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Nonequilibrium properties of a two-dimensionally isotropic interface in a two-phase mixture as described by the square gradient model

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In earlier work a systematic extension of the van der Waals square gradient model to nonequilibrium one-component systems was given. In this work the focus was on heat and mass transfer through the liquid-vapor interface as caused by a temperature difference or an over- or underpressure. We will give an extension of this approach to multicomponent nonequilibrium systems in the systematic context of nonequilibrium thermodynamics. An explicit expression for the pressure tensor is derived valid also for curved surfaces. It is shown how the Gibbs relation should be modified in the interfacial region, in both equilibrium and nonequilibrium. The two-dimensional isotropy of a curved interface is discussed. Furthermore, we give numerically obtained profiles of the concentration, the mole fraction, and the temperature, which illustrate the solution for some special cases.

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I. 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]. In 1893 van der Waals [2,3] was the first to introduced 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 mole fraction in binary mixtures. As the Helmholtz energy density given by van der Waals is no longer considered to be a function of the local density or local densities alone, there is no local equilibrium in the traditional sense in the interfacial region. 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 and co-workers [5,6]. We refer to his thesis for the relevant references. The gradient model is often used for a system, in which properties vary in only one direction. We do not restrict ourselves in this manner and do the analysis for the three-dimensional system.

Because of the lack of local equilibrium, the extension of nonequilibrium thermodynamics to a continuous description of an interface is not straightforward. In earlier work [7–9], coauthored by one of us (D.B.), we were able to show that such an extension was 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 [10–12] in this context. Very little work has been done on systems with a varying temperature [12] and on two-phase systems, however. The systematic treatment of heat and mass transport through the liquid-vapor interface, along the lines sketched in [7–9], was, to our knowledge, new. In this paper we will extend this approach to multicomponent nonequilibrium mixtures in three dimensions. Because we consider three-dimensional systems, it is possible to derive systematically all system properties which were postulated in the one-dimensional description [7–9].

The traditional local equilibrium hypothesis implies that in nonequilibrium 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 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.

We will follow the traditional procedure used in nonequilibrium thermodynamics. This requires several issues to be clarified. In Sec. II we present the equilibrium thermodynamics as it follows from the square gradient model. This model has been widely applied to flat interfaces of one-component mixtures in equilibrium. We extend it to the multicomponent mixtures in three-dimensional space, such that the interface may be curved. We derive all the thermodynamic properties, necessary for the equilibrium description. Particularly, we derive the general form of the pressure tensor which contain the familiar "parallel" and "perpendicular" pressures as its components. The equilibrium gradient model needs the equation of state which is used to describe the homogeneous mixtures. We give examples of them in Sec. III within the framework of the one-fluid approach. An important issue is the numerical values for the parameters, used in the gradient model. For the mixture we use mixing rules, similar to those used in the equation of state. We discuss this in Appendix A.

After that we are able to extend the thermodynamic description to nonequilibrium systems. This is explained in Sec. IV. To be able to derive the entropy production one needs the Gibbs relation. We show that within the interfacial region one can speak about two kinds of the Gibbs relation: the ordinary Gibbs relation and the spatial Gibbs relation. We discuss in Sec. V how these two equilibrium relations are combined to the nonequilibrium Gibbs relation. In Sec. VI we give the hydrodynamic equations. We use the so-called one-fluid approach which has been shown [13,14] to be appropriate for common mixtures.

In Sec. VII we discuss the consequences of the surface symmetry (two-dimensional isotropy). After deriving the entropy production and using the Curie principle, we give the linear relations between the thermodynamic fluxes and forces in Sec. VIII. It is found that, for instance, the resistances for transport through and into the interfacial region will in general contain square gradient contributions. In Sec. IX we give for some examples numerically obtained concentrations, mole fraction, and temperature profiles for a binary mixture with stationary mass and heat transport through the interfacial region. Concluding remarks and a discussion are given in the last section.

II. EQUILIBRIUM SQUARE GRADIENT MODEL

A mixture can be described by mass densities and temperature T as independent variables. We will use $\rho(\mathbf{r})$ as the total mass density of the mixture or $v(\mathbf{r})=1/\rho(\mathbf{r})$ as the mass specific volume and $\{\xi_1(\mathbf{r}),\ldots,\xi_{n-1}(\mathbf{r})\}$ as the mass fractions of components. We will write ξ instead of the set of arguments $\{\xi_1,\ldots,\xi_{n-1}\}$ and $\boldsymbol{\nabla}\xi$ instead of the set $\{\boldsymbol{\nabla}\xi_1,\ldots,\boldsymbol{\nabla}\xi_{n-1}\}$ to simplify the formulas.

In the square gradient model the specific Helmholtz energy can be written as

$$f(\mathbf{r}) = f_0(T,\rho,\xi) + \mathcal{K}(\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi), \tag{2.1}$$

where

$$\mathcal{K}(\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi) \equiv \frac{1}{2}\frac{\kappa}{\rho(\mathbf{r})}|\boldsymbol{\nabla}\rho(\mathbf{r})|^2 + \sum_{i=1}^{n-1}\frac{\kappa_i}{\rho(\mathbf{r})}\boldsymbol{\nabla}\rho(\mathbf{r})\cdot\boldsymbol{\nabla}\xi_i(\mathbf{r}) + \frac{1}{2}\sum_{i,j=1}^{n-1}\frac{\kappa_{ij}}{\rho(\mathbf{r})}\boldsymbol{\nabla}\xi_i(\mathbf{r})\cdot\boldsymbol{\nabla}\xi_j(\mathbf{r}). \tag{2.2}$$

All coefficients κ, κ_i, and κ_{ij} are assumed to be independent of the temperature (they may depend on the density and the mass fractions). The density distributions are such that they minimize the total Helmholtz energy

$$F = \int_V d\mathbf{r}\,\rho(\mathbf{r})f(\mathbf{r}). \tag{2.3}$$

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 $i=\overline{1,n-1}$, and the total mass $m=\int_V d\mathbf{r}\,\rho(\mathbf{r})$ are constants. The problem of minimizing the functional (2.3), having n constraints, can be done using the Lagrange method. Thus we minimize the integral

$$\Omega = \int_V d\mathbf{r}\,\rho(\mathbf{r})\left[f(\mathbf{r}) - \mu_n - \sum_{i=1}^{n-1}\psi_i\xi_i(\mathbf{r})\right] \equiv -\int_V d\mathbf{r}\,p(\mathbf{r}). \tag{2.4}$$

Here μ_n and ψ_i, where $i=\overline{1,n-1}$ (all integers from 1 to $n-1$), are the Lagrange multipliers, which are the chemical potential of the nth component and the quantities $\psi_k=\mu_k-\mu_n$, which we will call the "reduced chemical potentials," respectively. The Lagrange procedure gives for the chemical potentials

$$\mu_n = \frac{\partial}{\partial\rho}[\rho(f_0+\mathcal{K})] - \sum_{i=1}^{n-1}\psi_i\xi_i - \boldsymbol{\nabla}\cdot\left(\kappa\,\boldsymbol{\nabla}\rho + \sum_{i=1}^{n-1}\kappa_i\boldsymbol{\nabla}\xi_i\right),$$

$$\psi_k = \frac{\partial}{\partial\xi_k}(f_0+\mathcal{K}) - \frac{1}{\rho}\boldsymbol{\nabla}\cdot\left(\kappa_k\boldsymbol{\nabla}\rho + \sum_{i=1}^{n-1}\kappa_{ik}\boldsymbol{\nabla}\xi_i\right), \tag{2.5}$$

$$k=\overline{1,n-1},$$

which are constant through the surface in equilibrium, and the scalar pressure

$$p(\mathbf{r}) = \rho^2\frac{\partial}{\partial\rho}(f_0+\mathcal{K}) - \rho\,\boldsymbol{\nabla}\cdot\left(\kappa\,\boldsymbol{\nabla}\rho + \sum_{i=1}^{n-1}\kappa_i\boldsymbol{\nabla}\xi_i\right), \tag{2.6}$$

which is not constant.

Multiplying the first of the equations in Eq. (2.5) with $\boldsymbol{\nabla}\rho(\mathbf{r})$ and the other $(n-1)$ ones with $\boldsymbol{\nabla}\xi_k(\mathbf{r})$ and summing them all up,[1] we obtain the expression

$$\frac{d\sigma_{\alpha\beta}(\mathbf{r})}{dx_\alpha} = 0, \tag{2.7}$$

where we use the summation convention over double Greek subscripts, which label the coordinate axes. The tensor

$$\sigma_{\alpha\beta}(\mathbf{r}) = p(\mathbf{r})\delta_{\alpha\beta} + \gamma_{\alpha\beta}(\mathbf{r}) \tag{2.8}$$

is the pressure tensor. Furthermore, the tensor

$$\gamma_{\alpha\beta}(\mathbf{r}) = \kappa\frac{\partial\rho(\mathbf{r})}{\partial x_\alpha}\frac{\partial\rho(\mathbf{r})}{\partial x_\beta} + \sum_{i=1}^{n-1}\kappa_i\left(\frac{\partial\xi_i(\mathbf{r})}{\partial x_\alpha}\frac{\partial\rho(\mathbf{r})}{\partial x_\beta} + \frac{\partial\rho(\mathbf{r})}{\partial x_\alpha}\frac{\partial\xi_i(\mathbf{r})}{\partial x_\beta}\right) + \sum_{i,j=1}^{n-1}\kappa_{ij}\frac{\partial\xi_i(\mathbf{r})}{\partial x_\alpha}\frac{\partial\xi_j(\mathbf{r})}{\partial x_\beta} \tag{2.9}$$

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.

It is known that at the surface one can speak about the "parallel" and the "perpendicular" pressure [1], so the pres-

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[1] This method is a generalization of the one, given by Yang *et al.* [15] for a one-component system.

[2] The explicit expression for the pressure tensor in the square gradient model for a multicomponent mixture was, to the best of our knowledge, not given before.

sure reveals tensorial behavior. For a flat surface, when all the properties change in one direction only—say, x—one can show that $\sigma_{xx}(x)$ is the "perpendicular" pressure and $p(x) = \sigma_{yy}(x) = \sigma_{zz}(x)$ is the "parallel" pressure. For curved surfaces such an identification, however, can in general not be made.

From expression (2.4) for $p(\mathbf{r})$, we can see that the Helmholtz energy given in Eq. (2.1) and the quantities which are given in Eqs. (2.5) and (2.6) are related in the following way:

$$f(\mathbf{r}) = \mu_n + \sum_{i=1}^{n-1} \psi_i \xi_i(\mathbf{r}) - p(\mathbf{r}) v(\mathbf{r}). \tag{2.10}$$

It is then natural to define the specific internal energy, enthalpy, and Gibbs energy densities as follows:

$$u(\mathbf{r}) \equiv f(\mathbf{r}) + s(\mathbf{r})T,$$

$$h(\mathbf{r}) \equiv u(\mathbf{r}) + p(\mathbf{r})v(\mathbf{r}) = \mu_n + \sum_{i=1}^{n-1} \psi_i \xi_i(\mathbf{r}) + s(\mathbf{r})T,$$

$$g(\mathbf{r}) \equiv f(\mathbf{r}) + p(\mathbf{r})v(\mathbf{r}) = \mu_n + \sum_{i=1}^{n-1} \psi_i \xi_i(\mathbf{r}), \tag{2.11}$$

where the entropy is given by

$$s(\mathbf{r}) = -\frac{\partial}{\partial T} f(\mathbf{r}) = -\frac{\partial}{\partial T} f_0(T, v, \xi_1, \ldots, \xi_{n-1}). \tag{2.12}$$

It is important to realize that the thermodynamic relations (2.11) are true in the interfacial region only by definition. Analogous definitions were used in [7–9] for a one-dimensional one-component system and gave satisfactory results.

III. EQUATION OF STATE FOR A HOMOGENEOUS ONE-FLUID MIXTURE

To obtain the homogeneous specific Helmholtz energy we use the most common one-fluid equations of state[3]: (i) van der Waals equation of state

$$p_W(T, c, \zeta) = \frac{RTc}{1 - B(\zeta)c} - A(T, \zeta)c^2, \tag{3.1}$$

(ii) Soave-Redlich-Kwong equation of state

$$p_{SRK}(T, c, \zeta) = \frac{RTc}{1 - B(\zeta)c} - \frac{A(T, \zeta)}{1 - B(\zeta)c} c^2, \tag{3.2}$$

and (iii) Peng-Robinson equation of state

$$p_{PR}(T, c, \zeta) = \frac{RTc}{1 - B(\zeta)c} - \frac{A(T, \zeta)}{1 + 2B(\zeta)c - B^2(\zeta)c^2} c^2. \tag{3.3}$$

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

$$A(T, \zeta) = \sum_{i,k=1}^{n} a_{ik}(T) \zeta_i \zeta_k,$$

$$B(\zeta) = \sum_{k=1}^{n} b_k \zeta_k, \tag{3.4}$$

where usually $a_{ik}(T) = \sqrt{a_i(T) a_k(T)}$, and $a_k(T)$ and b_k are the corresponding coefficients for pure substances. The matrix $a_{ik}(T)$ is symmetric in its indices.

To find the homogeneous molar Helmholtz energy $f_0^{\nu}(T, c, \zeta)$ we integrate the equations of state over the volume at constant temperature and molar fractions of the components. The superscript ν here indicates a molar quantity. The integration constant should be chosen such that the specific Helmholtz energy of the system with a small mixture's concentration $(c \to 0)$ is equal to the specific Helmholtz energy for a mixture of ideal gases. Integrating the equation of state and using Eq. (B7) in Appendix B, we obtain following expression for the homogeneous molar Helmholtz energy:

$$f_0^{\nu}(T, c, \zeta) = -RT \ln\left(\frac{e}{cN_A} \frac{w(T, \zeta)}{\Lambda^3(T, \zeta)} [1 - B(\zeta)c] \right) - A(T, \zeta) c \varphi(B(\zeta)c), \tag{3.5}$$

where $\varphi(\omega)$ has corresponding expression for each equation of state,

$$\varphi_W(\omega) = 1,$$

$$\varphi_{SRK}(\omega) = \frac{1}{\omega} \ln(1 + \omega),$$

$$\varphi_{PR}(\omega) = \frac{1}{2\sqrt{2}\omega} \ln\left(1 + \frac{2\sqrt{2}\omega}{1 + \omega(1 - \sqrt{2})} \right). \tag{3.6}$$

IV. NONEQUILIBRIUM SURFACE

To describe nonequilibrium inhomogeneous systems we shall assume that all the relations between thermodynamic variables valid in equilibrium, which were discussed in the previous sections, remain valid away from equilibrium. Away from the surface this is the usual assumption made in nonequilibrium thermodynamics. In the interfacial regions it extends this assumption to places where the gradient contributions become important. As is said in [16], the validity of such a hypothesis can be verified only by experiment.

In nonequilibrium the density $\rho(\mathbf{r}, t)$ [or, alternatively, the volume per unit of mass $v(\mathbf{r}, t)$] and 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 on both position and time. All the other thermodynamic quantities may depend on position and time via their dependence on the temperature $T(\mathbf{r}, t)$, density $\rho(\mathbf{r}, t)$, and mass fractions $\xi(\mathbf{r}, t)$, found in Secs. II and III.

New variables which appear in the nonequilibrium description are the velocities of each component

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[3] In Sec. III and Appendix B we use densities per mole: the total molar concentration c and the molar fractions $\{\zeta_1, \ldots, \zeta_{n-1}\} \equiv \zeta$. Other densities per mole are denoted by the superscript ν.

$\{\mathbf{v}_1(\mathbf{r},t),\ldots,\mathbf{v}_n(\mathbf{r},t)\}$. We will, however, use the barycentric velocity of the whole mixture,

$$\mathbf{v}(\mathbf{r},t) = \frac{1}{\rho(\mathbf{r},t)}\sum_{i=1}^{n}\rho_i(\mathbf{r},t)\mathbf{v}_i(\mathbf{r},t), \tag{4.1}$$

and the diffusion fluxes,

$$\mathbf{J}_k \equiv \rho_k(\mathbf{v}_k - \mathbf{v}), \quad k = \overline{1,n-1}, \tag{4.2}$$

as independent variables. The mass densities of the components are $\rho_k=\rho\xi_k$ for $k=\overline{1,n-1}$ and $\rho_n=\rho-\Sigma_{i=1}^{n-1}\rho_i$.

V. GIBBS RELATION

An important part of the nonequilibrium description is the relation between the rate of change of thermodynamic potentials and the independent thermodynamic variables—in other words, the Gibbs relation. As with other thermodynamic relations, it should be extended from the equilibrium one. We shall therefore discuss the equilibrium Gibbs relation first and then go to the nonequilibrium description.

A. Equilibrium Gibbs relation

In a nonhomogeneous equilibrium system the thermodynamic properties may change from one equilibrium state to another as well as from one point in space to another within the same equilibrium state. This means that we should formulate two Gibbs relations, which we will call the ordinary Gibbs relation and the spatial Gibbs relation respectively.

Consider the variation of the total Helmholtz energy, $\delta F(T,\rho(\mathbf{r}),\xi(\mathbf{r}),\boldsymbol{\nabla}\rho(\mathbf{r}),\boldsymbol{\nabla}\xi(\mathbf{r}))$, due to a variation of the variables and their gradients:

$$\delta F(T,\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi) = \int_V d\mathbf{r}\{f(T,\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi)\delta\rho + \rho\delta f(T,\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi)\}, \tag{5.1}$$

where

$$\delta f(T,\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi) = \frac{\partial f}{\partial T}\delta T + \frac{\partial f}{\partial \rho}\delta\rho + \sum_{i=1}^{n-1}\frac{\partial f}{\partial \xi_i}\delta\xi_i + \frac{\partial f}{\partial \boldsymbol{\nabla}\rho}\delta\boldsymbol{\nabla}\rho + \sum_{i=1}^{n-1}\frac{\partial f}{\partial \boldsymbol{\nabla}\xi_i}\delta\boldsymbol{\nabla}\xi_i \tag{5.2}$$

is the total thermodynamic differential of the specific Helmholtz energy with respect to the thermodynamic variables and their gradients. Given Eqs. (2.1), (2.5), and (2.6), Eq. (5.2) becomes

$$\delta f(T,\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi) = \frac{\partial f_0}{\partial T}\delta T + \frac{p}{\rho^2}\delta\rho + \sum_{i=1}^{n-1}\psi_i\delta\xi_i + \frac{1}{\rho}\boldsymbol{\nabla}\cdot\delta\Theta, \tag{5.3}$$

where

$$\delta\Theta(\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi) \equiv \left(\kappa\boldsymbol{\nabla}\rho + \sum_{i=1}^{n-1}\kappa_i\boldsymbol{\nabla}\xi_i\right)\delta\rho + \sum_{k=1}^{n-1}\left(\kappa_k\boldsymbol{\nabla}\rho + \sum_{i=1}^{n-1}\kappa_{ik}\boldsymbol{\nabla}\xi_i\right)\delta\xi_k. \tag{5.4}$$

The total Helmholtz energy variation becomes then

$$\delta F(T,\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi) = \int_V d\mathbf{r}\left\{f(T,\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi)\delta\rho + \rho\left(\frac{\partial f_0}{\partial T}\delta T + \frac{p}{\rho^2}\delta\rho + \sum_{i=1}^{n-1}\psi_i\delta\xi_i\right)\right\} \tag{5.5}$$

since the boundary integral $\int_S dS\,\mathbf{n}_s\cdot\delta\Theta$ disappears, because we can choose boundaries of the system such that the normal component of the density gradients are zero everywhere along the boundaries. We will interpret the expression in parentheses as the total thermodynamic differential of the specific Helmholtz energy:

$$\delta f(T,\rho,\xi,\boldsymbol{\nabla}\rho,\boldsymbol{\nabla}\xi) = \frac{\partial f_0}{\partial T}\delta T + \frac{p}{\rho^2}\delta\rho + \sum_{i=1}^{n-1}\psi_i\delta\xi_i \tag{5.6}$$

or alternatively

$$\delta f(T,v(\mathbf{r}),\xi_1(\mathbf{r}),\ldots,\xi_{n-1}(\mathbf{r})) = -s(\mathbf{r})\delta T - p(\mathbf{r})\delta v(\mathbf{r}) + \sum_{i=1}^{n-1}\psi_i\delta\xi_i(\mathbf{r}). \tag{5.7}$$

We note the ambiguity in the definition of the total thermodynamic differential of the specific Helmholtz energy. The different expressions (5.3) and (5.6) for δf give the same expression (5.5) for δF, due to the cancellation 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. We will use Eq. (5.6), remembering this ambiguity.

Equation (5.7) has the form of the usual Gibbs relation for a homogeneous mixture. This implies 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. (5.7) the ordinary Gibbs relation. With the help of Eqs. (2.10) and (5.7) we obtain the Gibbs-Duhem relation

$$s(\mathbf{r})\delta T - v(\mathbf{r})\delta p(\mathbf{r}) + \delta\mu_n + \sum_{i=1}^{n-1}\xi_i(\mathbf{r})\delta\psi_i = 0. \tag{5.8}$$

Using the fact that the temperature and chemical potentials are constant in equilibrium and using Eqs. (2.7) and (2.10) together with Eq. (2.8), we obtain

$$\nabla_\beta f(\mathbf{r}) = -p(\mathbf{r})\nabla_\beta v(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i \nabla_\beta \xi_i(\mathbf{r}) + v(\mathbf{r})\nabla_\alpha \gamma_{\alpha\beta}(\mathbf{r}). \tag{5.9}$$

We will call Eq. (5.9) the spatial Gibbs relation. As the temperature is independent of the position, the expected $-s(\mathbf{r})\nabla_\beta T$ term is zero.

For the internal energy defined above, the ordinary Gibbs relation reads

$$\delta u(s(\mathbf{r}),v(\mathbf{r}),\xi(\mathbf{r})) = T\delta s(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i \delta\xi_i(\mathbf{r}) - p(\mathbf{r})\delta v(\mathbf{r}) \tag{5.10}$$

and the spatial Gibbs relations reads

$$\nabla u(\mathbf{r}) = T\ \nabla\ s(\mathbf{r}) + \sum_{i=1}^{n-1} \psi_i\ \nabla\ \xi_i(\mathbf{r}) - p(\mathbf{r})\ \nabla\ v(\mathbf{r}) - v(\mathbf{r})\frac{\partial \gamma_{\alpha\beta}(\mathbf{r})}{\partial x_\alpha}. \tag{5.11}$$

Notice in particular the last contribution on the right-hand side, which is only unequal to zero in the interfacial region.

B. Nonequilibrium Gibbs relation

Similar to the description of a homogeneous fluid, we extend the equilibrium Gibbs relations in the simplest way. One needs to make one important observation before such an extension, however: the equilibrium equation (5.10) 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:

$$T(\mathbf{r},t)\frac{\partial s(\mathbf{r},t)}{\partial t} = \frac{\partial u(\mathbf{r},t)}{\partial t} - \sum_{i=1}^{n-1} \psi_i(\mathbf{r},t)\frac{\partial \xi_i(\mathbf{r},t)}{\partial t} + p(\mathbf{r},t)\frac{\partial v(\mathbf{r},t)}{\partial t}. \tag{5.12}$$

We similarly use the equilibrium spatial Gibbs relation for the specific internal energy, Eq. (5.11), for nonequilibrium case:

$$T(\mathbf{r},t)\ \nabla\ s(\mathbf{r},t) = \nabla u(\mathbf{r},t) - \sum_{i=1}^{n-1} \psi_i(\mathbf{r},t)\ \nabla\ \xi_i(\mathbf{r},t) + p(\mathbf{r},t)\ \nabla\ v(\mathbf{r},t) - v(\mathbf{r},t)\frac{\partial \gamma_{\alpha\beta}(\mathbf{r},t)}{\partial x_\alpha}. \tag{5.13}$$

Contracting Eq. (5.13) with $\mathbf{v}(\mathbf{r},t)$ and summing with Eq. (5.12) we find

$$T(\mathbf{r},t)\frac{ds(\mathbf{r},t)}{dt} = \frac{du(\mathbf{r},t)}{dt} - \sum_{i=1}^{n-1} \psi_i(\mathbf{r},t)\frac{d\xi_i(\mathbf{r},t)}{dt} + p(\mathbf{r},t)\frac{dv(\mathbf{r},t)}{dt} - v(\mathbf{r},t)\mathrm{v}_\beta(\mathbf{r},t)\frac{\partial \gamma_{\alpha\beta}(\mathbf{r},t)}{\partial x_\alpha}, \tag{5.14}$$

where we used the substantial (barycentric) time derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla. \tag{5.15}$$

Equation (5.14) is the Gibbs relation for the nonequilibrium two-phase mixture including the interface. One can show that it reduces to the Gibbs relation used by Bedeaux *et al.* [7] for the case of a one-component fluid. The above analysis gives more insight into 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.* This defined all quantities and gave all relations needed for a nonequilibrium description using a generalization of the hypothesis of local equilibrium. We will further omit the arguments $(\mathbf{r},t)$ to simplify the notation.

Before we proceed further, we shall discuss an important issue here. One may wonder why we use the Gibbs relations for the specific internal energy, not for the specific Helmholtz energy, to extend them to nonequilibrium analysis. The Gibbs relations for the specific Helmholtz energy can be extended to nonequilibrium in the following way:

$$\frac{\partial f(\mathbf{r},t)}{\partial t} = -s(\mathbf{r},t)\frac{\partial T(\mathbf{r},t)}{\partial t} + \sum_{i=1}^{n-1} \psi_i(\mathbf{r},t)\frac{\partial \xi_i(\mathbf{r},t)}{\partial t} - p(\mathbf{r},t)\frac{\partial v(\mathbf{r},t)}{\partial t}, \tag{5.16}$$

$$\nabla f(\mathbf{r},t) = \sum_{i=1}^{n-1} \psi_i(\mathbf{r},t)\ \nabla\ \xi_i(\mathbf{r},t) - p(\mathbf{r},t)\ \nabla\ v(\mathbf{r},t) + v(\mathbf{r},t)\frac{\partial \gamma_{\alpha\beta}(\mathbf{r},t)}{\partial x_\alpha}. \tag{5.17}$$

For the ordinary Gibbs relations, like in the homogeneous description, there is no preference in the thermodynamic potential. Given Eq. (2.11), the equilibrium ordinary Gibbs relations (5.10) and (5.7) are equivalent. This is also true for the equilibrium spatial Gibbs relations (5.11) and (5.9). The nonequilibrium analogous of Eq. (2.11) makes the nonequilibrium ordinary Gibbs relations (5.12) and (5.16) also to be equivalent. The situation is different for the nonequilibrium spatial Gibbs relations, however.

The nonequilibrium spatial Gibbs relations (5.13) and (5.17) are *not* equivalent. The reason for that is that Eq. (5.9) does not contain the term proportional to ∇T, since $\nabla T=0$ in equilibrium. In nonequilibrium $\nabla T(\mathbf{r},t)\neq 0$ and the spatial Gibbs relation should have a form

$$\nabla f(\mathbf{r},t) = -s(\mathbf{r},t)\,\nabla T(\mathbf{r},t) + \sum_{i=1}^{n-1} \psi_i(\mathbf{r},t)\,\nabla \xi_i(\mathbf{r},t) - p(\mathbf{r},t)\,\nabla v(\mathbf{r},t) + v(\mathbf{r},t)\frac{\partial \gamma_{\alpha\beta}(\mathbf{r},t)}{\partial x_\alpha}, \tag{5.18}$$

which is not the same as Eq. (5.17).

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 nonequilibrium.

VI. HYDRODYNAMICS OF A ONE-FLUID MIXTURE

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

$$\frac{d\rho}{dt} = -\rho\,\nabla\cdot\mathbf{v},$$

$$\rho\frac{d\xi_k}{dt} = -\nabla\cdot\mathbf{J}_k, \quad k = \overline{1,n-1}, \tag{6.1}$$

where the dot indicates a contraction.

The momentum conservation law, or the equation of motion, can be written as

$$\rho\frac{d\mathrm{v}_\beta}{dt} = -\frac{\partial(\sigma_{\alpha\beta} + \pi_{\alpha\beta})}{\partial x_\alpha} + \rho g_\beta, \tag{6.2}$$

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

The law of energy conservation is (see [16])

$$\rho\frac{de}{dt} + \nabla\cdot(\mathbf{J}_e - \rho\mathbf{v}e) = 0, \tag{6.3}$$

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

$$e(\mathbf{r},t) = u(\mathbf{r},t) + \tau(\mathbf{r},t) + \phi(\mathbf{r}). \tag{6.4}$$

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

We restrict ourselves 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 components 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, this is the case. Thus, the specific kinetic energy is

$$\tau(\mathbf{r},t) = \frac{1}{2}\mathrm{v}^2(\mathbf{r},t). \tag{6.5}$$

From momentum conservation we obtain

$$\rho\frac{d\tau}{dt} = -\mathrm{v}_\beta\frac{\partial(\sigma_{\alpha\beta} + \pi_{\alpha\beta})}{\partial x_\alpha} + \rho\mathbf{v}\cdot\mathbf{g}. \tag{6.6}$$

For the internal energy we get

$$\rho\frac{du}{dt} = -\nabla\cdot\mathbf{J}_q - \pi_{\alpha\beta}\mathrm{v}_{\beta\alpha} - p\,\nabla\cdot\mathbf{v} + \mathrm{v}_\beta\frac{\partial\gamma_{\alpha\beta}}{\partial x_\alpha}, \tag{6.7}$$

where $\mathrm{v}_{\beta\alpha} \equiv \partial\mathrm{v}_\beta/\partial x_\alpha$ and where

$$\mathbf{J}_q \equiv \mathbf{J}_e - \rho\mathbf{v}e - p\mathbf{v} - \Pi\cdot\mathbf{v} \tag{6.8}$$

is the total heat flux.

We write the Gibbs relation (5.14) in the form

$$T\rho\frac{ds}{dt} = \rho\frac{du}{dt} - \sum_{i=1}^{n-1}\rho\psi_i\frac{d\xi_i}{dt} + p\rho\frac{dv}{dt} - \mathrm{v}_\beta\frac{\partial\gamma_{\alpha\beta}}{\partial x_\alpha}. \tag{6.9}$$

Using previous equations and performing algebraic transformations we obtain

$$\rho\frac{ds}{dt} = -\nabla\cdot\left[\frac{1}{T}\left(\mathbf{J}_q - \sum_{k=1}^{n-1}\psi_k\mathbf{J}_k\right)\right] + \mathbf{J}_q\cdot\nabla\frac{1}{T} - \sum_{k=1}^{n-1}\mathbf{J}_k\cdot\nabla\frac{\psi_k}{T} - \frac{1}{T}\pi_{\alpha\beta}\mathrm{v}_{\beta\alpha}. \tag{6.10}$$

VII. 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 gradient. The two-phase equilibrium state is not three-dimensionally isotropic.

Special care should be taken to determine the normal direction to the surface. With the help of the equilibrium analysis one can obtain the equilibrium densities distributions 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 then 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 any more. 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 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 $Q^{(dr)}$. 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 C for the details.

Consider the entropy production, which has the form

$$\sigma_s = S^{(3s)}R^{(3s)} + V^{(3v)} \cdot W^{(3v)} + T^{(3t)}{:}\Pi^{(3t)}, \tag{7.1}$$

where the double dot indicates double contraction. To be able to use the 2D Curie principle one may proceed along the steps explained in [16]. To clarify this we shall write this expression as a combination of independent 2D scalars, vectors, and tensors. The details are given in Appendix C; 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 **n** on the surface. We use the subscripts ⊥ and ∥ for this quantities. Because of the 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 (we refer to Appendix C for the details). This will be indicated by superscripts $2r$ as explained above.

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

$$S^{(3s)} = S^{(2s)} \equiv S^{(s)}. \tag{7.2}$$

Any 3D vector $V^{(3v)}$ can be written as [cf. the notation in Eq. (C1)]

$$V^{(3v)} = (V_\perp^{(s)}, V_\parallel^{(2v)}). \tag{7.3}$$

Any 3D tensor $T^{(3t)}$ can be written as [cf. the notation in Eq. (C4)]

$$T^{(3t)} = \begin{pmatrix} T_{\perp\perp}^{(s)} & T_{\perp\parallel}^{(2v)} \\ T_{\parallel\perp}^{(2v)} & T_{\parallel\parallel}^{(2t)} \end{pmatrix} = \begin{pmatrix} T_{\perp\perp}^{(s)} & T_{\perp\parallel}^{(2v)} \\ T_{\parallel\perp}^{(2v)} & \frac{1}{2}(\mathrm{Tr}\ T_{\parallel\parallel}^{(2t)})U^{(2t)} + \overset{\circ}{T}{}_{\parallel\parallel}^{(2t)} \end{pmatrix}, \tag{7.4}$$

where “Tr” indicates the trace of a tensor.

Combining these components we obtain for the entropy production

$$\sigma_s = \sigma_{s,scal} + \sigma_{s,vect} + \sigma_{s,tens}, \tag{7.5}$$

where

$$\sigma_{s,scal} = S^{(s)}R^{(s)} + V_\perp^{(s)}W_\perp^{(s)} + T_{\perp\perp}^{(s)}\Pi_{\perp\perp}^{(s)} + \frac{1}{2}(\mathrm{Tr}\ T_{\parallel\parallel}^{(2t)})(\mathrm{Tr}\ \Pi_{\parallel\parallel}^{(2t)}),$$

$$\sigma_{s,vect} = V_\parallel^{(2v)} \cdot W_\parallel^{(2v)} + 2T_\#^{(2v)} \cdot \Pi_\#^{(2v)},$$

$$\sigma_{s,tens} = \overset{\circ}{T}{}_{\parallel\parallel}^{(2t)}{:}\overset{\circ}{\Pi}{}_{\parallel\parallel}^{(2t)}, \tag{7.6}$$

where $T_\#^{(2v)} \equiv \frac{1}{2}(T_{\parallel\perp}^{(2v)} + T_{\perp\parallel}^{(2v)})$ and we have used the symmetry of the tensor $T^{(3t)}$. The 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.

VIII. PHENOMENOLOGICAL EQUATIONS

A. Force-flux relations

Comparing Eq. (6.10) with the balance equation for the entropy,

$$\rho\frac{ds}{dt} = -\boldsymbol{\nabla} \cdot \mathbf{J}_s + \sigma_s, \tag{8.1}$$

we conclude that the entropy flux and the rate of entropy production are given by

$$\mathbf{J}_s = \frac{1}{T}\left(\mathbf{J}_q - \sum_{k=1}^{n-1} \psi_k \mathbf{J}_k\right), \tag{8.2}$$

$$\sigma_s = \mathbf{J}_q \cdot \boldsymbol{\nabla}\frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_k \cdot \boldsymbol{\nabla}\frac{\psi_k}{T} - \frac{1}{T}\pi_{\alpha\beta}\mathrm{v}_{\beta\alpha}. \tag{8.3}$$

According to the second law σ_s is non-negative. Comparing Eq. (8.3) with Eqs. (7.5) and (7.6) we can write the entropy production for a 2D-isotropic surface as the sum of two-dimensional scalar, vectorial, and tensorial contributions

$$\sigma_{s,scal} = J_{q,\perp}\boldsymbol{\nabla}_\perp\frac{1}{T} - \sum_{k=1}^{n-1} J_{i,\perp}\boldsymbol{\nabla}_\perp\frac{\psi_k}{T} - (\boldsymbol{\nabla}_\perp \mathrm{v}_\perp)\frac{1}{T}\pi_{\perp\perp}$$

$$- \frac{1}{2}(\boldsymbol{\nabla}_\parallel \cdot \mathbf{v}_\parallel)\frac{1}{T}(\mathrm{Tr}\ \pi_{\parallel\parallel}),$$

$$\sigma_{s,vect} = \mathbf{J}_{q,\parallel} \cdot \boldsymbol{\nabla}_\parallel\frac{1}{T} - \sum_{k=1}^{n-1} \mathbf{J}_{i,\parallel} \cdot \boldsymbol{\nabla}_\parallel\frac{\psi_k}{T} - 2\mathbf{v}_\# \cdot \frac{1}{T}\pi_\#,$$

$$\sigma_{s,tens} = (\overset{\circ}{\boldsymbol{\nabla}_\parallel \mathbf{v}_\parallel}) : \frac{1}{T} \overset{\circ}{\boldsymbol{\pi}}_{\parallel\parallel}, \tag{8.4}$$

where $\mathbf{v}_\# \equiv \frac{1}{2}(\boldsymbol{\nabla}_\parallel \mathrm{v}_\perp + \boldsymbol{\nabla}_\perp \mathbf{v}_\parallel)$.

The linear force-flux equations for the scalar force-flux pairs are

$$\begin{aligned}
\boldsymbol{\nabla}_\perp \frac{1}{T} &= R_{qq,\perp\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{qk,\perp\perp} J_{k,\perp} - R_{q\pi,\perp\perp} \pi_{\perp\perp} \\
&\quad - R_{q\pi,\perp\parallel} \frac{1}{2} (\mathrm{Tr}\ \pi_{\parallel\parallel}), \\
\boldsymbol{\nabla}_\perp \frac{\psi_i}{T} &= R_{iq,\perp\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{ik,\perp\perp} J_{k,\perp} - R_{i\pi,\perp\perp} \pi_{\perp\perp} \\
&\quad - R_{i\pi,\perp\parallel} \frac{1}{2} (\mathrm{Tr}\ \pi_{\parallel\parallel}), \\
\frac{1}{T} \boldsymbol{\nabla}_\perp \mathrm{v}_\perp &= R_{\pi q,\perp\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{\pi k,\perp\perp} J_{k,\perp} - R_{\pi\pi,\perp\perp} \pi_{\perp\perp} \\
&\quad - R_{\pi\pi,\perp\parallel} \frac{1}{2} (\mathrm{Tr}\ \pi_{\parallel\parallel}), \\
\frac{1}{T} (\boldsymbol{\nabla}_\parallel \cdot \mathbf{v}_\parallel) &= R_{\pi q,\parallel\perp} J_{q,\perp} - \sum_{k=1}^{n-1} R_{\pi k,\parallel\perp} J_{k,\perp} - R_{\pi\pi,\parallel\perp} \pi_{\perp\perp} \\
&\quad - R_{\pi\pi,\parallel\parallel} \frac{1}{2} (\mathrm{Tr}\ \pi_{\parallel\parallel}).
\end{aligned} \tag{8.5}$$

For the vectorial force-flux pairs they are

$$\begin{aligned}
\mathbf{J}_{q,\parallel} &= L_{qq,\parallel\parallel} \boldsymbol{\nabla}_\parallel \frac{1}{T} - \sum_{k=1}^{n-1} L_{qk,\parallel\parallel} \boldsymbol{\nabla}_\parallel \frac{\psi_k}{T} - L_{q\pi,\parallel\#} \frac{1}{T} \mathbf{v}_\#, \\
\mathbf{J}_{i,\parallel} &= L_{iq,\parallel\parallel} \boldsymbol{\nabla}_\parallel \frac{1}{T} - \sum_{k=1}^{n-1} L_{ik,\parallel\parallel} \boldsymbol{\nabla}_\parallel \frac{\psi_k}{T} - L_{i\pi,\parallel\#} \frac{1}{T} \mathbf{v}_\#, \\
2\boldsymbol{\pi}_\# &= L_{\pi q,\#\parallel} \boldsymbol{\nabla}_\parallel \frac{1}{T} - \sum_{k=1}^{n-1} L_{\pi i,\#\parallel} \boldsymbol{\nabla}_\parallel \frac{\psi_k}{T} - L_{\pi\pi,\#\#} \frac{1}{T} \mathbf{v}_\#,
\end{aligned} \tag{8.6}$$

and for the tensorial force-flux pairs they are

$$\overset{\circ}{\boldsymbol{\pi}}_{\parallel\parallel} = L_\pi \frac{1}{T} (\overset{\circ}{\boldsymbol{\nabla}_\parallel \mathbf{v}_\parallel}) . \tag{8.7}$$

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 [17] 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 given form.

B. Phenomenological coefficients

The Onsager relations for the phenomenological coefficients are

$$\begin{gathered}
R_{qk,\perp\perp} = R_{kq,\perp\perp}, \quad L_{qk,\parallel\parallel} = L_{kq,\parallel\parallel}, \\
R_{q\pi,\perp\perp} = R_{\pi q,\perp\perp}, \quad L_{q\pi,\parallel\#} = L_{\pi q,\#\parallel}, \\
R_{q\pi,\perp\parallel} = R_{\pi q,\parallel\perp}, \quad L_{ik,\parallel\parallel} = L_{ki,\parallel\parallel}, \\
R_{ik,\perp\perp} = R_{ki,\perp\perp}, \quad L_{i\pi,\parallel\#} = L_{\pi i,\#\parallel}, \\
R_{i\pi,\perp\perp} = R_{\pi i,\perp\perp}, \\
R_{i\pi,\perp\parallel} = R_{\pi i,\parallel\perp}, \\
R_{\pi\pi,\perp\parallel} = R_{\pi\pi,\parallel\perp}.
\end{gathered} \tag{8.8}$$

As the ordinary Onsager relations, these are the consequence of 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 and 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 simulated. 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:

$$R = R^I + (R^{II} - R^I) \frac{\varphi - \varphi^I}{\varphi^{II} - \varphi^I} + \alpha (R^{II} + R^I) \frac{|\boldsymbol{\nabla}\varphi|^2}{|\boldsymbol{\nabla}\varphi_{eq}|^2_{\max}}, \tag{8.9}$$

where R^I and R^{II} are the resistivities for the coexisting homogeneous phases 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 $|\boldsymbol{\nabla}\varphi_{eq}|_{\max}$ 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 of an excess resistivity in the interfacial region. Particularly one can observe this fact in the molecular dynamic simulations [18]. The exact form of this term may be debated. It was chosen to model a rise of the resistivity in the interfacial region. The $|\boldsymbol{\nabla}\varphi|^2$ factor makes this term significant only in the interfacial region. It is scaled with $|\boldsymbol{\nabla}\varphi_{eq}|^2_{\max}$ in order to make this factor dimensionless and not far from unity. The $(R^{II}+R^I)$ factor gives the average value of the resistivity of both phases. The dimensionless factor α determines the magnitude of this effect. The homogeneous resistivities R^I and R^{II} are the known functions of the mass fraction and the temperature along the plane of coexistence.

For the conductivities used in Eqs. (8.6) and (8.7) one may use expressions analogous to Eq. (8.9). The conductivities along the surface are expected to be additive [17]. 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. Below we will only consider positive α's.

IX. TYPICAL PROFILES FOR THE BINARY MIXTURE

In order to illustrate the results which one can obtain using the above procedure, we have applied it to a special case. This requires a number of approximations connected to the specific mixture and geometry. We consider a flat liquid-vapor interface of the binary mixture of cyclohexane (first component) and n-hexane (second component) in nonequilibrium stationary conditions using the van der Waals equation of state. We only consider fluxes and gradients in the direction normal to the surface. Furthermore, we neglect viscous contributions. The force-flux relations then reduce to

$$\frac{d}{dx}\frac{1}{T} = R_{qq}J_q - R_{q1}J_1,$$

$$\frac{d}{dx}\frac{\psi}{T} = R_{1q}J_q - R_{11}J_1. \tag{9.1}$$

The differential equations for the temperature, density, and fraction profiles were solved using a numerical method for a two-point boundary-value problem. This was done using a collocation method implemented in the Matlab function bvp4c [19]. In this procedure we used the equilibrium profiles found previously as an initial state. Further details of the solution procedure will be given in the following paper. The numerical values of the homogeneous resistivities were taken from [20]. In all cases the integrated molar content for both components was kept equal to the equilibrium value.

The first aspect we will try to clarify is the influence of the additional resistivity to transport. We consider in particular two cases. In the first only, α_{qq}, the α factor for the heat resistivity coefficient R_{qq}, is unequal to zero, and in the second only, α_{11}, the α factor for the diffusion resistivity coefficient R_{11}, is unequal to zero. In Figs. 1–3 we plot the total molar concentration, the mole fraction, and the temperature for the case that only $\alpha_{qq} \neq 0$. The system is brought out of equilibrium by reducing the pressure on the vapor side to $0.95p_{eq}$, where p_{eq} is the equilibrium pressure. The temperatures on both ends of the box are kept equal to the equilibrium temperature T_{eq}. In Fig. 1 we see that the total molar concentration does not depend on the value of α_{qq} very much. This is different for the mole fraction which increases about 2% on the vapor side when α_{qq} increases from 0 to 10.

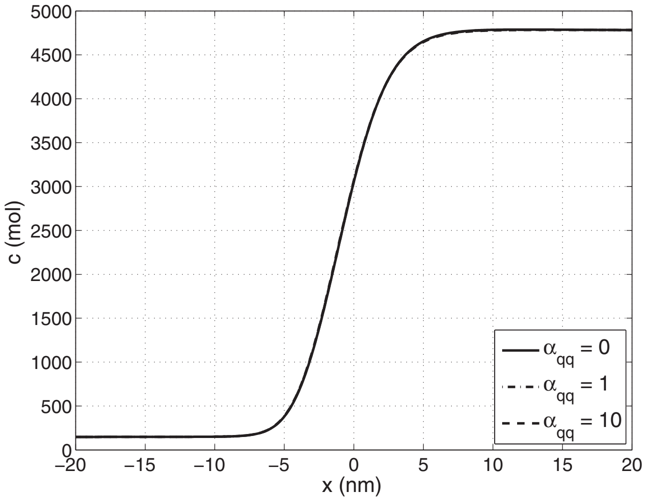

FIG. 1. Molar concentration profile for different α_{qq} at $p=0.95p_{eq}$ and $T_g=T_\ell=T_{eq}$.

The temperature decreases due to the evaporation. In all cases the extrapolated temperature in the liquid is higher then the value in the vapor, where we extrapolate to the inflection 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 the extrapolated profiles has increased to about 3 °C.

In Figs. 4 and 5 we plot the mole fraction and the temperature for the case that only $\alpha_{11} \neq 0$. Further conditions are the same as in the previous example. We did not plot the total molar concentration which is not very different from the one given in Fig. 1. 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 °C.

The third example considers the $\alpha_{qq} \neq 0$ case when the vapor pressure and temperature are kept equal to the equilibrium values and the liquid temperature is 5% higher then the

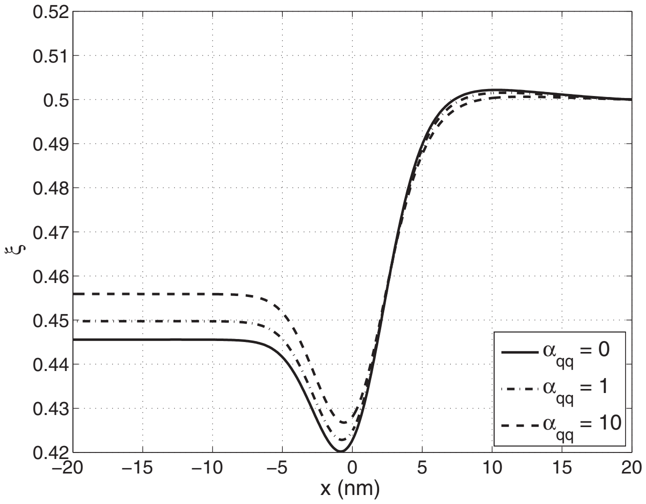

FIG. 2. Molar fraction profile for different α_{qq} at $p=0.95p_{eq}$ and $T_g=T_\ell=T_{eq}$.

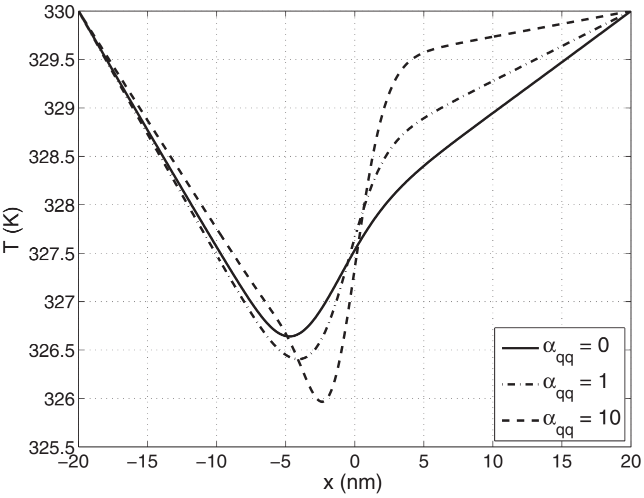

FIG. 3. Temperature profile for different α_{qq} at $p=0.95p_{eq}$ and $T_g=T_\ell=T_{eq}$.

equilibrium value. The total concentration profile is again similar to Fig. 1 and not given. Figures 6 and 7 give the mole fraction and temperature profiles. The change in the mole fraction went up to 12%. The temperature jump goes up to about 20 °C.

As a fourth example, we consider the $\alpha_{11}\neq 0$ case when the vapor pressure and temperature are kept equal to the equilibrium values and the liquid temperature is 5% higher then the equilibrium value. The total concentration profile is still similar to Fig. 1 and not given. Figures 8 and 9 give the mole fraction and temperature profiles. One can notice again the more dramatic behavior of the mole fraction and temperature profiles for large values of α_{11}.

Next we will discuss the influence of the pressure. We choose both α_{qq} and α_{11} equal to 1 for this case. The total concentration profiles are again similar to Fig. 1 and not given. In Figs. 10 and 11 we give the mole fraction and temperature profiles. The temperature profile goes down for evaporation and up for condensation as expected. The mole fraction in the vapor rises a little bit for condensation and decreases for evaporation.

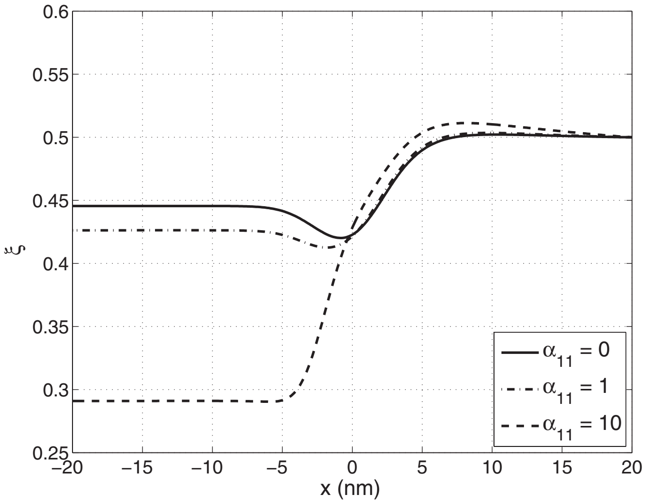

FIG. 4. Molar fraction profile for different α_{ii} at $p=0.95p_{eq}$.

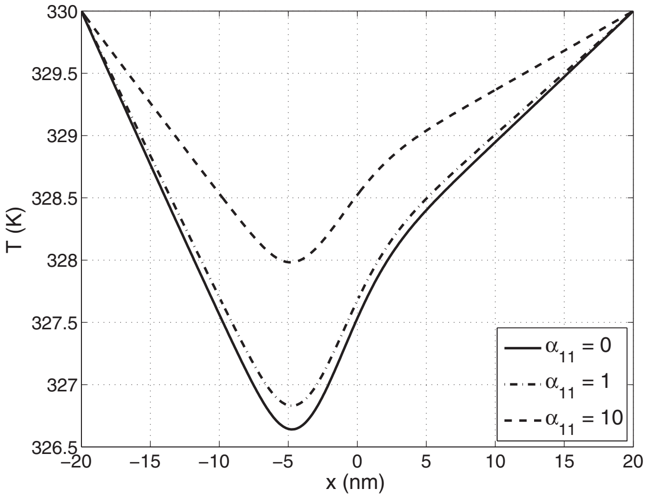

FIG. 5. Temperature profile for different α_{ii} at $p=0.95p_{eq}$.

In the last case we consider the influence of the temperature on the liquid side (see Figs. 12 and 13). The total concentration profile is again similar to Fig. 1 and not given. Lowering (raising) T_ℓ gives evaporation (condensation). This lowers (raises) the temperature on the vapor side as expected. The mole fraction decreases (raises) about 5% for condensation (evaporation). This is the opposite of what happens in the previous case.

X. DISCUSSION AND CONCLUSIONS

In this paper we have built the framework for the nonequilibrium description of the surface within the square gradient model. This required the following important steps.

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 multicomponent mixtures. The condition which the system should satisfy in equilibrium is that the total

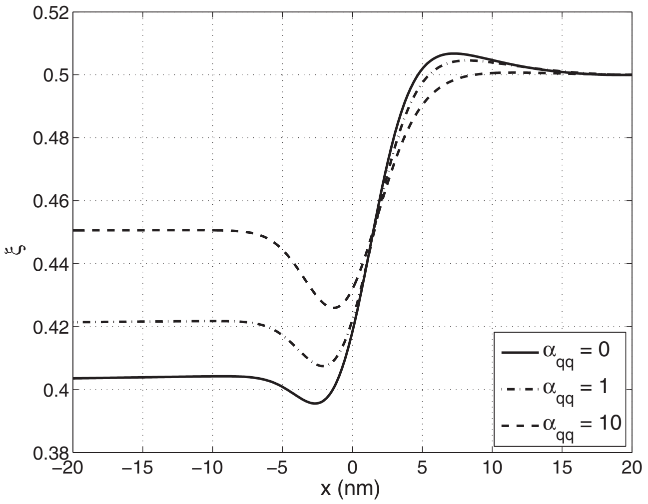

FIG. 6. Molar fraction profile for different α_{qq} at $p=p_{eq}$, $T_g=T_{eq}$, and $T_\ell=1.05T_{eq}$.

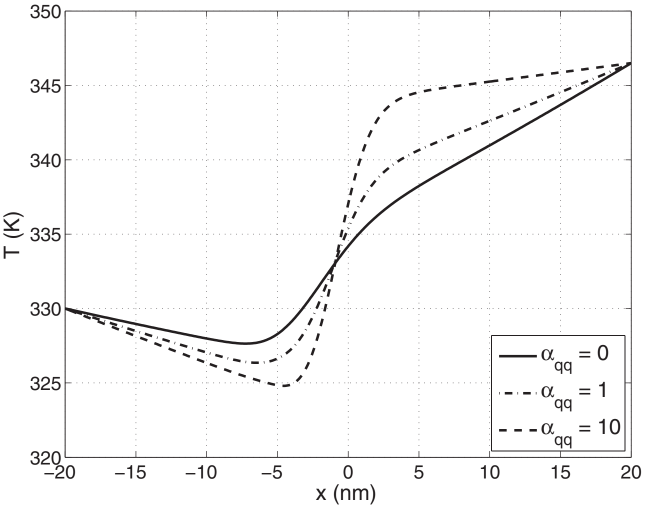

FIG. 7. Temperature profile for different α_{qq} at $p=p_{eq}$, $T_g=T_{eq}$, and $T_\ell=1.05T_{eq}$.

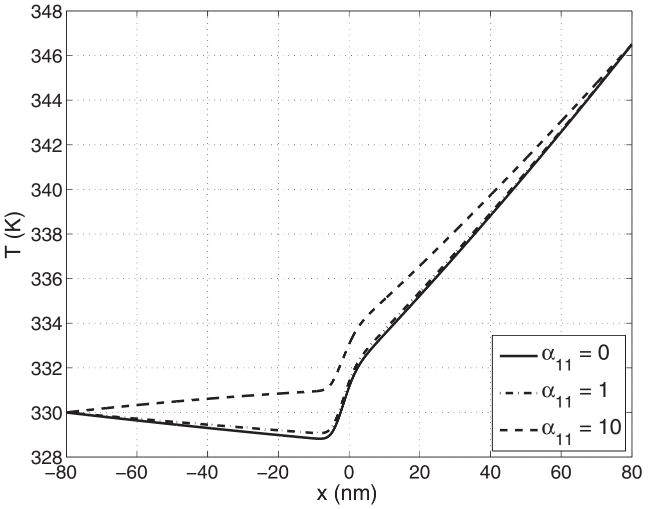

FIG. 9. Temperature profile for different α_{ii} at $p=p_{eq}$, $T_g=T_{eq}$, and $T_\ell=1.05T_{eq}$.

Helmholtz energy be minimal. With the help of the Lagrange method it was possible to derive the equations which the profile distribution should satisfy, given the fixed total mass 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.

It was 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. This means that local equilibrium for such a system is not satisfied. The local behavior of the mixture is determined not only by its local properties but also by its nearest surroundings. Moreover, in contrast to the homogeneous description, the local properties now vary in the space.

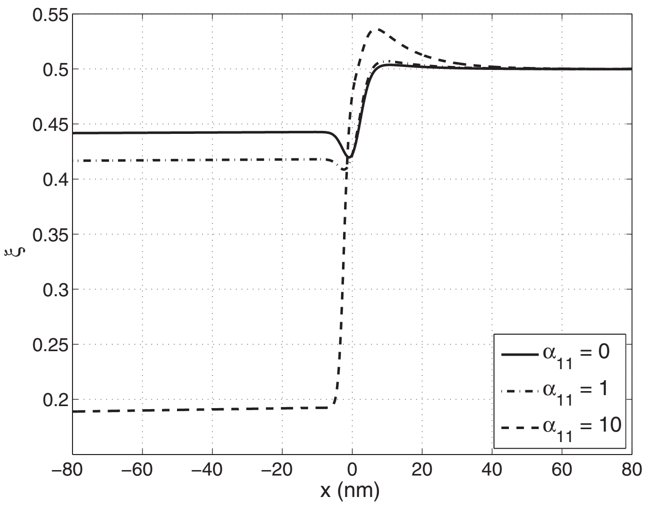

FIG. 8. Molar fraction profile for different α_{ii} at $p=p_{eq}$, $T_g=T_{eq}$, and $T_\ell=1.05T_{eq}$.

The equilibrium analysis gives the basis to extend the description to nonequilibrium systems.

An important part of the thermodynamic description is the relations between the rate of change of the thermodynamic variables: the Gibbs relations. In contrast to a homogeneous system, for an inhomogeneous system, in particular the interfacial region, thermodynamic variables vary also in space. 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 to speak also about the rates of change of the thermodynamic variables in space: the spatial 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 does not contribute to the ordinary Gibbs relations. Thus, the ordinary Gibbs relations have the ordinary form of the Gibbs relations for the homogeneous mixture. As the spatial derivatives of the temperature, chemical potentials, and pressure tensor are zero in equilibrium, we can determine the spatial Gibbs relation. The

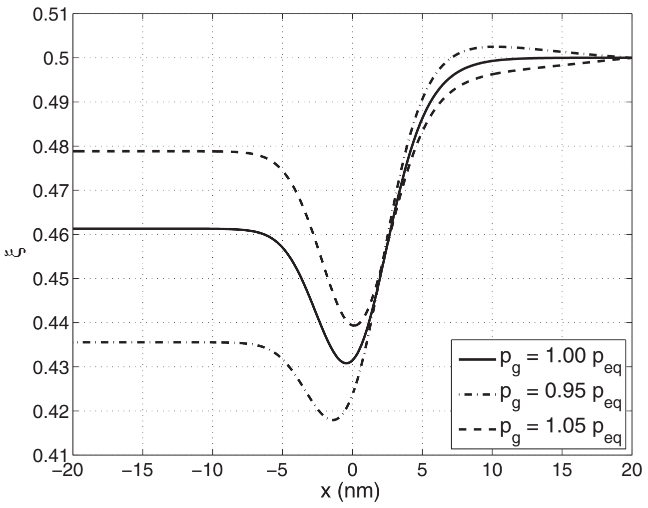

FIG. 10. Molar fraction profile for different p at $T_g=T_\ell=T_{eq}$.

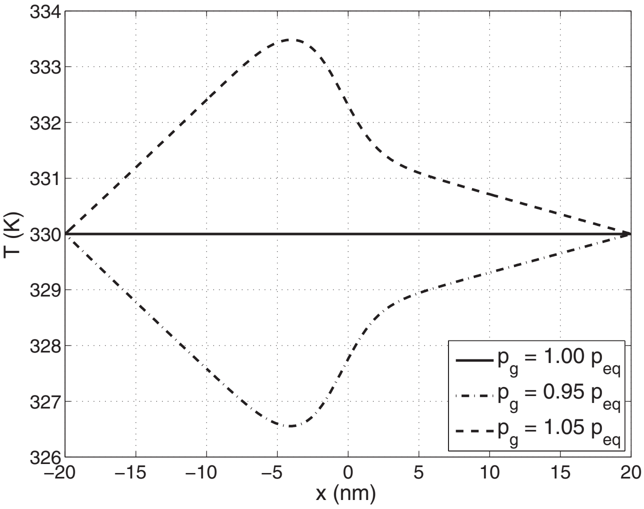

FIG. 11. Temperature profile for different p at $T_g = T_\ell = T_{eq}$.

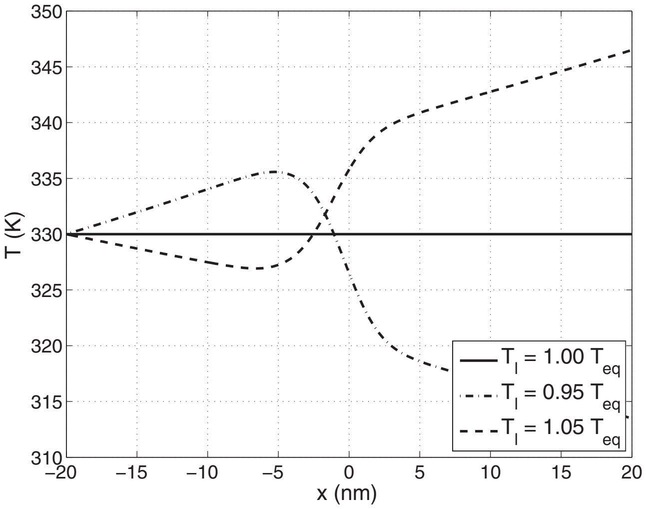

FIG. 13. Temperature profile for different T_ℓ at $T_g = T_{eq}$ and $p = p_{eq}$.

new term which appears because of the inhomogeneity is $\boldsymbol{\nabla}_\alpha \gamma_{\alpha\beta}(\mathbf{r})$, which is only unequal to zero close to the surface.

The next important step is to extend the equilibrium Gibbs relations to nonequilibrium. It was shown that the ordinary Gibbs relation corresponds to the partial time dependence of the thermodynamic variables and the spatial Gibbs relation corresponds to the partial space dependence of the thermodynamic variables. Combining these two equations we were able to write the nonequilibrium Gibbs relation. One should be careful understanding the Gibbs relation for a nonequilibrium inhomogeneous system. Unlike a homogeneous system, the properties may depend on position and time independently. That is the reason why one should distinguish the ordinary and spatial Gibbs relations. The differential between two states in the same spatial point corresponds to the partial time differential, not to the total time differential. Because the spatial Gibbs relation differs from the ordinary one, we have an essentially new term in the nonequilibrium Gibbs relation.

For the nonequilibrium 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. It is interesting that the components of the fluxes normal to the surface are scalar and couple therefore to reactions in the interfacial region. This is related to active transport, a phenomenon of great importance. We do not explicitly consider a reacting system in this paper, but may do so in a future publication. Having all these equations the nonequilibrium description of the surface is complete.

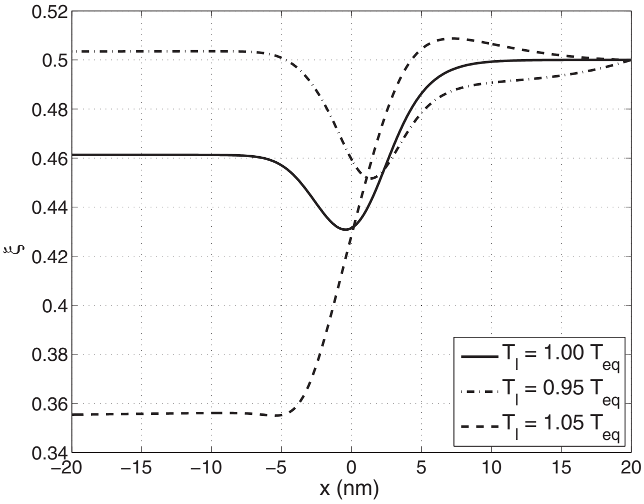

FIG. 12. Molar fraction profile for different T_ℓ at $T_g = T_{eq}$ and $p = p_{eq}$.

We applied the description to the special case of stationary heat and mass transport through and into a surface. Transport along the surface is in many respects like a two-dimensional analog of flow in a homogeneous medium. The presence of the surface has more influence on transports in the normal direction. We find that there is, for instance, a strong effect of the surface on the temperature and the concentration profiles. This effect increases when we increase the contribution proportional to the square gradient of the order parameter to the resistivity in the interfacial region.

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 multicomponent systems. Nonequilibrium molecular dynamic simulations of evaporation and condensation can 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 into 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 nonequilibrium molecular dynamic simulations and the discrete macroscopic description using the excess densities introduced by Gibbs [21]. In a future paper we intend to 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 [8]. 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 nonequilibrium thermodynamic a description of the surfaces this property is essential [22,23].

APPENDIX A: THE GRADIENT COEFFICIENTS

For a mixture modeling it is important to know the numerical values of the gradient coefficients. All these coefficients are in principle known functions of the densities. In practice they are not known for mixtures. Only the values for pure components are more or less known. Thus, it is necessary to express the cross coefficients in a form such that we can approximate them using pure-component values. From the equilibrium analysis for the specific quantities per unit of volume, which can be done analogously as was done in Sec. II, one can see that κ^v_{ij} are simply related to the pure-component coefficients. The superscript v here indicates quantities used in the description per unit of volume. On the other hand, the mass coefficients κ, κ_i, and κ_{ij} are related to the volume coefficients κ^v_{ij} as follows:

$$\kappa = \sum_{i,j=1}^{n-1} \xi_i \xi_j \mathrm{k}^v_{ij} + 2\sum_{i}^{n-1} \xi_i \mathrm{k}^v_i + \mathrm{k}^v,$$

$$\kappa_i = \rho \sum_{j=1}^{n-1} \xi_j \mathrm{k}^v_{ij} + \rho \mathrm{k}^v_i,$$

$$\kappa_{ij} = \rho^2 \mathrm{k}^v_{ij}, \tag{A1}$$

where

$$\mathrm{k}^v_{ij} \equiv \kappa^v_{ij} + \kappa^v_{nn} - \kappa^v_{in} - \kappa^v_{nj},$$

$$\mathrm{k}^v_i \equiv \kappa^v_{in} - \kappa^v_{nn},$$

$$\mathrm{k}^v \equiv \kappa^v_{nn}. \tag{A2}$$

Now we can introduce so-called mixing rules for the gradient coefficients. We will assume that, for instance, $\kappa^v_{ii} = \kappa^v_i$ is the coefficient for the pure component i. Cross coefficients can then be approximated by one of the so-called mixing rule for the gradient coefficients. We will assume the mixing rule

$$\kappa^v_{ij} = \sqrt{\kappa^v_i \kappa^v_j}. \tag{A3}$$

This mixing rule for the volume coefficients is analogous to the mixing rule for a_{ik} given in Sec. III.

APPENDIX B: HELMHOLTZ ENERGY OF A MIXTURE OF IDEAL GASES

According to [24] the total Helmholtz energy of a homogeneous mixture of ideal gases is

$$F_{0,id}[T,c,\zeta] = -RT\sum_{k=1}^{n} \nu_k \ln\left(\frac{e w_k(T)}{c_k N_A \Lambda_k^3(T)}\right), \tag{B1}$$

where ν_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:

$$\Lambda_k(T) \equiv \hbar N_A \sqrt{2\pi/M_k RT},$$

$$w_k(T) \equiv \sum_{\ell} \exp(-\varepsilon_k^{\ell}/k_B T), \tag{B2}$$

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:

$$F_{0,id}[T,c,\zeta] = -\nu RT \ln\left(\frac{e w(T,\zeta)}{c N_A \Lambda^3(T,\zeta)}\right) - RT\sum_{k=1}^{n} \nu_k \ln\left(\frac{c}{c_k}\frac{\Lambda^3(T)}{\Lambda_k^3(T,\zeta)}\frac{w_k(T)}{w(T,\zeta)}\right), \tag{B3}$$

where c is the total molar density of the mixture,

$$\Lambda(T,\zeta) \equiv \hbar N_A \sqrt{2\pi/M(\zeta)RT} \tag{B4}$$

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

$$M(\zeta) = \sum_{k=1}^{n} \zeta_k M_k = M_n + \sum_{k=1}^{n-1} \zeta_k (M_k - M_n) \tag{B5}$$

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

$$f_{0,id}(T,c,\zeta) = -RT \ln\left(\frac{e w(T,\zeta)}{c N_A \Lambda^3(T,\zeta)}\right) - RT\sum_{k=1}^{n} \zeta_k \ln\left[\zeta_k^{-1}\left(\frac{M_k}{M(\zeta)}\right)^{3/2}\frac{w_k(T)}{w(T,\zeta)}\right]. \tag{B6}$$

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

$$f_{0,id}(T,c,\zeta) = -RT \ln\left(\frac{e w(T,\zeta)}{c N_A \Lambda^3(T,\zeta)}\right), \tag{B7}$$

where

$$w(T,\zeta)=\exp\left\{\sum_{k=1}^{n}\zeta_k\ln\left[\zeta_k^{-1}\left(\frac{M_k}{M(\zeta)}\right)^{3/2}w_k(T)\right]\right\} \tag{B8}$$

can be considered as a mixing rule for the w. We note that Eq. (B7) together with Eq. (B8) does not impose any assumptions: it is nothing but Eq. (B6) written with the help of one-fluid terms.

APPENDIX C: TWO-DIMENSIONAL ISOTROPIC COMPONENTS IN THE THREE-DIMENSIONAL TENSORIAL QUANTITIES

As in Sec. VII, 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 $Q^{(dr)}$. 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, $Q^{(2t)}$ indicates the two-dimensional tensor—i.e., the quantity $\left(\begin{smallmatrix} q_{11} & q_{12}\\ q_{21} & q_{22}\end{smallmatrix}\right)$, where q_{ij} are numbers and $Q^{(3v)}$ 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 the 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 the 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

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

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,

$$V^{(3v)}=V^{(s_N)}N^{(3v)}+V^{(3v_N)}=(V^{(s_N)},V^{(2v_N)}). \tag{C1}$$

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

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

and

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

two vectorial quantities

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

and

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

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

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

Denoting

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

$$T_r^{(2v_N)}\equiv(T_{21}^{(3t)},T_{31}^{(3t)}),$$

we can write that

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

$$T_r^{(3v_N)}=(0,T_r^{(2v_N)}).$$

Thus[4]

$$T^{(3t)}=T_1^{(s_N)}N^{(3v)}N^{(3v)}+T_l^{(3v_N)}N^{(3v)}+N^{(3v)}T_r^{(3v_N)}+T^{(3t_N)}$$
$$=\begin{pmatrix}T_1^{(s_N)} & T_l^{(2v_N)}\\ T_r^{(2v_N)} & T^{(2t_N)}\end{pmatrix}. \tag{C2}$$

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

$$T_2^{(s_N)}\equiv\mathrm{Tr}\,T^{(2t_N)}=T_{32}^{(3t)}+T_{33}^{(3t)},$$

which obeys the relation

$$T_0^{(s)}=T_1^{(s_N)}+T_2^{(s_N)}. \tag{C3}$$

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 an independent pair. Introducing the traceless tensors

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

and

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

---

[4] Note that if the product of two tensorial quantities of rank $r>0$ is written without a centerdot $(\cdot)$, it means that this is the product, not the internal product.

where

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

we can write a 3D tensor as

$$\begin{aligned} T^{(3t)} &= T_1^{(s_N)} N^{(3v)} N^{(3v)} + T_l^{(3v_N)} N^{(3v)} + N^{(3v)} T_r^{(3v_N)} \\ &\quad + \tfrac{1}{2} T_2^{(s_N)} U^{(3t_N)} + \overset{\circ}{T}{}^{(3t_N)} \\ &= \begin{pmatrix} T_1^{(s_N)} & T_l^{(2v_N)} \\ T_r^{(2v_N)} & \tfrac{1}{2} T_2^{(s_N)} U^{(2t)} + \overset{\circ}{T}{}^{(2t_N)} \end{pmatrix}. \end{aligned} \tag{C4}$$

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