# Mean field theory of inhomogeneous fluid mixtures

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By using density functional theory, we analyze an inhomogeneous fluid mixture composed of an arbitrary number of species within mean field approximation. Under the assumption that the interfacial region behaves as an elastic continuous medium, we calculate the stress tensor and the equilibrium grand potential of the system for different surfaces. It is found that, unlike the single component system, there exist multiple coexistence regions induced by the diversity of interaction potentials between the different species. Surface properties are calculated for a step-like density profile and consistency with the monocomponent system is verified for both the same formalism and other approaches at the level of surface tension.

*Keywords:* Stress tensor; density functional theory; surface tension; density profile.

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## 1. Introduction

Density functional theory (DFT) for classical fluids has raised much interest in recent years. To a great extent, this is due to its versatility to be applied in different problems of various scales [1-5]. The theory assumes existence of a density functional corresponding to the intrinsic Helmholtz free energy $F[\rho(\vec{r})]$, which contains all the information about intermolecular interactions in the system. For a simple fluid in a coexistence state, the density profile of the interfacial region, $\rho(\vec{r})$, is a function of position. Its equilibrium value is obtained by solving the Euler-Lagrange (EL) equation that results from minimization of the grand potential functional [2]. The solution to the EL equation is not trivial as there is no exact expression for the free energy functional. Thus, instead of solving the equation, one may follow a completely different scheme which consists in manipulating the EL equation to obtain a force balance equation, which implies existence of a stress tensor. Following this alternative approach, a theory has been developed that describes correctly the monocomponent simple fluid in a liquid-vapor coexistence state. The most general expression of the stress tensor for this system has been calculated [6,7] and the result has been used, at the level of mean field, to obtain the contribution to the free energy from the interfacial region of surfaces with simple geometries, and also for an arbitrarily curved interface. For the simple geometries, the microscopic expressions for the surface properties have been calculated within two levels of approximation: for a step-like profile and a smooth one respectively [8,9]. In this work we extend the analysis to describe an inhomogeneous fluid mixture composed of $t$

components; in particular the microscopic expressions for the grand potential and surface properties are investigated for an asymptotic approximation of the density profile. Shortly, we shall obtain a theory for the system with an arbitrary number of components and show that the generalization maintains the same structure as the monocomponent case. The main purpose will be to provide a completely independent description from first principles.

Inhomogeneous fluid mixtures of several components represent a formidable challenge for equilibrium statistical mechanics due to the difficulty to carry out theoretical predictions and experimental measurements of their surface properties [10,11]. One of the crucial problems is that as the number of components increases, new mechanisms that modify surface properties between the different fluid phases are induced. The explanation on the relevance of these mechanisms when passing from a mixture to another with a different number of species is still unknown nowadays [12]. Remarkably, the most relevant physical property for mixtures is surface tension, which has been widely investigated from diverse viewpoints. In this sense, we consider important to highlight some works related to the analysis of this property and to our knowledge within the context of this investigation. The first one is the work of M. Sahini *et al*. They investigate the behavior of the surface tension of a binary mixture of $CO_2$ and hydrocarbons near the critical point using a square gradient theory [10]. A drawback of their theory, however, is the inability to correctly capture the surface properties. In another work, R. Penfold *et al*. perform a calculation to investigate the same physical quantity using a generalized van der

Waals theory, but for an Argon-Krypton mixture [12]. Their results are in agreement with numerical simulations and experimental data for this particular system. In a third work, T. Hiester *et al.* investigate the behavior of a binary mixture using an effective Hamiltonian [13]. Unlike the previous works, these authors derive microscopic expressions for the surface tension and rigidity constants, but their analysis is restricted to a two-component system. Although these three investigations, and many more in literature, contribute to understanding interfacial phenomena within mixtures, the topic is still an active field of research.

In this work we also derive all surface properties. Nevertheless, this investigation shows two clear differences when compared to previous studies. The first one is that here we consider the description of a fluid mixture with an arbitrary number of components instead of a binary system, and no restriction to a particular system is introduced. The second is that, as it will be shown shortly, we determine a microscopic expression, exact and simple, for the grand potential that depends on the densities of all species and the different interaction potentials between particles, which allows us to calculate the properties of the system without ambiguity. It is important to mention that in order to obtain microscopic expressions for the interfacial properties, we assume that the interface behaves as an elastic continuous medium which satisfies the corresponding Helfrich Hamiltonian [9].

The paper is organized as follows. In Sec. 2 we outline the fundamentals of the theory of several components. Sec. 3 briefly describes the procedure to obtain the stress tensor. The appropriate approximations we introduce to obtain specific results of the most relevant surface properties are performed in Sec. 4, and to conclude, in Sec. 5 we present some final remarks.

## 2. Density Functional Theory

Let us consider a grand canonical density functional for the $t$-component fluid consisting of particles of different species interacting via a spherically symmetric potential; to be introduced in explicit form shortly. The expression for this grand potential functional is

$$\Omega[\rho^1(\vec{r}), \dots, \rho^t(\vec{r})] = F[\rho^1(\vec{r}), \dots, \rho^t(\vec{r})]$$
$$+ \sum_{i=1}^{t} \int d\vec{r}\, [\mu^i - V_{\text{ext}}^i(\vec{r})]\rho^i(\vec{r}), \quad (1)$$

where $F[\rho^1(\vec{r}), \dots, \rho^t(\vec{r})]$ is the intrinsic Helmholtz free energy of the whole system, $\mu^i$, $V_{\text{ext}}^i(\vec{r})$, and $\rho^i(\vec{r})$ are the chemical potential, the external potential, and the density profile of the $i$-th specie respectively. Within the stress tensor theory being formulated here, the free energy is assumed known.

The intrinsic Helmholtz free energy contains information on all molecules of the different species, which are coupled to each other in such a way that results impossible to separate

expressions for different species; except for ideal gases. The equilibrium configuration is obtained from minimization of the grand potential functional, which allows for knowledge of the equilibrium density profile of each specie

$$\left. \frac{\delta\Omega[\rho^1(\vec{r}), \dots, \rho^t(\vec{r})]}{\delta\rho^i(\vec{r})} \right|_{\rho_0^i} = 0, \quad (2)$$

where $\rho_0^i$ is the equilibrium density profile of the $i$-th specie. The equilibrium of the whole system is obtained when the values of all equilibrium density profiles; *i.e.* $\rho_0^1, \dots, \rho_0^t$, are known. Under these conditions, the equilibrium grand potential can be written in the form

$$\Omega_0[\rho_0^1(\vec{r}), \dots, \rho_0^t(\vec{r})] = F[\rho_0^1(\vec{r}), \dots, \rho_0^t(\vec{r})]$$
$$+ \sum_{i=1}^{t} \int d\vec{r}\, [\mu^i - V_{\text{ext}}^i(\vec{r})]\rho_0^i(\vec{r}). \quad (3)$$

That is, the system is in thermodynamic equilibrium, which means thermal, chemical, and mechanical equilibrium. As pressure is a tensor, the last condition distinguishes this system from homogeneous fluids. In addition, mechanical equilibrium implies existence of force balance; this because any part of the interfacial region is not found rotating or displacing in a given direction. The EL equations can be manipulated to identify the conservation equation for each specie. To do so, we start by multiplying the EL equation by $\nabla\rho_0^i(\vec{r})$

$$\nabla\rho_0^i(\vec{r}) \left. \frac{\delta F[\rho^1(\vec{r}), \dots, \rho^t(\vec{r})]}{\delta\rho^i(\vec{r})} \right|_{\rho_0^i}$$
$$- \nabla\rho_0^i(\vec{r})[\mu^i - V_{\text{ext}}^i(\vec{r})] = 0. \quad (4)$$

Then, we introduce the relationship

$$\nabla[\rho_0^i(\vec{r})V_{\text{ext}}^i(\vec{r})] = \rho_0^i(\vec{r})\nabla V_{\text{ext}}^i(\vec{r}) + V_{\text{ext}}^i(\vec{r})\nabla\rho_0^i(\vec{r}). \quad (5)$$

After some manipulations carried out in Eq. (4), we get to

$$\left. \frac{\delta F}{\delta\rho^i} \right|_{\rho_0^i} \nabla\rho_0^i(\vec{r})$$
$$- \nabla\left\{ [\mu^i - V_{\text{ext}}^i(\vec{r})]\rho_0^i(\vec{r}) \right\} = \rho_0^i(\vec{r})\nabla V_{\text{ext}}^i(\vec{r}). \quad (6)$$

This is the force balance equation for an arbitrary specie. It is worth mentioning that Eq. (6) only contains partial information of the system; that is only on the coexistence region of the $i$-th specie. As the interest is on force balance in the whole system, we sum over all species to obtain

$$\nabla \cdot \boldsymbol{\sigma} = \sum_{i=1}^{t} \rho_0^i(\vec{r})\nabla V_{\text{ext}}^i(\vec{r}), \quad (7)$$

where $\boldsymbol{\sigma}$ is the stress tensor of all species, which is symmetric due to nature of the system [6].

It is a known fact that this stress tensor is not unique. There exists gauge freedom, as one can always add a symmetric tensor with vanishing divergence to $\boldsymbol{\sigma}$. Although this

feature could play down relevance to the tensor, the physical properties of the system have no dependence upon this arbitrariness. It is worthwhile emphasizing that a stress tensor constructed on the basis of general principles guarantees a better approach to the physical properties of the system.

Now, the properties of the system and the stress tensor itself can be studied in more detail by introducing the separation

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_0 + \boldsymbol{\sigma}_{\text{inh}}, \tag{8}$$

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

$$\boldsymbol{\sigma}_0 = \omega(\vec{r}, [\rho_0^1, \dots, \rho_0^t])\mathbf{I}$$
$$= \left[ f(\vec{r}, [\rho_0^1, \dots, \rho_0^t]) - \sum_{i=1}^{t} (\mu^i - V_{\text{ext}}^i(\vec{r}))\rho_0^i \right] \mathbf{I}, \tag{9}$$

with $\mathbf{I}$ being the unit tensor, and $\boldsymbol{\sigma}_{\text{inh}}$ is the contribution from the interfacial region, which satisfies the relation

$$\nabla \boldsymbol{\sigma}_{\text{inh}}(\vec{r}) = \sum_{i=1}^{t} \left[ \left. \frac{\delta F}{\delta \rho^i} \right|_{\rho_0^i} \nabla \rho_0^i(\vec{r}) \right]$$
$$- \nabla f(\vec{r}, [\rho_0^1, \cdots, \rho_0^t]). \tag{10}$$

Into these we have introduced the densities of grand potential and of Helmholtz free energy, $\omega(\vec{r}, [\rho_0^1, \dots, \rho_0^t])$ and $f(\vec{r}, [\rho_0^1, \dots, \rho_0^t])$, defined respectively as

$$\Omega[\rho_0^1, \dots, \rho_0^t] = \int d\vec{r}\, \omega(\vec{r}, [\rho_0^1, \dots, \rho_0^t]) \quad \text{and}$$

$$F[\rho_0^1, \dots, \rho_0^t] = \int d\vec{r}\, f(\vec{r}, [\rho_0^1, \dots, \rho_0^t]). \tag{11}$$

We emphasize that $F[\rho(\vec{r})]$ is non-local in terms of the density profile, which implies that any local term in this free energy gives no contribution to $\boldsymbol{\sigma}_{\text{inh}}$.

The separation in Eq. (8) is motivated by two reasons. The first one is that the $\boldsymbol{\sigma}_{\text{inh}}$ term originates exclusively from the non-local part of $F$, and the second is that within the region where the system is homogeneous, $\nabla \cdot \boldsymbol{\sigma}_{\text{inh}} = 0$ and the tensor $\boldsymbol{\sigma}_{\text{inh}}$ vanishes. On the other hand, the diagonal term $\boldsymbol{\sigma}_0$ originates from both local and non-local contributions to $F$, and is given by $\omega(\vec{r}, [\rho_0^1, \dots, \rho_0^t])\mathbf{I}$, when the stress tensor becomes $\boldsymbol{\sigma} = \sigma_0\mathbf{I}$. Moreover, this separation can be regarded as a phenomenological interpretation of the system. From the macroscopic point of view, there exist two well defined regions: those of the bulk phases and the interfacial region. In a microscopic scale, it is impossible to guarantee existence of decoupling between molecular interactions of both homogeneous and inhomogeneous regions. However, one may consider the dominant contribution to be contained in each region and not necessarily on the boundary molecules.

The geometric properties of the interfacial region, which we consider here as a mathematical surface, depend on its composition. Although it may be formed by a mixture of different species, these maintain identity as they do not form a new compound. The fact that each specie can be included in the surface is denoted by the script $i$ on the density profile, that is $\rho_i$ where $i = 1, 2, \dots, t$. Equidensity surfaces $\rho_0^i = \text{const.}^i$ define families of surfaces $r_n^i$ having normal vectors $\hat{n}^i(\vec{r}) = \nabla \rho^i(\vec{r})/|\nabla \rho^i(\vec{r})|$, which are defined only within the interfacial region, where $\nabla \rho^i \neq 0$. It will be shown in the following section that within this formalism we carry out a description of the system which considers all higher order derivatives of the density profile; assuming they vanish at the boundary of the system where density is homogeneous. In our analysis, we consider some simple geometries and the most general case of an arbitrarily deformed interfacial region and introduce a set of semi-orthogonal local unit vectors, $\hat{n}^i(\vec{r}), \hat{t}_1^i(\vec{r}), \hat{t}_2^i(\vec{r})$, where $\hat{t}_1^i(\vec{r})$ and $\hat{t}_2^i(\vec{r})$ are tangent vectors to the equidensity surfaces satisfying the conditions: $\hat{n}^i(\vec{r}) \cdot \hat{t}_\alpha^i(\vec{r}) = 0$, $\hat{t}_1^i(\vec{r}) \cdot \hat{t}_2^i(\vec{r}) \neq 0$, $\alpha = 1, 2$, $i = 1, \dots, t$. It is now possible to perform the separation of the stress tensor in terms of its local components: normal, tangent, and tangent normal [14]. Nevertheless, as the most relevant physical property of the system is the equilibrium grand potential, which represents the microscopic free energy, only the normal component of the stress tensor is required for its calculation. This can be written in the form

$$\sigma^N = \omega(\vec{r}, [\rho_0^1, \dots, \rho_0^t]) + \sigma_{\text{inh}}^N. \tag{12}$$

By integrating this component over the whole space one obtains the equilibrium grand potential [14,15]

$$\Omega_0 = \int d\vec{r}[\sigma^N(\vec{r}) - \sigma_{\text{inh}}^N(\vec{r})]. \tag{13}$$

It can be observed from this expression that the free energy separates naturally bulk and surface contributions independently of the surface geometry. The first term contains only bulk information, corresponding to terms of pressure by volume, whereas the second one captures the interfacial properties of the fluid mixture. Equation (13) is a key element within this theory as introduction of the normal component of stress tensor into the free energy allows, without ambiguity, calculation of all relevant properties of the system. In addition, further developments can be performed so as to obtain general results [6,9].

## 3. Stress Tensor Derivation

It was shown in the previous section that the EL equation of a multicomponent system leads to a force balance equation, which implies existence of a stress tensor $\boldsymbol{\sigma}$; unknown up to this point. Starting from general physical principles, this quantity may be constructed to any level of approximation of the free energy. For a non-local system of a single component, this task has been carried out by J. K. Percus and V. Romero-Rochín, modeling the system as a continuous medium [6,7]. Here we follow the same approach but for a $t$-component mixture. The key element for this analysis is the non-locality of the system. As in the interfacial

region density varies from point to point, an appropriate description must capture as much information as possible from the neighborhood of each point. This may be accomplished by including an arbitrary number of high-order derivatives of the density. In this sense the Lagrangian formulation for continuous systems and fields is the most appropriate because the Lagrangian allows incorporation of any number of derivatives of the dynamic variable under consideration [6,16,17]. For this system, the density and its derivatives are the relevant physical quantities which play a role analogous to the dynamic variables of position and velocity in classical mechanics; the difference being that these quantities depend on the vector position rather than on a parameter as time. On the other hand, the derivatives have a number of components that depend on the dimensionality of space. In this section we denote field variables by $\rho$, derivatives are indicated by a semicolon, components of the vector position and density are

denoted by Greek superscripts, species of the different components of the system are indicated by Latin superscripts, and the summation convention over repeated indices is assumed. We emphasize that only the most relevant aspects in the construction of the stress tensor are discussed without going into algebraic details.

The Lagrangian $L$ of the system depends on the densities $\rho^i(\vec{r})$ of all species and on an arbitrary number $c$ of their spatial derivatives, $\rho^i{}_{,\alpha_1\alpha_2\ldots\alpha_c}(\vec{r})$. From this we write the action

$$S = \int d\vec{r}\, L\big(\{\rho^1(\vec{r}), \rho^1{}_{,\alpha_1}(\vec{r}), \rho^1{}_{,\alpha_1\alpha_2}(\vec{r}), \ldots\}, \ldots,$$

$$\{\rho^t(\vec{r}), \rho^t{}_{,\alpha_1}(\vec{r}), \rho^t{}_{,\alpha_1\alpha_2}(\vec{r}), \ldots\}; \vec{r}\big), \tag{14}$$

and calculate its first variation

$$\delta S = \int d\vec{r}\, \left( \left\{ \frac{\partial L}{\partial \rho^1}\delta\rho^1 + \frac{\partial L}{\partial \rho^1{}_{,\alpha_1}}\delta\rho^1{}_{,\alpha_1} + \frac{\partial L}{\partial \rho^1{}_{,\alpha_1\alpha_2}}\delta\rho^1{}_{,\alpha_1\alpha_2} + \cdots \right\}, \ldots, \right.$$

$$\left. \left\{ \frac{\partial L}{\partial \rho^t}\delta\rho^t + \frac{\partial L}{\partial \rho^t{}_{,\alpha_t}}\delta\rho^t{}_{,\alpha_t} + \frac{\partial L}{\partial \rho^t{}_{,\alpha_t\alpha_2}}\delta\rho^t{}_{,\alpha_1\alpha_2} + \cdots \right\} \right) = \sum_{i=1}^{t}\sum_{s=0}^{c} \int d\vec{r}\, \frac{\partial L}{\partial \rho^i{}_{,\alpha_1\ldots\alpha_s}}\delta\rho^i{}_{,\alpha_1\ldots\alpha_s}. \tag{15}$$

To find the EL equation, successive integrations by parts of the density field are necessary. We consider these derivatives vanishing on the boundary of the hypervolume where the field is defined; that is

$$\delta\rho^j{}_{,\alpha_1\ldots\alpha_s}\big|_{\text{ext}} = 0, \tag{16}$$

where $s = 0, 1, 2, \ldots, c$, and $j = 1, 2, \ldots, t$. Physically, this is equivalent to state that the fluid is homogeneous at the boundary of the system. The condition for stationarity, $\delta S = 0$, leads to the equations of motion

$$\sum_{i=1}^{t}\sum_{s=0}^{c} (-1)^s \left( \frac{\partial L}{\partial \rho^i{}_{,\alpha_1\ldots\alpha_s}} \right)_{,\alpha_1\ldots\alpha_s} = 0, \tag{17}$$

which reduce to the single dynamic variable case. The same EL equations may alternatively be obtained from a modified Lagrangian $\hat{L}$, with the advantage that this formalism incorporates an infinite number of high-order derivatives and that allows for other extensions [6]. The proposal of modified Lagrangian is

$$\hat{L}\big(\{\rho^1_{\alpha_1\ldots\alpha_s}, \rho^1_{\alpha_1\ldots\alpha_s,\beta}\}, \ldots, \{\rho^t_{\alpha_1\ldots\alpha_s}, \rho^t_{\alpha_1\ldots\alpha_s,\beta}\}, p^{1\beta}_{\alpha_1\ldots\alpha_s}, \ldots, p^{t\beta}_{\alpha_1\ldots\alpha_s}; \vec{r}\big)$$

$$= L\big(\rho^1_{,\alpha_1\ldots\alpha_s}, \ldots, \rho^t_{,\alpha_1\ldots\alpha_s}; \vec{r}\big) + \sum_{i=1}^{t}\sum_{s=0}^{\infty} (\rho^i_{\alpha_1\ldots\alpha_s,\beta} - \rho^i_{\alpha_1\ldots\alpha_s\beta})p^{i\beta}_{\alpha_1\ldots\alpha_s}. \tag{18}$$

Writing the action for this Lagrangian and calculating its first variation, one obtains

$$\delta S = \sum_{i=1}^{t} \int d\vec{r}\, \left( \frac{\partial \hat{L}}{\partial \rho^i_{\alpha_1\ldots\alpha_s}}\delta\rho^i_{\alpha_1\ldots\alpha_s} + \frac{\partial \hat{L}}{\partial \rho^i_{\alpha_1\ldots\alpha_s,\beta}}\delta\rho^i_{\alpha_1\ldots\alpha_s,\beta} + \frac{\partial \hat{L}}{\partial p^{i\beta}_{\alpha_1\ldots\alpha_s}}\delta p^{i\beta}_{\alpha_1\ldots\alpha_s} \right). \tag{19}$$

Once again, repeated integrations by parts, using the fact that all derivatives of the density vanish at the boundary, and that $\rho^i_{\alpha_1\ldots\alpha_s}$ and $p^{i\beta}_{\alpha_1\ldots\alpha_s}$ are independent variables, give rise to the corresponding EL equations

$$\frac{\partial \hat{L}}{\partial \rho^i_{\alpha_1\ldots\alpha_s}} - \left( \frac{\partial \hat{L}}{\partial \rho^i_{\alpha_1\ldots\alpha_s,\beta}} \right)_{,\beta} = 0, \tag{20}$$

$$\frac{\partial \hat{L}}{\partial p^{i\beta}_{\alpha_1\ldots\alpha_s}} = 0. \tag{21}$$

By introducing in the latter the explicit form of the proposed Lagrangian for the system of several components, Eq. (18), one gets to the relationship

$$\rho^i_{\alpha_1\ldots\alpha_s,\beta} = \rho^i_{\alpha_1\ldots\alpha_s\beta}. \tag{22}$$

We now calculate the explicit EL equation for the density of an arbitrary specie by introducing Eq. (18) into Eq. (20). Evaluation of each term produces an equation that can be iterated, and that yields a result equivalent to that of a Lagrangian containing information on higher order derivatives explicitly. The resulting expression is

$$p^{i\beta_1}_{\alpha_1\ldots\alpha_s} = \frac{\partial L}{\partial\rho^i_{\alpha_1\ldots\alpha_s\beta_1}} - \left(\frac{\partial L}{\partial\rho^i_{\alpha_1\ldots\alpha_s\beta_1\beta_2}}\right)_{,\beta_2}$$
$$+ \left(\frac{\partial L}{\partial\rho^i_{\alpha_1\ldots\alpha_2\beta_1,\beta_2\beta_3}}\right)_{,\beta_2\beta_3} + \cdots, \tag{23}$$

where $p^{i\beta_1}_{\alpha_1\ldots\alpha_s} = 0$ for $s = -1$, which reproduces Eq. (17). Thus $L$ and $\hat{L}$ have some equivalence as they lead to the same equations of motion. From this point we perform a series of manipulations to relate these expressions to an exact quantity. Given that a functional derivative of the Lagrangian with respect to an arbitrary field variable is

$$\frac{\delta}{\delta\rho^i(\vec{r}')}L\left(\rho^1_{\alpha_1\ldots\alpha_s},\ldots,\rho^t_{\alpha_1\ldots\alpha_s};\vec{r}\right) = \sum_{s,\{\alpha\}}\sum_{i=1}^t \nabla_{\alpha_1}$$
$$\cdots\nabla_{\alpha_s}\delta(\vec{r}-\vec{r}')\frac{\partial L(\vec{r}\mid\rho^1,\ldots,\rho^t)}{\partial\rho^i_{\alpha_1\ldots\alpha_s}}, \tag{24}$$

we multiply this expression by $\prod_{j=1}^p\left(r'_{\beta_j} - R_{\beta_j}\right)$ and integrate over $\vec{r}'$ to obtain

$$\int d\vec{r}'\prod_{j=1}^p\left(r'_{\beta_j} - R_{\beta_j}\right)\frac{\delta L(\vec{r}\mid\rho^1,\ldots,\rho^t)}{\delta\rho^i(\vec{r}')} = \sum_{s,\{\alpha\}}\sum_{i=1}^t\nabla_{\alpha_1}$$
$$\cdots\nabla_{\alpha_s}\prod_{j=1}^p\left(r_{\beta_j} - R_{\beta_j}\right)\frac{\partial L(\vec{r}\mid\rho^1,\ldots,\rho^t)}{\partial\rho^i_{,\alpha_1\ldots\alpha_s}}, \tag{25}$$

and observe that each term with $s > p$ vanish, as after the $p$-th derivation it is a constant. All terms with $s < p$ also vanish by substituting $R_{\beta_j} = r_{\beta_j}$. The final result is then

$$\sum_{i=1}^t\frac{\partial L(\vec{r}\mid\rho^1,\ldots,\rho^t)}{\partial\rho^i_{,\beta_1\ldots\beta_p}(\vec{r})}$$
$$= \sum_{i=1}^t\frac{1}{p!}\int d\vec{r}'\prod_{j=1}^p r'_{\beta_j}\frac{\delta L(\vec{r}\mid\rho^1,\ldots,\rho^t)}{\delta\rho^i(\vec{r}+\vec{r}')}. \tag{26}$$

Now, an inhomogeneous fluid in a coexistence state, as a closed system, is invariant under the Galilean symmetry group. These symmetries are a consequence of the properties of the space-time in which the system is described, and may be analyzed using Noether's theorem. The homogeneity of time implies temporal translational invariance of the closed system, which translates into conservation of energy. On the other hand, from the homogeneity of space follows spatial translational invariance, which implies conservation

of the linear momentum. Finally, isotropy of space implies that the closed system has spatial rotational invariance, which in its turn guarantees conservation of the angular momentum. Such symmetries may be investigated using the fact that the Lagrangian is invariant under an infinitesimal coordinate transformation, from which one identifies the Noether current. The starting point is the first variation

$$\delta L(\{\rho^1_\eta,\rho^1_{\eta,\alpha}\},\ldots,\{\rho^t_\eta,\rho^t_{\eta,\alpha}\};\vec{r})$$
$$= \sum_{i=1}^t\left(\frac{\partial L}{\partial\rho^i_\eta}\delta\rho^i_\eta + \frac{\partial L}{\partial\rho^i_{\eta,\alpha}}\delta\rho^i_{\eta,\alpha}\right)$$
$$= \sum_{i=1}^t\nabla_\alpha\left(\frac{\partial L}{\partial\rho^i_{\eta,\alpha}}\delta\rho^i_\eta\right). \tag{27}$$

For $\delta = \nabla_\beta$, one identifies the stress tensor

$$\nabla_\beta L\big|_{\rho^i_0} = \nabla_\alpha\left(L\delta_{\alpha\beta}\right)$$
$$- \sum_{i=1}^t\nabla_\alpha\left(\rho^i_{\eta,\beta}\frac{\partial L}{\partial\rho^i_{\eta,\alpha}}\right) = \nabla_\alpha\sigma_{\alpha\beta}, \tag{28}$$

where

$$\sigma_{\alpha\beta} = L\delta_{\alpha\beta} - \sum_{i=1}^t\rho^i_{\eta,\beta}\frac{\partial L}{\partial\rho^i_{\eta,\alpha}}. \tag{29}$$

Equation (28) is the corresponding conservation law for the inhomogeneous fluid, which will be transparent when the first of the two terms in the middle be identified.

Assuming a system internally autonomous, we may separate the field contribution in a single term through $\mu^i(\vec{r})$ [6], identify $L$ as $\hat{L}$, and the $\rho^i_\sigma$ as $\rho^i_{\alpha_1\ldots\alpha_s}$, as well as the $p^{i\beta}_{\alpha_1\ldots\alpha_s}$. This leads us to propose the expression

$$\hat{L}\left(\rho^1_{,\alpha_1\ldots\alpha_s},\ldots\rho^t_{,\alpha_1\ldots\alpha_s};\vec{r}\right)$$
$$= L_0\left(\rho^1_{\alpha_1\ldots\alpha_s},\ldots,\rho^t_{\alpha_1\ldots\alpha_s}\right) - \sum_{i=1}^t\mu^i(\vec{r})\rho^i. \tag{30}$$

By carrying out the infinitesimal variation, once again one calculates the conserved quantity that Noether's theorem guarantees

$$\delta\hat{L} = \sum_{i=1}^t\sum_s\left(\frac{\partial\hat{L}}{\partial\rho^i_{\gamma_1\ldots\gamma_s,\alpha}}\right)_{,\alpha}\delta\rho^i_{\gamma_1\ldots\gamma_s}$$
$$+ \sum_{i=1}^t\sum_s\frac{\partial\hat{L}}{\partial\rho^i_{\gamma_1\ldots\gamma_s}}\delta\rho^i_{\gamma_1\ldots\gamma_s,\alpha}$$
$$= \sum_{i=1}^t\nabla_\alpha\left(\sum_s\frac{\partial\hat{L}}{\partial\rho^i_{\gamma_1\ldots\gamma_s,\alpha}}\delta\rho^i_{\gamma_1\ldots\gamma_s}\right), \tag{31}$$

then introducing $\delta = \nabla_\beta$, we find

$$\nabla_\alpha\left(\hat{L}\delta_{\alpha\beta} - \sum_{i=1}^t\sum_s\frac{\partial\hat{L}}{\partial\rho^i_{\gamma_1\ldots\gamma_s,\alpha}}\rho^i_{\gamma_1\ldots\gamma_s,\beta}\right) = \nabla_\beta\hat{L}\big|_{\rho^i_0}. \tag{32}$$

The corresponding Noether current is the stress tensor

$$\sigma_{\alpha\beta} = \hat{L}\delta_{\alpha\beta} - \sum_{i=1}^{t}\sum_{s}\frac{\partial\hat{L}}{\partial\rho^i_{\gamma_1\ldots\gamma_s,\alpha}}\rho^i_{\gamma_1\ldots\gamma_s,\beta}. \qquad (33)$$

Observe that $\nabla_\beta\hat{L}|_{\rho^i_0}$ in Eq. (32) is determined by calculating the derivative of $\hat{L}$ and evaluating at the equilibrium value. The result is

$$\nabla_\beta\hat{L}|_{\rho^i_0} = \sum_{i=1}^{t}\left(\mu^i(\vec{r})\rho^i_{,\beta} - \mu^i\rho^i_{,\beta} - \rho^i\mu^i_{,\beta}\right)$$

$$= -\sum_{i=1}^{t}\rho^i(\vec{r})\mu^i_{,\beta}(\vec{r}). \qquad (34)$$

Putting this expression as the right hand side of Eq. (32) yields the balance equation predicted by DFT.

A connection between concepts from the Lagrangian formulation and the equilibrium statistical mechanics can be made. The quantity $L_0(\vec{r}\mid\rho^1,\ldots,\rho^t) - \sum_{i=1}^{t}\mu^i(\vec{r})\rho^i(\vec{r})$ $= \omega(\vec{r}\mid\rho^1,\ldots,\rho^t)$ is identified as the grand potential density; that is, minus the pressure in an uniform fluid. In this sense one gets a rigorous derivation of the conservation law for $\sigma_{\alpha\beta}$ in Eq. (33), which is

$$\sigma_{\alpha\beta,\alpha} = -\sum_{i=1}^{t}\rho^i(\vec{r})\mu^i_{,\beta}(\vec{r}). \qquad (35)$$

In our problem, $\mu^i(\vec{r}) = \mu^i - V^i_{\text{ext}}(\vec{r})$, with $\mu^i$ being the value of the chemical potential of the $i$-th specie. We observe that the balance equation obtained from the minimization condition can be derived rigorously and in general from a Lagrangian formulation for continuous systems. We now proceed to express Eq. (33) in a direct functional form. This is accomplished by a purely algebraic procedure and the result is

$$\sigma_{\alpha\beta}(\vec{r}) = \left(L_0 - \sum_{i=1}^{t}\mu^i(\vec{r})\rho^i(\vec{r})\right)\delta_{\alpha\beta}$$

$$- \sum_{i=1}^{t}\int d\vec{r}\,'\int_0^1 d\lambda\, r'_\alpha\nabla_\beta\rho^i(\vec{r}+\lambda\vec{r}\,')$$

$$\times \frac{\delta L_0(\vec{r}-(1-\lambda)\vec{r}\,'\mid\rho^1,\ldots,\rho^t)}{\delta\rho^i(\vec{r}+\lambda\vec{r}\,')}. \qquad (36)$$

As previously discussed, the isotropy of space implies conservation of the angular momentum. However, for this to occur the stress tensor must be symmetric [6,15]. Equation (36) does not satisfy this condition as can be observed from direct exchange of indices. This can always be corrected by including in the stress tensor a term $\overline{\sigma}_{\alpha\beta}$ that has no physical consequences; neither local nor global [6]. After the symmetrization procedure we obtain

$$\overline{\sigma}_{\alpha\beta} = \nabla_\nu\sum_{i=1}^{t}\int d\vec{r}\,'\int_0^1 d\lambda\,\lambda r'_\beta\left(r'_\nu\nabla_\alpha\rho^i(\vec{r}+\lambda\vec{r}\,') - r'_\alpha\nabla_\nu\rho^i(\vec{r}+\lambda\vec{r}\,')\right)\frac{\delta L_0(\vec{r}-(1-\lambda)\vec{r}\,'\mid\rho^1,\ldots,\rho^t)}{\delta\rho^i(\vec{r}+\lambda\vec{r}\,')}. \qquad (37)$$

By adding this to Eq. (36) we get to the final form of the stress tensor for the whole system, which is symmetric, exact, and that satisfies all symmetry requirements

$$\sigma_{\alpha\beta}(\vec{r}) = \left(f(\vec{r};[\rho^1_0,\ldots,\rho^t_0]) - \sum_{i=1}^{t}(\mu^i - V^i_{\text{ext}}(\vec{r}))\rho^i_0\right)\mathbf{I}$$

$$- \sum_{i=1}^{t}\int d\vec{r}\,'\int_0^1 d\lambda\, r'_\alpha\nabla_\beta\rho^i(\vec{r}+\lambda\vec{r}\,')\frac{\delta L_0(\vec{r}-(1-\lambda)\vec{r}\,'\mid\rho^1,\ldots,\rho^t)}{\delta\rho^i(\vec{r}+\lambda\vec{r}\,')}$$

$$+ \nabla_\nu\sum_{i=1}^{t}\int d\vec{r}\,'\int_0^1 d\lambda\,\lambda r'_\beta\left(r'_\nu\nabla_\alpha\rho^i(\vec{r}+\lambda\vec{r}\,') - r'_\alpha\nabla_\nu\rho^i(\vec{r}+\lambda\vec{r}\,')\right)\frac{\delta L_0(\vec{r}-(1-\lambda)\vec{r}\,'\mid\rho^1,\ldots,\rho^t)}{\delta\rho^i(\vec{r}+\lambda\vec{r}\,')}. \qquad (38)$$

Notice that the first term corresponds to the contribution from bulk phases whereas the remaining part contains information on the interfacial region. The parameter $\lambda$ expresses gauge freedom in the stress tensor; relating two points in the fluid which is a non-local system, and the integral over this parameter shows that all points in the interfacial region are being considered. It is important to remark that the stress tensor given in Eq. (38) is the most general expression known within this topic, that is exact and for an arbitrary free energy.

## 4. Results

As previously mentioned, DFT assumes existence of the intrinsic Helmholtz free energy functional. In order to calculate thermodynamic properties it is necessary to introduce an approximation for this quantity. One may use any approximation capable of describing correctly the coexistence state; the most common in practice being the mean field model

$$F[\rho(\vec{r})] = \sum_{i=1}^{t} \int d\vec{r}\, f(\rho^i(\vec{r}))$$

$$+ \frac{1}{2} \sum_{i=1}^{t} \sum_{j=1}^{t} \int d\vec{r} \int d\vec{r}'\, \tilde{\omega}_{ij}(\vec{r} - \vec{r}')\rho^i(\vec{r})\rho^j(\vec{r}'), \quad (39)$$

where $\tilde{\omega}_{ij}$ is the interaction potential between two molecules of arbitrary species $i$ 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. Later on we shall discuss how for the interfacial region the second term is the relevant one as such region is characterized by a non-zero gradient of the density profile.

In our analysis, we are considering a $t$-component mixture for which there is a variety of interaction potentials $\tilde{\omega}_{ij}$ between molecules. As all interactions, either between molecules of the same or different species, are possible, there is a total of $t(t+1)/2$ interaction potentials, which implies existence of an equivalent number of coexistence regions. In addition, the dimension $t+1$ of the space of parameters, given by all chemical potentials of the different species and temperature, could allow free variation of one of the components without losing the coexistence state.

By carrying out the variation of the free energy density involved in the stress tensor, and performing the appropriate coordinate transformations, we get to the final expression for the stress tensor of the inhomogeneous region within this level of approximation

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

$$- \frac{1}{2} \sum_{ij} \nabla_\nu \int d\vec{r}' \int_0^1 d\lambda\, \rho_0^i(\vec{r} - (1-\lambda))\tilde{\omega}_{ij}(\vec{r}')r'_\beta[r'_\alpha \nabla_\nu \rho_0^j(\vec{r} + \lambda\vec{r}') - r'_\nu \nabla_\alpha \rho_0^j(\vec{r} + \lambda\vec{r}')]. \quad (40)$$

The contribution from the homogeneous region to the complete tensor, Eq. (38), suffers no considerable modifications. Now, the stress tensor $\sigma_{\text{inh}}^{\alpha\beta}(\vec{r})$ depends explicitly on the interaction potential between particles and on the equilibrium density profile $\rho_0^i$ of each specie. To obtain specific results, one needs to introduce an approximation for the density profile. This will be carried out in detail shortly.

As in this work we are interested only in the contribution to energy from the interfacial region, we calculate this quantity using the second term in Eq. (13), which we denote here as $\Omega_{\text{inh}}$ and depends on the density of all species, *i.e.* $\Omega_{\text{inh}} = \Omega_{\text{inh}}[\rho_0^1, \ldots, \rho_0^t]$. Nevertheless, to simplify expressions, we omit this dependence and write

$$\Omega_{\text{inh}} = -\int d\vec{r}\, \sigma_{\text{inh}}^N, \quad (41)$$

which captures all details in the interfacial region. At this point we consider important to mention some relevant aspects of the behavior of the system as a function of temperature. The fluid mixture is in a vapor phase. As temperature is lowered, the fluid reaches a liquid-vapor coexistence state composed of a low-density vapor phase and a high-density liquid phase. In this regime there exists a unique interfacial region with both phases being mixtures of particles of all species. Nevertheless, as temperature is lowered further, there appear different interfacial regions between particles of the same and mixed species [18]. In this lower-temperature regime there exist a variety of Gibbs dividing surfaces; explicitly one for each in- terfacial region. In this work we analyze both cases. For the system with a single Gibbs dividing surface we consider surfaces having the simple geometries of planes and spheres, whereas for the system having multiple Gibbs dividing surfaces we consider an arbitrarily curved surface.

Analogously to the single component system, the interfacial region of this multiple component fluid mixture may be modeled as an elastic continuous medium which, in the limit of large radii of curvature as compared with the range of the interaction potential, satisfies the Helfrich phenomenological Hamiltonian [9,19]

$$\Omega_{\text{inh}} = \sum_{ij} \int dS \left\{ \gamma - \kappa c_0 \frac{1}{2}[H_i + H_j]\delta_{ij} \right.$$

$$\left. + \kappa H_i H_j + \frac{1}{2}\bar{\kappa}[K_i + K_j]\delta_{ij} \right\}, \quad (42)$$

where $dS$ is the area element, $H_i = (1/R_1^i) + (1/R_2^i)$ and $K_i = 1/R_1^i R_2^i$ are the mean and Gaussian curvatures respectively with $R_1^i$ and $R_2^i$ being the principal radii of curvature, and the coefficients $\gamma$, $c_0$, $\kappa$, and $\bar{\kappa}$ are the surface tension, spontaneous curvature, bending rigidity, and the saddle-splay constant respectively. These interfacial coefficients depend on all densities of the system. For a surface of a system composed of a single specie, Eq. (42) corresponds to the usual Helfrich energy [9,20]. As is well known, such a model describes competition between two geometrical quantities: the surface tension and flexion constants. The first one measures capacity of the system to develop area whereas the second accounts for the energy cost for bending the surface.

Next we illustrate the calculation of the grand potential in Eq. (14); first for simple geometries and then for an arbitrary surface. In all cases the external potential is gravity acting in the negative $z$-direction.

### 4.1. Planar Surface

We start by considering one of the simplest examples; that of a planar geometry. The density profile is a function that depends only on the normal coordinate, which occurs also for the other surfaces here presented. Assuming $\hat{n}^i(\vec{r}) = \hat{k}$, then $\rho_0^i(\vec{r}) = \rho_0^i(z)$. As a consequence, the normal component of the stress tensor for this system is

$$\sigma_{\text{inh}}^{zz}(\vec{r}) = -\frac{1}{2}\sum_{ij}\int d\vec{r}' \int_0^1 d\lambda\, \rho_0^i(\vec{r} - (1-\lambda)\vec{r}')\tilde{\omega}_{ij}(\vec{r}')z'$$

$$\times \frac{\partial \rho_0^j(z + \lambda z')}{\partial z}. \qquad (43)$$

In order to obtain the microscopic expression for the grand potential, we integrate the normal component of this stress tensor over the whole space. After eliminating the parameter $\lambda$ we get to the result

$$\Omega_{\text{inh}} = -\frac{1}{4}\sum_{ij}\int dS \int d^2 R' |\vec{R}'|^2 \int dz$$

$$\times \int dz' \frac{d\rho_0^i(z)}{dz}\frac{d\rho_0^j(z')}{dz'}\int_0^\infty du\, \tilde{\omega}_{ij}(\vec{R}'^2 + u^2), \quad (44)$$

where $dS$ is a surface element and $\vec{R}' = (x', y')$ is a bidimensional vector on the interfacial plane. From Eq. (44) it is possible to identify the most general microscopic expression for surface tension, which depends on the exact density profile of each specie and on the different interaction potentials between species. Its value reduces to that of the monocomponent system as predicted by the scheme with fluctuations [21]. An asymptotic value for the surface tension may

be obtained by introducing in Eq. (44) the step-like approximation for the density profile

$$\rho_0^i(z) = \rho_{0l}^i\Theta(z_0 - z) + \rho_{0v}^{(i)}\Theta(z - z_0), \qquad (45)$$

where $\Theta(z)$ is the Heaviside step function: equals to 1 for $z \geq 0$ and 0 otherwise, and $z_0$ is the radius of the Gibbs dividing surface of the $i$-th specie, which in this case is the same for all species. This proposal introduces the location of the Gibbs dividing surface, on which the interfacial region is projected, and is a key element to be able to define surface properties. The approximation is valid when the drop size is very large as compared to the range of the interaction potential. By introducing this expression and evaluating the integrals one gets to the final expression for the grand potential of a planar interface which is formed by molecules of different species

$$\Omega_{\text{inh}} = \int dS \left\{ -\frac{\pi}{2}\sum_{ij}\Delta\rho_0^i\Delta\rho_0^j \int_0^\infty dr\, r^3\tilde{\omega}_{ij}(r^2) \right\}, \quad (46)$$

where $\Delta\rho_0^i(\vec{r}) = \rho_{0l}^i - \rho_{0v}^i$. The value of the surface tension that one identifies within this limit is in complete agreement with the result obtained using a different approach [18], and also reduces to the value of the monocomponent case from the same scheme [7,8].

### 4.2. Spherical Drop

The spherical surface is, without a doubt, the most interesting case for systems of one and several components because many systems present spherical symmetry naturally. The appropriate description of this interfacial region as well as its structural properties have been investigated since long ago for inhomogeneous fluids [20,22].

Such a symmetry requires the density profile to be a function that depends exclusively on the magnitude of the vector position; that is $\rho^i(\vec{r}) = \rho^i(|\vec{r}|)$. The normal vector on each coexistence surface is $\hat{n}^i(\vec{r}) = \nabla\rho^i(\vec{r})/|\nabla\rho^i(\vec{r})|$. The components of the stress tensor, in mean field, are

$$\sigma_{\text{inh}}^{rr} = -\frac{1}{2}\sum_{ij}\int d\vec{r}' \int_0^1 d\lambda\, |\vec{r}'|\cos\theta\cos\theta'\tilde{\omega}_{ij}(|\vec{r}'|)\rho_0^i(\vec{r} - (1-\lambda)\vec{r}')\frac{\partial\rho_0^j(\vec{r} + \lambda\vec{r}')}{\partial r}, \qquad (47)$$

$$\sigma_{\text{inh}}^{\theta\theta} = \sigma_{\text{inh}}^{\phi\phi} = -\frac{1}{4}\sum_{ij}\frac{\partial}{\partial r}\int d\vec{r}' \int_0^1 d\lambda\, \lambda|\vec{r}'|^2\sin\theta'^2\tilde{\omega}_{ij}(|\vec{r}'|)\rho_0^i(\vec{r} - (1-\lambda)\vec{r}')\frac{\partial\rho_0^j(\vec{r} + \lambda\vec{r}')}{\partial r}. \qquad (48)$$

As within this formalism, the calculation of the grand potential only requires information on the normal component of the stress tensor, we introduce Eq. (47) into Eq. (41) and carry out some manipulations and simplifications to obtain the grand potential

$$\Omega_{\text{inh}}[\rho_0(\vec{r})] = -\frac{1}{4}\sum_{ij}\int d\vec{r}\int d\vec{r}'\int_0^\infty ds\, \tilde{\omega}_{ij}(s + |\vec{r} - \vec{r}'|^2)\nabla'\rho_0^i(\vec{r}')\cdot\nabla\rho_0^j(\vec{r}), \qquad (49)$$

which depends on the exact expressions for the density profile of the spherical surface. Now, to calculate surface properties it is necessary to introduce an approximation for the density profile. Although the system is three-dimensional, the density profile depends exclusively on the normal coordinate; which is the only direction for changes of the profile and therefore the gradient acts only on that coordinate. Introducing the step-like approximation for the density profile

$$\rho_0^i(\vec{r}) = \rho_{0l}^i \Theta(R - r) + \rho_{0v}^i \Theta(r - R), \qquad (50)$$

where $R$ defines the radius of the Gibbs dividing surface and $r = |\vec{r}|$, and considering that locally the surface can be approximated by a plane plus correction terms, we perform two integrations and carry out further simplifications to get to the grand potential for this geometry

$$\Omega_{\text{inh}}[\rho_0(\vec{r})] = 4\pi R^2 \left\{ -\frac{\pi}{2} \sum_{ij} \Delta\rho_0^i \Delta\rho_0^j \int_0^\infty dr\, r^3 \tilde{\omega}_{ij}(r^2) + \frac{\pi}{8R^2} \sum_{ij} \Delta\rho_0^i \Delta\rho_0^j \int_0^\infty dr\, r^5 \tilde{\omega}_{ij}(r^2) \right\}. \qquad (51)$$

Notice the separation in two contributions: the first one corresponding to surface tension and the second due to the curvature of the system. Both expressions reduce to the single component case from the same formalism.

### 4.3. Arbitrary Surfaces

We now consider the case when the coexistence surfaces are arbitrarily curved. Once again, the interest is in obtaining the microscopic expression for the corresponding free energy. For this general case we introduce the normal component of the stress tensor, Eq. (38), into Eq. (41) to obtain

$$\Omega_{\text{inh}} = -\frac{1}{2} \sum_{ij} \int d\vec{r} \int d\vec{r}' \int_0^1 d\lambda\, \hat{n}_\alpha^i(\vec{r})\hat{n}_\beta^j(\vec{r})\rho_0^i(\vec{r} - (1-\lambda)\vec{r}')\tilde{\omega}_{ij}(|\vec{r}'|)r'_\alpha \nabla_\beta \rho_0^j(\vec{r} + \lambda\vec{r}')$$

$$-\frac{1}{2} \sum_{ij} \int d\vec{r}\, \hat{n}_\alpha^i(\vec{r})\hat{n}_\beta^j(\vec{r})\nabla_\nu \int d\vec{r}' \int_0^1 d\lambda \rho_0^i(\vec{r} - (1-\lambda))\tilde{\omega}_{ij}(|\vec{r}'|)r'_\beta[r'_\alpha\nabla_\nu\rho_0^j(\vec{r} + \lambda\vec{r}') - r'_\nu\nabla_\alpha\rho_0^j(\vec{r} + \lambda\vec{r}')]. \quad (52)$$

Aimed at simplifying the general microscopic expression for the free energy contribution from the interfacial region of the arbitrarily curved interface within a mean field approximation, we now introduce a change of variables of the form

$$\vec{r}^{(1)} = \vec{r} + \lambda\vec{r}', \qquad (53)$$

$$\vec{r}^{(2)} = \vec{r}', \qquad (54)$$

and use the relation for normal vectors of the different coexistence regions

$$r_\nu^{(2)}\nabla_\nu^{(1)}\left[\hat{n}_\alpha^i(\vec{r}^{(1)} - \lambda\vec{r}^{(2)})\hat{n}_\beta^j(\vec{r}^{(1)} - \lambda\vec{r}^{(2)})\right] = \frac{\partial}{\partial\lambda}\left[\hat{n}_\alpha^i(\vec{r}^{(1)} - \lambda\vec{r}^{(2)})\hat{n}_\beta^j(\vec{r}^{(1)} - \lambda\vec{r}^{(2)})\right]. \qquad (55)$$

We realize it is convenient to define an auxiliary function $W_{ij}(r_n'^2 + r_{t_1}'^2 + r_{t_2}'^2)$, which is short ranged and is related to the interaction potential $\tilde{\omega}_{ij}(|r_n'^2 + r_{t_1}'^2 + r_{t_2}'^2|)$ via

$$\frac{\partial}{\partial r_n'}W_{ij}(r_n'^2 + r_{t_1}'^2 + r_{t_2}'^2) = r_n'\tilde{\omega}_{ij}(|r_n'^2 + r_{t_1}'^2 + r_{t_2}'^2|). \qquad (56)$$

Introducing all these elements from Eqs. (53-56) into Eq. (52) and carrying out further simplifications, we obtain the final result

$$\Omega_{\text{inh}} = -\frac{1}{4} \sum_{ij} \int d\vec{r}^{(1)} \int d\vec{r}^{(2)} \int_0^\infty dt\, \tilde{\omega}_{ij}(t + (\vec{r}_n^{(1)} - \vec{r}_n^{(2)})^2 + (\vec{r}_t^{(1)} - \vec{r}_t^{(2)})^2)\partial_n^{(1)}\rho_0^i(\vec{r}^{(1)})\partial_n^{(2)}\rho_0^j(\vec{r}_n^{(2)}), \qquad (57)$$

where each vector has been written as $\vec{r}^{(i)} = r_n^{(i)}\hat{n}^{(i)} + r_{t_1}\hat{t}_1^{(i)} + r_{t_2}\hat{t}_2^{(i)}$. Notice that the density profile depends exclusively on the normal coordinate. This is one of the most relevant results from this theory; it is the simplest and exact microscopic expression within mean field known in the context of inhomogeneous fluids. For this general case, we consider a situation of average temperatures for which there exist multiple coexistence surfaces that can be composed of one or several species.

Notice that the microscopic grand potential in Eq. (57) depends exclusively on the $t$ density profiles and the $t(t+1)/2$ interaction potentials between molecules of the same or different species. The compact expression appears rather elegant as is, but within this level is still far from helpful to identify surface properties and to carry out comparisons with other viewpoints. It is necessary to introduce the Gibbs dividing surface, on which the calculation of the interfacial properties is projected. In general, for a system composed of several components and for a real density profile, this is a formidable task. Nevertheless, one may consider once again the asymptotic limit for the density profile that is relatively easy to implement

$$\rho_0^k(\vec{r}) = \rho_0^k(\vec{r}_n) = \rho_{0l}^k \Theta(r_{n0}^{(k)} - r_n) + \rho_{0v}^k \Theta(r_n - r_{n0}^{(k)}),\ (58)$$

where $r_{n0}^{(k)}$ is the radius of the Gibbs dividing surface, with $k = 1, 2, \ldots, t$.

By writing volume elements in the form $d\vec{r}^{(i)} = dr_n^{(i)} dS^{(i)}$, $i = 1, 2$, evaluations of the derivatives of the density profile become obvious. The resulting expression is

$$\Omega_{\text{inh}} = \frac{1}{4} \sum_{ij} \Delta\rho_0^i \Delta\rho_0^j \int dS^{(1)} \int dS^{(2)} \hat{n}_i^{(1)} \cdot \hat{n}_J^{(2)}$$

$$\times \int\limits_0^\infty dt\, \tilde{\omega}_{ij} \left( t + (r_{n0}^{(1)} - r_{n0}^{(2)})^2 + (\vec{r}_t^{(1)} - \vec{r}_t^{(2)})^2 \right),\quad (59)$$

with $\vec{r}_t^{(l)}$ being two-dimensional vectors on $S_1$ and $S_2$, and $l = 1, 2$ in this case. Observe that the information on the metric of the different coexistence surfaces is contained within the dot product of the normals, $\hat{n}_i^{(1)} \cdot \hat{n}_j^{(2)}$, the surface elements, and the interaction potential. According to this, the surface invariants are coupled to the index that labels each specie. Although this approximation for the density profile introduces simplifications to the integrand in the interfacial free energy, evaluation of one of the surface integrals still remains.

To perform the integration we use an approximation on one of the surfaces [8]; explicitly we introduce a local coordinate system in the neighborhood of a point $P$ lying on a Gibbs dividing surface of constant density for an arbitrary specie. This point defines the origin of the local coordinate system and we assume it located by the vector position $\vec{r}^{(1)}$. We choose the $z^i$ axis pointing in the normal direction so that $\hat{n}_i^{(1)}(\vec{r}) = \hat{k}$. Both coordinates $x$ and $y$ remain on the tangent plane, along the directions of the principal radii of curvature. Evidently, the Gibbs dividing surface is located at $r_n^{1i} = r_{n0}^{1i}$. Any other point $Q$ in the neighborhood of $P$, and located by the vector position $\vec{r}^{(2)}$, is on the Gibbs dividing surface at $r_n^{(2i)} = r_{n0}^{(2i)}$ and located outside the local tangent plane at a distance $z^i = r_{n0}^{(1i)} - r_{n0}^{(2i)}$. On the local coordinate system, this can be approximated as

$$z^i = \frac{1}{2} \left( \frac{x^2}{R_1^i} + \frac{y^2}{R_2^i} \right) + \cdots \qquad (60)$$

The normal vector at point $Q$, located by $\vec{r}^{(2)}$, is given by

$$\hat{n}_i^{(2)} = \frac{(-\frac{x}{R_1^i}, -\frac{y}{R_2^i}, 1)}{\left[ 1 + (\frac{x}{R_1^i})^2 + (\frac{y}{R_2^i})^2 \right]^{\frac{1}{2}}}, \qquad (61)$$

so that the metric in this coordinate system is $g(z^i) = 1 + [\nabla z^i(x, y)]^2 = 1 + (x/R_1^i)^2 + (y/R_2^i)^2$, where $(x/R_1^i) \ll 1$, $(y/R_2^i) \ll 1$. The surface element in the local system is $dS^{(2)} = [g(z^i)]^{\frac{1}{2}} dx dy$ and the scalar product of the normal vectors is $\hat{n}_i^{(1)} \cdot \hat{n}_i^{(2)} = [g(z^i)]^{-\frac{1}{2}}$.

The interaction potential captures interactions between two molecules in different points on the surface and so has an implicit dependence on the metric. For the purposes of this work, only the first order contribution is relevant. That is

$$\tilde{\omega}_{ij} \left( t + (r_{n0}^{(1)} - r_{n0}^{(2)})^2 + (\vec{r}_t^{(1)} - \vec{r}_t^{(2)})^2 \right)$$

$$= \tilde{\omega}_{ij} \left( t + \frac{1}{4} \left( \frac{x^2}{R_1^i} + \frac{y^2}{R_2^i} \right)^2 + x^2 + y^2 \right). \qquad (62)$$

Although the metric depends on the scalar product of the normal vectors $\hat{n}_i^{(1)}$ and $\hat{n}_i^{(2)}$ at two different points on the surface, in the end only information on one of the points transcends, as one of the normals is chosen in the direction of the unit vector $\hat{k}$. Power-expanding the interaction potential about $t + x^2 + y^2$ and evaluating each of the integrals, we obtain the expression for the grand potential correct to second order in the inverse of the radii of curvature for the surface composed of species $i$

$$\Omega_{\text{inh}} = -\sum_{ij} \int dS \left\{ \frac{\pi \Delta\rho_0^i \Delta\rho_0^j}{2} \int\limits_0^\infty dr\, r^3 \tilde{\omega}_{ij}(r^2) \right\}$$

$$+ \int dS \left[ \left( \frac{1}{R_1^i} \right)^2 + \left( \frac{1}{R_2^i} \right)^2 + \frac{2}{3R_1^i R_2^i} \right]$$

$$\times \left\{ \frac{3\pi \Delta\rho_0^i \Delta\rho_0^j}{64} \int\limits_0^\infty dr\, r^5 \tilde{\omega}_{ij}(r^2) \right\} + \cdots, \qquad (63)$$

where $dS^{(1)} = dS$ has been used. By introducing the mean and Gaussian curvatures, $H_i$ and $K_i$ respectively, into the surface under consideration one obtains the relationship

$$4H_i^2 - \frac{4}{3}K_i = \left( \frac{1}{R_1^i} \right)^2 + \left( \frac{1}{R_2^i} \right)^2 + \frac{2}{3R_1^i R_2^i}, \qquad (64)$$

which can be introduced into Eq. (63) to obtain a general result for the microscopic free energy for the interfacial region of the $t$-specie multicomponent system in terms of the surface invariants $H_i$ and $K_i$

$$\Omega_{\text{inh}} = -\sum_{ij} \int dS \left[ \frac{\pi \Delta\rho_0^i \Delta\rho_0^j}{2} \int\limits_0^\infty dr\, r^3 \tilde{\omega}_{ij}(r^2) \right.$$

$$\left. + \frac{3\pi \Delta\rho_0^i \Delta\rho_0^j}{64} (4H_i^2 - \frac{4}{3}K_i) \int\limits_0^\infty dr\, r^5 \tilde{\omega}_{ij}(r^2) \right]. \quad (65)$$

Observe its dependence on the different interaction potentials and on the principal curvatures of the surface under consideration, which is consistent with previous works that use the same viewpoint [8,9].

To identify microscopic expressions of surface properties it is necessary to compare Eq. (65) with the corresponding Helfrich phenomenological model for a fluid membrane of a $t$-component mixture, which is proposed in this work by Eq. (42). One issue to be noticed is the lack of contribution due to spontaneous curvature; also known as Tolman length. The reason behind this is the sharp approximation for the density profile, which prevents from capturing details arising from the smooth behavior of this quantity.

## 5. Final Remarks

The most relevant feature in this work resides in being able to extend, without ambiguity, the theory of inhomogeneous fluids of a single component to an arbitrary number of components. The starting point in this scheme is the EL equation, which is modified to obtain a force balance equation, that in its turn implies existence of a stress tensor. This quantity has been constructed using general symmetry considerations of a mechanical system and has resulted in the most general expression known within this topic. In order to obtain concrete results, an approximation for the free energy at the level of mean field has been introduced; which is appropriate for the equilibrium system far from the critical point and that, in addition, correctly captures the non-locality of the system.

We have analyzed the system in two different states: when it is found forming either one or multiple interfacial regions. All relevant properties have been calculated in both cases for different geometries. Expressions for the free energy corresponding to the planar, spherical, and arbitrarily curved surface, are in complete agreement with previous results; that is both the exact expression and that where the step-like approximation for the density profile is introduced. The result we obtain for the grand potential maintains the same structure from the monocomponent system. That is, it depends on the densities of the different species in the system, on the interaction potential, and is fully consistent with previous works that use the same scheme. The agreement with other approaches is maintained only at the level of surface tension. A noteworthy fact is that the analysis for an arbitrarily curved surface is justified only in the case of weakly deformed surfaces or for surfaces with very large radii of curvature as compared to range of the interaction potential. It is also important to mention that the expression for surface tension is a function of the number of species, which suggests the possibility of carrying out numerical calculations varying the number of molecules of some species and observe interfacial phenomena [13]. This requires, without a doubt, a rather detailed analysis which we shall consider in a future publication.

## Acknowledgments

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