

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:

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

and an expression for p :

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

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 ζ , 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 $\nabla \zeta_k(\mathbf{r})$ 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

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

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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<http://www.springer.com/978-3-642-15265-8>

Multicomponent Interfacial Transport
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Evaporation and Condensation

Glavatskiy, K.

2011, XVIII, 174 p., Hardcover

ISBN: 978-3-642-15265-8