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Interfacial properties of inhomogeneous fluids for a smooth profile

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We analyze single- and multi-component simple fluids in a liquid-vapor coexistence state, which forms an arbitrarily curved interface. Using an analytical approach, based upon density functional theory, we perform a power series expansion of the density profile on the principal curvatures to calculate the grand potential that represents the free energy of the system. In addition, we derive microscopic expressions for the interfacial properties. All results are in good agreement with other viewpoints at the level of surface tension and spontaneous curvature.

Keywords: Density functional theory; stress tensor; multi-component fluid.

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1. Introduction

The statistical mechanics description of two-dimensional extended objects is a topic of great relevance in condensed matter physics. The interest on it is due to the diversity of systems that may be modeled in this fashion [1–4]. Among those systems one can mention, for instance, micelles, microemulsions, interfaces, and biological or artificial membranes. The composition of such systems is diverse, ranging from simple to complex molecules. An important thermodynamical property of such systems is surface tension, which may be defined as the free energy per unit area and is a measure of the energy cost for the system to maintain the surface extended. In some cases the interfacial surface tension may be lowered by adding surfactants (tensoactive agents), which are part of the amphiphilic family. The molecules in the interfacial region are formed by two parts; one polar or hydrophilic (head) and the other non-polar or hydrophobic (tail). Surfactants adhere to the bulk phases leading to formation of soap films. At room temperature the amphiphilic bilayers show up generally as a fluid and form what is called a fluid membrane [5]. Under certain conditions these membranes close onto themselves forming bag-like structures which are known as vesicles. The elastic behavior of those systems is crucial to describe such structures. It is known that the relevant contributions to the elastic energy of an homogeneous fluid membrane are those from surface tension and from flexion; which in its turn are determined by area and curvature of the membrane. As in films formed by amphiphils surface tension is very small, or nearly null, the dominant contribution to its free energy is due to bending. Nevertheless, in many systems surface tension is not negligible and the corresponding energy contribution must be included [6, 7].

Tools employed to describe fluid membranes can also be used to describe the behavior of fluid interfaces, which may be formed in fluids of one or several components when they are in a liquid-vapor coexistence state [8–10]. For monocomponent systems there exists a single interfacial region separating both the liquid and vapor homogeneous phases. However, for multicomponent systems there exist multiple interfacial regions: those formed within the same component, but in different phases, and those from combinations of different components where the phases are not necessarily different [11]. Although interfacial regions have been studied since more than a century ago, their structure and conformation to different scales is still a topic of study; particularly in systems formed by several components [12, 13]. There exists vast literature on the theoretical and experimental description of these systems. On the theoretical context, two approximation schemes may be basically identified: the one in equilibrium and the other when fluctuations are included. In the former, driven forward originally by van der Waals [14], although the external field is what generates the interface, it is neglected. This scheme assumes existence of a smooth intrinsic interface with a density profile that interpolates smoothly between the bulk-phase densities of the coexistence state. On the other hand, in the scheme with fluctuations, driven forward by Buff *et al*. [15], the external field plays a crucial role as it controls fluctuations of the interface. It is assumed that the interface is non-smooth, having small undulations due to capillary waves. Within this viewpoint only the interfacial local positions are considered as statistical variables and the thickness of the interface is described as a result of the capillary wave fluctuations of a step-like density profile. Each of these viewpoints yields independent results for the width of the interfacial region.

On the one hand the equilibrium scheme, in all versions, is unable to capture the fact that the interface thickness diverges as gravity goes to zero. The fluctuation scheme, on the other hand, cannot account for the divergence of the interfacial thickness, on the scale of the bulk correlation length, when the system approaches the critical temperature. Nevertheless, it has been proved that far from the critical point, predictions for the interfacial properties from both schemes agree [16, 17]. We consider that these two viewpoints are complementary, and enrich comprehension of interfacial phenomena. In any of the situations previously described, if one deals with amphiphilic membranes or fluid interfaces, either with or without surface tension, the free energy can be represented in general by the Helfrich phenomenological model [18]

$$\Omega_S = \int dS[\gamma - 2\kappa c_0 H + \kappa H^2 + \bar{\kappa} K], \qquad (1)$$

where dS is the area element of the interface, $H = (1/R_1) + (1/R_2)$ and $K = 1/R_1 R_2$ are the mean and Gaussian local curvatures respectively with R_1 and R_2 being the principal radii of curvature on a given point in the surface. The coefficients are in its turn: γ the surface tension, κ and $\bar{\kappa}$ the bending constants, and c_0 the spontaneous curvature. These parameters are intrinsic properties of the media under study which, in particular for interfacial surfaces, should have a representation in terms of microscopic quantities. For the analysis of our system, we consider an ab-initio microscopic approach to derive independently the "Helfrich equivalent" and then identify the surface properties [10]. Following this route, and some variants, fluid interfaces having simple geometries as spherical or cylindrical for different approximations of the density profile have been studied [19]. There exists consensus respect to the points of agreement and discrepancy on the microscopic expressions predicted for the surface properties [9, 19]. Nevertheless, when it comes to describing the behavior of an interface given as a surface arbitrarily curved in a microscopic context, the analysis is more complicated. Much technical effort is required to carry out pertinent approximations and only a few have adventured on this task. A pioneer approximation in this context was carried out by R. P. K. Zia; in which the normal coordinates were introduced for the first time to investigate the behavior of the interface [20]. A drawback from this work is that the approximation was carried out on the squared gradient theory, also known as drum model, and is a known fact that this model is unable to correctly describe interfacial properties. In a later work, S. Dietrich *et al.* use density functional theory (DFT) as a basis to analyze a more microscopic model for both a monocomponent and a binary system. Their study is aimed at obtaining an effective Hamiltonian in each case [11, 21]. In order to obtain the interfacial properties, these authors account for the smooth variation of the density profile, include its deformation due to curvature, and use normal coordinates to introduce an adapted parametrization for the profile near the interface. In the present work we analyze the statistical mechanics nature of the free energy and the interfacial coefficients for an interface that is arbitrarily deformed, for systems composed of one or several components. Specifically, we consider a mean field approximation for the free energy of the interfacial region, which is the simplest approximation to describe the coexistence state of a simple fluid. The resulting energy functional can be expressed as a sum of two terms, each containing local and non-local information respectively [16, 19]. Our aim is to determine the grand potential of an arbitrarily deformed interface for a smooth density profile. To proceed we use DFT following the route of the stress tensor, and assume that the interface behaves as a bidimensional elastic continuous medium. The Gibbs dividing surface is then fixed properly, and the density profile is expanded in powers of the principal curvatures. Finally, a local approximation for the surface is performed, which indirectly affects the interaction potential, and the microscopic expressions for the surface are obtained. The results we obtain are in complete agreement with previous works and with the most relevant quantities from other viewpoints. The most relevant features in our work, which distinguish it from those previously cited, can be summarized as: (i) we start from an exact expression for the free energy at the level of mean field [10], (ii) instead of using normal coordinates, we carry out a local approximation for the surface, and (iii) by using the corresponding expression for the energy, the analysis is generalized to an arbitrary number of components [22].

This paper is organized as follows. In Sec. 2 we briefly outline the general aspects from this viewpoint. Section 3 is devoted to the monocomponent system. There we consider all relevant developments and results. Next, we carry out an analogous analysis but for the multicomponent system in Sec. 4, where in addition we obtain properties for the different surfaces. In Sec. 5 we compare our results with the most relevant works, and finally, in Sec. 6 we draw some concluding remarks.

2. Stress Tensor Theory

The description of the system may be carried out using the fact that the free energy representing the interface of a monocomponent simple fluid in a liquid-vapor coexistence state, according to DFT, can be written as [23–25]

$$\Omega[\rho(\vec{r})] = F[\rho(\vec{r})] + \int d\vec{r}[\mu - V_{\text{ext}}(\vec{r})]\rho(\vec{r}), \qquad (2)$$

where $F[\rho(\vec{r})]$ is the intrinsic Helmholtz free energy, μ is the chemical potential, and V_{ext} is the external potential. To obtain the equilibrium value for the density profile, ρ_0, it is necessary to minimize the grand potential density functional and solve the resulting Euler-Lagrange (E-L) equation. Alternatively, the E-L equation can be manipulated to identify a force-balance equation for a continuum medium in equilibrium [19, 26, 27]

$$\nabla \cdot \boldsymbol{\sigma} = \rho_0 \nabla V_{\text{ext}}, \qquad (3)$$

where $\boldsymbol{\sigma}$ is the stress tensor and $\rho_0 V_{\rm ext}(\vec{r})$ is the external force per unit area. This conservation equation implies existence of a stress tensor, which contains information of the whole system. That is, information on the bulk homogeneous phases as well as on the interfacial region. Although this quantity is not unique, because a term with zero divergence may be always added, within this theory it is the starting point for the calculation of relevant physical properties. Here we employ the most general expression known in literature, derived from a non-local field theory, and model the system as a continuous medium [16, 28]. By convenience, and to carry out a detailed analysis, we separate the stress tensor in two contributions: one for the homogeneous region and the other for the inhomogeneous one. The microscopic expression that results for the interfacial contribution within the van der Waals approximation for the monocomponent fluid is given by [10]

$$\begin{aligned}\sigma_S^{\alpha\beta}(\vec{r}) = &-\int d\vec{r}\,' \int_0^1 d\lambda\, \rho_0(\vec{r}-(1-\lambda)\vec{r}\,')\\ &\times \tilde{\omega}(\vec{r}\,') r'_\alpha \nabla_\beta \rho_0(\vec{r}+\lambda\vec{r}\,')\\ &-\frac{1}{2}\nabla_\nu \int d\vec{r}\,' \int_0^1 d\lambda\, \rho_0(\vec{r}-(1-\lambda)\vec{r}\,')\tilde{\omega}(\vec{r}\,')\\ &\times r'_\beta[r'_\alpha \nabla_\nu \rho_0(\vec{r}+\lambda\vec{r}\,') - r'_\nu \nabla_\alpha \rho_0(\vec{r}+\lambda\vec{r}\,')]. \quad (4)\end{aligned}$$

This quantity depends exclusively on the density profile and on the interaction potential, and is independent of the interfacial geometry. In fact, the geometry is defined by the density profile itself Superscripts α and β on the stress tensor denote its cartesian components; $\tilde{\omega}$ is the interaction potential between particles, which is short-ranged, and λ is a parameter that relates two fluid points on the interfase. Our goal is to determine the grand potential for an arbitrarily curved geometry by considering a smooth profile. Evidently, one expects to obtain more precise results and extra contributions absent for a step-like profile. We assume that each point $\vec{r}$ in space is described by a semi-orthogonal triple $(\hat{n}(\vec{r}), \hat{t}_1(\vec{r}), \hat{t}_2(\vec{r}))$, with $\hat{n}(\vec{r}) = \nabla\rho_0(\vec{r})/\mid \nabla\rho_0(\vec{r}) \mid$ being the normal vector and $\hat{t}_\alpha(\vec{r})$, $\alpha = 1, 2$ tangent vectors to the surface. They are such that $\hat{n}(\vec{r}) \cdot \hat{t}_\alpha(\vec{r}) = 0$, with $\alpha = 1, 2$ and $\hat{t}_1(\vec{r}) \cdot \hat{t}_2(\vec{r}) \neq 0$. Notice that the normal vector is defined only in the inhomogeneous region, where $\nabla\rho_0(\vec{r}) \neq 0$.

The free energy of the whole system is obtained by integrating the normal component of the stress tensor over all space. This normal component may be also separated in two contributions: one due to the homogeneous region and the other due to the inhomogeneous one [27]. As we are interested only in the interfacial region, we use the fact that the corresponding grand potential can be obtained from

$$\Omega_S[\rho_0(\vec{r})] = -\int d\vec{r}\sigma_S^N(\vec{r}), \quad (5)$$

where σ_S^N is the microscopic stress tensor of the inhomogeneous region. Eq. (5) is a completely general expression that may be used to derive surface properties, at the microscopic level, of any surface. Such derivations are carried out in Sec. 3 for a curved interface.

2.1. Fluid Mixture

We now provide a brief description, analogous to that at the beginning of this section, but for the system containing an arbitrary number of components [22]. Let us, therefore, consider a grand canonical density functional for the t-component fluid consisting of molecules of different constituents interacting via a spherically symmetric potential; to be introduced in explicit form shortly. The expression for this grand potential functional is

$$\begin{aligned}\Omega[\rho^1(\vec{r}), \ldots, \rho^t(\vec{r})] = &F[\rho^1(\vec{r}), \ldots, \rho^t(\vec{r})]\\ &+\sum_{i=1}^{t} \int d\vec{r}\,[\mu^i - V_{\rm ext}^i(\vec{r})]\rho^i(\vec{r}), \quad (6)\end{aligned}$$

where $F[\rho^1(\vec{r}), \ldots, \rho^t(\vec{r})]$ is the intrinsic Helmholtz free energy of the whole system, μ^i, $V_{\rm ext}^i(\vec{r})$, and $\rho^i(\vec{r})$ are the chemical potential, the external potential, and the density profile of the i-th component respectively. Molecules from different constituents are related each other through an interaction potential which depends on the level of approximation under consideration. Throughout this study we assume an approximation at the level of mean field, which is introduced explicitly later on.

The equilibrium density profile for each component ρ_0^i is obtained following the same procedure as in the monocomponent system. The difference, in this case, being the appearance of a system of t coupled E-L equations whose solution is more complicated. Explicitly, it is necessary to minimize Eq. (6); which yields the corresponding E-L equation. Then, in analogy to the monocomponent treatment, we carry out pertinent manipulations so as to write it as the force-balance equation

$$\begin{aligned}\left.\frac{\delta F}{\delta\rho^i}\right|_{\rho_0^i} &\nabla\rho_0^i(\vec{r}) - \nabla\{[\mu^i - V_{\rm ext}^i(\vec{r})]\rho_0^i(\vec{r})\}\\ &= \rho_0^i(\vec{r})\nabla V_{\rm ext}^i(\vec{r}). \quad (7)\end{aligned}$$

This partial balance is not sufficient to represent the conservation equation of the whole system. The appropriate result is obtained from Eq. (7) by summing over all components. That yields

$$\nabla\cdot\boldsymbol{\sigma} = \sum_{i=1}^{t} \rho_0^i(\vec{r})\nabla V_{\rm ext}^i(\vec{r}), \quad (8)$$

where $\boldsymbol{\sigma}$ now denotes the stress tensor of the fluid mixture, which is symmetric by nature of the system [28]. This quantity contains information on both, the homogeneous phases and the interfacial region. However, it is not unique as one may always add a term with vanishing divergence and the external force per unit area remains invariant. To proceed, we separate the stress tensor in two contributions: one for each region, corresponding to homogeneous and inhomogeneous densities

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_0 + \boldsymbol{\sigma}_S, \tag{9}$$

where $\boldsymbol{\sigma}_0$ is the homogeneous contribution from the bulk phases of all components, given as

$$\begin{aligned}\boldsymbol{\sigma}_0 &= \omega(\vec{r},[\rho_0^1,\ldots,\rho_0^t])\mathbf{I}]) \\ &= \left[f(\vec{r},[\rho_0^1,\ldots,\rho_0^t]) - \sum_{i=1}^{t}(\mu^i - V_{\mathrm{ext}}^i(\vec{r}))\rho_0^i\right]\mathbf{I},\end{aligned} \tag{10}$$

with $\mathbf{I}$ being the unit tensor, and the contribution from the interfacial region, $\boldsymbol{\sigma}_S$, that satisfies the relationship

$$\begin{aligned}\nabla\cdot\boldsymbol{\sigma}_S(\vec{r}) = \sum_{i=1}^{t}&\left[\left.\frac{\delta F}{\delta\rho^i}\right|_{\rho_0^i}\nabla\rho_0^i(\vec{r})\right] \\ &- \nabla f(\vec{r},[\rho_0^1,\cdots,\rho_0^t]).\end{aligned} \tag{11}$$

In addition, we introduce the densities of grand potential and Helmholtz free energy, $\omega(\vec{r},[\rho_0^1,\ldots,\rho_0^t])$ and $f(\vec{r},[\rho_0^1,\ldots,\rho_0^t])$, defined respectively through

$$\Omega[\rho_0^1,\ldots,\rho_0^t] = \int d\vec{r}\,\omega(\vec{r},[\rho_0^1,\ldots,\rho_0^t]), \tag{12}$$

$$F[\rho_0^1,\ldots,\rho_0^t] = \int d\vec{r}\,f(\vec{r},[\rho_0^1,\ldots,\rho_0^t]). \tag{13}$$

By considering the system as a continuum medium and using general symmetry arguments, a non-local field theory has been constructed which predicts the following expression for the stress tensor [22, 28]

$$\begin{aligned}\sigma^{\alpha\beta}(\vec{r}) = &\left(f(\vec{r},[\rho_0^1,\ldots,\rho_0^t]) - \sum_{i=1}^{t}(\mu^i - V_{\mathrm{ext}}^i(\vec{r}))\rho_0^i\right)\mathbf{I} \\ &- \sum_{i=1}^{t}\int d\vec{r}\,'\int_0^1 d\lambda\, r'_\alpha\nabla_\beta\rho_0^i(\vec{r}+\lambda\vec{r}\,') \\ &\times\frac{\delta L_0(\vec{r}-(1-\lambda)\vec{r}\,' \mid \rho_0^1,\ldots,\rho_0^t)}{\delta\rho_0^i(\vec{r}+\lambda\vec{r}\,')} \\ &+ \nabla_\nu\sum_{i=1}^{t}\int d\vec{r}\,'\int_0^1 d\lambda\,\lambda r'_\beta \\ &\times\left(r'_\nu\nabla_\alpha\rho_0^i(\vec{r}+\lambda\vec{r}\,') - r'_\alpha\nabla_\nu\rho_0^i(\vec{r}+\lambda\vec{r}\,')\right) \\ &\times\frac{\delta L_0\big(\vec{r}-(1-\lambda)\vec{r}\,' \mid \rho_0^1,\ldots,\rho_0^t\big)}{\delta\rho_0^i(\vec{r}+\lambda\vec{r}\,')}.\end{aligned} \tag{14}$$

There exists a direct relation between concepts from Lagrangian mechanics and equilibrium statistical mechanics. The quantity $L_0(\vec{r}\mid\rho_0^1,\ldots,\rho_0^t) - \sum_{i=1}^{t}\mu^i(\vec{r})\rho_0^i(\vec{r}) = \omega(\vec{r}\mid\rho_0^1,\ldots,\rho_0^t)$ is identified as the grand potential density; that is, minus the pressure in an uniform fluid [28]. The first term in brackets in Eq. (14) is the contribution σ_0, corresponding to the bulk homogeneous phases, whereas the remaining part is that from the interfacial region σ_S, recognizable because $\nabla\rho_0(\vec{r}) \neq 0$ there. In this theory the non-local functional $F[\rho(\vec{r})]$ enters just as an ingredient. We assume that the mean field approximation is sufficient to capture all relevant details of the fluid mixture in the liquid-vapor coexistence state. Higher order approximations to the free energy yield more detailed information, as they allow to measure correlations between different points. Nevertheless, this information is relevant when the system presents long-range fluctuations, which occurs as it approaches to the critical point.

Once again the free energy of the system may be obtained by integrating the normal component of the stress tensor over the whole space. The separation of the stress tensor introduced before implies that the grand potential may also be separated in two contributions [22]. The contribution from the bulk homogeneous phases may be considered known. In many cases it corresponds to terms of pressure by volume, or to the free energy of a hard sphere system. On the other hand, the microscopic expression for the free energy of the interfacial region is the most relevant physical quantity, which we will investigate for inhomogeneous systems. The fact that all surface properties may be derived from this contribution, lead us to concentrate exclusively on it. Our starting point is the exact result

$$\Omega_S = -\int d\vec{r}\sigma_S^N, \tag{15}$$

where the expression for σ_S depends on the free energy approximation and captures information on the t-component system. As previously mentioned, we consider an approximation at the level of mean field, which proposes the Helmholtz free energy as

$$\begin{aligned}F[\rho_0(\vec{r})] = \sum_{i=1}^{t}\int d\vec{r}\,f(\rho_0^i(\vec{r})) + \frac{1}{2}\sum_{i=1}^{t}\sum_{j=1}^{t}\int d\vec{r} \\ \times\int d\vec{r}\,'\,\tilde{\omega}_{ij}(\vec{r}-\vec{r}\,')\rho_0^i(\vec{r})\rho_0^j(\vec{r}\,'),\end{aligned} \tag{16}$$

with $\tilde{\omega}_{ij}$ being the interaction potential between two molecules of arbitrary components i and j. The first term in this expression contains information only on the system local contribution, which can be for an ideal gas or hard spheres. The second captures the non-local behavior of the system, which is the most relevant contribution to describe its liquid-vapor coexistence state. By introducing this approximation into the stress tensor, Eq. (14), and identifying the contribution to the interfacial region, we find

$$\begin{aligned}\sigma_S^{\alpha\beta}(\vec{r}) = -\frac{1}{2}\sum_{ij}\int d\vec{r}\,'\int_0^1 d\lambda\,\rho_0^i(\vec{r}-(1-\lambda)\vec{r}\,') \\ \times\tilde{\omega}_{ij}(\vec{r}\,')r'_\alpha\nabla_\beta\rho_0^j(\vec{r}+\lambda\vec{r}\,')\end{aligned}$$

$$-\frac{1}{2}\sum_{ij}\nabla_\nu\int d\vec{r}\,'\int_0^1 d\lambda\,\rho_0^i(\vec{r}-(1-\lambda)\vec{r}\,')\tilde{\omega}_{ij}(\vec{r}\,')$$
$$\times r'_\beta\left[r'_\alpha\nabla_\nu\rho_0^j(\vec{r}+\lambda\vec{r}\,')-r'_\nu\nabla_\alpha\rho_0^j(\vec{r}+\lambda\vec{r}\,')\right]. \quad (17)$$

We perform a general analysis, for the system composed of an arbitrary number t of components, for which there exists a variety of interaction potentials $\tilde{\omega}_{ij}$ between pairs of molecules. As all interactions, either between molecules of the same or different constituents, are possible, there is a total of $t(t+1)/2$ interaction potentials, which implies existence of an equivalent number of coexistence regions.

3. Interfacial Free Energy and Curvature Expansion for the Density Profile

We consider an arbitrarily curved interface for a density profile that depends exclusively on the normal coordinate. By using Eqs. (4) and (5) we get to the general microscopic grand potential [10]

$$\Omega_S[\rho_0(\vec{r})]=-\frac{1}{4}\int d\vec{r}\int d\vec{r}\,'\int_0^\infty ds$$
$$\times\nabla\rho_0(\vec{r})\cdot\nabla'\rho_0(\vec{r}\,')\tilde{\omega}(s+(\vec{r}-\vec{r}\,')^2). \quad (18)$$

This result, exact at the level of mean field, describes the behavior of an arbitrarily curved interface in equilibrium. All details of the interfacial region are there contained as it depends on the full profile of the curved interface. In order to obtain explicit expressions for surface properties it is necessary to approximate the density profile and the surface representing the interfacial region. The aim in this study is to perform the most general approximation to the density profile within this scheme.

We start by writing the volume element as $d\vec{r}=dS(r_n)dr_n$, where the surface element dS depends on the metric under consideration. By decomposing vectors in their normal and tangent components respectively, the expression for the interaction potential gets slightly modified. After this, we fix the Gibbs dividing surface by assuming it located at $r_n=R_n$, and then expand the density profile about this surface. Explicitly, we use $r_n=R_n+z$ and propose an expansion in powers of the principal curvatures of the form

$$\rho_0(\vec{r}_n)=\rho(R_n+z)$$
$$=\rho_0(z)+\rho_1(z)H+\rho_2(z)H^2+\rho_3(z)K, \quad (19)$$

where H and K are the mean and Gaussian curvatures respectively, ρ_0 is the density profile of the local plane, and ρ_α, $\alpha=1,2,3$, are corrections to the profile due to curvatures. Within this representation the volume element becomes $dS(r_n)dr_n=dS(R_n)dz$. The interaction potential is also affected by this choice of Gibbs dividing surface. Now its argument has the dependence

$$\tilde{\omega}\Big(s+(\vec{r}_n-\vec{r}\,'_n)^2+(\vec{r}_t-\vec{r}\,'_t)^2\Big)=\tilde{\omega}\Big(s+(\vec{r}_t-\vec{r}\,'_t)^2$$
$$+(R_n-z_1)^2+(R'_n-z_2)^2$$
$$-2(R_n-z_1)(R'_n-z_2)\hat{n}(\vec{r})\cdot\hat{n}'(\vec{r}\,')\Big). \quad (20)$$

Also, for this dividing surface, the density profile is expanded and introduced into the interaction potential. The grand potential then becomes

$$\Omega_S=-\frac{1}{4}\int dS(r_n)\int_{-\infty}^{\infty}dz_1\int dS(r'_n)\int_{-\infty}^{\infty}dz_2$$
$$\times\int_0^\infty ds\,\hat{n}(\vec{r})\cdot\hat{n}'(\vec{r}\,')\tilde{\omega}\Big(s+(\vec{r}_t-\vec{r}\,'_t)^2+(R_n-z_1)^2$$
$$+(R'_n-z_2)^2-2(R_n-z_1)(R'_n-z_2)\hat{n}\cdot\hat{n}'\Big)$$
$$\times\Big\{\rho'_0(z_1)\rho'_0(z_2)+H[\rho'_1(z_1)\rho'_0(z_2)+\rho'_0(z_1)\rho'_1(z_2)]$$
$$+H^2[\rho'_0(z_1)\rho'_2(z_2)+\rho'_1(z_1)\rho'_1(z_2)+\rho'_2(z_1)\rho'_0(z_2)]$$
$$+K[\rho'_3(z_1)\rho'_0(z_2)+\rho'_0(z_1)\rho'_3(z_2)]\Big\}. \quad (21)$$

That is, a function of the principal curvatures of the system and of the diverse contributions from the density profile. A drawback is that it also depends on two surface integrals. To obtain explicit forms for the microscopic expressions of the surface properties, it is necessary to approximate one of these

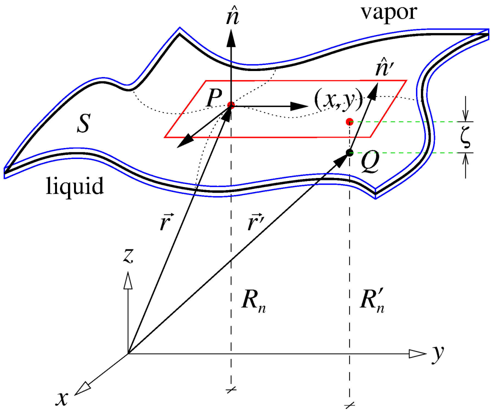

FIGURE 1. Schematic picture showing the local approximation for surface S about a point P. Points P and Q are located by vectors $\vec{r}$ and $\vec{r}\,'$ respectively, and the normal vectors to the surface at those points are $\hat{n}$ and $\hat{n}'$. Point P is chosen as the origin of the local coordinate system whereas Q lies outside the tangent plane. Its projection onto this tangent plane has coordinates (x,y). The radius of location of the Gibbs dividing surface is at R_n. The distance from Q to the local plane (projection of $\hat{n}'$ onto $\hat{n}$) is $R_n-R'_n=\zeta$, with ζ seen from the local system as a paraboloid.

integrals. This may be accomplished by choosing two arbitrary points on the surface, located by vectors $\vec{r}$ and $\vec{r}\,'$, and taking one of them as the origin of the new coordinate system, with its horizontal plane being the tangent plane to the surface at such point [10, 29, 30]. The distance that separates these points is of the order of the interaction potential range, *i.e.* the length-scale over which a molecule is related to others. Although this separation could be small, only one of the points lies on the tangent plane. Figure 1 shows this setting where the point P, located by $\vec{r}$, is chosen as the origin of the local coordinate system. The other point, Q, located by $\vec{r}\,'$, has in-plane coordinates (x, y). Denoting the magnitudes of the normal components of vector positions $\vec{r}$ and $\vec{r}\,'$ as R_n and R_n' respectively, the difference between these components, as measured from the local system, is $R_n - R_n' = \zeta = 1/2\left(x^2/R_1 + y^2/R_2\right)$, which corresponds to the height ζ of the arbitrary point $\vec{r}\,'$ on the Gibbs dividing surface as seen from the local coordinate system. By using this parametrization, the metric on the surface becomes $g = 1 + x^2/R_1^2 + y^2/R_2^2$. A normal vector to the surface at Q is $\hat{n}' = (-\nabla\zeta, 1)/\sqrt{g}$, which is easily obtained from the quadratic approximation. Then, by choosing the normal vector to the surface at P as $\hat{n} = \hat{k}$, the product of normals becomes $\hat{n}\cdot\hat{n}' = 1/\sqrt{g}$.

Evidently, election of the Gibbs dividing surface as well as manipulations on the density profile depend only on the normal components. This choice of local coordinate system, in addition, make the tangent components of vectors $\vec{r}$ and $\vec{r}\,'$ have coordinates $\vec{r}_t = (0, 0)$ and $\vec{r}_t\,' = (x, y)$, respectively. From this we find the approximation to the product $\hat{n}\cdot\hat{n}'$, in terms of the radii of curvature, given as $\hat{n}\cdot\hat{n}' \approx 1 - 1/2\left(x^2/R_1^2 + y^2/R_2^2\right)$. We employ this result to approximate the argument of the interaction potential and then power expand it, in terms of the inverse radii of curvature, about the value $s + x^2 + y^2 + (z_1 - z_2)^2$. This yields

$$\begin{aligned}
&\tilde{\omega}\Big(s+(\vec{r}_t-\vec{r}_t\,')^2+(R_n-z_1)^2+(R_n'-z_2)^2-2(R_n-z_1)(R_n'-z_2)\hat{n}\cdot\hat{n}'\Big)=\tilde{\omega}\Big(s+(\vec{r}_t-\vec{r}_t\,')^2+(z_1-z_2)^2\\
&+(R_n-R_n')^2+2(z_1-z_2)(R_n-R_n')\Big)=\tilde{\omega}\Big(s+x^2+y^2+(z_1-z_2)^2+(z_1-z_2)\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)+\frac{1}{4}\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)^2\Big)\\
&=\tilde{\omega}\Big(s+x^2+y^2+(z_1-z_2)^2\Big)+\tilde{\omega}'\Big(s+x^2+y^2+(z_1-z_2)^2\Big)\Big[(z_1-z_2)\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)+\frac{1}{4}\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)^2\Big]\\
&+\frac{1}{2}\tilde{\omega}''\Big(s+x^2+y^2+(z_1-z_2)^2\Big)\Big[(z_1-z_2)\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)+\frac{1}{4}\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)^2\Big]^2+\cdots
\end{aligned}\tag{22}$$

It will be shown later on in this section that this approximation is sufficient to capture the most relevant details of the system and to obtain the terms containing physical meaning.

As we are interested only in the most relevant contributions to the surface, terms with curvatures larger than H^2 and K, or equivalently larger than the inverse radii of curvature squared, will be ignored. By also considering that $dS(r_n') = \sqrt{g}dxdy$, we get to an expression for the grand potential in terms of the difference $z_1 - z_2$

$$\begin{aligned}
\Omega=&-\frac{1}{4}\int dS(R_n)\int_{-\infty}^{\infty}dz_1\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dz_2\int_{0}^{\infty}ds\times\Big[\tilde{\omega}(s+x^2+y^2+(z_1-z_2)^2)+\frac{1}{4}\tilde{\omega}'(s+x^2+y^2+(z_1-z_2)^2)\\
&\times\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)^2\Big]\Big[\rho_0'(z_1)\rho_0'(z_2)+H[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_1'(z_2)]+H^2[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]\\
&+K[\rho_3'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_3'(z_2)]\Big]-\frac{1}{4}\int dS(R_n)\int_{-\infty}^{\infty}dz_1\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dz_2\int_{0}^{\infty}ds\,(z_1-z_2)\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)\\
&\times\Big[\tilde{\omega}'(s+x^2+y^2+(z_1-z_2)^2)+\frac{1}{2}\tilde{\omega}''(s+x^2+y^2+(z_1-z_2)^2)(z_1-z_2)\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)+\cdots\Big]\\
&\times\Big[\rho_0'(z_1)\rho_0'(z_2)+H[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_1'(z_2)]+H^2[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]\\
&+K[\rho_3'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_3'(z_2)]\Big]=\Omega_0+\Omega_{z_1-z_2}.
\end{aligned}\tag{23}$$

Notice the separation in two contributions: The first integral, that we call Ω_0, is independent of the difference $z_1 - z_2$. However the second one, here denoted $\Omega_{z_1-z_2}$, is proportional, up to quadratic terms, to $z_1 - z_2$. We first work the term Ω_0 to identify its contribution to the free energy of the interfacial region. The aim is to express this quantity in terms of the interaction potential, and not on its derivative. We expect it to depend explicitly on the curvatures. Its expression is easily identified from Eq. (23) and reads

$$\begin{aligned}\Omega_0 = -\frac{1}{4}\int dS(R_n)\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz_2 \int_{0}^{\infty} ds\Big[\tilde{\omega}(s+x^2+y^2+(z_1-z_2)^2)+\frac{1}{4}\tilde{\omega}'\\ (s+x^2+y^2+(z_1-z_2)^2)\times\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)^2\Big]\Big[\rho_0'(z_1)\rho_0'(z_2)+H[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho1'(z_2)]\\ +H^2[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]+K[\rho_3'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_3'(z_2)]\Big].\end{aligned} \tag{24}$$

Integrations respect to x and y may be easily carried out. Then, by using the relation between radii of curvature and principal curvatures, $\frac{1}{R_1^2}+\frac{1}{R_2^2}+\frac{2}{3R_1R_2}=H^2-\frac{4}{3}K$, one finds the expression for Ω_0 in powers of the principal curvatures

$$\begin{aligned}\Omega_0 = -\frac{1}{4}\int dS(R_n)\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2\Big[2\pi\int_{0}^{\infty} dr\, r^3\tilde{\omega}(r^2+(z_1-z_2)^2)-\frac{3}{16}\pi\int_{0}^{\infty} dr\, r^5\tilde{\omega}(r^2+(z_1-z_2)^2)\Big(H^2-\frac{4}{3}K\Big)\Big]\\ \times\Big[\rho_0'(z_1)\rho_0'(z_2)+H[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_1'(z_2)]+H^2[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]\\ +K[\rho_3'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_3'(z_2)]\Big].\end{aligned} \tag{25}$$

We now concentrate on those terms that depend on the difference z_1-z_2, which could imply a dependence on the Gibbs dividing surface. This contribution, correct to quadratic order on the inverse radii of curvature, may be read directly from Eq. (23)

$$\begin{aligned}\Omega_{z_1-z_2} = -\frac{1}{4}\int dS(R_n)\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz_2 \int_{0}^{\infty} ds\times(z_1-z_2)\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)\Big[\tilde{\omega}'(s+x^2+y^2+(z_1-z_2)^2)\\ +\frac{1}{2}\tilde{\omega}''(s+x^2+y^2+(z_1-z_2)^2)(z_1-z_2)\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)+\cdots\Big]\Big[\rho_0'(z_1)\rho_0'(z_2)+H[\rho_1'(z_1)\rho_0'(z_2)\\ +\rho_0'(z_1)\rho_1'(z_2)]+H^2[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]\\ +K[\rho_3'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_3'(z_2)]\Big]=\Omega^{(1)}_{z_1-z_2}+\Omega^{(2)}_{z_1-z_2},\end{aligned} \tag{26}$$

where now $\Omega^{(1)}_{z_1-z_2}$ and $\Omega^{(2)}_{z_1-z_2}$ denote contributions linear and quadratic on the difference z_1-z_2 respectively; each requiring a separate analysis as their dependence on the interaction potential is different. The first term is

$$\begin{aligned}\Omega^{(1)}_{z_1-z_2} = -\frac{1}{4}\int dS(R_n)\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz_2 \int_{0}^{\infty} ds\times(z_1-z_2)\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)\tilde{\omega}'(s+x^2+y^2+(z_1-z_2)^2)\\ \times\Big[\rho_0'(z_1)\rho_0'(z_2)+H[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_1'(z_2)]+H^2[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]\\ +K[\rho_3'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_3'(z_2)]\Big],\end{aligned} \tag{27}$$

in which, analogously to the previous term, we perform the integrations over x and y independently. Maintaining the contribution to quadratic order on the curvatures we find

$$\begin{aligned}\Omega^{(1)}_{z_1-z_2} = -\frac{1}{4}(-\frac{\pi}{2})H\int dS(R_n)\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \int_{0}^{\infty} drr^3\times(z_1-z_2)\tilde{\omega}'(r^2+(z_1-z_2)^2)\\ \times\Big[\rho_0'(z_1)\rho_0'(z_2)+H[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_1'(z_2)]\Big].\end{aligned} \tag{28}$$

This expression can be interpreted as the first order term in the series expansion of the two-point correlation function, which gets canceled out by symmetry. Introducing appropriate changes of variables, this expression can be manipulated further to realise that it cancels indeed. It is important to mention that throughout these manipulations, the principal curvatures are taken as constants, which is so because the Gibbs dividing surface has been fixed in advance. We now look at the term that depends quadratically on the difference $z_1 - z_2$

$$\Omega^{(2)}_{z_1-z_2} = -\frac{1}{4}\int dS(R_n)\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dx \int\limits_{-\infty}^{\infty} dy \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} ds \times (z_1-z_2)^2\Big(\frac{x^2}{R_1}+\frac{y^2}{R_2}\Big)^2\,\frac{1}{2}\,\tilde{\omega}''(s+x^2+y^2+(z_1-z_2)^2)$$
$$\times\bigg[\rho_0'(z_1)\rho_0'(z_2) + H[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_1'(z_2)] + H^2[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]$$
$$+ K[\rho_3'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_3'(z_2)]\bigg]. \tag{29}$$

Once again, we evaluate the integrals over x and y, and maintain only quadratic order contributions on the curvatures to get

$$\Omega^{(2)}_{z_1-z_2} = -\frac{3\pi}{16}\Big(H^2-\frac{4}{3}K\Big)\int dS(R_n)\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr r^3 \times (z_1-z_2)^2\ \tilde{\omega}(r^2+(z_1-z_2)^2)\rho_0'(z_1)\rho_0'(z_2). \tag{30}$$

This contribution can be interpreted as the second order term in the series expansion of the two-point correlation function, which is non-zero by symmetry. By adding all contributions we obtain the final result

$$\Omega_S = -\frac{\pi}{2}\int dS(R_n)\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2\bigg\{\int\limits_{0}^{\infty} dr\, r^3\tilde{\omega}(r^2+(z_1-z_2)^2)\Big[\rho_0'(z_1)\rho_0'(z_2)+H[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_1'(z_2)]$$
$$+H^2[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]+K[\rho_3'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_3'(z_2)]\Big]$$
$$+\frac{3}{8}\int\limits_{0}^{\infty} dr[\,(z_1-z_2)^2r^3-\frac{1}{4}\,r^5]\tilde{\omega}(r^2+(z_1-z_2)^2)\Big(H^2-\frac{4}{3}K\Big)\rho_0'(z_1)\rho_0'(z_2)\bigg\}. \tag{31}$$

Observe that the order in the approximation of this microscopic free energy is the same as in the expansion of the interaction potential (22).

Equation (31) provides the most general expression for an arbitrarily curved surface and for a smooth density profile within this approximation scheme; which is consistent with the limit case of a step-like density profile. The result is also consistent with that obtained for spherical and cylindrical surfaces using a smooth profile. Microscopic expressions for the interfacial properties are obtained by direct comparison of the previous expression with Eq. (1). Thus, for this system

$$\gamma = -\frac{\pi}{2}\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr\, r^3\tilde{\omega}(r^2+(z_1-z_2)^2)\rho_0'(z_1)\rho_0'(z_2), \tag{32}$$

$$\kappa c_0 = \frac{\pi}{4}\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr\, r^3\tilde{\omega}(r^2+(z_1-z_2)^2)[\rho_1'(z_1)\rho_0'(z_2)+\rho_0'(z_1)\rho_1'(z_2)], \tag{33}$$

$$\kappa = -\frac{\pi}{2}\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr\, r^3\tilde{\omega}(r^2+(z_1-z_2)^2)[\rho_0'(z_1)\rho_2'(z_2)+\rho_1'(z_1)\rho_1'(z_2)+\rho_2'(z_1)\rho_0'(z_2)]$$
$$-\frac{3\pi}{16}\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr\,(z_1-z_2)^2r^3\tilde{\omega}(r^2+(z_1-z_2)^2)\rho_0'(z_1)\rho_0'(z_2)$$
$$+\frac{3\pi}{64}\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr\, r^5\tilde{\omega}(r^2+(z_1-z_2)^2)\rho_0'(z_1)\rho_0'(z_2), \tag{34}$$

$$\bar{\kappa} = -\frac{\pi}{2}\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr\, r^3 \tilde{\omega}(r^2 + (z_1 - z_2)^2)[\rho_3'(z_1)\rho_0'(z_2) + \rho_0'(z_1)\rho_3'(z_2)]$$
$$+ \frac{\pi}{4}\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr\, (z_1 - z_2)^2 r^3 \tilde{\omega}(r^2 + (z_1 - z_2)^2)\rho_0'(z_1)\rho_0'(z_2)$$
$$- \frac{\pi}{16}\int\limits_{-\infty}^{\infty} dz_1 \int\limits_{-\infty}^{\infty} dz_2 \int\limits_{0}^{\infty} dr\, r^5 \tilde{\omega}(r^2 + (z_1 - z_2)^2)\rho_0'(z_1)\rho_0'(z_2), \tag{35}$$

are the surface tension, the spontaneous curvature, and the rigidity constants respectively. Observe that these coefficients inherit the generalities of the microscopic free energy (31), and that to be able to evaluate all properties numerically the third order corrections to the density profile, ρ_3, are necessary. This is a formidable task, initiated recently, that has already provided some significant advances [31]. We shall consider this problem in a future publication.

4. Multicomponent System

Here we carry out an analysis analogous to that in the previous section, but for the system composed of an arbitrary number of constituents. For this purpose, the normal component of the stress tensor for the inhomogeneous region, Eq. (14), is integrated over the whole space, Eq. (15), to obtain the contribution to the free energy from the interfacial region. By assuming density profiles that define an arbitrarily deformed interfacial region, which may be described using a semi-orthogonal system of vectors at each point, one finds the microscopic grand potential [22]

$$\Omega_S = -\frac{1}{4}\sum_{ij}\int d\vec{r}\int d\vec{r}\,'\int\limits_{0}^{\infty} ds\,\tilde{\omega}_{ij}$$
$$\times \left(s + (\vec{r}_n^{\,(1)} - \vec{r}_n^{\,(2)})^2 + (\vec{r}_t^{\,(1)} - \vec{r}_t^{\,(2)})^2\right)$$
$$\times\, \partial_n^{(1)}\rho_0^i(\vec{r}^{\,(1)})\partial_n^{(2)}\rho_0^j(\vec{r}_n^{\,(2)}). \tag{36}$$

The staring point for our study is precisely this exact microscopic expression, which captures the non-local character of the free energy. In contrast to the monocomponent system, in which there is only one density profile and one interaction potential, there now exist a large amount of these quantities. Equation (36) depends on all exact densities of an arbitrarily deformed surface. Such a form is inconvenient to exploit its analytic potential when studying the interfacial region, although it favors numerical analyzes, which are beyond the scope of this work. To obtain useful microscopic expressions of the interfacial properties, it is necessary to approximate the density profile. The approximation we use, accounts for the smooth decay of the density profile of each component density. Before proceeding to the analysis, we consider it relevant to briefly discuss the behavior of the fluid mixture with temperature. At high temperatures the system is expected to be found in a vapor phase mixture, obeying its corresponding mechanical equilibrium condition. As temperature is slightly lowered, there appears a liquid-vapor coexistence state in which both homogeneous phases are found in a mixed state. If temperature is lowered even further, multiple coexistence regions between the diverse components of the system are formed. These coexistence regions range from those of a single component to those of multiple ones. The latter is the most general state and thus the one we are interested to describe in this work.

Now we go onto fixing the Gibbs dividing surface for the i-th component; having density ρ^i. Let us assume its radius located at $r_n^i = R_n^i$ and expand the density profile about this surface by introducing the change $r_n^i = R_n^i + z$. When the choice is made, we get a mathematical surface on which the concepts from differential geometry can be associated without ambiguity. By performing a power-expansion of the density profile on the principal curvatures we get to

$$\rho_0^i(\vec{r}_n) = \rho_0^i(R_n^i + z)$$
$$= \rho_0^i(z) + \rho_1^i(z)H_i + \rho_2^i(z)H_i^2 + \rho_3^i(z)K_i, \tag{37}$$

where H_i and K_i are the mean and Gaussian curvatures, ρ_0^i is the profile of the local plane, and ρ_α^i are corrections to the density profile due to curvature. This expansion is obtained for each profile in the grand potential. The interaction potential between two arbitrary components i and j also captures these details. It is

$$\tilde{\omega}_{ij}\left(s + (\vec{r}_n^{\,i} - \vec{r}\,'^{j}_{n})^2 + (\vec{r}_t - \vec{r}\,'_t)^2\right)$$
$$= \tilde{\omega}_{ij}\Big(s + (\vec{r}_t - \vec{r}_t\,')^2 + (R_n^i - z_1)^2$$
$$+ (R_n'^j - z_2)^2 - 2(R_n^i - z_1)(R_n'^j - z_2)\hat{n}^i\cdot\hat{n}'^j\Big). \tag{38}$$

To proceed we introduce the volume element $d\vec{r} = dS(r_n)dr_n = dS(R_n)dz$ into the grand potential; observing that the surface element dS depends on the metric under consideration. Thus, it is evident that in order to obtain microscopic expressions for the most relevant properties of the system, one of the surface integrals in the grand potential must be evaluated. Following the same approach as for the monocomponent system; that is, assuming the surface for the i-th component locally approximated by a paraboloid, we calculate the metric and obtain an approximate expression for the product of the normals, so as to approximate the interaction potential. By introducing these approximations and the expansion for the density profile into the microscopic grand potential we obtain

$$\Omega = -\frac{1}{4}\sum_{ij}\int dS(r_n)\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{0}^{\infty} ds\tilde{\omega}_{ij}\bigg(s + x^2 + y^2 + (z_1 - z_2)^2 + (z_1 - z_2)\Big(\frac{x^2}{R_1^j} + \frac{y^2}{R_2^j}\Big) + \frac{1}{4}\Big(\frac{x^2}{R_1^j} + \frac{y^2}{R_2^j}\Big)^2\bigg)\Big\{\rho_0^{\prime i}(z_1)\rho_0^{\prime j}(z_2) + H_i\rho_1^{\prime i}(z_1)\rho_0^{\prime j}(z_2) + H_j\rho_0^{\prime i}(z_1)\rho_1^{\prime j}(z_2) + H_j^2\rho_0^{\prime i}(z_1)\rho_2^{\prime j}(z_2) + H_iH_j\rho_1^{\prime i}(z_1)\rho_1^{\prime j}(z_2) + H_i^2\rho_2^{\prime i}(z_1)\rho_0^{\prime j}(z_2) + K_i\rho_3^{\prime i}(z_1)\rho_0^{\prime j}(z_2) + K_j\rho_0^{\prime i}(z_1)\rho_3^{\prime j}(z_2) + \cdots\Big\}. \tag{39}$$

Then, we expand the interaction potential between components i and j, $\tilde{\omega}_{ij}$, about $s + x^2 + y^2 + (z_1 - z_2)^2$ and order terms in powers of the difference $z_1 - z_2$. These terms may now be analyzed, following the analogy with the monocomponent case, to obtain the final result for the contribution to the free energy from the interfacial region

$$\Omega_S = -\frac{\pi}{2}\sum_{ij}\int dS(R_n)\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \bigg[\int_{0}^{\infty} dr\, r^3\tilde{\omega}_{ij}(r^2 + (z_1 - z_2)^2))\Big\{\rho_0^{\prime i}(z_1)\rho_0^{\prime j}(z_2) + H_i\rho_1^{\prime i}(z_1)\rho_0^{\prime j}(z_2) + H_j\rho_0^{\prime i}(z_1)\rho_1^{\prime j}(z_2) + H_j^2\rho_0^{\prime i}(z_1)\rho_2^{\prime j}(z_2) + H_iH_j\rho_1^{\prime i}(z_1)\rho_1^{\prime j}(z_2) + H_i^2\rho_2^{\prime i}(z_1)\rho_0^{\prime j}(z_2) + K_i\rho_3^{\prime i}(z_1)\rho_0^{\prime j}(z_2) + K_j\rho_0^{\prime i}(z_1)\rho_3^{\prime j}(z_2)\Big\} + \frac{3}{8}\int_{0}^{\infty} dr\, [(z_1 - z_2)^2 r^3 - \frac{1}{4}r^5] \times \tilde{\omega}_{ij}(r^2 + (z_1 - z_2)^2)\Big(H_j^2 - \frac{4}{3}K_j\Big)\rho_0^{\prime i}(z_1)\rho_0^{\prime j}(z_2)\bigg]. \tag{40}$$

This expression implies that the Hamiltonian of the system depends on the arbitrary number of components, and that may be expanded in powers of the curvatures. This is an important result, as it allows for the knowledge, in approximate form, of the expression of the grand potential for a smooth profile.

Microscopic expressions for the interfacial properties of the multicomponent system can also be identified as the coefficients of the surface invariants, in analogy to Eq. (1). However, we consider the free energy Eq. (40) as the most relevant result, which is consistent with the monocomponent system, Eq. (31). Expressions for the microscopic free energy of the mono- and multi-component systems, Eqs. (31) and (40) respectively, clearly reproduce the asymptotic values of this quantity in the limit of a step-like density profile within this viewpoint [10, 22]. It is important to point out that the use of the same, van der Waals, mean-field model to describe the liquid-vapor coexistence state, as used in other viewpoints, is not a guarantee of identical expressions for the interfacial properties. Discrepancies do occur as a result of different approximations and simplifications, which are mainly due to the arbitrariness in election of the Gibbs dividing surface. Although discrepancies are observed in expressions for the rigidity constants [8,24], it is expected to find agreement with the main terms.

5. Comparison with other Works

Here we compare our results with predictions from other theoretical frameworks. For the monocomponent system, we take the microscopic grand potential either from Eq. (31) or setting $t = 1$ into Eq. (40). Only the most relevant aspects and results from these models are presented.

5.1. Squared Laplacian

The starting point for the description of this model is Eq. (16) with $t = 1$, *i.e.* for a single component. First, one introduces the assumption of small density gradients, which means that $\rho_0(\vec{r}\,')$ can be expanded about $\rho_0(\vec{r})$. This yields a free energy functional that depends on the equilibrium density at one point. Power-expanding this expression; maintaining terms up to squared laplacian, one obtains

$$f[\rho(\vec{r})] = \int d\vec{r}\bigg[f_0(\rho(\vec{r})) + \frac{1}{2}A(\rho(\vec{r}))\left(\nabla\rho(\vec{r})\right)^2 - \frac{1}{4}B(\rho(\vec{r}))\left(\nabla^2\rho(\vec{r})\right)^2\bigg], \tag{41}$$

where the coefficients f_0, A and B are given respectively by

$$f_0(\rho(\vec{r})) = kT\Big[\rho(\vec{r})\,\left[\ln(\lambda^3\rho(\vec{r})) - 1\right]$$

$$-\frac{1}{2}\rho^2(\vec{r})\int d\vec{r}\,'c(\vec{r}\,';\rho(\vec{r}))\Bigg], \tag{42}$$

$$A(\rho(\vec{r}))=\frac{kT}{3!}\int d\vec{r}\,'r'^2c(\vec{r}\,';\rho(\vec{r})), \tag{43}$$

$$B(\rho(\vec{r}))=\frac{2kT}{5!}\int d\vec{r}\,'r'^4c(\vec{r}\,';\rho(\vec{r})). \tag{44}$$

In these expressions, λ is the de Broglie thermal wavelength, $c(\vec{r}\,';\rho(\vec{r}))$ is the direct correlation function of a homogeneous and isotropic fluid of density $\rho(\vec{r})$, f_0 is the free energy density of an uniform fluid, and the coefficients A and B are the second and four moments of $c(\vec{r}\,';\rho(\vec{r}))$ respectively. Using this model, Robledo et al. described a monocomponent inhomogeneous fluid with interfacial surface arbitrarily curved [32]. According to DFT, the equilibrium grand potential is

$$\Omega_{\rm eq}=\Omega_{\rm bulk}[\rho_{\rm eq}(\vec{r})]+\Omega_{\rm surf}[\rho_{\rm eq}(\vec{r})], \tag{45}$$

where $\rho_{\rm eq}$ corresponds to the equilibrium density profile, which is obtained by minimizing the grand potential functional in Eq. (2). The result is

$$\Omega_{\rm eq}=-p_0V_{\rm in}-PL_nV_{\rm out}+\int dS\Bigg\{[A\left(\rho'\right)^2-B\left(\rho''\right)^2] + J\int dr_nB\rho'\rho''+\frac{1}{2}(J^2-2K) \times\int dr_nr_n^2[A\left(\rho'\right)^2-B\left(\rho''\right)^2]\Bigg\}. \tag{46}$$

Introduction of the same approximation for the density profile, Eq. (19), into this leads to

$$\Omega_{\rm eq}=-p_0V_{\rm in}-PL_nV_{\rm out}+\Omega_{\mathcal{S}}, \tag{47}$$

where $\Omega_{\mathcal{S}}$ denotes the contribution from the interfacial surface

$$\begin{aligned}\Omega_{\mathcal{S}}=&\int dS\int dr_n\left(\left[A\left(\rho_0'\right)^2-B\left(\rho_0''\right)^2\right]\right)+H\int dS\\ &\times\int dr_n[2A\rho_0'\rho_1'-2B\rho_0''\rho_1''+2B\rho_0'\rho_0'']+H^2\int dS\\ &\times\int dr_n\Big(A[2\rho_0'\rho_2'+\rho_1'^2]-B[2\rho_0''\rho_2''+\rho_1''^2]+2B\\ &\times[\rho_0'\rho_1''+\rho_1'\rho_0'']+2r_n^2[A\left(\rho_0'\right)^2-B\left(\rho_0''\right)^2]\Big)+K\int dS\\ &\times\int dr_n\left(\rho_3'\rho_0-B\rho_3''\rho_0''-[A\rho_0'^2+B\rho_0''^2]r_n^2\right).\end{aligned} \tag{48}$$

From this we read the microscopic expressions for the interfacial coefficients

$$\gamma=\int dr_n[A\left(\rho_0'\right)^2-B\left(\rho_0''\right)^2], \tag{49}$$

$$\kappa c_0=-\frac{1}{2}\int dr_n[2A\rho_0'\rho_1'-2B\rho_0''\rho_1''+2B\rho_0'\rho_0''], \tag{50}$$

$$\begin{aligned}\kappa=&\int dr_n\Big(A[2\rho_0'\rho_2'+\rho_1'^2]-B[2\rho_0''\rho_2''+\rho_1''^2]\\ &+2B[\rho_0'\rho_1''+\rho_1'\rho_0'']+2r_n^2[A\left(\rho_0'\right)^2-B\left(\rho_0''\right)^2]\Big),\end{aligned} \tag{51}$$

$$\bar{\kappa}=\int dr_n\left(\rho_3'\rho_0-B\rho_3''\rho_0''-[A\rho_0'^2+B\rho_0''^2]r_n^2\right). \tag{52}$$

By direct comparison of the expressions in this work and the squared laplacian model respectively, we observe the following: for the surface tension, Eqs. (32) and (49), show analytical discrepancy. This is due to the fact that Eq. (32) is exact at mean field level, whereas Eq. (49) corresponds to the first two terms of a series expansion. Comparison on the Tolman length, Eqs. (33) and (50), show agreement only in the first term. Eq. (50) has terms that cannot be reproduced in more detailed analyses, as the one in this and previous works [19, 31]. By comparing the results for the rigidity constants κ and $\bar{\kappa}$, Eqs. (34) and (35) with (51) and (52) respectively, we observe coincidence of some terms in the case $\rho(z_1)=\rho(z_2)$. Setting this condition, however, implies loosing information on the non-local behavior of the system, which is an effect from the squared laplacian approximation. Better coincidence is expected with a model using and equivalent level of approximation on the free energy.

5.2. Mean Field

Blokhuis *et al.* analyze the liquid-vapor coexistence state of a monocomponent simple fluid. Their starting point is the free energy functional [9, 31]

$$\Omega[\rho]=\int d\vec{r}\,[f_{\rm hs}(\rho(\vec{r}))-\mu\rho(\vec{r})] +\frac{1}{2}\int d\vec{r}\int d\vec{r}_{12}U(r)\rho(\vec{r}_1)\rho(\vec{r}_2), \tag{53}$$

where μ is the chemical potential and $U(r)$ is the short-range interaction potential. For the reference free energy, they assume the form of Carnahan-Starling

$$f_{\rm hs}(\rho)=k_BT\rho\ln\rho+k_BT\rho\frac{4\eta-3\eta^2}{(1-\eta)^2}, \tag{54}$$

where $\eta=\pi\rho d^3/6$ and d is the molecular diameter. These authors consider spherical and cylindrical liquid-droplets and expand both the density profile and chemical potential in powers of the inverse radii of curvature, as in Eq. (19). The results they obtain for the interfacial coefficients are [31]

$$\sigma = -\frac{1}{4}\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^2 (1-s^2)\rho_0'(z_1)\rho_0'(z_2), \tag{55}$$

$$\delta\sigma = \frac{1}{4}\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^2 (1-s^2)\rho_0'(z_1)\rho_1'(z_2), \tag{56}$$

$$\begin{aligned} k = &-\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^2 (1-s^2)\rho_0'(z_1)\rho_{c,2}'(z_2 - \frac{1}{8}\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^2 (1-s^2)\rho_1'(z_1)\rho_1'(z_2) \\ &- \frac{1}{4}\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^2 (1-s^2) z_1^2 \rho_0'(z_1)\rho_0'(z_2 + \frac{1}{64}\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^4 (1-s^2)(1+3s^2)\rho_0'(z_1)\rho_0'(z_2), \end{aligned} \tag{57}$$

$$\begin{aligned} \bar{\kappa} = &\frac{1}{2}\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^2 (1-s^2)\rho_0'(z_1)[4\rho_{c,2}'(z_2) - \rho_{s,2}'(z_2)] + \frac{1}{4}\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^2 (1-s^2) z_1^2 \rho_0'(z_1)\rho_0'(z_2) \\ &- \frac{1}{96}\int\limits_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U(r) r^4 (1-s^2)(1+7s^2)\rho_0'(z_1)\rho_0'(z_2), \end{aligned} \tag{58}$$

for the surface tension, Tolman length, and the bending and Gaussian rigidity respectively. Subscripts s and c accordingly label spheres and cylinders, and the $\rho_i(z)$ denote corrections to the density profile due to curvatures. Explicitly, these quantities measure deviations, of order i, of the density profile from a planar surface.

In the analysis of Blokhuis *et al*. the free energy contains the same level of approximation that we used here, and so one would expect identical expressions for the interfacial coefficients. By comparing Eqs. (32) and (55) one finds that both expressions for the surface tension are equivalent. In order to compare the Tolman length, Eqs. (33) and (56) respectively, one needs to make the correspondence $\rho_1 \to \rho_{s,1}/2 = \rho_1/2$. By doing this, one finds that both expressions are identical. Then, to compare the coefficient of H^2 in Eq. (31), the two correspondences $\kappa \to k/2$ and $\rho_2 \to \rho_{c,2}$ are needed. It can be observed that, one to one, the terms in (34) and (57) coincide, although the factors are not identical. Finally, to compare the coefficient of K in Eq. (31), the two correspondences $\bar{\kappa} \to \bar{k}$ and $\rho_3 \to [\rho_{s,2} - 4\rho_{c,2}]$ are necessary. Once again, all terms in both Eqs. (35) and (58) correspond identically; although they also show discrepancies on numerical factors. As a summary of this comparison, we find full agreement in the microscopic form of the rigidity constants, but discrepancies on the numerical factors, whose origin is certainly due to approximations as the free energy is the same in both works. Notice, however, that in their analysis these authors only consider the spherical and cylindrical geometries, whereas we analyze an arbitrarily curved surface. A comparison with multicomponent mixtures is not possible, as no equivalent analysis for a smooth profile has been reported.

6. Conclusions

Starting from the most general, microscopic and exact, expression for the grand potential within mean field approximation, Eqs. (18) and (36), we have derived the effective Hamiltonian for an arbitrarily curved interface of single- and multi-component simple fluids in a liquid-vapor coexistence state, considering a smooth density profile. Then, from this result, we have been able to generalize microscopic expressions for surface properties obtained in previous works. Important considerations that make this generalization worthwhile are: (i) Incorporation of a smooth profile, (ii) For an arbitrarily curved surface, (iii) With extension to a system of an arbitrary number of components. In particular, for the monocomponent system, we introduce a smooth profile that captures the geometry of the interfacial region and therefore contains more detailed information on particle interactions than in the case of a step-like profile. The treatment of this single-component fluid is based essentially on two approximations: (a) A power-series expansion of the density profile on the principal curvatures up to second order. Within this approximation, the lowest order term corresponds to a plane profile, whereas the other contributions capture the effects of surface curvature. (b) The other one, necessary to obtain concrete results, consists in approximating the surface locally by a paraboloid. This is valid when the average radius of curvature is very large as compared to the range of the interaction potential. Although the interaction between two molecules is considered short-ranged, technically only one of them is located on the local plane, which reveals that this approximation really captures the effects of curvature even at very small scales. Nevertheless, this in no way avoids the fact that this approximation is appropriate for weakly curved surfaces. Both approximations, (a) and (b), are captured in the interaction potential, which depends directly on the radius of the Gibbs dividing surface, and on the radii of curvature defined on the local coordinate system. This fact is employed to perform an expansion of the interaction potential in powers of the principal curvatures, which allows us to obtain a final expression for the grand potential of the interfacial region. As described above, the results obtained are in agreement with other viewpoints for the surface tension and the Tolman length, but differ on the values predicted for the rigidity coefficients [31, 33].

To carry out the description of the multicomponent system, we consider an arbitrary number t of density profiles, which enter directly into the grand potential. Contrary to the single component case, where only one interfacial region may exist, here there exist multiple coexistence regions and intermolecular interactions. The coexistence surfaces may be due to a single component or to a mixture of different ones. As a generalization to the monocomponent system, the approximations used on each component are basically those described previously, except that we now consider different Gibbs dividing surfaces. From the results obtained, only the microscopic surface tension may be compared, which shows agreement with other viewpoints [11, 12]. The theory here presented can, in addition, be used to describe nucleation of fluid drops of any geometry and number of components. A task that is still pending concerns numerical evaluation of all results for single- and multiple-component systems. We shall consider this study in a future publication.

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