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Stress tensor of liquid-vapor states of inhomogeneous fluids

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The theory of the stress tensor of nonuniform fluids by means of density functional theory is reviewed. We present a general, symmetric, stress tensor valid for any free energy density functional with translational and rotational invariance. We specialize to the nonlocal van der Waals free energy density functional of a simple fluid and study inhomogeneous liquid-vapor coexistence states, separated by either a planar or a spherical interface. It is shown that the stress tensor contains all the information regarding the mechanical equilibrium of the state of the system. On the one hand, it leads to the expected expressions and relationships of the interfacial quantities and, on the other, it allows for a correct separation of the bulk and interfacial contributions to the free energy. [S1063-651X(96)07305-9]

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I. INTRODUCTION

The description of the liquid-vapor coexistence states is one of the central problems of the study of nonuniform fluids [1–4]. Among the difficulties that one faces is the appropriate separation of contributions of the free energy arising from the bulk and the interface between the two phases; this is particulary important when the description is attempted at a microscopic level. Related to this issue is the elucidation of the corresponding stress, or pressure, tensor of the fluid. That is, since the density of the fluid is inhomogeneous, it is no longer true that the pressure is uniform and isotropic everywhere. This lack of uniformity and isotropy is, in fact, responsible for the surface tension that develops between the liquid and vapor phases, and thus, the importance of studying the stress or pressure tensor of these states. There have been many important attempts in obtaining general expressions for the stress tensor and in relating these to measurable quantities such as the surface tension [5,6]. As is known, one of the most uncomfortable properties of such a tensor is that it appears not to be unique, in the sense (see below) that the condition for mechanical equilibrium leaves a sort of ''gauge'' freedom in the determination of the stress tensor; that is, the condition of the balance of forces is a statement about the *divergence* of the tensor and thus, it seems, one is free to add to the stress tensor, the curl of another tensor without altering the equilibrium condition.

In this article we present a very general representation of the stress tensor within density functional theory that only requires translational and rotational invariance of the free energy density. A similar expression was already shown by one of the authors [6] but it was not symmetric. We also review the argument previously shown [7] that, once the stress tensor is known, one can express the free energy in terms of its bulk and interfacial contributions. Then, specializing to the nonlocal van der Waals model for the free energy density functional we explicitly verify and illustrate that the stress tensor has the correct mechanical properties of the fluid, and this indeed leads to the above-mentioned separation of the free energy. We shall examine the case in which a planar interface is present and the case of a spherical drop of liquid in coexistence with its vapor.

But before we enter into the discussion of the stress tensor within density functional theory, we shall discuss some thermodynamics of the liquid-vapor states. This is important since thermodynamic and mechanical arguments are very clear as to how different terms contribute to the free energy, while the path from the microscopic point of view of statistical mechanics is not always unambiguous. Thus we shall first state what we are trying to achieve.

Working in the grand canonical ensemble is particularly simple for our purposes. Namely, for a homogeneous system, we know that the grand potential $\Omega(V,\mu,T)$, a function of the volume, temperature and chemical potential, is given by

$$\Omega(V,\mu,T)=-p(\mu,T)V, \tag{1.1}$$

where $p(\mu,T)$ is the thermodynamic pressure.

When a system finds itself in a coexistence liquid-vapor state separated by a planar interface, we expect from general considerations of thermodynamics that the grand potential should now be written as

$$\Omega=-pV+\gamma S, \tag{1.2}$$

where γ is surface tension of the interface and S its area. The pressure is no longer isotropic and, indeed, the surface tension is mechanically related to the difference of stresses as [2]

$$\gamma=\int dz(\sigma^T-\sigma^N), \tag{1.3}$$

where σ^N and σ^T are the components of the stress tensor *normal* and *tangential* to the interfacial surface; z is the coordinate normal to the interface. The pressure that appears in Eq. (1.2) is equal to (minus) the normal stress, $p=-\sigma^N$, constant everywhere and equal to the pressure of the ''Maxwell equal areas'' construction [8].

When the state corresponds to a drop of (say) liquid in its vapor, the grand potential is now

$$\Omega = -p_l V_l - p_v (V - V_l) + \gamma S, \tag{1.4}$$

where p_l and p_v are the pressures of the liquid and vapor phases, respectively; V_l is the volume of the drop and S its area. By the Young-Laplace equation the pressures and the surface tension are related as

$$p_l - p_v = 2\frac{\gamma}{R}, \tag{1.5}$$

where R is the radius of the drop. Again, the pressure is equal to (minus) the component of the stress tensor normal to the interface.

The previous results are all based on general aspects of thermodynamics and mechanical equilibrium and do not involve any microscopic details of statistical mechanics. It should be clear that if an account is taken of the microscopic nature of the fluid particles, the above expressions may only be approximate in the sense that there may not be a clear cut separation of ''bulk'' and ''surface'' because the interfacial region actually occupies volume.

For our purposes, we point out that complete thermodynamic equilibrium in a system requires thermal equilibrium (same temperature everywhere), chemical equilibrium (for a one-species fluid, same chemical potential everywhere) and mechanical equilibrium. For homogeneous systems, the latter translates into equal (isotropic) pressure everywhere, but for an inhomogeneous fluid, the corresponding mechanical equilibrium condition is now the equation of balance of forces

$$\boldsymbol{\nabla} \cdot \tilde{\sigma} = -\mathbf{f}_{\mathrm{ext}} \tag{1.6}$$

where $\tilde{\sigma}$ is the stress tensor and $\mathbf{f}_{\mathrm{ext}}$ is the *external* force per unit of volume.

II. THE STRESS TENSOR VIA DENSITY FUNCTIONAL THEORY

Density functional theory asserts that the grand potential, can be written as [1–3]

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] - \int d\mathbf{r}[\mu - V_{\mathrm{ext}}(\mathbf{r})]\rho(\mathbf{r}), \tag{2.1}$$

where $F[\rho(\mathbf{r})]$ is the intrinsic Helmholtz free energy density functional and $V_{\mathrm{ext}}(\mathbf{r})$ is an external potential.

We assume that the free energy is expressed as

$$F[\rho(\mathbf{r})] = \int d\mathbf{r} f(\mathbf{r};\rho), \tag{2.2}$$

with $f(\mathbf{r};\rho)$ a free energy density whose dependence on $\mathbf{r}$ arises through its, in general, nonlocal dependence on the density $\rho(\mathbf{r})$. We also consider that $f(\mathbf{r};\rho)$ is translationally and rotationally invariant as a consequence of the nature of the internal interactions of the particles in the fluid; we shall make use of these properties below.

In this theory it is assumed that $F[\rho(\mathbf{r})]$ is a known function of the temperature T. The chemical potential is that given by μ in Eq. (2.1). Therefore the equilibrium state and the actual value of the grand potential $\Omega[\rho(\mathbf{r})]$ at equilibrium is found by minimizing (actually extremizing) $\Omega[\rho(\mathbf{r})]$, that is, by solving the Euler-Lagrange equation

$$\left.\frac{\delta F}{\delta \rho(\mathbf{r})}\right|_{\rho_0} = \mu - V_{\mathrm{ext}}(\mathbf{r}). \tag{2.3}$$

The function $\rho_0(\mathbf{r})$ is the equilibrium density profile for the given values of T and μ. But the Euler-Lagrange equation *is* also the condition for mechanical equilibrium: namely, by multiplying Eq. (2.3) by the gradient of the equilibrium density, $\boldsymbol{\nabla}\rho_0(\mathbf{r})$, we obtain

$$\left.\frac{\delta F}{\delta \rho(\mathbf{r})}\right|_{\rho_0} \boldsymbol{\nabla}\rho_0(\mathbf{r}) - \boldsymbol{\nabla}\{[\mu - V_{\mathrm{ext}}(\mathbf{r})]\rho_0(\mathbf{r})\} = \rho_0(\mathbf{r})\boldsymbol{\nabla} V_{\mathrm{ext}}(\mathbf{r}). \tag{2.4}$$

Since the right-hand side of this equation is (minus) the external force per unit of volume acting on the fluid, the left-hand side can be identified as the divergence of the stress tensor in its equilibrium state. That is, Eq. (2.4) corresponds to

$$\boldsymbol{\nabla} \cdot \tilde{\sigma}(\mathbf{r}) = \rho_0(\mathbf{r})\boldsymbol{\nabla} V_{\mathrm{ext}}(\mathbf{r}). \tag{2.5}$$

As we discuss below one can find very general expressions for a symmetric stress tensor satisfying the balance force equation (2.5). But before presenting such a tensor, we review the arguments given in Ref. [7] regarding the different ''bulk'' and ''surface'' contributions of the stress tensor for liquid-vapor type of inhomogeneities.

The argument is that, once we know the stress tensor, we can separate it into two pieces

$$\tilde{\sigma}(\mathbf{r}) = \tilde{\sigma}_0(\mathbf{r}) + \tilde{\sigma}_{\mathrm{inh}}(\mathbf{r}), \tag{2.6}$$

where

$$\tilde{\sigma}_0(\mathbf{r}) = \{f(\mathbf{r};\rho_0) - [\mu - V_{\mathrm{ext}}(\mathbf{r})]\rho_0(\mathbf{r})\}\tilde{1} \tag{2.7}$$

and $\tilde{1}$ is the unit tensor. If the tensor $\tilde{\sigma}_{\mathrm{inh}}(\mathbf{r})$ is defined in such a way that

$$\boldsymbol{\nabla} \cdot \tilde{\sigma}_{\mathrm{inh}}(\mathbf{r}) = \left.\frac{\delta F}{\delta \rho(\mathbf{r})}\right|_{\rho_0} \boldsymbol{\nabla}\rho_0(\mathbf{r}) - \boldsymbol{\nabla} f(\mathbf{r};\rho_0), \tag{2.8}$$

then, by construction $\boldsymbol{\nabla}\cdot[\tilde{\sigma}_0(\mathbf{r}) + \tilde{\sigma}_{\mathrm{inh}}(\mathbf{r})]$ equals the left-hand side of Eq. (2.4). As mentioned above, in general, $F[\rho_0(\mathbf{r})]$ is a nonlocal functional of $\rho_0(\mathbf{r})$. Clearly, any term local in the density (such as the ideal gas) cannot contribute to $\tilde{\sigma}_{\mathrm{inh}}(\mathbf{r})$. Moreover, if the system is in a *homogeneous* state, $[\boldsymbol{\nabla}\rho_0(\mathbf{r}) = \mathbf{0}$ everywhere$]$ then, not only $\boldsymbol{\nabla}\cdot\tilde{\sigma}_{\mathrm{inh}}(\mathbf{r})$ vanishes, but the tensor itself does so: For homogeneous states one clearly wants

$$\tilde{\sigma}(\mathbf{r}) = -p(\mu,T)\tilde{1} \tag{2.9}$$

in order to recover the thermodynamic result Eq. (1.1), and it follows from Eqs. (2.6) and (2.7) that $\widetilde{\sigma}_{\rm inh}(\mathbf{r})=0$. Thus the above separation is motivated by the facts that $\widetilde{\sigma}_{\rm inh}(\mathbf{r})$ arises only from the nonlocal part of $F[\rho_0(\mathbf{r})]$ and by its vanishing in homogeneous fluid states.

Now, for a liquid-vapor type of inhomogeneity, the equilibrium density $\rho_0(\mathbf{r})$ is uniform everywhere, except at the interfacial region where it changes ''abruptly'' from one of its bulk values to the other. This change is registered by the gradient of the density $\boldsymbol{\nabla}\rho_0(\mathbf{r})$ being zero everywhere but at the interfacial region where it is ''sharply'' peaked; the gradient of the density also defines the normal $\hat{\mathbf{n}}$ to the interfacial ''surface.'' An important result thus follows from the proposed separation of the stress tensor Eq. (2.6): Consider the component of the stress tensor *normal* to the interfacial surface

$$\sigma^N(\mathbf{r})=\{f(\mathbf{r};\rho_0)-[\mu-V_{\rm ext}(\mathbf{r})]\rho_0(\mathbf{r})\}+\sigma^N_{\rm inh}(\mathbf{r}), \qquad (2.10)$$

where $\sigma^N=\hat{\mathbf{n}}\cdot\widetilde{\sigma}\cdot\hat{\mathbf{n}}$. By integrating this equation throughout the whole volume we find

$$\Omega=\int d\mathbf{r}\sigma^N(\mathbf{r})-\int d\mathbf{r}\sigma^N_{\rm inh}(\mathbf{r}). \qquad (2.11)$$

The claim is that this equation is the generalization of the thermodynamic expression, Eq. (1.1), for inhomogeneous fluids: The first term in the right-hand side is the generalization of the *bulk* term ''$-pV$'' (and reduces to it in the case of homogeneous fluids). Close to the interface σ^N has the physical meaning of the pressure acting *on* the interfacial surface. And far from the interface the fluid becomes uniform, and in those regions, σ^N truly becomes the thermodynamic pressure, i.e., $\sigma^N\to(1/3){\rm Tr}\widetilde{\sigma}=-p(\mu,T)$. The second term in Eq. (2.11) is, therefore, the *surface* contribution to the free energy since, as discussed above, $\sigma^N_{\rm inh}$ is different from zero only in the interfacial region, where $\boldsymbol{\nabla}\rho_0(\mathbf{r})\neq\mathbf{0}$. Of course, since the interfacial region actually has a finite width, the separation may seem arbitrary. However, and this is the purpose of the next section, one can show that the second term in Eq. (2.11) leads to the correct identification of the surface tension and higher-order surface contribution.

We now return to present a very general symmetric stress tensor that satisfies Eq. (2.5). Because of the proposed separation of the tensor given in Eq. (2.6) we only need to be concerned with the tensor $\widetilde{\sigma}_{\rm inh}$. Consider the following expression:

$$\begin{aligned}\sigma^{\alpha\beta}_{\rm inh}(\mathbf{r})=&-\int d\mathbf{r}'\int_0^1 d\lambda\,\frac{\delta f(\mathbf{r}-(1-\lambda)\mathbf{r}';\rho_0)}{\delta\rho_0(\mathbf{r}+\lambda\mathbf{r}')}\\&\times r'_\alpha\nabla_\beta\rho_0(\mathbf{r}+\lambda\mathbf{r}')\\&-\boldsymbol{\nabla}_\nu\int d\mathbf{r}'\int_0^1 d\lambda\,\lambda\frac{\delta f(\mathbf{r}-(1-\lambda)\mathbf{r}';\rho_0)}{\delta\rho_0(\mathbf{r}+\lambda\mathbf{r}')}\\&\times r'_\beta[r'_\alpha\boldsymbol{\nabla}_\nu\rho_0(\mathbf{r}+\lambda\mathbf{r}')-r'_\nu\boldsymbol{\nabla}_\alpha\rho_0(\mathbf{r}+\lambda\mathbf{r}')],\end{aligned} \qquad (2.12)$$

where the indices represent the components of the involved quantities in Cartesian coordinates, summation over repeated indices is assumed, and the gradient operators act on the variable $\mathbf{r}$. The first term on the right-hand side is, by itself, a solution to Eq. (2.8) but it is not symmetric [6]; the second term, the novelty here, is needed to symmetrize it. This is shown below, but first we verify that $\widetilde{\sigma}_{\rm inh}$ obeys Eq. (2.8): Taking the divergence of the tensor we readily note that the contribution of the second term on the right-hand side of Eq. (2.12) vanishes identically; hence we obtain

$$\begin{aligned}\boldsymbol{\nabla}\cdot\widetilde{\sigma}_{\rm inh}(\mathbf{r})=&-\int d\mathbf{r}'\int_0^1 d\lambda\,\mathbf{r}'\cdot\boldsymbol{\nabla}\left\{\frac{\delta f(\mathbf{r}-(1-\lambda)\mathbf{r}';\rho_0)}{\delta\rho_0(\mathbf{r}+\lambda\mathbf{r}')}\right.\\&\left.\times\boldsymbol{\nabla}\rho_0(\mathbf{r}+\lambda\mathbf{r}')\right\}\\=&-\int d\mathbf{r}'\int_0^1 d\lambda\,\frac{\partial}{\partial\lambda}\left\{\frac{\delta f(\mathbf{r}-(1-\lambda)\mathbf{r}';\rho_0)}{\delta\rho_0(\mathbf{r}+\lambda\mathbf{r}')}\right.\\&\left.\times\boldsymbol{\nabla}\rho_0(\mathbf{r}+\lambda\mathbf{r}')\right\}\\=&\int d\mathbf{r}\left[\boldsymbol{\nabla}\rho_0(\mathbf{r})\frac{\delta f(\mathbf{r}';\rho_0)}{\delta\rho_0(\mathbf{r})}-\boldsymbol{\nabla}'\rho_0(\mathbf{r}')\frac{\delta f(\mathbf{r};\rho_0)}{\delta\rho_0(\mathbf{r}')}\right],\end{aligned} \qquad (2.13)$$

which using the translational invariance of $f(\mathbf{r};\rho_0)$, see below, is Eq. (2.8).

In order to show that the tensor $\widetilde{\sigma}_{\rm inh}$, Eq. (2.12), is symmetric, we first rewrite it as

$$\begin{aligned}\sigma^{\alpha\beta}_{\rm inh}=&-\int d\mathbf{r}\int_0^1 d\lambda[r'_\alpha\boldsymbol{\nabla}_\beta\rho_0(\mathbf{r}+\lambda\mathbf{r}')+r'_\beta\boldsymbol{\nabla}_\alpha\rho_0(\mathbf{r}+\lambda\mathbf{r}')]\\&\times\frac{\delta f(\mathbf{r}-(1-\lambda)\mathbf{r}';\rho_0)}{\delta\rho_0(\mathbf{r}+\lambda\mathbf{r}')}\\&-\int d\mathbf{r}\int_0^1 d\lambda\,\lambda r'_\alpha r'_\beta\boldsymbol{\nabla}_\nu\left(\boldsymbol{\nabla}_\nu\rho_0(\mathbf{r}+\lambda\mathbf{r}')\right.\\&\left.\times\frac{\delta f(\mathbf{r}-(1-\lambda)\mathbf{r}';\rho_0)}{\delta\rho_0(\mathbf{r}+\lambda\mathbf{r}')}\right)\\&+\int d\mathbf{r}(r'_\alpha-r_\alpha)\boldsymbol{\nabla}_\beta\rho_0(\mathbf{r}')\frac{\delta f(\mathbf{r};\rho_0)}{\delta\rho_0(\mathbf{r}')},\end{aligned} \qquad (2.14)$$

where an integration by parts was performed. The first two terms are manifestly symmetric, and in order to show that the third one is also symmetric we have to appeal to the translational and rotational invariance of the free energy density $f(\mathbf{r};\rho_0)$. Translational invariance means [6] that

$$\boldsymbol{\nabla}f(\mathbf{r};\rho_0)=\int d\mathbf{r}\boldsymbol{\nabla}'\rho_0(\mathbf{r}')\frac{\delta f(\mathbf{r};\rho_0)}{\delta\rho_0(\mathbf{r}')}, \qquad (2.15)$$

while rotational invariance translates into [9]

$$\mathbf{r}\times\boldsymbol{\nabla}f(\mathbf{r};\rho_0)=\int d\mathbf{r}\mathbf{r}'\times\boldsymbol{\nabla}'\rho_0(\mathbf{r}')\frac{\delta f(\mathbf{r};\rho_0)}{\delta\rho_0(\mathbf{r}')}. \qquad (2.16)$$

Combining these two equations yields

$$\int d\mathbf{r}(\mathbf{r}-\mathbf{r}')\times\boldsymbol{\nabla}'\rho_0(\mathbf{r}')\frac{\delta f(\mathbf{r};\rho_0)}{\delta\rho_0(\mathbf{r}')}=0, \qquad (2.17)$$

which shows that the last term in Eq. (2.14) is, indeed, symmetric.

The stress tensor here shown is certainly not unique since one can always add to it a divergenceless symmetric tensor. In this regard, it is interesting to note the striking similarity between this expression Eq. (2.12) and its counterpart through the virial route [2,3,5] in terms of the density-density correlation function: Both expressions depend on a parametric integral (over λ) connecting two spatial points in the fluid. In the virial expression it has been shown [10] that one can choose different parametric integrals, giving rise to different stress tensors, without altering physically measurable quantities such as the surface tension. We expect that the same type of differences can be found in the present case with similarly, as we show below, the surface tension being independent of the parametric integral over λ.

Although in order to show that an expression for the stress tensor is correct, it is sufficient to show that it obeys the force balance equation (2.5), it may be of interest to have a systematic way of constructing such types of tensors. This is the more so since, after all, the present density functional theory is not exclusive of statistical physics but belongs to a wider class of field theories. Such an explicit construction, however, is out of the scope of the present discussion and deserves a separate treatment [11].

III. COEXISTING LIQUID-VAPOR STATES

Thus far, the density inhomogeneity $\rho_0(\mathbf{r})$ and the stress tensor are quite general. In this section we shall analyze the cases of liquid-vapor states with the phases separated by a planar and a spherical interface. In order to make explicit and illustrate some of the results, we shall specialize to the van der Waals nonlocal free energy functional; we shall later point out results that are more general. For the van der Waals model we use

$$F[\rho(\mathbf{r})]=\int d\mathbf{r} f_0(\rho(\mathbf{r})) + \frac{1}{2}\int\int d\mathbf{r} d\mathbf{r}'\, \widetilde{\omega}(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r})\rho(\mathbf{r}'). \quad (3.1)$$

This free energy may be thought of as arising from a functional expansion up to second order terms. The first term on the right-hand side is local in the density and represents the ‘‘reference’’ fluid, usually taken as the locally homogeneous contribution due to the hard-core part of the intermolecular potential. The kernel in the second term is proportional to the direct correlation function [1,3]; it is considered to be density-independent, and assumed spherically symmetric; the latter property ensures both translation and rotation invariance. Since we are considering simple fluids with short-range attractive interactions, the kernel $\widetilde{\omega}(|\mathbf{r}-\mathbf{r}'|)$ is correspondingly short ranged [1,3].

In order to evaluate the stress tensor of the preceding section we need the following expression:

$$\frac{\delta f(\mathbf{r};\rho)}{\delta\rho(\mathbf{r}')}=\frac{d f_0(\rho(\mathbf{r}))}{d\rho(\mathbf{r})}\delta(\mathbf{r}-\mathbf{r}') + \tfrac{1}{2}\,\delta(\mathbf{r}-\mathbf{r}')\int d\mathbf{r}''\widetilde{\omega}(\mathbf{r}-\mathbf{r}'')\rho(\mathbf{r}'') + \tfrac{1}{2}\,\rho(\mathbf{r})\widetilde{\omega}(|\mathbf{r}-\mathbf{r}'|). \quad (3.2)$$

Because of the factors of $\mathbf{r}'$ in the tensor $\widetilde{\sigma}_{\text{inh}}$, cf. Eq. (2.12), only the last term of the above equation contributes.

A. A planar interface

In this case, the density profile depends on only one coordinate, say z. For short-range intermolecular interactions one expects that, far from the critical point, the width of the interface is of the order of the range of the potential (we call it ξ_b). We assume that an arbitrarily weak external field is applied so that, say, the Gibbs dividing surface is pinned at $z=0$. Mechanical stability of a planar interface requires the stress normal to the interface (namely, the ‘‘pressure’’) to be the same in both phases; therefore one can construct a density profile approaching the bulk values of vapor and liquid densities ρ_g and ρ_l, as $z\rightarrow\pm\infty$, corresponding to the unique chemical potential and bulk pressure of Maxwell equal areas construction μ_{coex} and $p(\mu_{\text{coex}},T)$. Such an inhomogeneous solution exists for the van der Waals model Eq. (3.1) for zero external fields [12].

Several conclusions can be drawn from the assumed dependence of the profile $\rho_0(z)$, and *directly* from the stress tensor:

The stress tensor given by Eqs. (2.6), (2.7), (2.12), and (3.2), clearly, depends only on z and can be written as

$$\widetilde{\sigma}(z)=\sigma^N(z)\hat{\mathbf{z}}\hat{\mathbf{z}}+\sigma^T(z)(\hat{\mathbf{x}}\hat{\mathbf{x}}+\hat{\mathbf{y}}\hat{\mathbf{y}}), \quad (3.3)$$

in an obvious notation, with the ‘‘inhomogeneous’’ part of the stress tensor given by

$$\sigma^N_{\text{inh}}(z)=-\frac{1}{2}\int d\mathbf{r}'\int_0^1 d\lambda\, \widetilde{\omega}(|\mathbf{r}'|)\rho_0[z-(1-\lambda)z']z' \times\frac{d\rho_0(z+\lambda z')}{dz}, \quad (3.4)$$

and

$$\sigma^T_{\text{inh}}(z)=-\frac{1}{2}\frac{d}{dz}\int d\mathbf{r}'\int_0^1 d\lambda\, \widetilde{\omega}(|\mathbf{r}'|)\rho_0[z-(1-\lambda)z']x'x' \times\frac{d\rho_0(z+\lambda z')}{dz}. \quad (3.5)$$

For a planar liquid-vapor interface one can calculate the surface tension by means of its so-called mechanical definition

$$\gamma_{\mathrm{mech}}=\int_{-\infty}^{\infty}dz(\sigma^{T}(z)-\sigma^{N}(z))$$

$$=\frac{1}{2}\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'\int d^{2}R\int_{0}^{1}d\lambda\,\tilde{\omega}(R^{2}+z'^{2})$$

$$\times z'\rho_{0}[z-(1-\lambda)z']\frac{d\rho_{0}(z+\lambda z')}{dz}, \tag{3.6}$$

which after a change of variables $z+\lambda z'\rightarrow z$ and $z-(1-\lambda)z'\rightarrow z'$ and some manipulations can be cast as

$$\gamma_{\mathrm{mech}}=-\frac{1}{4}\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'\,\frac{d\rho_{0}(z)}{dz}\,\frac{d\rho_{0}(z')}{dz'}$$

$$\times\int d^{2}R|\mathbf{R}|^{2}\tilde{\omega}[\mathbf{R}^{2}+(z-z')^{2}]. \tag{3.7}$$

In the above expressions $\mathbf{R}=(x,y)$ is a two-dimensional (2D) vector over the interfacial plane. Two comments are in order: First, we note that the above expression is independent of the parametric integral over λ and consistent with the independence of the particular representation of the stress tensor. And, second, we can verify that it agrees with the Triezenberg-Zwanzig expression for the surface tension [13] of a planar interface:

$$\gamma_{\mathrm{TZ}}=-\frac{kT}{4}\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'\,\frac{d\rho_{0}(z)}{dz}\,\frac{d\rho_{0}(z')}{dz'}$$

$$\times\int d^{2}R|\mathbf{R}|^{2}C(\mathbf{R};z,z'), \tag{3.8}$$

where $C(\mathbf{R};z,z')$ is the direct correlation function of the fluid, defined by

$$C(\mathbf{R}-\mathbf{R}';z,z')=\frac{1}{kT}\,\frac{\delta^{2}F[\rho]}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}\bigg|_{\rho_{0}}. \tag{3.9}$$

For the van der Waals model the only part of $C(\mathbf{R};z,z')$ that contributes to the surface tension is $\tilde{\omega}(|\mathbf{r}|)$ and, therefore, $\gamma_{\mathrm{mech}}=\gamma_{\mathrm{TZ}}$.

We are now in a position of evaluating the general result Eq. (2.11) regarding the form of the grand potential. We find the expected thermodynamic result:

$$\Omega=\int d\mathbf{r}\sigma^{N}(z)-\int d\mathbf{r}\sigma_{\mathrm{inh}}^{N}(z)=-p(\mu_{\mathrm{coex}},T)V+\gamma_{\mathrm{TZ}}A, \tag{3.10}$$

where V is the total volume and A the interfacial area. In the above expression we have already identified the coefficient of the area A as, precisely, the surface tension given in Eq. (3.7), see also Eq. (3.4). As to the identification of the first term, namely, $\sigma^{N}(z)=-p(\mu_{\mathrm{coex}},T)$, this follows from the force balance equation (2.5) (in the absence of external fields) with the form of the stress tensor given by Eq. (3.3), namely,

$$\frac{d}{dz}\sigma^{N}(z)=0, \tag{3.11}$$

and the fact that far from the interface the full stress tensor becomes constant with $\mathrm{Tr}\tilde{\sigma}=-3p(\mu_{\mathrm{coex}},T)$.

B. A spherical drop

Now we assume that the density profile depends on only the radial coordinate $|\mathbf{r}|=r$, and that the temperature and chemical potential are such that the state is a drop of liquid in its vapor. We shall assume that the system is enclosed in a large, closed, volume so that the drop is stable. Again, and for the van der Waals model it has been shown to be the case [12], the width of the interfacial region is of the order of the range ξ_{b} of the intermolecular interactions (far from the critical temperature), and the size of the drop depends on the value of the chemical potential. That is, for $\mu<\mu_{\mathrm{coex}}$ one finds a drop of liquid whose ''radius'' becomes larger the closest μ approaches μ_{coex}. As is well known, the radius of the drop is not uniquely defined but if the drop is large, meaning that the width of the interface ξ_{b} is very small compared to any of the definitions of the radius, we can speak of the radius $R(\mu,T)$ as a given quantity and refer to the differences when needed.

Again, several conclusions can be reached from the radial symmetry of the profile:

The stress tensor given by Eqs. (2.6), (2.7), (2.12), and (3.2) only depends on r and its only components different from zero are:

$$\tilde{\sigma}(r)=\sigma^{N}(r)\hat{\mathbf{r}}\hat{\mathbf{r}}+\sigma^{T}(r)(\hat{\theta}\hat{\theta}+\hat{\phi}\hat{\phi}), \tag{3.12}$$

where $\hat{\mathbf{r}}$, $\hat{\theta}$, and $\hat{\phi}$ are the unit vectors of spherical coordinates. The explicit expressions of the normal and tangential components of the tensor can be read off from the general expressions, e.g., $\sigma_{N}=\hat{\mathbf{r}}\cdot\tilde{\sigma}\cdot\hat{\mathbf{r}}$. Clearly, the result (3.12) does not depend on the particular form of $\rho_{0}(r)$ but only on its assumed radial dependence.

Evaluation of the general form of the grand potential, Eq. (2.11), yields

$$\Omega=\int d\mathbf{r}\sigma^{N}(r)-\frac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{d\rho_{0}(r)}{dr}\,\frac{d\rho_{0}(r')}{dr'}\int_{0}^{\infty}ds$$

$$\times\tilde{\omega}[s+(\mathbf{r}-\mathbf{r}')^{2}]. \tag{3.13}$$

Without further knowledge of the density profile this is as far as we can get. Nevertheless, it is important to realize that the second term, which contains the ''surface'' contribution to the free energy, is again independent of the parametric integral over λ just as in the planar case.

In order to show that, indeed, the contributions to the free energy separate into ''bulk'' and ''surface'' with the correct properties we can make use of the clear cut separation of length scales for large drops and approximate the density $\rho_{0}(r)$ as a ''sharp'' steplike profile. That is, we can write

$$\rho_{0}(r)\approx\rho_{l}\Theta(R-r)+\rho_{v}\Theta(r-R)+O(\xi_{b}/R), \tag{3.14}$$

where $\Theta(x)$ is the Heaviside step function, equal to one for positive values of its argument and zero otherwise, and ρ_{l} and ρ_{v} are the bulk liquid and vapor densities for the given values of μ and T. The last term in the above equation means corrections of the order of the ratio of the width ξ_{b} of the profile to the radius $R(\mu,T)$ of the drop. Dietrich and Napiorkowski [14] and Keller and Merchant [15] have also used this density profile in related interfacial problems.

Substitution of the approximate profile (3.14) into the second term in Eq. (3.13) (that we call Ω_S) yields

$$\begin{aligned}\Omega_S &\cong 4\pi R^2\left[-\frac{\pi}{2}(\Delta\rho)^2\int_0^\infty dr r^3\tilde{\varpi}(r^2)\right.\\ &\left.\quad+\frac{1}{R^2}\frac{\pi}{24}(\Delta\rho)^2\int_0^\infty dr r^5\tilde{\varpi}(r^2)\right]+O(\xi_b/R)\\ &\cong 4\pi R^2\left(\gamma_p+k_s\frac{1}{R^2}\right)+O(\xi_b/R),\end{aligned} \tag{3.15}$$

where $\Delta\rho=\rho_l-\rho_v$. In the second line γ_p is the surface tension of the plane, Eq. (3.7), for the approximate profile (3.14). The coefficient k_s is a *rigidity* coefficient but due to the spherical symmetry we cannot identify the so-called bending and splay (or Gaussian) contributions [16]. In this regard there is an ongoing controversy as to the actual form and origin of these curvature corrections but it is out of the scope of this article to review the different points of view [4,14,15,17,18]. Nevertheless, it can be verified that the rigidity coefficient is related to the *fourth* transverse moment of the direct correlation function [19] in an analogous way in which the surface tension is related to the second moment of the direct correlation function, see Eq. (3.8). It is of interest to note that due to the approximation in the density there are no linear contributions in the curvature nor higher order than two.

We now need to verify that the identification of $\sigma^N(r)$ in Eq. (3.13) as the "pressure," is appropriate. For this we use the equation for mechanical equilibrium, $\nabla\cdot\tilde{\sigma}=0$, written as

$$\frac{\partial\sigma^N(r)}{\partial r}+\frac{2}{r}\sigma^N(r)-\frac{2}{r}\sigma^T(r)=0, \tag{3.16}$$

which, after integration over r, becomes the well-known Young-Laplace equation relating the differences in pressures "inside" and "outside" the drop:

$$\begin{aligned}\sigma^N(0)-\sigma^N(\infty)&=\int_0^\infty dr\left(\frac{2}{r}\sigma^N(r)-\frac{2}{r}\sigma^T(r)\right)\\ &\cong-\frac{2}{R}\gamma_p+O(\xi_b/R),\end{aligned} \tag{3.17}$$

where in the second line we have made use of the approximately sharp profile Eq. (3.14). We thus identify $\sigma^N(0)=-p_l$ and $\sigma^N(\infty)=-p_v$, the pressures of the bulk liquid and vapor phases, respectively. It is important to note that the results (3.15) and (3.17) are consistent with each other within the approximation used. That is, the above two results could also be derived directly from the (approximate) grand potential

$$\Omega\cong-p_lV_l-p_vV_v+\Omega_S, \tag{3.18}$$

with $V_l=4\pi R^3/3$ the volume of the drop and the surface free energy Ω_S given by Eq. (3.15). Clearly, corrections such as Tolman's length [20] will arise from the higher-order terms in (ξ_b/R).

It is of interest to point out here that using a Taylor expansion of the nonlocal term in the free energy one can obtain the well-known *local* van der Waals "square-gradient" free energy density functional and its generalization to "square-Laplacian;" within such a local model one can also calculate explicit expressions of the stress tensor [21,19], and the mechanical properties and free energies of the nonuniform states discussed in this section.

IV. REMARKS

We have presented a representation of the stress tensor of inhomogeneous states valid for any free energy density functional with rotational and translational invariance. This result appears to be the counterpart of the expression for the stress tensor which is obtained directly from the microscopic forces and that involves the density-density correlation function [2]; this is partially corroborated by the fact that, on the one hand, the Kirkwood-Buff [22] expression for the surface tension follows from the latter tensor, while the corresponding Triezenberg-Zwanzig expression follows from the form of the stress tensor here shown.

For the van der Waals model and for liquid-vapor-like density profiles we have been able to show that the grand potential can be straightforwardly written in terms of bulk and surface contributions that, in turn, are consistent with the mechanical definition and the Triezenberg-Zwanzig expression of the surface tension and with the force balance equation. That is, the equation for mechanical equilibrium implies that the normal component of the stress tensor is constant for the planar interface, while for the spherical one that the normal stress satisfy the Young-Laplace equation; these, together with the asymptotic value of the normal stress as the bulk thermodynamic pressure, allows us to make the correct identification of the bulk term. Thus we have shown that the stress tensor so obtained leads to the correct mechanical properties of the liquid-vapor inhomogenous state.

Although one needs an explicit form of the free energy density in order to show the inner consistency of the different results mentioned in the previous paragraph, one can find, nevertheless, quite general expressions for the grand potential using only the planar or spherical symmetry of the density profile. That is, one can show, directly from the stress tensor that

$$\Omega=\int d\mathbf{r}\sigma^N(\mathbf{r})+\int d\mathbf{r}\int d\mathbf{r}'\frac{\delta f(\mathbf{r};\rho_0)}{\delta\rho_0(\mathbf{r}')}(\mathbf{r}'-\mathbf{r})\cdot\nabla'\rho_0(\mathbf{r}'), \tag{4.1}$$

valid for $\rho_0=\rho_0(z)$ and $\rho_0=\rho_0(r)$ but not valid for arbitrary inhomogeneities (this may be so because an arbitrary inhomogeneity needs a particular external field to sustain it). However we cannot proceed further, nor can we show the other mechanical properties, without making extra assumptions on the structure of the free energy density $f(\mathbf{r};\rho)$. It is, nevertheless, interesting to observe that Ω is independent of the parametric integral over λ.

As a final comment, we observe that with the knowledge of a stress tensor $\sigma_{\alpha\beta}$ one may be tempted to calculate the mechanical free energy associated to it. Namely, one can evaluate the product $\sigma_{\alpha\beta}du_{\alpha\beta}$, with $du_{\alpha\beta}$ the differential of the strain tensor [23]. However, due to the form of the stress tensor used here [see Eqs. (2.6) and (2.7)],

$$\sigma_{\alpha\beta}=\omega\delta_{\alpha\beta}+\sigma_{\alpha\beta}^{\text{inh}} \tag{4.2}$$

with $\omega=f-(\mu-V_{\text{ext}})\rho$, and the fact that the differential of volume is $d\mathbf{r}=\delta_{\alpha\beta}du_{\alpha\beta}$, it follows that

$$\omega d\mathbf{r}=\sigma_{\alpha\beta}du_{\alpha\beta}-\sigma_{\alpha\beta}^{\text{inh}}du_{\alpha\beta}=\sigma^{N}d\mathbf{r}-\sigma_{\text{inh}}^{N}d\mathbf{r} \tag{4.3}$$

valid for *any* geometry of (density) level surfaces. The above result can be easily shown to be correct since the density level surfaces can be used to define a semiorthogonal coordinate system $(\hat{\mathbf{n}},\mathbf{t}_1,\mathbf{t}_2)$, with $\hat{\mathbf{n}}=\boldsymbol{\nabla}\rho_0/|\boldsymbol{\nabla}\rho_0|$ and $\mathbf{t}_1$ and $\mathbf{t}_2$ vectors orthogonal to $\hat{\mathbf{n}}$ but not necessarily between them [24]: the ‘‘trick’’ is to use $\delta_{\alpha\beta}=n_\alpha n_\beta+g_{ij}t_\alpha^i t_\beta^j$ with g_{ij} the 2D metric of the level surfaces. Thus the expression of the grand potential in terms of the normal components of the stress tensor bears the same information as the mechanical free energy associated with the full stress tensor.

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