HEAT AND MASS TRANSFER DURING NUCLEATION

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ABSTRACT

In this paper we discuss a systematic procedure to assess the nucleation rate with the help of the non-equilibrium square gradient model, which is also known as H-model or diffuse-interface model. We first distinguish between the density (concentration) gradient caused by the phase coexistence in equilibrium and the density (concentration) gradient caused by the non-equilibrium conditions in bulk phases. The non-equilibrium description of the interfacial region requires a proper Gibbs relation, which is formulated in our theory. Non-equilibrium thermodynamics uses the constitutive relations between thermodynamic forces and thermodynamic fluxes. It does not provide the values of the transport coefficients. We use the transport coefficients in the interfacial region which follow from the square gradient model. Furthermore, the nonzero curvature of the surface modifies the expressions for thermodynamic quantities in the interfacial region. Next we combine all these pieces in a systematic picture, which gives a consistent description of heat and mass transport across curved interfaces.

INTRODUCTION

Nucleation is a dynamic process which involves formation and growth of small nuclei of one phase in another phase [1]. One could think of formation of bubbles in liquid or drops in a multicomponent fluid. This process requires formation of an interface between two phases, a region where the density or concentration gradient are large. Furthermore, during nucleation matter and heat are being transfered across the interface, which moves the system towards equilibrium. The interface poses an additional barrier to transport [2]. This barrier will affect the standard Fourier's or Fick's laws in the interfacial region, where the transport coefficients become dependent on the density gradients. For small nuclei of the new phase the curvature is rather high which will also modify the values of the integrated transport coefficients [3]. The knowledge of the integrated surface transfer coefficients, which determine the barrier of the interface to heat and mass transfer, is useful for a correct prediction of the nucleation rate.

In this paper we provide a systematic procedure to describe a non-equilibrium interface of a bubble or droplet, which combines non-equilibrium thermodynamics with the square gradient model for a curved interface. Following [4], we distinguish the following steps which are essential in any non-equilibrium thermodynamic theory: i) equilibrium thermodynamics; ii) Gibbs relation; iii) balance equations; iv) constitutive relations. It is the aim of this paper to emphasize the difference between these parts and at the same time to bring them together. We will go through these steps for spherical interface of one-component fluid, however, the established framework is not restricted to this particular case.

One of the interesting topics is the origin of so-called non-equilibrium capillary forces, that are believed to cause the self-propelled motion of bubbles [5]. Analyzing the structure of the interface in equilibrium and non-equilibrium, we show that one should distinguish between the gradients of the density (concentration) in the interfacial region on the one hand and the gradients of the chemical potential or the pressure on the other hand [2]. The former ones are present even in equilibrium system and therefore cannot cause the motion of bubble interface nor the bubble as a whole. In contrast, the latter ones are the genuine measure of non-equilibrium and are not reduced to the interfacial density gradients.

The paper is organized as follows. First, we summarize the square gradient model for equilibrium interface. In particular, we discuss the different quantities all of which have a meaning of pressure. It is important to distinguish between them, especially when coming to non-equilibrium. We identify the meaning of these pressures. Next, we extend the equilibrium description to non-equilibrium. Care should be taken when extending these quantities in the interfacial region. In particular, we formulate the Gibbs relation for the interfacial region which differs from the one for a homogeneous phase. Furthermore, formulating the balance equations we identify the fluxes, which are a measure of non-equilibrium. Next, we formulate and discuss the constitutive relations between the fluxes and the thermodynamic forces in the context of linear irreversible thermodynamics. We discuss that on macro scale the surface can be viewed as a separate thermodynamic system, which, in particular, increases the number of dissipative fluxes by one. Now it is not only a diffusion flux, but also a component flux, which leads to dissipation. We also discuss a particular example of a simple system, where the above considerations are implemented. Finally, we give the concluding remarks.

SQUARE GRADIENT MODEL FOR EQUILIBRIUM SPHERICAL INTERFACE

In square gradient model one starts with the expression for the Helmholtz energy density $f^v(\mathbf{r})$ which can be represented as a sum of two terms [3]: the local contribution $f_0^v(\rho(\mathbf{r}), T)$, and the gradient contribution $f_{\nabla\rho}^v(\nabla\rho(\mathbf{r}))$,

$$f^v(\mathbf{r}) = f_0^v(\rho(\mathbf{r}), T) + f_{\nabla\rho}^v(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) \tag{1}$$

where T is the temperature, $\rho(\mathbf{r})$ is the local density, while $\nabla\rho(\mathbf{r})$ is the density gradient. For a spherical interface the density gradient has only nonzero component $\rho'(r)$, the derivative of the density with respect to the radial position r. For the sake of clarity we provide the description for a one-component system. The general analysis for multicomponent systems forming planar interface can be found in [6].

The local contribution $f_0^v(\rho(r), T)$ is determined by an equation of state. A particular choice of the equation of state is not important for the present analysis. In all further calculations we use van der Waals equation of state. Equation (1) can be considered as a Taylor expansion in the density derivatives, since in the interfacial region the density change abruptly. Therefore, the gradient contribution $f_{\nabla\rho}(\rho(r), \rho'(r))$ contains the first non-local terms in the Taylor expansion

$$f_{\nabla\rho}^v(\rho, \rho') = \frac{1}{2}\kappa\rho'(r)^2 \tag{2}$$

The coefficient $\kappa(\rho)$ is independent of the temperature but may depend on the density. Without restriction in generality we will consider it to be independent of the density as well.

For a closed system with fixed total volume and mass the density distribution is such that it minimizes the total grand potential $\Omega = \int dr\, 4\pi r^2 \left(f^v(r) - \mu_e\rho(r)\right)$, where μ_e is the equilibrium chemical potential of the system. The density distribution satisfies therefore the equation

$$\mu_e = \frac{\partial f_0^v(\rho, T)}{\partial\rho} - \kappa\left(\rho'' + \frac{2}{r}\rho'\right) \tag{3}$$

We note, that the system considered is highly inhomogeneous, which contains the density gradients even in equilibrium. However, the condition of thermodynamic equilibrium requires that the chemical potential is constant through the system. Indeed, that is the case: the chemical potential μ_e, being the Lagrange multiplier of the variational minimization procedure, is a number which characterizes the whole system. Even though each term in Eq. (3) depends substantially on the position, the entire right hand side of Eq. (3) is independent of the position.

The pressure

In the interfacial region the pressure is no longer a scalar: it becomes a tensor. It is convenient therefore to consider its structure in general tensorial form. The tensorial pressure $\sigma_{\alpha\beta}$ can be represented as

$$\sigma_{\alpha\beta}(\mathbf{r}) = p(\mathbf{r})\delta_{\alpha\beta} + \gamma_{\alpha\beta}(\mathbf{r}) \tag{4}$$

where

$$p(\mathbf{r}) = \mu_e\rho(\mathbf{r}) - f^v(\mathbf{r}) \tag{5}$$

is the thermodynamic pressure and

$$\gamma_{\alpha\beta}(\mathbf{r}) = \nabla_\alpha\rho(\mathbf{r})\nabla_\beta\rho(\mathbf{r}) \tag{6}$$

is the tension tensor. Here $\delta_{\alpha\beta}$ is the Kronecker symbol and ∇_α represents the partial derivative with respect to the α coordinate. In equilibrium in the absence of external field it satisfies the relation

$$\nabla_\alpha\sigma_{\alpha\beta}(\mathbf{r}) = 0 \tag{7}$$

where the summation convention over double Greek symbol is used. In the presence of external field the right hand side of Eq. (7) contains the density of external field.

Identification of the scalar and tensorial terms in Eq. (4) is arbitrary. For instance, the thermodynamic pressure

$$p(\mathbf{r}) = p_0(\rho, T) - \kappa\rho\nabla^2\rho - \frac{1}{2}\kappa|\nabla\rho|^2 \tag{8}$$

where $p_0(\rho, T)$ is the homogeneous pressure which is given by an equation of state. Equation (4) can therefore be written as

$$\sigma_{\alpha\beta} = p_0(\rho, T)\delta_{\alpha\beta} + \varpi_{\alpha\beta} \tag{9}$$

where

$$\varpi_{\alpha\beta}(\mathbf{r}) \equiv \gamma_{\alpha\beta}(\mathbf{r}) - \kappa\left(\rho\nabla^2\rho + \frac{1}{2}\kappa|\nabla\rho|^2\right)\delta_{\alpha\beta} \tag{10}$$

is the Korteweg tensor [7].

When using the pressure tensor in the interfacial region, it is common to speak of the scalar and tensorial parts separately. The particular identification may depend on the application one uses it for. In this paper we show that distinguishing the thermodynamic pressure and the tension tensor is natural in the context of non-equilibrium thermodynamics.

For instance, the expression for the thermodynamic pressure, Eq. (5), has the same functional form as in a homogeneous phase. This is important when one introduces the hypothesis of local equilibrium in non-equilibrium description. Furthermore, integral of the tension tensor over the interfacial region determines the surface tension. Finally, since Eq. (7) represents the condition of mechanical equilibrium, it is the gradient of the total pressure tensor $\sigma_{\alpha\beta}$, not the Korteweg tensor $\varpi_{\alpha\beta}$, which changes the momentum of the system. We will see this when we discuss the balance equations.

For a spherical system the pressure tensor has a diagonal form with two independent components, the normal pressure $p_n(r) = p(r) + \kappa\rho'(r)^2$ and the tangential pressure $p_\tau(r) = p(r)$. The condition of mechanical equilibrium becomes
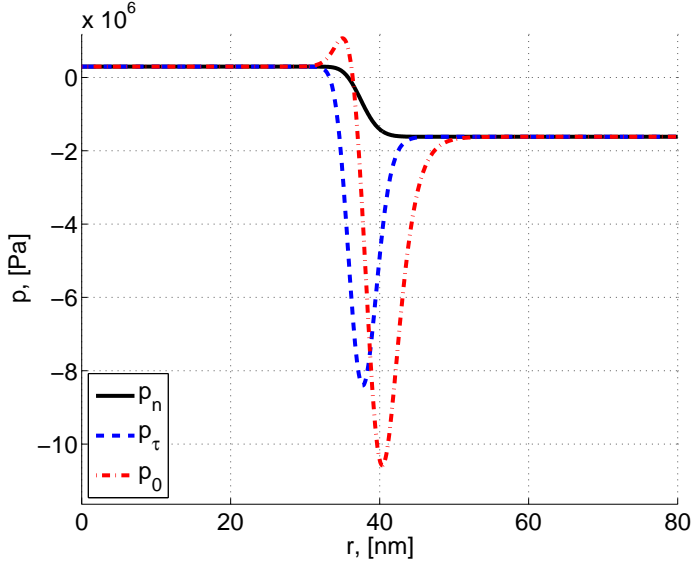
$$p_n'(r) + \frac{2}{r}\kappa\rho'(r)^2 = 0 \tag{11}$$

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Figure 1. Profile of the normal, tangential and homogeneous pressure across the interfacial region for cyclohexane at 330 K
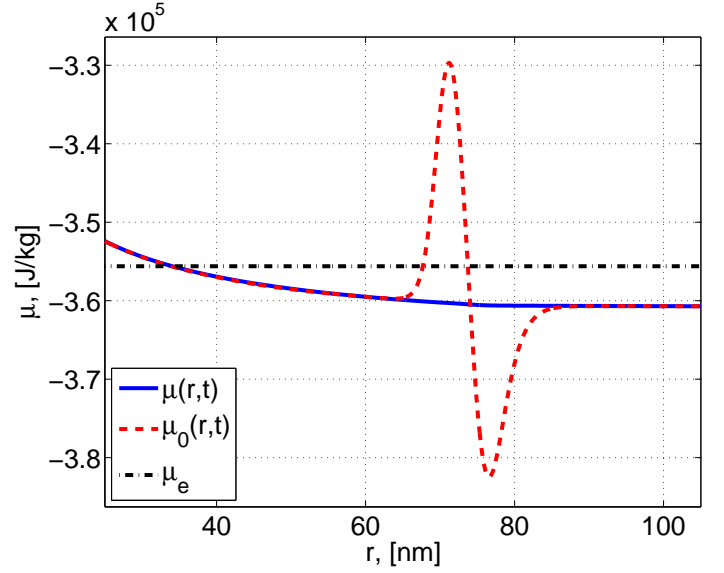

Figure 2. Profile of the non-equilibrium chemical potential, non-equilibrium homogeneous chemical potential and the equilibrium total chemical potential for cyclohexane. Equilibrium temperature is 330 K, while the non-equilibrium boundary temperature is 10 K higher than equilibrium value in the center.

Variations in the pressure are of two kinds. First, due to nonzero curvature, the normal pressure is not constant across the interfacial region. The second term in Eq. (11) represents the local form of the Laplace pressure and is nonzero for a spherical interface. It is substantial for small bubbles and decreases when the bubble grows, becoming zero for a planar interface. Next, there exist variations in pressure which lead to the surface tension. They are present in the system even in the case of zero curvature. For a planar interface the normal pressure is constant through the interface, while the thermodynamic pressure has a large negative dip. The variation of the tension tensor is the opposite. Figure 1 represents typical profiles of the various pressures for a spherical bubble of cyclohexane in equilibrium at $T = 330$ K.

LOCAL EQUILIBRIUM AND BALANCE EQUATIONS

In order to use the above thermodynamic analysis in non-equilibrium, one has to assume that there exist so-called local equilibrium, i.e. that all the thermodynamic quantities and relations in non-equilibrium have the same functional form as in equilibrium. In formulating the local equilibrium hypothesis it is important to do the correct identification of the thermodynamic quantities. In homogeneous phase, where the spatial variations of all the quantities are small, this is straightforward. However, in the interfacial region, where the density changes a lot, care should be taken. For instance, as was discussed above, in the interfacial region one can identify at least three different quantities with the meaning of pressure: the normal pressure $p_n(r)$, the tangential pressure $p_\tau(r)$ and the homogeneous pressure p_0.

We start with introducing the density $\rho(r,t)$ and the temperature $T(r,t)$ as independent thermodynamic variables. Next we define the non-equilibrium local Helmholtz energy $f^v(r,t)$ in the interfacial region in the same way as in equilibrium, see Eq. (1). In non-equilibrium the total grand potential does not have a minimum, so it is not possible to perform a variational minimization procedure. Thus, the pressure and the chemical potential have to be defined independently. We use Eq. (3) and Eq. (5) for this.

Namely, the non-equilibrium chemical potential is

$$\mu(r,t) = \mu_0(\rho(r,t), T(r,t)) - \kappa \left(\rho''(r,t) + \frac{2}{r}\rho'(r,t) \right) \quad (12)$$

and the non-equilibrium thermodynamic pressure is

$$p(r,t) = \mu(r,t)\rho(r,t) - f^v(r,t) \quad (13)$$

We note, that unlike μ_e, the non-equilibrium chemical potential $\mu(r,t)$ is not constant through the system. However, the spatial variation of $\mu(r,t)$ is much less than the spatial variation of $\mu_0(\rho(r,t), T(r,t))$. The former one is determined by the rate of non-equilibrium perturbation, which is considered to be small, and vanishing in equilibrium. The latter one is determined by the rate of the density variation in the interfacial region, which is large and non-zero even in equilibrium. Typical variations of the chemical potential are represented in Figure 2.

The non-equilibrium normal pressure is defined with the help of Eq. (4) as

$$p_n(r,t) = p(r,t) + \kappa\rho'(r,t)^2 \quad (14)$$

Gibbs relation

An important part of specifying local equilibrium is to provide the rates of change of thermodynamic quantities, the Gibbs relation. A particular Gibbs relation can be justified only by the validity of the results, which follow from the analysis. We can, however, provide arguments which elucidate a particular form of the Gibbs relation.

In an inhomogeneous equilibrium system such as interfacial region the local thermodynamic properties can vary in two different dimensions. First, they can change when the whole system changes its thermodynamic state from, for instance, one

temperature to another. Since the temperature and the chemical potential are constant in equilibrium system, it means that every small element of the system follows the same change in thermodynamic state, but locally. For a one-component system this can be described by the ordinary Gibbs relation

$$T\,\delta s(r) = \delta u(r) + p(r)\,\delta v(r) \tag{15}$$

where symbol δ denotes a change in a thermodynamic state of the entire system. Furthermore, $u(r) = f^v(r)v(r) - Ts(r)$ is the specific internal energy, $s(r) = v(r)\partial f^v(r)/\partial T)$ is the specific entropy, and $v(r) = 1/\rho(r)$ is the specific volume. Next, the thermodynamic properties in an inhomogeneous equilibrium system vary in space. This variation is not arbitrary and is constrained by the conditions of mechanical equilibrium, Eq. (4) and the conditions of the thermodynamic equilibrium, $T(r) = const$ and $\mu(r) = const$. Using Eq. (5), we obtain

$$T\,\nabla_\alpha s(r) = \nabla_\alpha u(r) + p(r)\,\nabla_\alpha v(r) - v(r)\nabla_\beta \gamma_{\alpha\beta}(r) \tag{16}$$

Equation (16) has the form of Eq. (15) except the las term. Since it accounts for spatial changes of thermodynamic properties, we will call it the spatial Gibbs relation. We note, that both Eq. (15) and Eq. (16) are exact in equilibrium.

The next step is to formulate the non-equilibrium Gibbs relation. One can observe that the change of a thermodynamic quantity in thermodynamic state at a given spatial position corresponds to the partial time derivative of this quantity, while its change in spatial position at a given thermodynamic state corresponds to the partial spatial derivative. Multiplying Eq. (16) with barycentric flow velocity $\mathbf{v}$ and adding it to Eq. (15) we obtain

$$T\frac{ds}{dt} = \frac{du}{dt} + p\frac{dv}{dt} - J_{m,\alpha}v^2\,\nabla_\beta\gamma_{\alpha\beta} \tag{17}$$

where $\mathbf{J}_m \equiv \rho\mathbf{v}$ is the mass flux across the interface and we have omitted the arguments (r,t), as now all the quantities depend on position and time. Equation (17) is the Gibbs relation for a non-equilibrium interfacial region. The last term is nonzero only in the interfacial region and vanishes in the homogeneous phase, leading to the ordinary form of the Gibbs relation. The last term can be considered as a work required to transfer an element of specific volume v across the interface. We note that it is the tension tensor which comes to the non-equilibrium Gibbs relation, not the Korteweg tensor.

Balance equations

For a one-component system we can write four balance equations, for mass, energy, momentum and entropy respectively:

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot\mathbf{J}_m \tag{18}$$

$$\frac{\partial e^v}{\partial t} = -\nabla\cdot\mathbf{J}_e \tag{19}$$

$$\frac{\partial\rho v_\alpha}{\partial t} = -\nabla_\beta J_{p,\alpha\beta} \tag{20}$$

$$\frac{\partial s^v}{\partial t} = -\nabla\cdot\mathbf{J}_s + \sigma_s \tag{21}$$

Here $\mathbf{J}_m$, $\mathbf{J}_e$, $J_{p,\alpha\beta}$, $\mathbf{J}_s$ are the mass flux, the energy flux, the momentum flux and the entropy flux respectively. Furthermore, e^v is the total energy density, s^v is the entropy density and σ_s is the local entropy production. The form of the balance equations in an inhomogeneous region is the same as in an homogeneous region. In particular, the momentum flux $J_{p,\alpha\beta}$ consists of the kinetic term $\rho v_\alpha v_\beta$ and the mechanical pressure tensor $\sigma_{\alpha\beta}$. When there is no flux, the momentum balance equation, Eq. (20), reduces to the condition of mechanical equilibrium, Eq. (4). It is clear, therefore, that it is the total pressure tensor $\sigma_{\alpha\beta}$ which contributes to the momentum flux.

Using the Gibbs relation, Eq. (17), and the above balance equations we can derive the expression for the entropy production. In spherical coordinates it takes the following form

$$\sigma_s = J_q\left(\frac{1}{T}\right)' \tag{22}$$

where the heat flux $J_q \equiv J_e - J_m(u + v^2/2 + pv)$ is the measurable heat flux.

CONSTITUTIVE RELATIONS AND TRANSPORT CO-EFFICIENTS

We must provide constitutive relations between the thermodynamic driving forces and the fluxes. In case of one-component system the thermodynamic force is the radial temperature gradient, $(1/T)'$ while the flux is the heat flux J_q. In order for the entropy production to be positive, they must be related linearly, i.e.

$$\left(\frac{1}{T}\right)' = r_{qq}(r)J_q \tag{23}$$

where $r_{qq}(r)$ is the local resistivity to the heat transfer. A particular expression for the resistivity coefficient does not follow from the theory and must be given in addition. In the context of the square gradient theory we model the resistivity coefficient similarly to the local Helmholtz energy, Eq. (1), i.e.:

$$r_{qq}(r) = r_{qq,0}(\rho,T) + r_{qq,\nabla\rho}(\rho,\nabla\rho) \tag{24}$$

In this form the resistivity coefficient resembles the equilibrium profiles of the density and the density gradient. Even though it depends on the density gradient, it does not contribute to the driving force, as is expected in linear non-equilibrium thermodynamics. All the effects of non-equilibrium perturbation are therefore due to the nonzero heat flux J_q.

In equilibrium thermodynamics a smooth variation of local density profile across the interface leads to the surface excess properties, such as the interfacial tension or the Laplace pressure. For small bubbles or droplets these properties modify the state of the system such that the surface becomes its important part, together with the bulk phases. A similar situation is observed in non-equilibrium. Due to smooth variation of the local resistivity profile $r_{qq}(r)$ across the interface, the surface possesses excess resistance to the heat transfer. Additional resistance is particularly large for small bubbles or droplets as it may be comparable to the bulk resistance.

In a continuous description of a one-component non-equilibrium system there exist only one irreversible flux, the

heat flux, which is caused by the temperature gradient, as suggested, in particular, by Eq. (23). However, description in terms of the excess interfacial properties, in particular for bubble and droplets, reveals existence of the cross effects. Thus, the temperature gradient across the interface causes the mass flux, while the gradient in the chemical potential causes the heat flux. These phenomena are the essence of nucleation process, so the correct account for these phenomena is crucial for understanding the nucleation. The reason for the existence of the irreversible mass flux in the one-component system is the presence of surface. Its velocity does not necessarily coincide with the barycentric velocity of the fluid. This leads to the mass flux across the interface. This flux carries along additional heat due to the temperature gradient.

One can perform the analysis of non-equilibrium transport for a discrete system (see e.g. [8] or [2]) and in stationary states obtain the following constitutive relations

$$\Delta \frac{1}{T} = R_{qq} J_q^g + R_{qm} J_m$$

$$-\Delta \frac{\mu}{T} + h^g \Delta \frac{1}{T} = R_{mq} J_q^g + R_{mm} J_m \quad (25)$$

where Δ indicates the difference between the extrapolated to the surface bulk values of the corresponding quantities. Furthermore, h^g is the specific enthalpy in the gas phase and J_q^g is the measurable heat flux in the same phase. Equation (25) suggests that there exist mass flux J_m across the interface, which depends both on the temperature difference and the chemical potential difference across the interface.

The coefficients R_{qq}, R_{qm}, R_{mq}, R_{mm} represent the excess interfacial resistances to the heat and mass transfer. Just like the local resistivity coefficient $r_{qq}(r)$, they can depend only on equilibrium properties of the system and do not depend on the non-equilibrium perturbation. They are related to the local resistivity profile in the following way:

$$R_{qq}(x) = \mathfrak{E}[r_{qq}](x)$$

$$R_{mq}(x) = R_{qm}(x) = \mathfrak{E}[r_{qq}(h^g - h)](x) \quad (26)$$

$$R_{mm}(x) = \mathfrak{E}[r_{qq}(h^g - h)^2](x)$$

where

$$\mathfrak{E}[q](x) \equiv \int_{r^g}^{r^\ell} dr \frac{x^2}{r^2} \left(q(r) - q^g \Theta(x - r) - q^\ell \Theta(r - x) \right) \quad (27)$$

In this expression Θ is the Heaviside step function, while r^g and r^ℓ are the positions in the homogeneous region of the gas and liquid phase. Furthermore, q^g and q^ℓ are the extrapolated to the position x homogeneous values of the quantity q. $\mathfrak{E}[q]$ represents therefore the excess of a quantity $q(r)$ across the interfacial region above the homogeneous values. Figure 3 illustrates the idea of excess: it is basically the difference between the shaded areas of different color. The value of the excess depends on the position of the dividing surface. Depending on the kind of profile it can be either positive or negative, such as in Figure 3(a), if the profile changes monotonically across the interface, or always positive, such as in Figure 3(b), if the profile has

a peak inside the interfacial region. Equations (26) show that interfacial resistances are the excesses of local profiles, which are the combinations of resistivity profile and the enthalpy profile.

A PARTICULAR SOLUTION FOR STATIONARY STATES

We consider here an example of solution for a bubble in stationary states. The balance equations 18-21 take the following form

$$(r^2 J_m)' = 0$$

$$(r^2 J_e)' = 0$$

$$(r^2 J_p)' = 2 r p(r) \quad (28)$$

$$(r^2 J_s)' = \sigma_s$$

where the momentum flux $J_p = p_n + \rho v^2$. Unlike the planar interface the mass, energy and momentum fluxes are not constant through the interfacial region. Due to spherical symmetry, it is $r^2 J_m$ and $r^2 J_e$ which are constant. In addition, $r^2 J_p$ is not even constant.

For a planar interface stationary states are typically realized by keeping different values of the temperature and pressure on the boundaries of the system. This leads to a flux of matter and energy into the system at one side of it and out of the system at the other side. An equivalent picture for a spherically symmetric system would be to control the temperature and pressure at the spherical boundary. This would lead to a flux of matter and energy through that boundary. In stationary states this flux should be compensated by the corresponding source or sink in the center of the bubble. Equation (28) suggests that this could be realized either if the flux of matter or energy is zero everywhere or if they are infinite in the center. In the first case we get equilibrium, while the second case is unphysical. In other words the stationary non-equilibrium state for a bubble or a droplet is not possible. It can either be in equilibrium, or grow (shrink).

The interfacial property of a bubble do not depend, however, on its motion. Besides, the most convenient condition to study these properties is stationary state. In order to circumvent the above problem in stationary state we need to allow matter and energy to be sinked not in the center of the bubble, but at some finite radius. Our system would be therefore have not only the outer boundary of the radius L^o, but also the inner boundary of radius L^i. The gas-liquid interfacial region lies entirely inside the layer between these boundaries. With this geometry we can control the temperature and pressure at the both boundaries.

To illustrate a particular solution we consider the case when there is no mass flux across the boundary. In this case Eq. (23) allows an analytic solution for the temperature:

$$\frac{1}{T(x)} = \frac{1}{T^i} + \left(\frac{1}{T^o} - \frac{1}{T^i} \right) \int_{L^i}^x dr \frac{r_{qq(r)}}{r^2} \bigg/ \int_{L^i}^{L^o} dr \frac{r_{qq(r)}}{r^2} \quad (29)$$

The local resistivity profile depend only on equilibrium properties of the system. Equation (24) can take the following form

$$r_{qq}(r) = r_{qq}^i + (r_{qq}^o - r_{qq}^i) \frac{\rho_{eq}(r) - \rho_{eq}^i}{\rho_{eq}^o - \rho_{eq}^i} + \alpha (r_{qq}^o + r_{qq}^i) \frac{|\nabla \rho_{eq}|^2}{|\nabla \rho_{eq}|^2_{max}} \quad (30)$$
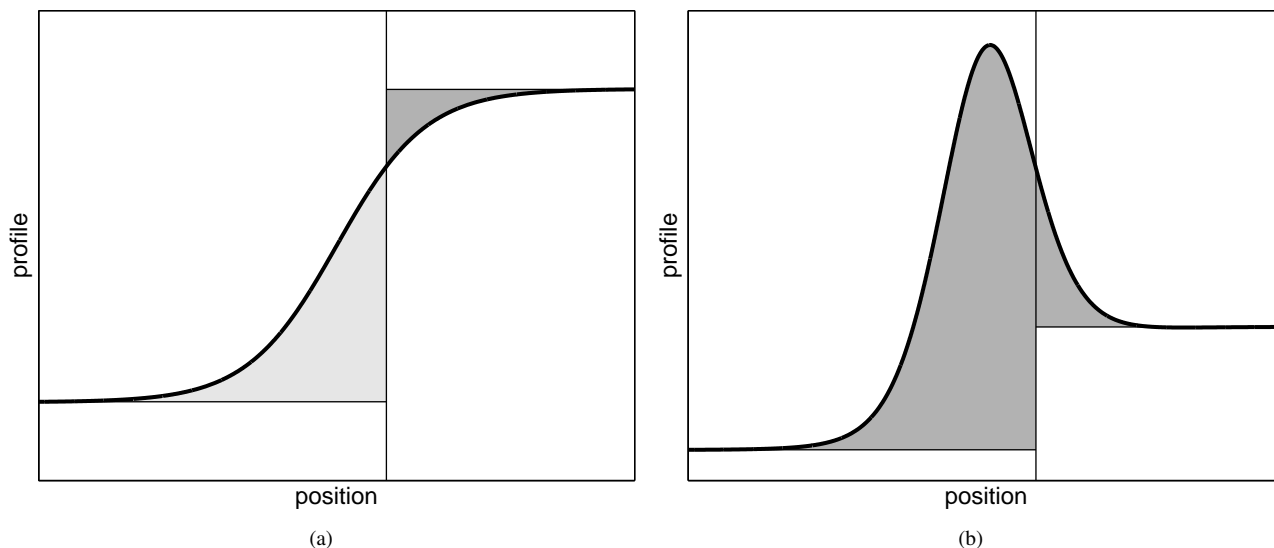
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Figure 3. Illustration of the interfacial excess. The excess is the difference between the shaded areas of different color. (a) Depending on the position of the dividing surface the excess may be both positive and negative; (b) Irrespectively of the position of the dividing surface, the excess is always positive.
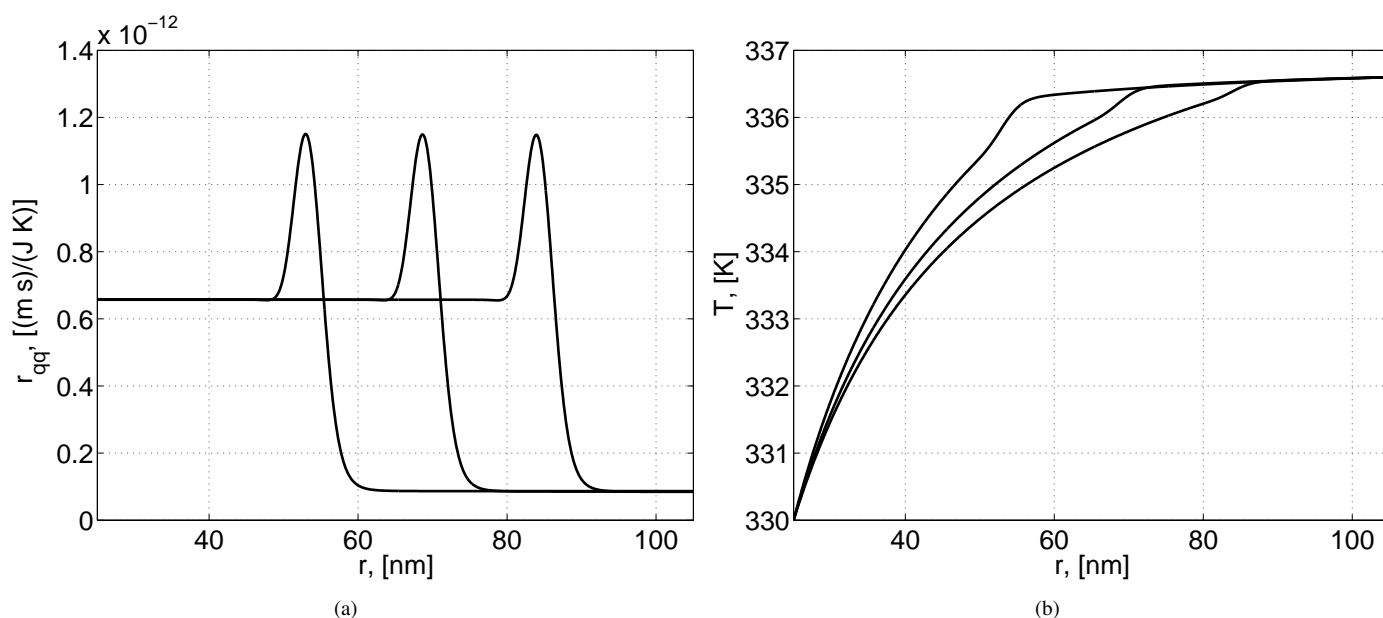

Figure 4. Local resistivity profiles (a) and temperature profiles (b) for spherical layer filled with various amounts of cyclohexane, boundaries of which are kept at 330 K and 336.6 K.

where superscripts i and o denote the values of the resistivity and the density at the boundaries. Typical resistivity profiles for different bubble sizes are given in Figure 4(a). Position of the peaks in the profiles correspond to the positions of the interfacial region. This lead to the temperature profiles illustrated in Figure 4(b). We see that the temperature profiles has different slopes in the gas and liquid phases. This is natural, since the gas and liquid resistivity are different. Higher gas resistivity leads to the more steep temperature profile in the gas phase. Another interesting thing is that the extrapolated temperature profiles in the gas and liquid phases are different at the interface.

CONCLUSIONS

In this article we have presented a systematic procedure for the description of a non-equilibrium spherical interface. We considered separately the equilibrium square gradient model, non-equilibrium constitutive equations and the extension of the equilibrium thermodynamic quantities in an inhomogeneous region to non-equilibrium. We emphasized the importance of this extension as it allows one to identify correctly the forces which drive the system away from equilibrium.

In particular we have summarized the role of pressure. It was shown that one can identify several quantities with a meaning of the pressure, namely the thermodynamic pressure, the normal and tangential pressure, the tension tensor and the Korteweg tensor. In particular, the thermodynamic pressure is used in the definition of local thermodynamic potentials, such as local Helmholtz energy or local internal energy, and in the Gibbs relation. In addition, the tension tensor appears in the Gibbs relation for an inhomogeneous region, which illustrates an ad-

ditional work required to transfer a volume element across the interface. In contrast, the normal pressure is present in balance equation for momentum, i.e. equation of motion.

We have discussed that non-equilibrium fluxes are determined by the gradients of the chemical potentials rather than the gradients of the densities. While the variations of the thermodynamic quantities, such as p_0 or μ_0, determined from the equation of state are large across the interfacial region, the non-equilibrium flux of matter is determined by the slow variation in the total chemical potential.

We have discussed the origin of an additional resistance met by a bubble to heat and mass transfer, which is caused by the interface. The excess resistance is essentially determined by the peak in the local resistivity profile caused by the large density gradients in the interfacial region. As the surface can be considered as a separate thermodynamic phase, its resistance is determined by the equilibrium properties, just like the resistance of the homogeneous phase.

Finally we considered a simple example of a bubble in non-equilibrium conditions. It illustrated the typical profiles of local properties which are developed in non-equilibrium bubble or droplet.

NOMENCLATURE

Vectors are indicated by the bold phase, tensors are indicated by two Greek subscripts.

$_0$ Subscript indicating the homogeneous phase
f^v Helmholtz energy density [J/m^3]
h Specific enthalpy [J/kg]
J_m Mass flux [kg/(m^{2}s)]
J_e Energy flux [J/(m^{2}s)]
J_q Measurable heat flux [J/(m^{2}s)]
J_p Momentum flux [Pa]
J_s Entropy flux [J/(m^{2}K)]
p Thermodynamic pressure [Pa]
p_n Normal pressure [Pa]
p_τ Tangential pressure [Pa]
r Position [m]
r_{qq} Local heat resistivity coefficient [(m s)/(J K)]
R_{qq} Excess heat resistance coefficient [(m^{2}s)/(J K)]
R_{qm} Excess heat resistance coefficient [(m^{2}s)/(kg K)]
R_{mm} Excess heat resistance coefficient [(m^{2}s)/(kg^2 K)]

s Specific entropy [J/kg]
T Temperature [K]
t Time [s]
u Specific internal energy [J/kg]
v Specific volume [m^3/kg]
v Velocity [m/s]
α, β Spatial components of vectors and tensors []
$\mathfrak{E}$ Excess operator []
$\gamma_{\alpha\beta}$ Tension tensor [Pa]
κ Square gradient coefficient [J m^5/kg^2]
μ Chemical potential [J/kg]
ρ Mass density [kg/m^3]
σ_s Entropy production [J/(m^{3}K)]
$\sigma_{\alpha\beta}$ Pressure tensor [Pa]
$\varpi_{\alpha\beta}$ Korteweg tensor [Pa]

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