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Interfacial properties of liquid-vapor interfaces with planar, spherical, and cylindrical geometries in mean field

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Following the route of the stress tensor we study the free energy of a fluid liquid-vapor interface in the van der Waals approximation for planar, cylindrical and spherical interfaces. By performing a systematic expansion in powers of the inverse of the curvature radii, and appropriately defining the Gibbs dividing surface, we find unambiguous expressions for the surface tension, the spontaneous curvature, the bending rigidity and the Gaussian rigidity.

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I. INTRODUCTION

Under the assumption that the interface between liquid and vapor of a single component fluid can be viewed as a continuum two-dimensional elastic object the interfacial free energy has been proposed to have the so-called Helfrich's form [1],

$$\Omega_S = \int ds(\gamma - 2\kappa c_0 J + \kappa J^2 + \bar{\kappa} K) \tag{1}$$

where dS is the element of area of the interface, $J=(1/R_1)+(1/R_2)$ is the local mean curvature, $K=1/R_1R_2$ is the local Gaussian curvature, and R_1 and R_2 are the principal radii of curvature at a given point on the surface. The coefficients are, γ the surface tension, κ and $\bar{\kappa}$ the bending and the Gaussian, or saddle-splay, rigidities, and c_0 the spontaneous curvature. These coefficients are properties of the elastic medium itself, and for a fluid interface, they should be expressible in terms of microscopic quantities of the fluid, such as the intermolecular potential as well as in terms of thermodynamic properties of the macroscopic state.

There are a variety of points of view to analyze the *planar* liquid-vapor interface of a simple fluid [2,3] that lead to the same value of the surface tension. However, when the surface is curved the matter becomes more complicated and a lot of theoretical work has been devoted to the determination of the interfacial coefficients in the context of a more microscopic theory [4–17], and it is remarkable that there still exist discrepancies in the values of the rigidity constants. As far as the surface tension is concerned, there is full agreement of all the theories with the well-known Yvon-Triezenberg-Zwanzig expression [18].

One of the approaches that has an old tradition is one in which the surface energy is analyzed in terms of the inverse of the radius of curvature of the surface. This approach was initiated by Tolman [19] in 1949, who calculated a first order correction to the surface tension for a spherical drop. In a later work Fisher and Wortis [20] used Landau theory to analyze a spherical interface and they also obtained an expression for the first order correction of the surface energy for the spherical interface. Then, Giessen *et al.* [15] extended the study of Fisher and Wortis, and by a direct identification of the surface energy using spherical and cylindrical geometries, obtained the interfacial properties up to second order corrections in the radii of curvature.

In the present paper we provide a systematic calculation of the interfacial coefficients using the general approach of density functional theory, through the route of the stress tensor and within the van der Waals approximation [4–6]. As we shall see, we find agreement with the results of Refs. [15,20], which were calculated through different approaches. We base our study on the most general expression of the stress tensor, valid for any free energy density functional that satisfies translational and rotational invariance [6]. As we shall explain below, the free energy can be expressed in terms of the stress tensor, and the obtained expression is then compared with Helfrich's form.

Besides the technical and systematic approach here used, it is important to emphasize the role of the concept of the "Gibbs dividing surface" [3] in this study. In an actual liquid-vapor fluid coexistence state the interface is not really a two-dimensional object but, rather, it is a very thin region of molecular size (far away from the critical point) that is called the interfacial region. Therefore, it is common to consider an imaginary surface where the surface tension and the other interfacial properties act.

In the present work, since the properties of the nonuniform fluid enter through the assumption of the existence of a free energy density functional, the concept of a Gibbs dividing surface plays no a priori role. The inhomogeneous region where the interface is located is determined by the density

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profile itself, which in turn is the result of the equilibrium state. The theory that we follow here makes first an identification of which part of free energy belongs to the bulk phases and which other part belongs to the interfacial region. One may call such a term simply the "surface" free energy. When the surface is planar, one is lead to identify right away a free energy *per* unit of surface, and this turns out to be the well-known value for the surface tension [18], which is independent of the choice of the surface of tension. However, when the surface is curved, there appears not to be an unambiguous way to define the "surface" and this may well be one of the reasons for the discrepancies alluded above. The ambiguity can be removed if one assumes that the size of, say, the drop of liquid is large compared with the size of the interfacial region. In such a case one can perform an expansion in terms of the inverse of the radii of curvature and the coefficients of those terms may then be identified with the interfacial constants of the fluid. Because of the nature of the expansion, those coefficients should be independent of the choice of the surface; that is, they should be valid for any value of the size of the drop. Thus, one must assume the existence of an appropriate Gibbs dividing surface, and this actually determines the values of the curvature radii. By following this procedure, which is essentially the same proposed by Fisher and Wortis and used by Giessen *et al.* [15], we arrive at unambiguous results for the surface properties. Thus, the agreement of our work with those references indicates that the different routes agree, first because correctly isolate the interfacial contributions, and second because of the appropriate choice of the Gibbs dividing surface in this order of approximation. As a further verification, we also provide the extreme limit of drops so large that the density profile can be approximated by a steplike function, namely, with an interfacial region of zero width, in which case the Gibbs dividing surface is uniquely defined; we find that our previous results reduce to the latter in the limit of very large curvature radii.

The paper is organized as follows. Section II deals with a brief review of the stress tensor and of the identification of the interfacial free energy. In Sec. III the interfacial free energy is explicitly calculated, within the approximations mentioned above, and three geometries are analyzed, planar, spherical, and cylindrical. With these three we can calculate all the interfacial coefficients. We conclude in Sec. IV with a brief summary.

II. THE STRESS TENSOR

For a fluid to be in thermodynamic equilibrium it must satisfy thermal, chemical, and mechanical equilibrium. For a homogeneous fluid, the latter is equivalent to the condition that the pressure has the same value in all spatial points of the fluid. However, for an inhomogeneous fluid the pressure is no longer a constant everywhere neither is it isotropic. In such a class of states the mechanical equilibrium condition is now expressed in terms of the stress tensor [21],

$$\nabla \cdot \tilde{\sigma} = -\vec{f}_{\mathrm{ext}}, \tag{2}$$

where $\tilde{\sigma}$ is the stress tensor and $\vec{f}_{\mathrm{ext}}$ is the external force per unit of volume. The divergence of the stress tensor is the force that the fluid exerts on itself and this is balanced by the external force. In the absence of external forces (or when the only existing external forces are those exerted at the boundaries by identical "walls" everywhere) the fluid is homogeneous within the volume and one recovers $\tilde{\sigma}=-p\tilde{1}$, with p the hydrostatic pressure [22]. Below we discuss how one can envisage an inhomogeneous liquid-vapor coexistence state to be established by imposing appropriate boundary conditions, which in turn, play the role of the external field.

According to the density functional theory [2,23] the grand potential for a simple one-component fluid can be written as

$$\Omega[\rho(\vec{r})] = F[\rho(\vec{r}),T] - \int d\vec{r}(\mu - V_{\mathrm{ext}}(\vec{r}))\rho(\vec{r}) \tag{3}$$

where $F[\rho,T]$ is the intrinsic Helmholtz free energy density functional, also a function of the temperature T, V_{ext} is the potential of the external force, and μ is the chemical potential.

At equilibrium, the grand potential is a minimum and the solution to the ensuing Euler-Lagrange equation is the equilibrium density profile $\rho_0(\vec{r})$,

$$\left.\frac{\delta F[\rho(\vec{r}),T]}{\delta\rho}\right|_{\rho_0} = \mu - V_{\mathrm{ext}}(\vec{r}). \tag{4}$$

We emphasize that the equilibrium profile is determined by the external fields and the intensive thermodynamic variables T and μ. It has been shown by several authors [3,5,6,24,25] that the Eq. (4) is completely equivalent to the equation for mechanical equilibrium, Eq. (2). Romero-Rochín and Percus [6,26], starting from Eq. (4), have derived an expression for the stress tensor for an arbitrary free energy density functional $F[\rho]$; this result will be used below.

In an inhomogeneous liquid-vapor state the equilibrium density profile $\rho_0(\vec{r})$ is uniform in each of its bulk liquid and vapor phases and is nonuniform only in the interfacial region that separates the two phases. In this region the density profile changes abruptly from one of its bulk values to the other. The experienced change is reflected in the gradient of the density profile $\nabla\rho_0(\vec{r})$, which is zero everywhere except in the interfacial region where it is sharply peaked [4–6]. The geometry of the interface is thus ingrained in the density profile. Therefore, we can use the family of surfaces $\rho_0(\vec{r})=\text{constant}$ as one of a set of curvilinear coordinates to describe the system. The corresponding unit vectors are the normal to the constant density surfaces,

$$\hat{n}(\vec{r}) = \frac{\nabla\rho_0(\vec{r})}{|\nabla\rho_0(\vec{r})|} \tag{5}$$

and two other unit vectors tangential to the surfaces. Here, we shall limit ourselves to the simple orthogonal sets Cartesian, spherical and cylindrical, but one can also consider more complicated geometries [4].

Taking into account these geometrical considerations, Romero-Rochín, Varea, and Robledo [5] showed that the grand potential, Eq. (3), can be expressed solely in terms of the *normal* component of the stress tensor,

$$\Omega = \int dr\sigma^N(\vec{r}) - \int dr\sigma^N_{\mathrm{inh}}(\vec{r}). \tag{6}$$

The quantity $\sigma^N = \hat{n}\cdot\tilde{\sigma}\cdot\hat{n}$ is the full normal component of stress tensor while and $\sigma^N_{\mathrm{inh}}(\vec{r})$ is the part of the normal component of the stress tensor that arises only if there is an inhomogeneity. This will be explicitly written below. The purpose here is to point out that if the inhomogeneity of the fluid is of the form of a liquid-vapor interface, the second term in the right-hand side (rhs) is different from zero only at the interface. That is, far from the interface, σ^N equals (minus) the hydrostatic pressure and σ^N_{inh} vanishes. Thus, all the interfacial properties are described by the second term of Eq. (6). We call such a part the *interfacial* contribution to the grand potential and this is the subject of our present study,

$$\Omega_S = -\int dr\sigma^N_{\mathrm{inh}}(\vec{r}). \tag{7}$$

To reiterate, the contribution to the free energy, or grand potential, arising from the interfacial surface is completely contained in the above expression. The purpose of this paper is to explicitly calculate such a contribution for a (short-range) fluid in a mean field approximation, for large curvature radii, and for different geometries.

The mean-field, van der Waals free energy density functional is given by

$$F[\rho(\vec{r})] = \int d\vec{r} f_0(\rho(\vec{r})) + (1/2)\int\int d\vec{r}d\vec{r}'\tilde{w}(|\vec{r}-\vec{r}'|)\rho(\vec{r})\rho(\vec{r}'), \tag{8}$$

where $f_0(\rho(\vec{r}))$ is the local free energy density which in the absence of inhomogeneities yields the repulsive part of the van der Waals equation of state. $\tilde{w}(|\vec{r}-\vec{r}'|)$ is the direct correlation function of the fluid in the uniform phases and, in this approximation, is the attractive part of the interaction potential assumed to be of short range ξ_B [2,3].

As mentioned above, a general expression for the stress tensor for an arbitrary free energy density functional $F[\rho]$ is known [6]. Evaluating such an expression for the van der Waals model yields the inhomogeneous part of the stress tensor as

$$\begin{aligned}\sigma^{\alpha\beta}_{\mathrm{inh}}(\vec{r}) = &-\frac{1}{2}\int d\vec{r}'\int_0^1 d\lambda\rho_0(\vec{r}-(1-\lambda)\vec{r}')\tilde{w}(|\vec{r}'|)r'_\alpha \\ &\times\boldsymbol{\nabla}_\beta\rho_0(\vec{r}+\lambda\vec{r}') - \frac{1}{2}\boldsymbol{\nabla}_\nu\int d\vec{r}'\int_0^1 d\lambda\lambda \\ &\times\rho_0(\vec{r}-(1-\lambda)\vec{r}')\tilde{w}(|\vec{r}'|)r'_\beta \\ &\times[r'_\alpha\boldsymbol{\nabla}_\nu\rho_0(\vec{r}+\lambda\vec{r}') - r'_\nu\nabla_\alpha\rho_0(\vec{r}+\lambda\vec{r}')],\end{aligned} \tag{9}$$

where the greek indices indices Cartesian components. The normal component is $\sigma^N_{\mathrm{inh}} = \hat{n}_\alpha\sigma^{\alpha\beta}_{\mathrm{inh}}\hat{n}_\beta$.

Substitution of the normal component of the above tensor into the expression for the interfacial grand potential, Eq. (7), yields,

$$\begin{aligned}\Omega_S = &-\frac{1}{2}\int d\vec{r}\int d\vec{r}'\int_0^1 d\lambda\tilde{w}(|\vec{r}'|)\rho_0(\vec{r}-(1-\lambda)\vec{r}') \\ &\times\boldsymbol{\nabla}_\alpha\rho_0(\vec{r}+\lambda\vec{r}')\{r'_\beta\hat{n}_\alpha(\vec{r})\hat{n}_\beta(\vec{r}) - 2\lambda r'_\nu r'_\beta\hat{n}_\nu(\vec{r})\boldsymbol{\nabla}_\alpha\hat{n}_\beta(\vec{r}) \\ &+\lambda r'_\beta r'_\nu\hat{n}_\alpha(\vec{r})\boldsymbol{\nabla}_\nu\hat{n}_\beta(\vec{r}) + \lambda r'_\beta r'_\nu\hat{n}_\beta(\vec{r})\boldsymbol{\nabla}_\nu\hat{n}_\alpha(\vec{r})\}.\end{aligned} \tag{10}$$

Let us make a few observations. First, if the fluid is homogeneous everywhere, $\boldsymbol{\nabla}\rho_0 = 0$ and this contribution vanishes. Second, we need to know the density profile in order to evaluate the free energy, that is, we are supposed to have solved the Euler-Lagrange equation. For the van der Waals model it is known [27] that one can construct solutions to the Euler-Lagrange equation for simple geometries that yield planar, spherical or cylindrical interfaces. This can be done by imposing boundary conditions in which the fluid is in the liquid phase at one "extreme" and at the vapor phase in the other one. These boundary conditions can be thought to arise from appropriate external fields. The way we shall proceed is to *assume* those solutions exist, and with general geometrical considerations, we shall transform Eq. (10) in order to make it appear as Helfrich's free energy. This is explicitly performed in the following sections.

III. THE INTERFACIAL FREE ENERGY

Following the program explained above, we now consider that the equilibrium density profile represents a liquid-vapor interface with the geometries planar, cylindrical, and spherical. These coordinate sets have the property that their three unit vectors are orthogonal everywhere, allowing for a simplification of the interfacial free energy that yields exact expressions that can be further approximated.

Let us use the following notation for those coordinates, respectively, (x,y,z), $(R,\phi,z)q$, and (r,θ,ϕ), with $R = (x^2+y^2)^{1/2}$ the radial cylindrical coordinate. That the density profile has one of the said geometries means that

$$\begin{aligned}\rho_0 &= \rho_0(z) \quad \text{planar}, \\ \rho^c_0 &= \rho^c_0(R) \quad \text{cylindrical}, \\ \rho^s_0 &= \rho^s_0(r) \quad \text{spherical},\end{aligned} \tag{11}$$

and the corresponding normal unit vectors are $\hat{k}$, $\hat{R}$, and $\hat{r}$. It turns out that for these geometries the interfacial grand potential can be written in a very simple form. Referring to Eq. (10), one notices that this expression seemingly depends on the parameter λ, which would indicate a type of gauge dependence. This is not so since the λ integral can be done. The "trick" is to realize that, in general, the following identity is true:

$$r'_\alpha\boldsymbol{\nabla}_\alpha\rho_0(\vec{r}+\lambda\vec{r}') = \frac{\partial}{\partial\lambda}\rho_0(\vec{r}+\lambda\vec{r}'). \tag{12}$$

With this, the grand potential (10) can be transformed in any of the two following expressions:

$$\Omega_S = -\frac{1}{4}\int d\vec{r}\int d\vec{r}'\int_0^\infty ds\, \nabla\rho_0(\vec{r})\cdot\nabla\rho_0(\vec{r}')\tilde{w}(s+(\vec{r}-\vec{r}')^2) \tag{13}$$

and

$$\Omega_S = \frac{1}{2}\int d\vec{r}\int d\vec{r}'\, r_\alpha\tilde{w}(|\vec{r}'|)\{\rho_0(|\vec{r}-\vec{r}'|)\nabla_\alpha\rho_0(|\vec{r}|) - \rho_0(|\vec{r}|)\nabla_\alpha\rho_0(|\vec{r}-\vec{r}'|)\}, \tag{14}$$

where in both it is understood that the dependence of the density is one with the corresponding symmetries given by Eq. (11). These two expressions are the *exact* interfacial contributions to the free energy for the symmetries at hand, for the van der Waals model, Eq. (8). The first form will be useful for the approximation of a "steplike" profile, whereas the second one is more amenable for a systematic expansion in terms of the inverse of the radii of curvature, as we now discuss.

As we see from Eqs. (13) and (14), in order to calculate the interfacial grand potential we need to know "only"the equilibrium density profile $\rho_0(\vec{r})$ in any of the forms given by Eq. (11). Those solutions must be obtained from the Euler-Lagrange equation which yields the minimization of the free energy, for a given model of the kernel $\tilde{\omega}(|\vec{r}-\vec{r}'|)$. In the following section we make a small digression on the form and general properties of those solutions.

A. The density profile

The equilibrium density profile $\rho_0(\vec{r})$ minimizes the grand potential and is found as the solution of the Euler-Lagrange equation,

$$\frac{\partial f_0(\rho(\vec{r}),T)}{\partial\rho(\vec{r})} + \int d\vec{r}'\,\tilde{\omega}(|\vec{r}-\vec{r}'|)\rho(\vec{r}') - \mu = 0. \tag{15}$$

This equation must be supplemented by appropriate boundary conditions that yield a density profile with the required symmetry; accordingly, the chemical potential μ must be adjusted. Thus, for planar symmetry one assumes $\rho_0(z)$ such that for $z\to-\infty$, $\rho(z)\to\rho_l$ and for $z\to+\infty$, $\rho(z)\to\rho_v$, where ρ_l and ρ_v are the liquid and vapor coexisting densities given by the bulk density van der Waals equation of state, i.e., by the equal-areas Maxwell construction of the isotherm with temperature T. This is obtained by a particular value of the chemical potential, that we denote by μ_{coex}. It can be shown, by approximate methods [3] and by explicit numerical calculations [27], that the width of the interface is of the order of the range ξ_B of the potential, namely, of the kernel $\tilde{\omega}(|\vec{r}-\vec{r}'|)$. For cylindrical symmetry, the boundary conditions are at $R=0$, say $\rho_0^c\to\rho_l^c$ and at $R\to\infty$, $\rho_0^c\to\rho_v^c$; and for the spherical one at $r=0$, say $\rho_0^s\to\rho_l^s$ and at $r\to\infty$, $\rho_0^c\to\rho_v^c$. In both cases, the value of the chemical potential μ cannot take the value μ_{coex}; it will be greater or lower depending on the phase "inside" the drop. We are assuming here a drop of liquid in its vapor and the the values of the bulk densities for the spherical and the cylindrical symmetries differ from those of the planar case. Since the bulk values correspond to a metastable liquid drop in equilibrium with a stable vapor, an interfacial region of width ξ_B will develop where the gradient of the density becomes different from zero. The radius R_0 of the drop is contained within this region. As the radius R_0 of the drop grows indefinitely, all the mentioned differences vanish.

Thus, irrespective of the particular form of the kernel $\tilde{\omega}(|\vec{r}-\vec{r}'|)$, and following Fisher and Wortis [20] and Giessen *et al.* [15], one can propose that the density profiles and the chemical potentials for cylindrical and spherical symmetries, in the limit of large radius of curvature, may be expanded in a series of powers of the inverse of the radius of curvature. Thus for the cylindrical symmetry one first makes the change of variables $R=z+R_c$ and the expansion reads

$$\rho_0^c(R) = \rho_0(z) + \frac{1}{R_c}\rho_1^c(z) + \frac{1}{R_c^2}\rho_2^c(z) + \cdots, \tag{16}$$

where R_c is the radius of the cylindrical drop and now z may take values from $-\infty$ to ∞. For the spherical case, the change of variables is $r=z+R_s$, with R_s the radius of the spherical drop and the expansion is now

$$\rho_0^s(r) = \rho_0(z) + \frac{1}{R_s}\rho_1^s(z) + \frac{1}{R_s^2}\rho_2^s(z) + \cdots. \tag{17}$$

The chemical potential must be expanded accordingly,

$$\mu^c = \mu_{\text{coex}} + \frac{1}{R_c}\mu_1^c + \frac{1}{R_c^2}\mu_2^c + \cdots, \tag{18}$$

$$\mu^s = \mu_{\text{coex}} + \frac{1}{R_s}\mu_1^s + \frac{1}{R_s^2}\mu_2^s + \cdots. \tag{19}$$

The radii of curvature R_c and R_s determine the location of the Gibbs dividing surface and its precise value is found as part of the solution by demanding that the interfacial coefficients must be independent of the location of the surface; this will be done in detail below. As already mentioned, the radii of curvature will be located within the region where the gradient of the density is different from zero. In the strict limit of infinite radii the profile and the chemical potential must approach those of the planar profile.

In order to obtain the functions $\rho_1^{c,s}(z)$ and $\rho_2^{c,s}(z)$, one would have to solve the Euler-Lagrange equation for a given kernel $\tilde{\omega}(|\vec{r}-\vec{r}'|)$. Very interestingly, Giessen *et al.* [15] have found that in order to be consistent with the above expansions in the limit of large curvatures, the functions $\rho_1^{c,s}(z)$ and $\rho_2^{c,s}(z)$ are not independent but must obey

$$2\rho_1^c(z) = \rho_1^s(z) \equiv \rho_1(z) \tag{20}$$

and

$$4\rho_2^c(z) = \rho_2^s(z) \equiv \rho_2(z). \tag{21}$$

The demonstration of these equalities is by no means simple and we refer the reader to Ref. [15] for details. These equalities will prove to be essential for obtaining the interfacial elastic coefficients.

A more radical approximation to the density profile, that should be valid in the limit of very large radius of curvature,

$R \gg \xi_B$, may be obtained by assuming a "steplike" function,

$$\rho_0(z) = \rho_l \theta(z_0 - z) + \rho_v \theta(z - z_0), \tag{22}$$

for the plane,

$$\rho_0^c(R) = \rho_l \theta(R_c - R) + \rho_v \theta(R - R_c), \tag{23}$$

for the cylinder

$$\rho_0^s(r) = \rho_l \theta(R_s - r) + \rho_v \theta(r - R_s), \tag{24}$$

and for the sphere. $\theta(x)$ is the step function, z_0 the location of the interface in the planar geometry. In this approximation, because the radii are very large, one can assume that the bulk values of the coexisting densities are the same in the same geometries and correspond to those of the Maxwell equal-areas construction. The interfacial coefficients found from employing the steplike approximation will be shown to be the limit of the more detailed expansion in powers of $1/R_{c,s}$.

In the following sections we analyze the different geometries separately and from the results there obtained we shall find the expressions for the interfacial properties γ, κ, $\bar{\kappa}$, and c_0.

B. A planar interface

In this case, the density profile is considered to depend only on the z direction, $\rho_0 = \rho_0(z)$. Substituting into the interfacial grand potential, Eq. (13), one finds

$$\Omega_S = -\frac{1}{4} \int d\vec{r} \int d\vec{r}\,' \int_0^\infty ds \frac{d}{dz}\rho_0(z) \frac{d}{dz'}\rho_0(z') \tilde{w}[s + (\vec{r} - \vec{r}\,')^2]. \tag{25}$$

With a change of variables and by making use of the following identity:

$$\int d^2R |\vec{R}|^{2n} \int_0^\infty ds \tilde{w}[s + R^2 + (z - z')^2] = \frac{1}{2(n+1)} \int d^2R |\vec{R}|^{2(n+1)} \tilde{w}(R^2 + (z - z')^2] \tag{26}$$

with n a positive integer and $\vec{R} = x\hat{i} + y\hat{j}$ a two-dimensional vector, one readily obtains the interfacial free energy contribution to the planar interface,

$$\Omega_S = -S \frac{1}{4} \int dz \int dz' \frac{d}{dz}\rho_0(z) \frac{d}{dz'}\rho_0(z') \times \int d^2R |\vec{R}|^2 \tilde{w}[R^2 + (z - z')^2], \tag{27}$$

where $S = \int d^2R'$ is the area of the planar interface. From this equation one immediately identifies the surface tension

$$\gamma = -\frac{1}{4} \int dz \int dz' \frac{d}{dz}\rho_0(z) \frac{d}{dz'}\rho_0(z') \times \int d^2R |\vec{R}|^2 \tilde{w}[R^2 + (z - z')^2]. \tag{28}$$

This expression equals the celebrated exact expression of Yvon, Triezenberg, and Zwanzig [18] for the surface tension; in this case, for the van der Waals model. It has also been obtained by all the authors working in this field.

A simpler form can be obtained by assuming the "steplike" profile, Eq. (22), yielding

$$\frac{d}{dz}\rho_0(z) = -\Delta\rho\, \delta(z_0 - z), \tag{29}$$

where $\Delta\rho = \rho_l - \rho_v$ is the difference of liquid and vapor bulk densities. Substituting into Eq. (28) one finds the surface tension for this approximation,

$$\gamma^{(0)} = -\frac{\pi}{2}(\Delta\rho)^2 \int_0^\infty dr r^3 \tilde{w}(r^2). \tag{30}$$

The index (0) shall be used to denote the interfacial coefficients at this level of approximation. This expression has also been found by several authors in the field.

C. A cylindrical interface

Now we suppose that we have an inhomogeneous fluid system in the shape of a cylindrical "drop" of liquid of radius R_c in coexistence with its vapor. Although this case seems a bit unrealistic the Euler-Lagrange equation admits such a solution with the appropriate boundary conditions, as discussed before.

We refer now to the expression given by Eq. (14) for the grand potential. Assuming $\rho_0(\vec{r}) = \rho_0^c(R)$, we get,

$$\Omega_S = \frac{1}{2} \int d\vec{r} \int d\vec{r}\,' r_\alpha \tilde{w}(|\vec{r}\,'|)\{\rho_0^c(|\vec{R} - \vec{R}'|)\nabla_\alpha \rho_0^c(|\vec{R}|) - \rho_0^c(|\vec{R}|)\nabla_\alpha \rho_0^c(|\vec{R} - \vec{R}'|)\}, \tag{31}$$

where r_α still denotes the three-dimensional vector. Our goal is to make an expansion up to second order in $1/R_c$. The main point to realize here is that the kernel vanishes for $|\vec{r}\,'| \gg \xi_B$, therefore, all the primed variables cannot become greater than ξ_B, whereas the unprimed variables will mainly contribute for $|\vec{r}| \sim R_c$ since it is in that region where the gradient of the density is different from zero. Thus, effectively, $|\vec{r}\,'| \ll |\vec{r}|$, and the small parameter for the expansion turns out to be $\epsilon = R' \cos\phi / (R - R' \cos\phi)$. Therefore, one can proceed first with a systematic expansion of the integrand in Eq. (31) up to third order in ϵ. Next, we introduce the change of variables $R = z'' + R_c$, which also changes the differential of volume as

$$d\vec{r} = R dR d\phi dz = R_c\left(1 + \frac{z''}{R_c}\right) dz'' d\phi dz. \tag{32}$$

Note that we can safely take $z'' \to \pm\infty$ because the gradient of the density vanishes everywhere, except at the interfacial region. Then, one makes the ansatz of the expansion of the density in powers of $1/R_c$ given by Eq. (16). This procedure is straightforward and yields a formidable expression that we do not write here. By a systematic expansion up to second in powers of $1/R_c$, the interfacial grand potential is thus obtained,

$$\Omega_S = S\int dz\int dz'\int d^2R\tilde{w}[R^2+(z-z')^2]\Bigg[\Bigg(-\frac{1}{4}R^2\rho_0'(z)\rho_0'(z')-\frac{R^2}{4R_c}\rho_0'(z)\rho_1'(z')+\frac{3R^4}{128R_c^2}\rho_0'(z)\rho_0'(z') - \frac{R^2}{16R_c^2}[2\rho_0'(z)\rho_2'(z')+\rho_1'(z)\rho_1'(z')]\Bigg)-\Bigg(\frac{R^2}{8R_c}(z+z')\rho_0'(z)\rho_0'(z')+\frac{R^2}{32R_c^2}(z-z')^2\rho_0'(z)\rho_0'(z')+\frac{R^2}{4R_c^2}(z+z')\rho_0'(z)\rho_1'(z')\Bigg)\Bigg], \tag{33}$$

where $S=2\pi R_c\int dz$ is the area of an infinite cylinder of radius R_c. The use of the identity Eq. (26) proved to be very useful to arrive at the above result.

We note that the last three terms in Eq. (33) depend on the particular choice of the Gibbs dividing surface of the *planar* interface. This would imply that the grand potential itself would depend on such a choice, and this cannot be possible. Therefore, by demanding that these terms vanish, this in turn *defines* the position R_c of the surface of tension at which the interfacial properties are attached. This requirement is essentially the same used by Blokhuis and collaborators [13–15] and is equivalent to demanding that the Laplace equation, including the elastic contributions, acquires its phenomenological form. The latter condition was used by Fisher and Wortis [20] to define the surface of tension and, as shall indicate in the following section devoted to the spherical symmetry, our choice leads to their same condition in the appropriate limit. Summarizing, the location of the radius R_c is defined by demanding that the free energy is independent of the choice of the Gibbs dividing surface, and is given by

$$\int dz\int dz'\int d^2R\tilde{w}[R^2+(z-z')^2]R^2\Bigg(\frac{1}{8}(z+z')\rho_0'(z)\rho_0'(z') + \frac{1}{32R_c}(z-z')^2\rho_0'(z)\rho_0'(z')+\frac{1}{4R_c}(z+z')\rho_0'(z)\rho_1'(z')\Bigg) = 0. \tag{34}$$

The remaining terms of the interfacial grand potential Ω_S, Eq. (33), can now be compared with Helfrich's free energy, Eq. (1), for a cylindrical surface of radius R_c, i.e., with

$$\Omega_S = \int ds\left(\gamma - 2\kappa c_0\frac{1}{R_c}+\kappa\frac{1}{R_c^2}\right), \tag{35}$$

where the Gaussian rigidity does not appear since the Gaussian curvature vanishes for a cylinder. Thus, comparing Eq. (33) with Eq. (35), one obtains first the surface tension γ which is exactly the same expression obtained in the planar interface, Eq. (28).

The spontaneous curvature is found from the first order term as

$$\kappa c_0 = \frac{1}{8}\int dz\int dz'\frac{d}{dz}\rho_0(z)\frac{d}{dz'}\rho_0(z') \times\int d^2R|\vec{R}|^2\tilde{w}[R^2+(z-z')^2], \tag{36}$$

which agrees exactly with the expression obtained by Blokhuis and collaborators [13–15]. These authors have argued that this term, proportional to the first correction to the surface tension is at the same time the so-called Tolman's length δ, that is, $\kappa c_0 = -\gamma\delta$. This point of view was also originally advocated by Fisher and Wortis [20].

The bending rigidity takes the value,

$$\kappa = \int dz\int dz'\int d^2R\tilde{w}[R^2+(z-z')^2]\Bigg(\frac{3}{128}|\vec{R}|^4\rho_0'(z)\rho_0'(z') - \frac{1}{16}|\vec{R}|^2[2\rho_0'(z)\rho_2'(z')+\rho_1'(z)\rho_1'(z')]\Bigg). \tag{37}$$

This is one of the main results of this paper. That is, we claim that this is the bending rigidity in mean-field for a liquid-vapor interface. Certainly, we expect that the higher order corrections $\rho_1(z)$ and $\rho_2(z)$ contribute less than the planar profile ρ_0, and, therefore, from the above equation one finds that even if only the planar profile is known, a very accurate expression may be found for the bending rigidity, especially if the radius of curvature R_c is sufficiently larger than the range ξ_B of the intermolecular potential. This is further supported by the simple calculation with a steplike profile, as we now show.

In the limit of the steplike profile for a cylinder, Eq. (23), one can proceed by directly substituting such a profile into the exact interfacial grand potential for cylindrical symmetry, Eq. (31), yielding,

$$\Omega_S^{(0)} = -\frac{1}{4}(\Delta\rho)^2R_c\int dS_1(R_c)\int_{-\infty}^{\infty}dz_2\int_0^{\infty}ds\int_{-1}^{1}\frac{dxx}{(1-x^2)^{\frac{1}{2}}}\tilde{w} \times[s+(z_1-z_2)^2+2R_c^2(1-x)] + \frac{1}{4}(\Delta\rho)^2R_c\int dS_1(R_c)\int_{-\infty}^{\infty}dz_2\int_0^{\infty}ds\int_{-1}^{1}\frac{dxx}{(1-x^2)^{\frac{1}{2}}}\tilde{w} \times[s+(z_1-z_2)^2+2R_c^2(1+x)], \tag{38}$$

where $dS_1(R_c)=dz_1R_cd\phi$ is the surface differential of a cylinder of radius R_c. With the further changes of variables $y=2R_c^2(1-x)$ in the first integral and $y'=2R_c^2(1+x)$ in the second one, the above expression can be greatly simplified. One finds integrals whose upper limit is proportional to R_c: since the corresponding integrands fall to zero within ξ_B, we can safely extend those limits to infinity. The final result of the grand potential in this limit is [28]

$$\Omega_S^{(0)} = -\int dS\left(\frac{(\Delta\rho)^2}{2}\pi\int_0^\infty drr^3\tilde{w}(r^2) - \frac{3(\Delta\rho)^2}{64R_c^2}\pi\int_0^\infty drr^5\tilde{w}(r^2)\right). \tag{39}$$

The surface tension takes the same value $\gamma^{(0)}$ as in the planar case, Eq. (30). The spontaneous curvature is

$$c_0^{(0)} = 0, \tag{40}$$

and the bending rigidity is

$$\kappa^{(0)} = \frac{3}{64}(\Delta\rho)^2\pi\int_0^\infty drr^5\tilde{w}(r^2), \tag{41}$$

which, indeed, are the limits of Eqs. (36) and (37) when $\rho_1(z)=\rho_2(z)=0$ and the planar profile $\rho_0(z)$ is the steplike one given by Eq. (22).

D. A spherical interface

In this case we assume that the density profile bears a spherical symmetry, $\rho_0^s=\rho_0^s(|\vec{r}|)$, and that it represents a liquid-vapor state. We consider the case of a spherical drop of liquid in its vapor. The procedure is completely analogous to the cylindrical case. That is, we first consider the interfacial free energy with spherical symmetry,

$$\Omega_S = \frac{1}{2}\int d\vec{r}\int d\vec{r}\,' r_\alpha\tilde{w}(|\vec{r}\,'|)\{\rho(|\vec{r}-\vec{r}\,'|)\boldsymbol{\nabla}_\alpha\rho(|\vec{r}|) - \rho(|\vec{r}|)\boldsymbol{\nabla}_\alpha\rho(|\vec{r}-\vec{r}\,'|)\}, \tag{42}$$

where $\vec{r}=x\hat{i}+y\hat{j}+z\hat{k}$ is the three-dimensional radial vector. Again, because we assume $R_s \gg \xi_B$, we find that a small parameter is $\epsilon=r'\cos\theta/(r-r'\cos\theta)$ and a analogous expansion to the cylindrical case can be performed. We use the change of variables $r=z''+R_s$, where R_s is the radius of the sphere, to be determined, and again z'' may be extended to ±∞. The differential of volume transforms now as

$$d\vec{r} = \sin\theta d\theta d\phi r^2 dr = \sin\theta d\theta d\phi R_s^2\left(1 + 2\frac{z''}{R_s} + \frac{z''^2}{R_s^2}\right)dz''. \tag{43}$$

By a further substitution of the ansatz for the profile given by Eq. (17) and expanding up to second order in $1/R_c$, one finds the interfacial grand potential,

$$\begin{aligned}\Omega_S = S\int dz\int dz'\int d^2R\tilde{w}[R^2+(z-z')^2]\Bigg[\Bigg(&-\frac{1}{4}\rho_0'(z)\rho_0'(z')R^2 - \frac{R^2}{2R_s}\rho_0'(z)\rho_1'(z') + \frac{R^4}{16R_s^2}\rho_0'(z)\rho_0'(z')\\ &- \frac{R^2}{4R_s^2}[2\rho_0'(z)\rho_2'(z') + \rho_1'(z)\rho_1'(z')]\Bigg) + \frac{3}{96R_s^2}R^6\rho_0''(z)\rho_0''(z') - \frac{3}{R_s^2}(z-z')\rho_0(z)\rho_1(z') - \frac{R^2}{4R_s}(z+z')\rho_0'(z)\rho_0'(z')\\ &- \frac{R^2}{4R_s^2}zz'\rho_0'(z)\rho_0'(z') - \frac{2R^2}{R_s^2}(z+z')\rho_0'(z')\rho_1'(z)\Bigg],\end{aligned} \tag{44}$$

where $S=4\pi R_s^2$ is the area of a sphere of radius R_s. In a similar fashion as in the cylindrical case, the last five terms yield a dependence of the free energy on the location of the Gibbs dividing surface. Thus, by imposing the vanishing of those terms, the radius R_s gets determined,

$$\begin{aligned}\int dz\int dz'\int d^2R\tilde{w}[R^2+(z-z')^2]\\ \times\Bigg(\frac{3}{96R_s}R^6\rho_0''(z)\rho_0''(z') - \frac{3}{R_s}(z-z')\rho_0(z)\rho_1(z')\\ - \frac{R^2}{4}(z+z')\rho_0'(z)\rho_0'(z') - \frac{R^2}{4R_s}zz'\rho_0'(z)\rho_0'(z')\\ - \frac{2R^2}{R_s}(z+z')\rho_0'(z')\rho_1'(z)\Bigg) = 0.\end{aligned} \tag{45}$$

The remaining terms in Eq. (45) are to be compared with the Helfrich's free energy for a spherical surface,

$$\Omega_S = \int ds\left(\gamma - 4\frac{\kappa c_0}{R_s} + \frac{1}{R_s^2}(4\kappa+\bar{\kappa})\right). \tag{46}$$

We find that the surface tension γ, again, takes the same value as in the planar and cylindrical symmetries, Eq. (28). The spontaneous curvature c_0 (or Tolman's length), takes also the same value as in the cylindrical case, see Eq. (36), and now, from this symmetry, we find an expression for the combination $4\kappa+\bar{\kappa}$,

$$\begin{aligned}4\kappa+\bar{\kappa} = \int dz\int dz'\int d^2R\tilde{w}[R^2+(z-z')^2]\Bigg(\frac{R^4}{16}\rho_0'(z)\rho_0'(z')\\ - \frac{R^2}{4}[2\rho_0'(z)\rho_2'(z') + \rho_1'(z)\rho_1'(z')]\Bigg).\end{aligned} \tag{47}$$

Assuming that the expression for the bending rigidity κ is that found in the cylindrical case, Eq. (37), we can solve from the previous equation for the Gaussian rigidity,

$$\bar{\kappa} = -\frac{1}{32}\int dz \int dz' \rho_0'(z)\rho_0'(z') \int d^2R |\vec{R}|^4 \tilde{w}[R^2 + (z-z')^2]. \tag{48}$$

This is also one of the main results of this paper. It is the Gaussian rigidity for the van der Waals liquid-vapor interface. It is of interest to realize that it depends only on the planar profile $\rho_0(z)$. The result found by Blokhuis and collaborators [13–15] is also given only in terms of $\rho_0(z)$ but it is written in a very different form from Eq. (48). The procedure by which those authors have arrived at their result is by no means simple and we have not been able to reduce it to our result; since their procedure yielded the same surface tension and spontaneous curvature as ours, we expect the rigidities to be also the same.

For completeness we present the results found in the approximation of a steplike profile such as that given by Eq. (24). Again, we substitute such a profile into the interfacial free energy Ω_S, Eq. (42), finding

$$\Omega_S = -4\pi \frac{(\Delta\rho)^2}{4} R_s^4 \left(2\pi \int_{-1}^{1} dx x \int_0^\infty ds \tilde{w}(s + 2R_s^2 - 2R_s^2 x) \right). \tag{49}$$

By making the change of variable $r = 2R_s^2 - 2R_s^2 x$ one finds integrals whose upper limit is proportional to R_s^2. Since the integrands falls off for lengths longer than ξ_B, we can extend those limits to infinity. The result can be cast as [28],

$$\Omega_S^{(0)} = -4\pi R^2 \left(\frac{\pi}{2}(\Delta\rho)^2 \int_0^\infty dr r^3 \tilde{w}(r^2) - \frac{\pi}{8R_s^2}(\Delta\rho)^2 \int_0^\infty dr r^5 \tilde{w}(r^2) \right). \tag{50}$$

Comparing with Helfrich's form, Eq. (46), one finds the surface tension $\gamma^{(0)}$ already given by Eq. (30), the spontaneous curvature in this approximation is $c_0^{(0)}$, and the combination $4\kappa^{(0)} + \bar{\kappa}^{(0)}$ is

$$4\kappa^{(0)} + \bar{\kappa}^{(0)} = \frac{(\Delta\rho)^2 \pi}{8} \int_0^\infty dr r^5 \tilde{w}(r^2), \tag{51}$$

which, needless to say, is the limit of Eq. (47). With the use of $\kappa^{(0)}$ given by Eq. (41), we can solve for $\bar{\kappa}^{(0)}$,

$$\bar{\kappa}^{(0)} = -\frac{1}{16}(\Delta\rho)^2 \pi \int_0^\infty dr r^5 \tilde{w}(r^2), \tag{52}$$

which, of course, can be found directly by taking a steplike profile in the expression for $\bar{\kappa}$, Eq. (48).

IV. FINAL REMARKS

Following the route of the stress tensor, with its general expression for an arbitrary free energy density functional, we have obtained the interfacial constants for the van der Waals fluid, as a result of a power series in the inverse of the curvature radii. These coefficients are, the surface tension γ, Eq. (28), the spontaneous curvature c_0, Eq. (36), the bending rigidity κ, Eq. (37), and the Gaussian rigidity $\bar{\kappa}$, Eq. (48). We have also found their corresponding values in the limit of a steplike profile, Eqs. (30), (40), (41), and (52).

We want to emphasize, nonetheless, that with the present scheme one can obtain the *exact* interfacial contribution of the free energy for the van der Waals fluid, and that for the simple geometries here considered the expression is formally the same, namely,

$$\Omega_S = -\frac{1}{4}\int d\vec{r} \int d\vec{r}' \int_0^\infty ds\, \nabla\rho(\vec{r}) \cdot \nabla\rho(\vec{r}')\tilde{w}[s + (\vec{r} - \vec{r}')^2]. \tag{53}$$

Our approximations here are the leading order terms for any other more accurate calculation. However, it is only in a expansion in terms of the curvatures that one can identify the interfacial coefficients.

Several results are important to point out. First, the well-known dependence of the surface tension on the second moment of the direct correlation function [18] and the dependence of the rigidities on its fourth moment are also here verified [29]. The bending rigidity is found to be negative, in agreement with numerical simulations [30], experiments [31], and calculations by the route of the fluctuations [32,33]. Our results are more general than those obtained by square-gradient and square-Laplacian theories, since the latter are already approximations to the van der Waals free energy given by Eq. (8). More importantly, perhaps, is the agreement of our results with those of Blokhuis and collaborators [13–15] and with Fisher and Wortis [20] at first order. The is important because this field has been plagued by discrepancies in the values of the elastic coefficients. The differences are not easy to discern since different authors use different approaches to identify interfacial coefficients [7,8,16,17]. The fact that the approach here used via the stress tensor is different from that of Refs. [15,20] yielding the same results, we believe, it is an indicative that the concept of the Gibbs dividing surface, used in these works, leads to unambiguous interfacial quantities.

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