

Microscopic expressions for interfacial bending constants and spontaneous curvature

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We derive the interfacial-curvature free energy for a simple fluid from density-functional theory, and find a form matching that for a two-dimensional shearless elastic media. The fourth moment of the direct correlation function and the density gradient determine the bending moduli κ and $\bar{\kappa}$, while the spontaneous curvature c_0 is given by asymmetry in the density. We obtain the critical indices of these quantities and corrections to the Laplace equation for curved interfaces.

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The statistical-mechanical description of two-dimensional shapes is a rich field, with novel and previously unforeseen features, currently undergoing rapid development [1]. Attention to this subject has been spurred, in part, by studies where the objects of interest are interfaces with small or even vanishing surface tension, such as those occurring in microemulsions, lyotropic liquid crystals, and bilayer vesicle solutions [2]. Generally, fluctuations of an interface between coexisting phases, say a liquid and its vapor, are governed by the surface tension γ , but in the case of the above-mentioned systems the interfacial fluctuations are determined solely by curvature effects [1-3]. The determination of these effects has been accomplished *phenomenologically* via the consideration that the interface forms an incompressible, two-dimensional fluid, with shape fluctuations regulated by its elastic-curvature free energy. This free energy, known also by the name of Helfrich [4], can be written, per unit area, as

$$f_H = \kappa(J - c_0)^2 + \bar{\kappa}K, \tag{1}$$

where $J = c_1 + c_2$ is the mean curvature and $K = c_1c_2$ is the Gaussian curvature of the interface and c_1 and c_2 are the principal curvatures. The bending modulus κ and the saddle-splay constant $\bar{\kappa}$ measure, respectively, changes in f_H due to deviations from the spontaneous curvature c_0 , and due to the Gaussian curvature. Minimization of f_H determines the stability of the various possible interfacial shapes or structures.

In view of these developments it is of interest to consider the microscopic origins of the moduli κ and $\bar{\kappa}$, and of the spontaneous curvature c_0 , and to provide the necessary statistical-mechanical foundation to the Helfrich-free-energy terms, just as it has been done some time ago for the case of the surface tension [5-7]. Here we restrict ourselves to the simplest case of the liquid-vapor interface of a simple one-component fluid, and consider the free energy for the density inhomogeneity $\rho(\mathbf{r})$, i.e., the free-energy density functional $F[\rho(\mathbf{r})]$, descriptive of a macroscopic interface and obtain, besides the customary surface tension term, the form corresponding to f_H and find the expressions for κ , $\bar{\kappa}$, and c_0 in terms of the molecular distribution functions. This exercise can be done in two different ways: (i) Through the examina-

tion of the general form that $F[\rho(\mathbf{r})]$ assumes for an unspecified nonplanar equilibrium interface. (ii) By considering the changes on $F[\rho(\mathbf{r})]$ produced by arbitrary shape fluctuations on a specific geometry for the equilibrium interface. We shall undertake both approaches here. Along the first route we analyze the density functional in the local form obtained via the gradient expansion. This will allow us to obtain an expression for the stress tensor, to examine the Gibbs equation, and to derive the curvature corrections to the Laplace equation. Finally, we consider briefly the second route to f_H , and analyze shape fluctuations about a planar interface that do not change its topology, therefore with this choice we have access only to κ . The expression we find for κ in terms of the inhomogeneous direct correlation function reduces to that obtained via the gradient expansion in the appropriate limit. We also determine the critical indices for κ , $\bar{\kappa}$, and c_0 .

The free-energy density functional $F[\rho(\mathbf{r})]$ can be approximated by a spacially local expression [5-7] by performing first a functional expansion around a density $\rho(\mathbf{r})$, and then an expansion of the density $\rho(\mathbf{r})$ around the field point \mathbf{r} . See Ref. [7] for details. This procedure yields up to density square Laplacians the form $F[\rho(\mathbf{r})] = \int d\mathbf{r} f(\rho(\mathbf{r}))$ where

$$f(\rho(\mathbf{r})) = f_0(\rho(\mathbf{r})) + \frac{1}{2}A(\rho(\mathbf{r}))[\nabla\rho(\mathbf{r})]^2 - \frac{1}{4}B(\rho(\mathbf{r}))[\nabla^2\rho(\mathbf{r})]^2, \tag{2}$$

with

$$f_0(\rho(\mathbf{r})) = kT \left[\rho(\mathbf{r}) \{ \ln[\lambda^3\rho(\mathbf{r})] - 1 \} + \frac{1}{2}\rho(\mathbf{r})^2 \int d\mathbf{r}' c(\mathbf{r}';\rho(\mathbf{r})) \right], \tag{3a}$$

$$A(\rho(\mathbf{r})) = \frac{1}{6}kT \int d\mathbf{r}' \mathbf{r}'^2 c(\mathbf{r}';\rho(\mathbf{r})), \tag{3b}$$

and

$$B(\rho(\mathbf{r})) = \frac{2}{5!}kT \int d\mathbf{r}' \mathbf{r}'^4 c(\mathbf{r}';\rho(\mathbf{r})). \tag{3c}$$

In the above expressions λ is the Broglie thermal length, $c(\mathbf{r}';\rho(\mathbf{r}))$ is the direct correlation function for a uniform

fluid with density $\rho(\mathbf{r})$. $f_0(\rho(\mathbf{r}))$ is the free-energy density for a uniform fluid of density $\rho(\mathbf{r})$, and A and B are the second and fourth moments, respectively, of the reference fluid uniform direct correlation function. That is, the reference fluid state changes from point to point and f_0 , A , and B are functions of ρ . In writing Eq. (2) above we have neglected boundary terms, the removal of which is equivalent to having assumed uniformity at the system boundaries. Higher-order terms in f involve either higher derivatives of the density or functional derivatives of the correlation function or both. As we shall see, via a rather lengthy exercise, the elastic curvature free energy arises from the Laplacian square term, just as the surface tension originates from the square gradient term.

In our local approximation the equilibrium density $\rho(\mathbf{r})$ follows from the minimization of $\Omega[\rho] = \int d\mathbf{r} \{f(\rho(\mathbf{r})) - [\mu - v(\mathbf{r})]\rho(\mathbf{r})\}$ with vanishing variations of derivatives of the density at the boundary, where μ is the chemical potential and $v(\mathbf{r})$ an external field. Variation of $\Omega[\rho]$ yields

$$\mu - \mu_0 + v(\mathbf{r}) + \frac{1}{2}A'(\nabla\rho)^2 + A\nabla^2\rho + \frac{3}{4}B'(\nabla^2\rho)^2 + \frac{1}{2}B\nabla^4\rho + B'(\nabla\rho \cdot \nabla)\nabla^2\rho + \frac{1}{2}B''(\nabla\rho)^2\nabla^2\rho = 0, \quad (4)$$

where the primes stand for differentiation with respect to ρ , and μ_0 is the chemical potential of the reference fluid. Equation (4) can be transformed into that for mechanical equilibrium for the fluid by multiplying it by $\nabla\rho$, since then it can be written as $\nabla \cdot \sigma = -\rho\nabla v$, where σ can be identified as the stress tensor of the inhomogeneous fluid. This tensor is symmetrical and is given by

$$\sigma = (\mu\rho - v\rho - f)\mathbb{1} + A\nabla\rho\nabla\rho + \frac{1}{2}\{\nabla\rho\nabla(B\nabla^2\rho) - B\nabla^2\rho\nabla\nabla\rho + \nabla \times [B\nabla\rho \times \nabla\nabla\rho - \mathbb{1} \times B(\nabla\rho \cdot \nabla)\nabla\rho]\}, \quad (5)$$

where $\mathbb{1}$ is the unit tensor. It is convenient to write Eq. (5) in the form $\sigma = (\mu\rho - v\rho - f)\mathbb{1} + \sigma^{(2)} + \sigma^{(4)}$ where the superscripts (2) and (4) denote the terms in σ proportional to A and B , respectively.

The Euler-Lagrange equation (4) describes a wide range of equilibrium nonuniformities in a simple fluid, many of which may extend over the entire volume of the system [since the choice of external field $v(\mathbf{r})$ is arbitrary]. We shall be interested here only in *surface-confined* nonuniformities representative of coexisting two-phase states like a liquid and its vapor. In them the associated density profile changes *abruptly* from a region of high uniform density to a region of low uniform density. By *abruptly* we mean spatial regions with a width of the order of the correlation length ξ . We shall assume that the spatial region over which the density change occurs, and which is described as a surface at a macroscopic scale, is of arbitrary geometry. More precisely, $\rho(\mathbf{r}) = \text{const}$ defines a family of surfaces, denoted by $\mathbf{r}_n(x, y, z)$, with unit normal \mathbf{n} given by $\mathbf{n} = [\partial_n \rho(\mathbf{r}_n)]^{-1} \nabla \rho(\mathbf{r}_n)$, with $\partial_n = \mathbf{n} \cdot \nabla$. Clearly, the normal is only defined within the interfacial region since $\nabla \rho$ vanishes outside it. We can introduce now a semiorthogonal set of coordinates with the vectors \mathbf{n} , \mathbf{t}_1 , and \mathbf{t}_2 ,

where \mathbf{t}_1 and \mathbf{t}_2 are tangential to the surface but $\mathbf{t}_1 \cdot \mathbf{t}_2$ may differ from zero. In terms of these coordinates the stress tensor in Eq. (5) breaks up into three components: (i) normal (scalar)

$$\sigma^N = n^i n^j \sigma_{ij} = (\mu\rho - v\rho - f) + n^i n^j \sigma_{ij}^{(2)} + n^i n^j \sigma_{ij}^{(4)}, \quad (6a)$$

(ii) tangential (2×2 tensor)

$$\sigma_{\mu\nu}^T = (\mu\rho - v\rho - f) t_\mu^i t_\nu^j \delta_{ij}, \quad (6b)$$

(iii) normal-tangential (2 vector)

$$\sigma_\mu^{NT} = t_\mu^i n^j \sigma_{ij}^{(4)}, \quad (6c)$$

where italic-lettered subscripts denote three-dimensional Cartesian coordinates and Greek-lettered ones two-dimensional surface components. Explicit expressions for the tensor components in Eqs. (6) in terms of the surface metric tensor $g_{\mu\nu} = t_\mu^i t_\nu^j \delta_{ij}$, the surface curvature tensor $K_{\mu\nu} = t_\mu^i t_\nu^j \partial_i n_j$, the first or mean curvature $J = \nabla \cdot \mathbf{n} = \text{Tr} K_{\mu\nu} = c_1 + c_2$ and the second or Gaussian curvature $K = \frac{1}{2}[\mathbf{n} \cdot \nabla^2 \mathbf{n} + (\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2] = \det K_{\mu\nu} = c_1 c_2$ [8], can easily be obtained [9].

Now, the free energy associated with a stress tensor is $\sigma_{ij} du_{ij}$ where u_{ij} is the strain tensor. Thus, from Eq. (5), the identity $d\mathbf{r} = \delta_{ij} du_{ij} = du_{ii}$, and Eqs. (6), we obtain $f d\mathbf{r} = (\mu\rho - \sigma^N + \sigma^{N(2)} + \sigma^{N(4)}) d\mathbf{r}$, which, when integrated over the whole volume, with $d\mathbf{r} = d\mathbf{r}_n dS$ and neglecting boundary terms, yields

$$F = \int d\mathbf{r} [\mu\rho - \sigma^N] + \int d\mathbf{r}_n dS A(r_n)(\partial_n \rho)^2 + \int d\mathbf{r}_n dS B(r_n)(\partial_n \rho)^2 [K - (J + \partial_n \ln \partial_n \rho)^2]. \quad (7)$$

For the interfacial profile $(\partial_n \rho)^2$ is a sharply peaked function centered around some \mathbf{r}_0 and with a width of the order of the fluid correlation length ξ . Therefore, when we consider scale lengths larger than ξ , the locus of the \mathbf{r}_0 defines a *coexistence surface* at which the integrals on dS in Eq. (7) become evaluated. This property makes the integrals over $d\mathbf{r}_n$ independent of those over dS , and we obtain the familiar expression [5–7] for the surface tension as well as the sought-after expressions for κ , $\bar{\kappa}$, and c_0 . These are, respectively,

$$\gamma = \int d\mathbf{r}_n A(\mathbf{r}_n)(\partial_n \rho)^2, \quad (8a)$$

$$\kappa = -\bar{\kappa} = - \int d\mathbf{r}_n B(\mathbf{r}_n)(\partial_n \rho)^2, \quad (8b)$$

and

$$c_0 = -\partial_n \ln \partial_n \rho(\mathbf{r}_0). \quad (8c)$$

Thus, the last term in the free energy in Eq. (7) has indeed the form assumed by Helfrich, but both κ and $\bar{\kappa}$ depend in the same way on the fourth moment of the direct correlation function and on $(\partial_n \rho)^2$. The fact that these quantities differ only in sign indicates that the interfacial region behaves as a two-dimensional elastic medium with Poisson ratio of $\frac{1}{2}$, i.e., it cannot support shear stress [10] and is therefore fluid as expected. The expression found for c_0 in Eq. (8c) can be interpreted to be a measure of the asymmetry of the profile. It is worth not-

icing that the square-Laplacian term in the density functional in Eq. (2) leads only to elastic-curvature terms in Eq. (7), i.e., different moments of the correlation in Eqs. (3) contribute terms to the interfacial free energy with different physical content. Of course, $\gamma - \kappa c_0^2$ is the change in free energy due to a change in area. We note that the employment of a gradient expansion implies that long-ranged (algebraically decaying) molecular interactions cannot be treated properly, and that the bending moduli may not be well defined. This is because for such interactions after a finite number all moments of $c(\mathbf{r};\rho)$ do not exist. Below we consider expressions for them in terms of the moments of the inhomogeneous fluid direct correlation function.

Having now validated the form of the Helfrich term f_H with the methods of statistical mechanics, we determine a correction term, brought about by the presence of f_H , to the well-known Laplace equation that relates the pressure difference $\Delta\sigma^N$ across a curved interface with its tension γ . This follows readily from the evaluation of the work δW done in a normal displacement $\delta\zeta$ of a curved interface. This work is

$$\delta W = -\delta \int d\xi dS \sigma^N + \gamma \delta \int dS + \kappa \delta \int dS (J - c_0)^2 + \bar{\kappa} \delta \int dS K, \quad (9)$$

which, when taking $\delta\zeta$ to be arbitrary, together with $\delta J = (J^2 - 2K)\delta\zeta$ and $\delta K = -JK\delta\zeta$, leads to

$$\Delta\sigma^N = \gamma J - \kappa(J - c_0)(J^2 - 4K + Jc_0). \quad (10)$$

We note that the pressure difference does not depend on the saddle-splay constant κ , and that equal pressures do not necessarily imply $J=0$. In fact, in the limit when γ goes to zero, $\Delta\sigma^N$ vanishes if $J=c_0$ or $J^2 - 4K + Jc_0 = 0$. The first case $J=c_0$ may be taken to be an operational definition for the spontaneous curvature c_0 . If in addition to γ and $\Delta\sigma^N$, c_0 is also zero, the solutions of Eq. (10) correspond to principal curvatures c_1 and c_2 that may vary across the surface provided they satisfy any of the conditions $c_1=c_2$ or $c_1=-c_2$.

We determine now the critical behavior associated with κ , $\bar{\kappa}$, and c_0 . First we recall the dependence of the moments of the direct correlation function on the correlation length. For a uniform fluid the (classical) small-wave-number k expression for the structure factor S in Fourier space can be written as

$$S^{-1}(k;\rho) = \chi^{-1} + \frac{1}{2} \frac{d^2c(0)}{dk^2} k^2 + \frac{1}{4!} \frac{d^4c(0)}{dk^4} k^4 + \dots = \chi^{-1} (1 + \xi_1^2 k^2 + \xi_2^4 k^4 + \dots), \quad (11)$$

where χ is the isothermal compressibility. Since in our problem the only length scale is given by ξ , we have $\xi_1 \approx \xi_2 \approx \xi$, also χ and ξ diverge as $t^{-\gamma}$ and $t^{-\nu}$ with $\gamma = (2-\eta)\nu$ at the critical point where t is the reduced temperature. On the other hand, the integrations over \mathbf{r}_n and the square derivatives $(\partial_n \rho)^2$ in Eqs. (8a) and (8b) behave in the critical region as $\xi \sim t^{-\nu}$ and $(\Delta\rho \xi^{-1})^2 \sim t^{2(\beta+\nu)}$, respectively, where $\Delta\rho$ is the density difference between the two bulk phases. Therefore the interfacial free energy per unit area $f - f_0 = \gamma + f_H$ behaves as $\xi(\Delta\rho)^2 \chi^{-1} (1 + \xi^2/R^2)$ where R is a typical radius of curvature which must vanish as fast as ξ diverges when the critical point is approached. This is in order to maintain the independence of the integrations over $d\mathbf{r}_n$ from those over dS in Eq. (7), and still have meaningful definitions for γ , κ , $\bar{\kappa}$, and c_0 , as in Eqs. (8). Thus we find that all the terms in f_H share the same critical index as the surface tension γ , i.e., $\mu = -\nu + 2\beta - \gamma = 2 - \alpha - \nu$. The spontaneous curvature $c_0 = -\partial_z \ln \partial_z \rho = (\partial\rho/\partial z)^{-1} (\partial^2\rho/\partial z^2)$ behaves as $\xi(\Delta\rho)^{-1} \Delta\rho \xi^{-2} = \xi^{-1}$ and we have that $c_0 \sim t^\nu$.

As mentioned above, the rigidity κ can also be evaluated via the calculation of the change in grand potential for a planar interface at $z=0$ due to the increase in mean curvature caused by a small fluctuation in density. We follow the parallel treatment for the surface tension [11]. The change in (zero field) grand potential $\Omega[\rho] = F - \mu \int d\mathbf{r} \rho$ due to a change in density $\delta\rho(\mathbf{r})$ at fixed chemical potential μ is

$$\Delta\Omega = \Omega[\rho_0 + \delta\rho] - \Omega[\rho_0] = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \Big|_{\rho_0} \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') + \dots, \quad (12)$$

where ρ_0 is the equilibrium density distribution. To lowest order $\Delta\Omega$ is quadratic in $\delta\rho$ and depends on

$$C^{(2)}(\mathbf{r}, \mathbf{r}') = \frac{1}{kT} \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \Big|_{\rho_0} = \frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho_0(\mathbf{r})} - c^{(2)}(\mathbf{r}, \mathbf{r}'), \quad (13)$$

where $c^{(2)}(\mathbf{r}, \mathbf{r}')$ is the inhomogeneous fluid direct correlation function. For a planar interface $\rho_0 = \rho_0(z)$ and $C^{(2)} = C^{(2)}(|\mathbf{R}|; z, z')$ with $\mathbf{R} = (x - x', y - y')$, and small and rigid surface deviations $\zeta(x, y)$ with respect to $z=0$ yield density fluctuations of the form $\delta\rho(\mathbf{r}) = \rho_0(z - \zeta(x, y)) - \rho_0(z) \approx \zeta(x, y) \partial\rho_0/\partial z$. Consideration of these forms into Eq. (12) and expansion of $\zeta(x', y')$ to fourth order with respect to $\zeta(x, y)$ leads to

$$\Delta\Omega = \frac{1}{2kT} \int \int dz dz' \frac{\partial\rho_0}{\partial z} \frac{\partial\rho_0}{\partial z'} \left[\frac{1}{4} \int d\mathbf{R} |\mathbf{R}|^2 C^{(2)}(\mathbf{R}; z, z') \int dx dy \zeta(x, y) \left[\frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right] + \frac{1}{(2)(4!)} \int d\mathbf{R} |\mathbf{R}|^4 C^{(2)}(\mathbf{R}; z, z') \int dx dy \zeta(x, y) \left[\frac{\partial^4 \zeta}{\partial x^4} + 2 \frac{\partial^4 \zeta}{\partial x^2 \partial y^2} + \frac{\partial^4 \zeta}{\partial y^4} \right] \right], \quad (14)$$

where the zeroth-, first-, and third-order terms have vanished [the former because $\rho_0(z)$ satisfies the equilibrium condition, and the latter because of symmetry]. The familiar [5,6] expression for γ and that for κ in terms of $C^{(2)}(\mathbf{R};z,z')$ and $\partial\rho_0/\partial z$ follow from Eq. (14) by integration by parts, with the condition that derivatives of ζ vanish at the boundaries, and with the recognition of the forms for the changes in area and mean curvature introduced by the deformation $\zeta(x,y)$. We find

$$\gamma = -\frac{1}{4kT} \int \int dz dz' \frac{\partial\rho_0}{\partial z} \frac{\partial\rho_0}{\partial z'} \int d\mathbf{R} |\mathbf{R}|^2 C^{(2)}(\mathbf{R};z,z') \quad (15a)$$

and

$$\kappa = \frac{1}{(3)(4!)kT} \int \int dz dz' \frac{\partial\rho_0}{\partial z} \frac{\partial\rho_0}{\partial z'} \int d\mathbf{R} |\mathbf{R}|^4 C^{(2)}(\mathbf{R};z,z'). \quad (15b)$$

Finally, we note that in the local limit of the *inhomogeneous* $C^{(2)}$, its moments contain higher-order *local* moments. That is, Eq. (15a) reduces to $\gamma - \kappa c_0^2$, with γ , κ , and c_0 given by Eqs. (8). Thus Eqs. (15) capture in fact the total change in free energy due to changes in area and mean curvature.

The density-functional approach to inhomogeneous fluids has proven to be extremely fruitful in the description of the liquid-vapor interface [5–7]. It has pointed out the central role of the Ornstein-Zernike direct correlation function in providing a general picture of this problem. This function appears (as the kernel) in an integral equation for the density profile and renders a route for calculating the surface tension. Here we have extend-

ed the analysis of the long-wavelength behavior of the direct correlation function and clarified its relationship with the properties of the interfacial shape fluctuations. We found these fluctuations associated with a free-energy expression with the phenomenological form proposed by Helfrich to study shapes of surfactant membranes. For a simple one-component fluid the curvature free energy corresponds to that for two-dimensional shearless elastic media, and its magnitude is of the order of $\xi^2/R^2 \ll 1$ with respect to that of the surface tension contribution. Whether κ and $\bar{\kappa}$ appear related in a different manner for other types (e.g., multicomponent) of interfaces is a matter of further study. We already know [12] that for simple models of the electrical double layer the relationship between κ and $\bar{\kappa}$ depends on the conducting properties of the electrode. An important feature in the analysis presented here is the clarification of the fact that the interfacial quantities γ , κ , $\bar{\kappa}$, and c_0 are actually functionals of the surface S defined by the interface [see the derivation of Eq. (7)]. This implies corrections to these quantities when S departs from a planar shape [13]. Also, when the spatial extent, or width, of the inhomogeneity exceeds the value of the fluid's correlation length it is no longer meaningful to associate the above interfacial quantities with it. For instance, the capillary-wave broadening of the interfacial width, as described by long-range transverse correlations developing in the interface [11], implies such loss of definition for the surface tension.

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