mass fraction profiles in Eqs. 8.32 and 8.33 in equilibrium. This leads to the relation $\tilde{h}_i = h_{i, \text{eq}} - \mathbf{g} \cdot \mathbf{r}$ and $\tilde{h} = h_{\text{eq}} - \mathbf{g} \cdot \mathbf{r}$.

8.5 Results for the Two Component Mixture

8.5.1 Integral Relations

In this section we deduce the integral relations for a binary mixture. The formulae given in this section is not restricted to a particular binary mixture however. We do that for the sake of convenience as well as because we will apply them to the particular two component mixture. For simplicity of notation we will not write subscript eq for enthalpies, keeping in mind that all of them should be evaluated at equilibrium.

The relations (8.32, 8.33) between resistivities in case of binary mixture take the following form

$$\begin{aligned}
r_{qq}^e &= r'_{qq} \\
r_{q1}^e &= -r'_{qq} \tilde{h}_1 + r'_{q1} \xi_2 \\
r_{q2}^e &= -r'_{qq} \tilde{h}_2 - r'_{q1} \xi_1 \\
r_{11}^e &= r'_{qq} \tilde{h}_1^2 - 2r'_{q1} \xi_2 \tilde{h}_1 + r'_{11} \xi_2^2 \\
r_{21}^e &= r'_{qq} \tilde{h}_2 \tilde{h}_1 + r'_{q1} (\xi_1 \tilde{h}_1 - \xi_2 \tilde{h}_2) - r'_{11} \xi_1 \xi_2 \\
r_{22}^e &= r'_{qq} \tilde{h}_2^2 + 2r'_{q1} \xi_1 \tilde{h}_2 + r'_{11} \xi_1^2
\end{aligned} \tag{8.34}$$

and

$$\begin{aligned}
r_{qq}^e &= r_{qq} \\
r_{q1}^e &= -r_{qq} \tilde{h} + r_{q1} \xi_2 \\
r_{q2}^e &= -r_{qq} \tilde{h} - r_{q1} \xi_1 \\
r_{11}^e &= r_{qq} \tilde{h}^2 - 2r_{q1} \xi_2 \tilde{h} + r_{11} \xi_2^2 \\
r_{21}^e &= r_{qq} \tilde{h}^2 + r_{q1} (\xi_1 - \xi_2) \tilde{h} - r_{11} \xi_1 \xi_2 \\
r_{22}^e &= r_{qq} \tilde{h}^2 + 2r_{q1} \xi_1 \tilde{h} + r_{11} \xi_1^2
\end{aligned} \tag{8.35}$$

respectively. Using Eqs. 8.25 and 8.28 we therefore obtain

$$\begin{aligned}
R_{qq}^g &= \mathfrak{E}_r \{ r'_{qq} \} \\
R_{q1}^g &= \mathfrak{E}_r \{ -r'_{qq} (h_1 - h_1^g) + r'_{q1} \xi_2 \} \\
R_{q2}^g &= \mathfrak{E}_r \{ -r'_{qq} (h_2 - h_2^g) - r'_{q1} \xi_1 \} \\
R_{11}^g &= \mathfrak{E}_r \{ r'_{qq} (h_1 - h_1^g)^2 - 2r'_{q1} \xi_2 (h_1 - h_1^g) + r'_{11} \xi_2^2 \} \\
R_{12}^g &= \mathfrak{E}_r \{ r'_{qq} (h_1 - h_1^g) (h_2 - h_2^g) + r'_{q1} (\xi_1 (h_1 - h_1^g) - \xi_2 (h_2 - h_2^g)) - r'_{11} \xi_1 \xi_2 \} \\
R_{22}^g &= \mathfrak{E}_r \{ r'_{qq} (h_2 - h_2^g)^2 + 2r'_{q1} \xi_1 (h_2 - h_2^g) + r'_{11} \xi_1^2 \}
\end{aligned} \tag{8.36}$$

and

$$\begin{aligned}
R_{qq}^g &= \mathfrak{E}_r \{ r_{qq} \} \\
R_{q1}^g &= \mathfrak{E}_r \{ -r_{qq} (h - h_1^g) + r_{q1} \xi_2 \} \\
R_{q2}^g &= \mathfrak{E}_r \{ -r_{qq} (h - h_2^g) - r_{q1} \xi_1 \} \\
R_{11}^g &= \mathfrak{E}_r \{ r_{qq} (h - h_1^g)^2 - 2r_{q1} \xi_2 (h - h_1^g) + r_{11} \xi_2^2 \} \\
R_{12}^g &= \mathfrak{E}_r \{ r_{qq} (h - h_1^g) (h - h_2^g) + r_{q1} (\xi_1 (h - h_1^g) - \xi_2 (h - h_2^g)) - r_{11} \xi_1 \xi_2 \} \\
R_{22}^g &= \mathfrak{E}_r \{ r_{qq} (h - h_2^g)^2 + 2r_{q1} \xi_1 (h - h_2^g) + r_{11} \xi_1^2 \}
\end{aligned} \tag{8.37}$$

Furthermore, we used that $\tilde{h}_i - \tilde{h}_i^g = h_i - h_i^g$ in both equations. Equations 8.36 and 8.37 are the integral relations for the resistances associated with the measurable heat flux for a binary mixture. They clearly do not depend on the reference chosen for the enthalpies.

We further need the values for the local resistivities. In Chap. 3, we developed a scheme which uses r coefficients in calculation. We therefore use the following expressions

$$\begin{aligned} r_{qq}(x) &= r_{qq}^g + (r_{qq}^\ell - r_{qq}^g) q_0(x) + \alpha_{qq}(r_{qq}^\ell + r_{qq}^g) q_1(x) \\ r_{q1}(x) &= r_{q1}^g + (r_{q1}^\ell - r_{q1}^g) q_0(x) + \alpha_{q1}(r_{q1}^\ell + r_{q1}^g) q_1(x) \\ r_{11}(x) &= r_{11}^g + (r_{11}^\ell - r_{11}^g) q_0(x) + \alpha_{11}(r_{11}^\ell + r_{11}^g) q_1(x) \end{aligned} \quad (8.38)$$

where $q_0(x)$ and $q_1(x)$ for each resistivity are modulatory curves for the resistivity profiles: $q_0(x)$ is a smooth arctan-like function which changes its value from 0 to 1 within the range $[x^{g,s}; x^{\ell,s}]$ and $q_1(x)$ is zero on the boundaries of the $[x^{g,s}; x^{\ell,s}]$ interval and has a peak proportional to the square gradient of the density inside this interval. Thus, the first two terms in each expression for the resistivity represents a smooth transitions from the gas bulk resistivity to the liquid bulk resistivity, while the third term represents a peak in the resistivity proportional to the square gradient of the density.

The bulk values r^ℓ and r^g are related to the measurable transport coefficients such as heat conductivity, the diffusion coefficient and the Soret coefficient. We refer for the details to Chap. 4.

8.5.2 Numerical Data

Consider the binary mixture of cyclohexane and n -hexane used earlier. Furthermore, we consider a planar interface between liquid and vapor. The mixture is in a box with gravity directed along axes x from left to right. The gas phase is therefore in the left part of the box and the liquid is in the right part.

We compare the resistivities found in Chap. 7 to the values obtained from Eq. 8.37. The relative difference between them is almost the same within the whole range of temperatures and chemical potential differences considered: $T = \{325, \dots, 335\}$ and $\psi = \{400, \dots, 1,000\}$. We therefore give the data only for $T_{\text{eq}} = 330$ and $\psi_{\text{eq}} = 700$. In Table 8.1 we give the relative errors for gas and liquid side coefficients. The data are obtained for α -amplitudes, values of which were found to fit best kinetic theory in Chap. 7.

The relative differences are not more then a few per mill. It is larger only for R_{12}^ℓ which is discussed below.

We also do a consistency check. Consider Eq. 8.26 for two component mixture, which has a form

Table 8.1 Relative error in percent between the gas- and liquid-side coefficients obtained by “perturbation cell” and “integral relations” methods at $T_{\text{eq}} = 330$ and $\psi_{\text{eq}} = 700$ for $\beta = 0.0002$ and $\alpha_{qq} = 9, \alpha_{1q} = 0, \alpha_{11} = 3$

Phase	R_{qq}	R_{11}	R_{22}	R_{q1}	R_{q2}	R_{12}
Gas	0.019	0.065	0.0589	0.020	0.020	0.097
Liquid	0.019	0.006	0.0004	0.036	0.035	6.234

Table 8.2 Relative error in percent between the left- and right-hand side of Eq. 8.39 for coefficients obtained by “perturbation cell” and “integral relations” methods at $T_{\text{eq}} = 330$ and $\psi_{\text{eq}} = 700$ for $\beta = 0.0002$ and $\alpha_{qq} = 9, \alpha_{1q} = 0, \alpha_{11} = 3$

Phase	Integral relations			Perturbation cell		
	X_q	X_1	X_2	X_q	X_1	X_2
Gas	0.059	0.038	0.297	0.047	0.087	0.867
Liquid	0.059	0.172	0.027	0.047	0.217	0.014

$$\begin{aligned}
 X_q &= R'_{qq} J'_q + R'_{q1} J'_{\xi_1} + R'_{q2} J'_{\xi_2} \\
 X_1 &= R'_{1q} J'_q + R'_{11} J'_{\xi_1} + R'_{12} J'_{\xi_2} \\
 X_2 &= R'_{2q} J'_q + R'_{21} J'_{\xi_1} + R'_{22} J'_{\xi_2}
 \end{aligned} \tag{8.39}$$

The left-hand side of each equation must be equal to the right-hand side. The difference therefore reflects the error. We give the relative error between the left and the right-hand side of Eq. 8.39 in percent in Table 8.2. As a testing perturbation, we used one of those used in the perturbation cell method.

Again, the relative difference is not more than a few per mill. Given that this is the case even for a few percent difference in one of the coefficients, we may conclude that the values of the forces are insensitive to the precise value of this resistivity coefficient. This also indicates that the value of this coefficient obtained in Chap. 7 has a 6% error. This does not necessarily affect, however, the accuracy of the integral relations.

8.6 Discussion and Conclusions

In this chapter we have derived integral relations for the resistances to the transport of heat and mass across the interface for mixtures. We have given relations between the local resistivity profiles and the overall interfacial resistances.

The integral relations make it possible to calculate the interfacial resistances in a relatively simple way, using only the equilibrium profiles of the system. This is important especially for mixtures, for which the computation of a non-equilibrium profiles is much more time consuming.

The integral relations give an insight in the origin of the interfacial resistances. According to Eqs. 8.36 and 8.37 the interfacial resistances depend on the variation of the enthalpy across the interface. The transport coefficients depend on the

equilibrium enthalpies which vary a lot through the interface. One can see from the above formulae, that the dependence on the enthalpy of evaporation (the difference between the enthalpies of the liquid and gas phases) is crucial not only for the diagonal diffusion coefficient, but also for the off-diagonal coefficients. This is an important result since cross coefficients are usually neglected in the description of the interfacial phenomena.

Another factor which affects the overall interfacial resistance is the local resistivity profile. For instance, for the heat resistance this is the only factor. It is noticeable that an interfacial resistance depends on the whole profile of a local resistivity, not only on its bulk values. It is therefore crucial to have complete information about the local resistivity profiles. We have used sums of a function that smoothly connects the liquid and the vapor values and a peak proportional to the square gradient of the density. In principle one can use any model for this and further investigation are required. We have shown in the previous chapter, by comparison with the predictions from kinetic theory, that the local resistivities do have a peak in their profile and that the overall resistances therefore depend on the amplitudes of these peaks. Within the current theory these amplitudes are adjustable parameters.

The integral relations are in fact mathematical equalities. Given the local resistivities defined through the local force–flux relations, for instance r^e from Eqs. 8.23 and 8.24 follows. One can therefore consider Eq. 8.25 as a definition of the overall interfacial resistances R^e used in Eq. 8.24. It means that the force–flux relations (8.26) for the whole surface follow from the local force–flux relations. One therefore does not need the excess entropy production Eq. 8.14 to obtain Eq. 8.24.

This allows us to use them as a test for the accuracy of the numerical solution of the non-equilibrium case. Given that both local and overall linear laws are true independently, the different methods to obtain the overall resistivities give information about the accuracy of the method. The discussion below Tables 8.1 and 8.2 is based on this observation.

8.A Local Resistivities

We need to relate the resistivities r^e from Eq. 8.23 to the resistivities r' from Eq. 8.29. This is done by comparing the coefficients at the same fluxes in these equations. To do this we need to translate the set of fluxes used in Eq. 8.29 $\{J'_q, J_1, \dots, J_{n-1}\}$, to the set of fluxes used in Eq. 8.23, $\{J_e, J_{\xi_1}, \dots, J_{\xi_n}\}$. This is done with the help of the relation

$$\begin{aligned} J_i &= J_{\xi_i} - \xi_i \sum_{k=1}^n J_{\xi_k} \\ J'_q &= J_e - \sum_{k=1}^n \tilde{h}_k J_{\xi_k} \end{aligned} \tag{8.40}$$

Substituting J'_q and J_i into the first of Eq. 8.29 we obtain

$$\nabla_{\perp} \frac{1}{T} = r'_{qq} J_e + \sum_{i=1}^{n-1} J_{\xi_i} \left(r'_{qi} - r'_{qq} \tilde{h}_i - \sum_{k=1}^{n-1} r'_{qk} \xi_k \right) - J_{\xi_n} \left(r'_{qq} \tilde{h}_n + \sum_{k=1}^{n-1} r'_{qk} \xi_k \right) \quad (8.41)$$

Comparing it with the first of Eq. 8.23 we obtain

$$\begin{aligned} r'_{qq} &= r^e_{qq} \\ r'_{qi} &= -r'_{qq} \tilde{h}_i - \sum_{k=1}^{n-1} r'_{qk} \xi_k + r'_{qi}, \quad i = \overline{1, n-1} \\ r'_{qn} &= -r'_{qq} \tilde{h}_n - \sum_{k=1}^{n-1} r'_{qk} \xi_k \end{aligned} \quad (8.42)$$

which are the first three equations of Eq. 8.32.

In order to obtain the remaining relations we consider the second of Eq. 8.23, which gives

$$\begin{aligned} - \sum_{j=1}^n \xi_j \nabla_{\perp} \frac{\tilde{\mu}_j}{T} &= J_e \sum_{j=1}^n r^e_{jq} \xi_j + \sum_{i=1}^n J_{\xi_i} \sum_{j=1}^n r^e_{ji} \xi_j \\ \left(-\nabla_{\perp} \frac{\tilde{\mu}_j}{T} \right) - \left(-\nabla_{\perp} \frac{\tilde{\mu}_n}{T} \right) &= J_e (r^e_{jq} - r^e_{nq}) + \sum_{i=1}^n J_{\xi_i} (r^e_{ji} - r^e_{ni}), \quad i = \overline{1, n-1} \end{aligned} \quad (8.43)$$

Furthermore, we use Eq. 8.8. Together with the second of Eq. 8.29 it gives

$$\begin{aligned} - \sum_{i=1}^n \xi_i \nabla_{\perp} \frac{\tilde{\mu}_i}{T} &= - \sum_{i=1}^n \xi_i \tilde{h}_i \nabla_{\perp} \frac{1}{T} \\ - \nabla_{\perp} \frac{\psi_j}{T} &= -\eta_j \nabla_{\perp} \frac{1}{T} + r'_{jq} J'_q + \sum_{i=1}^{n-1} r'_{ji} J_i \end{aligned} \quad (8.44)$$

Substituting $\nabla_{\perp}(1/T)$ from Eq. 8.41 and J'_q and J_i from Eq. 8.40 we obtain the left-hand side of Eq. 8.44 expressed in terms of the fluxes J_e and J_{ξ_i} and the resistivities r' . Comparing the result with Eq. 8.43 we obtain the following equations sets

$$\begin{aligned} \sum_{k=1}^n r^e_{kq} \xi_k &= -r'_{qq} \sum_{k=1}^n \xi_k \tilde{h}_k \\ r^e_{jq} - r^e_{nq} &= -r'_{qq} \eta_j + r'_{jq}, \quad j = \overline{1, n-1} \end{aligned} \quad (8.45a)$$

$$\begin{aligned}
\sum_{k=1}^n r_{kj}^e \zeta_k &= \left(r'_{qq} \tilde{h}_i + \sum_{k=1}^{n-1} r'_{qk} \zeta_k - r'_{qi} \right) \sum_{k=1}^n \zeta_k \tilde{h}_k \\
r_{ji}^e - r_{ni}^e &= \left(r'_{qq} \tilde{h}_i + \sum_{k=1}^{n-1} r'_{qk} \zeta_k - r'_{qi} \right) \eta_j \\
&\quad - \sum_{k=1}^{n-1} r'_{jk} \zeta_k - r'_{jq} \tilde{h}_i + r'_{ji}, \quad i = \overline{1, n-1}
\end{aligned} \tag{8.45b}$$

$$\begin{aligned}
\sum_{k=1}^n r_{kn}^e \zeta_k &= \left(r'_{qq} \tilde{h}_n + \sum_{k=1}^{n-1} r'_{qk} \zeta_k \right) \sum_{k=1}^n \zeta_k \tilde{h}_k \\
r_{jn}^e - r_{nn}^e &= \left(r'_{qq} \tilde{h}_n + \sum_{k=1}^{n-1} r'_{qk} \zeta_k \right) \eta_j \\
&\quad - \sum_{k=1}^{n-1} r'_{jk} \zeta_k - r'_{jq} \tilde{h}_n, \quad j = \overline{1, n-1}
\end{aligned} \tag{8.45c}$$

solving which we obtain the relations (8.46) between the remaining resistivities.

As one can confirm the symmetry of the r' -matrix leads to the symmetry of the r^e -matrix and vice versa. We therefore do not give the expressions for r_{jq}^e, r_{nq}^e and r_{jn}^e in Eq. 8.32.

The relations (8.33) between the r^e - and r -resistivities are derived in the similar manner.

$$\begin{aligned}
r_{jq}^e &= -r'_{qq} \tilde{h}_j - \sum_{k=1}^{n-1} r'_{kq} \zeta_k + r'_{jq}, \quad j = \overline{1, n-1} \\
r_{nq}^e &= -r'_{qq} \tilde{h}_n - \sum_{k=1}^{n-1} r'_{kq} \zeta_k \\
r_{ji}^e &= r'_{qq} \tilde{h}_j \tilde{h}_i + \sum_{k=1}^{n-1} \zeta_k \left(r'_{kq} \tilde{h}_i + r'_{qk} \tilde{h}_j \right) - \left(r'_{jq} \tilde{h}_i + r'_{qi} \tilde{h}_j \right) \\
&\quad + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r'_{kl} \zeta_k \zeta_l - \sum_{k=1}^{n-1} \zeta_k \left(r'_{ki} + r'_{jk} \right) + r'_{ji}, \quad j, i = \overline{1, n-1} \\
r_{jn}^e &= r'_{qq} \tilde{h}_j \tilde{h}_n + \sum_{k=1}^{n-1} \zeta_k \left(r'_{kq} \tilde{h}_n + r'_{qk} \tilde{h}_j \right) - r'_{jq} \tilde{h}_n \\
&\quad + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r'_{kl} \zeta_k \zeta_l - \sum_{k=1}^{n-1} r'_{jk} \zeta_k, \quad j = \overline{1, n-1} \\
r_{ni}^e &= r'_{qq} \tilde{h}_n \tilde{h}_i + \sum_{k=1}^{n-1} \zeta_k \left(r'_{kq} \tilde{h}_i + r'_{qk} \tilde{h}_n \right) - r'_{qi} \tilde{h}_n \\
&\quad + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r'_{kl} \zeta_k \zeta_l - \sum_{k=1}^{n-1} r'_{ki} \zeta_k, \quad i = \overline{1, n-1} \\
r_{nn}^e &= r'_{qq} \tilde{h}_n^2 + \tilde{h}_n \sum_{k=1}^{n-1} \zeta_k \left(r'_{kq} + r'_{qk} \right) + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r'_{kl} \zeta_k \zeta_l
\end{aligned} \tag{8.46}$$

Reference

1. Johannessen E, Bedeaux D (2006) Integral relations for the heat and mass transfer resistivities of the liquid–vapor interface. *Phys A* 370:258–274

Chapter 9

Conclusions and Perspectives

9.1 This Thesis

The aim of the thesis was to build a theoretical approach which allows to describe a fluid behavior during evaporation or condensation in multi-component mixtures. This was done in the seven previous chapters. Each chapter contains the detailed discussion and conclusions of the addressed issue. Here we summarize the work.

In order to describe a nonuniform equilibrium mixture with an interface between two coexisting phases, it is necessary to consider contributions to the Helmholtz energy which depend on the gradients of, for instance, the density. In [Chap. 2](#) we extended the analysis of van der Waals [1] and Cahn and Hilliard [2] to multi-component mixtures. Given the contributions to the Helmholtz energy proportional to the square gradients of component's densities or mass fractions, we gave explicit expressions for most thermodynamic quantities in the interfacial region. The analysis was done in three-dimensional space which does not restrict the applications to planar interfaces.

An important characteristic of the interfacial region is that the pressure has tensorial behavior. One can speak about the pressure tensor which can be represented as a sum of a scalar pressure and a tension tensor, $\sigma_{\alpha\beta} = p\delta_{\alpha\beta} + \gamma_{\alpha\beta}$. Both terms depend on the density gradients. Furthermore, the tension tensor

$$\gamma_{\alpha\beta}(\mathbf{r}) = \sum_{i,j=1}^n \kappa_{\rho_i\rho_j} \frac{\partial \rho_i}{\partial x_\alpha} \frac{\partial \rho_j}{\partial x_\beta} \quad (9.1)$$

is the quantity which determines the surface tension and has a significant importance in the interfacial dynamic description of a mixture.

Another important consequence of equilibrium being attained in a non-homogeneous region, is that one has to speak about two kinds of Gibbs relations between thermodynamic quantities which vary in space: the ordinary Gibbs relation

$$\delta u = T \delta s - p \delta v + \sum_{i=1}^{n-1} \psi_i \delta \zeta_i \quad (9.2)$$

being established between two different states at the same position, and the spatial Gibbs relation

$$\nabla_\beta u = T \nabla_\beta s - p \nabla_\beta v + \sum_{i=1}^{n-1} \psi_i \nabla_\beta \zeta_i + v \nabla_\alpha \gamma_{\alpha\beta} \quad (9.3)$$

being established between different positions in the same state. The former has the same form as usual Gibbs relation, but all the quantities in it have gradient contributions. The latter has an additional term which is nonzero only in the interfacial region.

In earlier work [3–5] a systematic extension of the square gradient model to non-equilibrium one-component systems was given. In Chap. 3 we gave an extension of this approach to multi-component non-equilibrium systems in the systematic context of non-equilibrium thermodynamics [6]. We discussed the thermodynamics of the homogeneous phases, the non-equilibrium Gibbs relation, the hydrodynamics of one-fluid mixtures, and the surface symmetry together with the resulting force–flux relations.

The research area of thermodynamic equations of homogeneous mixtures is very large. In this thesis we did not intend neither to cover it nor to give any contribution to it. We used common equations of state [7], which together with normalizing conditions (coinciding with the standard expressions in the limit of rare gases [8]), are expected to give an adequate description of homogeneous mixtures. Furthermore, we used common mixing rules. For particular systems which are not well described by these equations, one should use the appropriate ones. This does not affect the present analysis.

A crucial part of non-equilibrium thermodynamics is the Gibbs relation. In non-equilibrium one does not derive it and may only assume a reasonable expression. This relation should be therefore tested on further applications. We used the Gibbs relation

$$T \frac{ds}{dt} = \frac{du}{dt} - \sum_{i=1}^{n-1} \psi_i \frac{d\zeta_i}{dt} + p \frac{dv}{dt} - v(v_\beta - v_\beta^s) \frac{\partial \gamma_{\alpha\beta}}{\partial x_\alpha} \quad (9.4)$$

which is different from the common relation in homogeneous phase. It was chosen such that it is Galilean invariant and reduces to the above two equilibrium Gibbs relations. We were able to build a non-contradictory theory with a number of numerical predictions. It is therefore possible to test it in experiments and applications.

In the non-equilibrium description one obtains the expression for entropy production and the resulting force–flux relations. In principle, any thermodynamic force depend linearly on any thermodynamic flux. But according to the Curie

symmetry principle [9] coupling is allowed only between forces and fluxes of the same tensorial order. A thin surface is no longer three-dimensionally isotropic. Because its thickness is very small compared to the curvature radii, for many applications it may be considered as two-dimensionally isotropic. We have discussed how the two-dimensional isotropy modifies the phenomenological relations in the interfacial region and allows coupling which is different from the bulk one.

The local phenomenological coefficients may be measured in a bulk phase but not in the surface. One has therefore to model the continuous expressions for the phenomenological coefficients in the interfacial region. We used a form of these coefficients which has two terms: one is a smooth transition from one bulk value to another, the other term models a peak which is nonzero only in the interfacial region. The further calculations confirm that the local resistivities have to have a nonzero peak term in order to make the entropy production be nonnegative. This result was also observed for one-component systems [5, 10].

In Chap. 4 we applied the general analysis described in Chap. 3 to the binary mixture of cyclohexane and *n*-hexane. We used the square gradient model for the continuous description of a non-equilibrium surface and obtained numerical profiles of various thermodynamic quantities in various stationary state conditions. It was, for instance, shown that, like in one-component systems, the temperature profile has a peak or a dip in the interfacial region. Details of the numerical procedure were given and discussed.

The next step in the description was to make a link to a macroscopic non-equilibrium description of surfaces [11]. In such a description one uses the assumption that a surface under non-equilibrium conditions may be considered as an autonomous phase with its own temperature and other thermodynamic characteristics which are related by the common thermodynamic relation

$$u^s = T^s s^s - \gamma^s + \sum_{i=1}^n \mu_i^s \Gamma_i^s \quad (9.5)$$

where u^s, s^s, γ^s , and Γ_i^s are the Gibbs excess densities of the internal energy, entropy, pressure, and concentration, respectively. In Chap. 5 we focused on the verification of this hypothesis of local equilibrium of the surface. It uses temperature and chemical potentials of a surface and the excess densities. We gave a definition of the temperature and chemical potentials of the surface and verified that these quantities are independent of the choice of the dividing surface. We then verified numerically for a binary mixture that the surface in a stationary state satisfies Eq. 9.5. The excess densities are found to be in good approximation equal to their equilibrium values at the stationary state temperature and chemical potentials of the surface.

In the last three chapters we calculated the interfacial transfer coefficients for evaporation and condensation of mixtures. They show how the whole surface resists the transfer of heat and mass. We used the continuous profiles of various thermodynamic quantities, obtained in Chap. 4 using the square gradient model. Furthermore, we introduced the Gibbs surface and obtained the excess entropy

production for a surface. Following the traditional non-equilibrium thermodynamic approach, we introduced the surface transfer coefficients which we were able to determine from the continuous solution. The knowledge of these coefficients is important for industrial applications which involve transport through a surface, such as distillation. The square gradient approach gives an independent way to determine the transfer coefficients for surfaces. The general framework for this was established in [Chap. 6](#) for stationary states. We used different methods to obtain the overall interfacial resistances which are described in [Chaps. 7](#) and [8](#).

The analysis in [Chap. 7](#) used the numerical solution of a non-equilibrium stationary state, while in [Chap. 8](#) we derived integral relations between the local resistivity profiles and the overall interfacial resistances. For instance, for the thermal resistance in the case of planar surface we got

$$R_{qq} = \int_x dx r_{qq}^{\text{ex}} \quad (9.6)$$

which is the same as in one-component systems [[12](#)]. The number of coefficients in mixtures is larger and, for instance, for the thermal diffusion resistance to the second component of a binary mixture we got in the case of planar surface

$$R_{q2} = \int_x dx \{r_{qq}(h_2 - h_2^g) - r_{q1}\xi_1\}^{\text{ex}} \quad (9.7)$$

Similar relations were obtained for the other resistances.

The analysis presented in these chapters allowed us to make a number of statements regarding the interfacial heat and mass transfer resistances. By comparing our results with kinetic theory predictions [[13](#)] we showed in [Chap. 7](#) that local resistivity profiles must have a peak in the interfacial region. This peak has its origin in the density gradients. The results of both kinetic theory and molecular dynamics simulations [[10](#)] support the existence of small peaks in the local resistivities in the interfacial region. Next, having the diagonal coefficients matched to the values from kinetic theory, we found that the values of the cross resistivities are one order of magnitude higher than the ones from kinetic theory. This indicates that kinetic theory underestimates the interfacial transfer coefficients in real fluids, in agreement with earlier findings [[14](#)].

In [Chap. 8](#) we have shown that interfacial resistances depend among other things on the enthalpy profile across the interface. Since this variation is substantial (the enthalpy of evaporation is one of the main differences between liquid and vapor phases) the interfacial resistivities are also substantial. Particularly, the surface puts up much more resistance to the heat and mass transfer than the homogeneous phases over a comparable distance. This is the case not only for pure heat conduction and diffusion, but also for the cross effects like thermal diffusion.

9.2 Perspectives

The presented approach points to various further research. This includes considering phenomena within the presented framework as well as linking it to the other areas, outlined in the introduction.

First of all, the results of this thesis, supporting the work by Kjelstrup and Bedeaux [11], may be used for description of distillation processes. Experimental results would be useful to verify a number of assumptions which were made in our theory, particularly the non-equilibrium Gibbs relation and the peak in local resistivity profiles.

The next-door target is to study mixtures in different domains of the phase diagram as well as mixtures with different kinds of phase diagrams. Thus, it is interesting and important to study evaporation and condensation in mixtures with infinite dilution, not also with approximately equal distribution of components. It is also necessary to study mixtures with non-similar components. All this can be done applying the present theory directly. One has to choose an appropriate homogeneous thermodynamic description of a desired mixture and specify the desired domain in a phase space.

9.2.1 Applications and Extensions

We studied transport through the surface in detail. The established framework also allows us to study transport processes along the surface. This includes the study of phenomena such as slip, thermal slip and the Marangoni effect [15].

We did the numerical calculations for planar interfaces. The analysis presented has no such restriction on the geometry of the surface. We may therefore study evaporation of spherical droplets, and use the two-dimensional isotropy of the surface. A relevant application here is the nucleation of sub-micrometer droplets. There are many experiments and molecular dynamic simulations in that area, but again, not much work is available for mixtures. If the radius of a droplet is much larger than the interfacial thickness, the general analysis presented in the thesis may be applied to such a system directly. Including the appropriate curvature corrections it may also be applied to droplets with a radius comparable to the interfacial thickness.

We have studied in details the evaporation and condensation. The square gradient model for multi-component systems describes not only liquid–vapor coexistence and transport, but also mixing-demixing phenomena [16]. A relevant application is an osmotic pressure difference due to a temperature difference. The developed analysis may be applied to these phenomena directly as well.

Heat and mass transport through the surface are important in many biological systems [17]. Biological cells have a semi-penetrable surface which allows transport of different components, depending on the conditions. This is also a

mixing-demixing process. One may consider cells to have a 2D isotropic surface. The transport processes in structures, which in equilibrium do not pose the 2D isotropy, differs. Taking into account the symmetry of such surfaces, one may modify the force–flux relations and apply the analysis to, for instance, cylindrical cells.

We did not study chemical reactions at the surface in this thesis. They contribute to the entropy production and being scalar phenomena couple to the heat and mass transport through the surface [6]. This is the subject of active transport, a process also happening in biological systems [15].

There is a number of other transport processes which happen in non-equilibrium systems, particularly, the transport of charge [11]. This is of interest in many applications, such as fuel cells or electrolysis. The present theory may not be applied to them directly, but one may proceed along the lines of this work in order to get the description of these processes.

9.2.2 Relation to Other Fields

It is desirable to have an independent way to verify the non-equilibrium continuous description. This can be done using molecular dynamics simulations. Both the continuous description and molecular dynamics uses a small set of input parameters which are related. These are, for instance, the molecular diameter together with the depth of interaction potential in molecular dynamic simulations and transport coefficients together with the van der Waals mixture coefficients for continuous description. Both the continuous description and molecular dynamics allows one to obtain macroscopic surface properties within the theory developed by Kjelstrup and Bedeaux [11]. As a continuation of this work one may choose the same system both for the continuous description and for molecular dynamics and compare the resulting macroscopic properties. They must be consistent.

Another source of justification is the microscopic theoretical descriptions. A number of quantities come to the continuous mesoscopic description as parameters. These are, among others, the local resistivities and the gradient coefficients κ . It is possible in principle to obtain the values of the gradient coefficients from microscopic theories, either from the statistical mechanics [18], or from kinetic theory [19]. It would be nice to get expressions for these coefficients in mixtures from statistical mechanics. This, for instance, can give an idea for mixing rules of the gradients coefficients, which currently are just empirical expressions.

There are microscopic expressions for the bulk transfer coefficients, the Green–Kubo relations. One can also obtain the microscopic expressions for the overall interfacial resistances [15]. They are not available for the local interfacial resistivities, however. It would be nice to obtain the microscopic expressions for the resistivity profiles and, in particular, for the amplitudes of local resistivities.

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Appendix A

Symbols List and Notation Convention

Here we give the symbols used throughout the thesis. The meaning of the symbols used only in particular sections of the thesis or “foobar” symbols is explained in the text.

Vectorial quantities are typefaced bold, while scalar quantities are typefaced with the ordinary font. Tensorial quantities are usually typefaced with the ordinary font and two Greek indices are used as subscripts to distinguish them from scalars. We use the summation convention over double Greek subscripts.

All the quantities may have subscripts and superscripts, which specify the exact meaning of this quantity. Specific quantities may be per unit of mass, per unit of mol, or per unit of volume. We give the dimensionality for mass units associated quantities only. A thermodynamic quantity with a subscript indicating a component number is a partial specific quantity of those component Tables [A.1](#), [A.2](#), [A.3](#), [A.4](#).

Table A.1 Superscripts: indicate quantities, associated with

<i>b</i>	A bulk
<i>g</i>	Gas bulk
<i>ℓ</i>	Liquid bulk
<i>s</i>	An interface or a dividing surface
<i>m</i>	Mass specific quantity
<i>v</i>	Molar specific quantity
<i>v</i>	Density per unit of volume

Table A.2 Subscripts

0	Bulk quantity
i, j, k, n	Mixture component number
α, β	Cartesian coordinate component
\parallel	Parallel to the surface component of spatial coordinates
\perp	Perpendicular to the surface component of spatial coordinates
eq	Equilibrium quantity
q	Heat associated quantity

Table A.3 Operations

\equiv	Definition
\cdot	Contraction sign
$'$	Measurable quantity (for J'_q and r'); Spatial derivative (for all other quantities)
$\overline{1, n}$	Enumeration of all integers from 1 to n
$\hat{\phi}$	Excess of ϕ
$\tilde{\phi}, \phi^*$	Quantity, which has the meaning of ϕ but is different from ϕ according to the context
\hat{T}	Traceless part of a tensor T
∇	Nabla-operator
$\nabla_{\alpha}, \partial/\partial x_{\alpha}$	Partial derivative with respect to x_{α} coordinate
δ, ∂, d	Differentials
$\delta_{\alpha\beta}$	Kroneker symbol
$d\mathbf{r}$	Infinitesimal volume element
$d\mathbf{S}$	Infinitesimal external boundary element

Table A.4 Physical quantities

α	[-]	Amplitude of the local resistivity
β	[-]	A small number, rate of the deviation from equilibrium
Γ	[mol/m ²]	Relative adsorption
$\gamma_{\alpha\beta}$	[Pa]	Tension tensor
ζ	[-]	Mole fraction
\mathcal{K}	[J/kg], [J/m ³]	Square gradient contribution
$\kappa_{\rho\rho}$	[J m ⁵ /kg ²]	Square gradient coefficient associated with the overall density
$\kappa_{\rho\xi_i}$	[J m/kg]	Square gradient coefficients associated with the overall density and the fraction of i th component
$\kappa_{\xi_i\xi_j}$	[J/m ³]	Square gradient coefficients associated with the fractions of i th and j th components
$\kappa_{\rho_i\rho_j}$	[J m ⁵ /kg ²]	Square gradient coefficients associated with the densities of i th and j th components
Λ	[m]	De Broglie wavelength
λ	[J/(m K s)]	Heat conductivity
μ	[J/kg]	Chemical potential

(continued)

Table A.4 (continued)

v	[mol]	Number of moles
ξ	[-]	Mass fraction
$\pi_{\alpha\beta}$	[Pa]	Viscous pressure tensor
ρ	[kg/m ³]	Mass density
$\sigma_{\alpha\beta}$	[Pa]	Pressure tensor
σ_s	[J/(K m ³)]	Entropy production
ϕ		“Foobar” variable
ψ	[J/kg]	Reduced chemical potential (chemical potential difference)
A, B		van der Waals coefficients for mixture
a_{ij}, b_i		van der Waals coefficients for components
c	[mol/m ³]	Molar concentration
D	[m ² /s]	Diffusion coefficient
e	[J/kg]	Specific total energy
F	[J]	Total Helmholtz energy
f	[J/kg]	Specific Helmholtz energy
g	[J/kg]	Specific Gibbs energy
h	[J/kg]	Specific enthalpy
$\eta_{1, 2, 3}$	[-]	Lamé coefficients
J	[J/(s m ²)], [kg/s m ²]	Any flux (of matter, energy, heat)
J_q'	[J/(s m ²)]	Measurable heat flux
i, j	[-]	Component number
M	[kg/mol]	Molar mass
m	[kg]	Mass
n	[-]	Number of components
p	[Pa]	Pressure
\mathbf{r}	[m]	Position
r		Local resistivity coefficient
R		Overall interfacial resistance coefficient
R	[J/(K mol)]	Universal gas constant
S	[J/K]	Total entropy
s	[J/(K kg)]	Specific entropy
s_T	[1/K]	Soret coefficient
T	[K]	Temperature
U	[J]	Total internal energy
u	[J/kg]	Specific internal energy
V	[m ³]	Total volume
v	[m ³ /kg]	Specific volume
\mathbf{v}	[m/s]	Velocity
x	[m]	Cartesian coordinate

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