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Interfacial Width and Shape Fluctuations and Extensions of the Gaussian Model of Capillary Waves

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Interfacial density fluctuations are studied at the level of the Gaussian model of capillary waves by means of density functional theory. We consider nonrigid fluctuations and arrive at exact Triezenberg–Zwanzig-type expressions for new interfacial coefficients. These include a width tension, a width rigidity, and other coefficients linked to both shape and width distortions. We find for these coefficients magnitudes of the same orders as those of their tangential counterparts. The corresponding capillary-wave model describes the effect of fluctuations when the density is slowly varying, and the recognition of the additional quantities and their roles may help in the understanding of ellipsometric studies near critical points.

KEY WORDS: Interfacial density fluctuations; density functional theory; direct correlation function; Triezenberg–Zwanzig expressions; interfacial width coefficients; generalized capillary-wave model.

1. INTRODUCTION

A central effort in developing a microscopic theory of interfaces is the derivation of exact expressions relating the surface tension γ, and other interfacial coefficients like the bending rigidity κ, to integrals involving the one- and two-particle correlation functions.[1] A great deal of our current understanding of fluctuations and correlations at fluid interfaces stems from these exact expressions. For instance, the capillary-wave model of the

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liquid-vapor interface focuses on thermal distortions of the interface, represented by rigid density fluctuations that exclude local width fluctuations, and, both, the original version of this model[2–5] and a recent extension,[6] that incorporates bending and other higher-order terms, are consistent with the exact Triezenberg–Zwanzig[4] expression for γ and with its counterpart for κ.[7,8] The behavior of the liquid-vapor interfacial width W in the limit of vanishing gravitational field mgz has been the subject of much scrutiny[1,4,5,6] in which capillary-wave models have played a major role by relating the behavior of W in bulk dimension d with the scaling properties that the interfacial density correlations develop as $g \to 0$.

Here we argue that in order to understand with generality density fluctuations at fluid interfaces it is insufficient to consider only the costumary (tangential) interfacial coefficients, like γ and κ, as restoring forces. We demonstrate that it is important to include new coefficients that define other restoring forces associated to deformations normal to the interface and to the coupling of these with the tangential modes. This is accomplished by deriving an exact expression for the second order variation of the grand potential $\delta\Omega$ of a planar interface due to a general nonrigid density fluctuation $\delta\rho$. We derive from $\delta\Omega$ Triezenberg–Zwanzig-like expressions for the known coefficients (albeit in local-height form described below) and obtain others of the same type corresponding to the new interfacial quantities. A physical interpretation for the latter coefficients is drawn out, and a density functional expression (reminiscent of that obtained from a capillary-wave model) for W that incorporates these coefficients is briefly discussed. The expression captures behavior for the interfacial displacement correlations, presumably conspicuous close to liquid-vapor criticality, that results from local width fluctuations taking place in interfacial regions described by slowly-varying densities. We consider too a local limit for $\delta\Omega$ that corresponds to a free energy functional with square-gradient and square-laplacian terms, and find that the new coefficients are of the same order of magnitude as the traditional ones.

2. NONRIGID INTERFACIAL DENSITY FLUCTUATIONS

To begin we consider the fluctuation formula

$$\delta\Omega = \frac{KT}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \delta\rho(\mathbf{r}_1)\, C(\mathbf{r}_1, \mathbf{r}_2)\, \delta\rho(\mathbf{r}_2) \tag{2.1}$$

for a planar geometry, for which the equilibrium density and direct correlation function have the spatial dependence $\rho_0(z)$ and $C(|\mathbf{R}_{12}|, z_1, z_2)$, respectively, with coordinates $\mathbf{r} = (\mathbf{R}, z)$ where $\mathbf{R}$ is a $(d-1)$-dimensional vector. A general nonrigid density fluctuation is described by

$$\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_0(z) \simeq -\zeta(\mathbf{R}, z)\, \rho_0'(z), \tag{2.2}$$

where $\zeta(\mathbf{R}, z)$ is interpreted as the displacement of an equilibrium equidensity plane located at z due to the fluctuation in density. A rigid fluctuation corresponds to a displacement function $\zeta(\mathbf{R})$ independent of z. It is fruitful to expand Eq. (2.1) in terms of $\delta z = (z_2 - z_1)/2$ around a central height coordinate $\bar{z} = (z_1 + z_2)/2$. The result can be written in the following form[9]

$$\delta\Omega = \int d\mathbf{R} \int d\bar{z} \sum_{m,n} \left| \nabla_{\mathbf{R}}^m \frac{\partial^{(n)}}{\partial \bar{z}^{(n)}} \zeta(\mathbf{R}, \bar{z}) \right|^2 K_{mn}(\bar{z}), \tag{2.3}$$

where

$$K_{mn}(\bar{z}) = (-1)^m \sum_{j=0}^{\infty} \sum_{k=0}^{2j} \binom{2j}{k} (-1)^k \left(-\frac{1}{2}\right)^{2j} a_n^{jk} \frac{\partial^{(2j-2n)}}{\partial \bar{z}^{(2j-2n)}} M_{mj}(\bar{z}), \tag{2.4}$$

where

$$M_{mj}(\bar{z}) = \frac{1}{(2m!!)^2} \frac{1}{2j!} \int d\,\delta z\, |\mathbf{R}|^{2m} (\delta z)^2\, \mathscr{C}(|\mathbf{R}|, \bar{z}, \delta z), \tag{2.5}$$

and where

$$\mathscr{C}(|\mathbf{R}|, \bar{z}, \delta z) \equiv (k, T/2)\, \rho_0'(\bar{z} - \delta z)\, C(|\mathbf{R}|, \bar{z} - \delta z, \bar{z} + \delta z)\, \rho_0'(\bar{z} + \delta z). \tag{2.6}$$

The constants a_n^{jk} can be obtained from the decomposition of the integrals

$$\int d\bar{z} \left(\frac{\partial^{(2j-k)}}{\partial \bar{z}^{(2j-k)}} \zeta(\bar{z}) \right) A(\bar{z}) \left(\frac{\partial^{(k)}}{\partial \bar{z}^{(k)}} \zeta(\bar{z}) \right) = \sum_n^j a_n^{jk} \left| \frac{\partial^{(n)}}{\partial \bar{z}^{(n)}} \zeta(\bar{z}) \right|^2 \left(\frac{\partial^{(2j-2n)}}{\partial \bar{z}^{(2j-2n)}} A(\bar{z}) \right). \tag{2.7}$$

For small j and k the decomposition can be readily carried out and we find, up to fourth order in derivatives of ζ,

$$\delta\Omega = \int d\mathbf{R} \int d\bar{z} \left\{ K_{00} |\zeta|^2 + K_{10} \left| \frac{1}{2} \nabla_{\mathbf{R}} \zeta \right|^2 + K_{01} \left| \frac{\partial}{\partial \bar{z}} \zeta \right|^2 \right.$$
$$\left. + K_{20} |\nabla_{\mathbf{R}}^2 \zeta|^2 + K_{11} (\nabla_{\mathbf{R}}^2 \zeta) \left(\frac{\partial^2}{\partial \bar{z}^2} \zeta \right) + K_{02} \left| \frac{\partial^2}{\partial \bar{z}^2} \zeta \right|^2 \right\}, \tag{2.8}$$

with $K_{00}=M_{00}+M''_{01}+M^{iv}_{02}$, $K_{10}=2(M_{10}+M''_{11})$, $K_{01}=-4(M_{01}+2M''_{02})$, $K_{20}=M_{20}$, $K_{11}=-2M_{11}$, and $K_{02}=8M_{02}$, where the primes indicate derivatives with respect to $\bar{z}$.

3. INTERFACIAL COEFFICIENTS FOR COUPLED WIDTH AND SHAPE FLUCTUATIONS

We interpret the various terms in Eq. (2.8) by noting first that the inverse of the first Ivon equation[10] can be rewritten as $K_{00}=-\rho'_0(\bar{z})\,\varphi'(\bar{z})$ where $\varphi'(z)$ is the spatial derivative of an external potential that varies only in the z direction. Secondly, the quantities $\frac{1}{2}|\nabla_{\mathbf{R}}\zeta|^2$ and $|\nabla_{\mathbf{R}}\zeta|^2$ in Eq. (2.8) can be seen to be, respectively, the increments in area and mean curvature due to the fluctuation at the equidensity surface located at $\bar{z}$. Therefore the moments K_{10} and K_{20} can be identified, respectively, as the (local) surface tension $\gamma_T(\bar{z})$ and bending rigidity $\kappa_T(\bar{z})$ per unit length at height $\bar{z}$. Next, we recognize that the quantity $(\partial\zeta/\partial\bar{z})^2$ measures a relative change in the interfacial width at the equidensity surface $\bar{z}$ (the entire change due to a uniform dilation normal to the interface), while $(\partial^2\zeta/\partial\bar{z}^2)^2$ provides a gauge for the nonuniformity of a dilation normal to the interface (measures the effect of distortions to the density profile that preserve width). These types of deformations suggest that we identify the moments K_{01} and K_{02}, respectively, with a width tension $\gamma_N(\bar{z})$ and a width rigidity $\kappa_N(\bar{z})$ per unit length. Finally, $(\nabla^2_{\mathbf{R}}\zeta)(\partial^2\zeta/\partial\bar{z}^2)$ measures the coupling of nonuniform normal dilations with tangential changes in surface curvature. Thus, a tangential-normal rigidity $\kappa_{TN}(\bar{z})$ can be defined via K_{11}.

For the less complicated term $n=0$ in Eq. (2.7), the coefficients a_0^{jk} turn out to be the mean of two Kronecker delta functions and one finds

$$K_{m0}(\bar{z})=(-1)^m\sum_{j=0}^{\infty}\left(\frac{1}{2}\right)^{2j}\frac{\partial^{(2j)}}{\partial\bar{z}^{(2j)}}M_{mj}(\bar{z}), \tag{3.1}$$

so that the like terms in Eq. (2.3) can be rewritten as

$$\begin{aligned}&\int d\mathbf{R}\int d\bar{z}\,|\nabla^m_{\mathbf{R}}\zeta(\mathbf{R},\bar{z})|^2\,K_{m0}(\bar{z})\\&\quad=\int d\mathbf{R}\int d\bar{z}\int d\,\delta z\,\frac{(-1)^m}{(2m!!)^2}\,|\nabla^m_{\mathbf{R}}\zeta(\mathbf{R},\bar{z})|^2\,|\mathbf{R}|^{2m}\,\mathscr{C}\left(|\mathbf{R}|,\bar{z}+\frac{\delta z}{2},\delta z\right).\end{aligned} \tag{3.2}$$

When the fluctuations considered are rigid only the above terms contribute to $\delta\Omega$, and, since in this case the integrations over $\mathbf{R}$ and $\bar{z}$ can be decoupled, we recover the known expressions that relate the external field

$\phi(z)$, the interfacial tension γ and the bending rigidity κ, respectively, to the zeroth, the second and the fourth transverse moments of the direct correlation function. That is, by considering the first three terms in Eq. (2.3) with $n = 0$, those with $m = 0$, 1, and 2, we arrive at the usual identifications[11, 6] for these quantities.

The formally exact, nonlocal, expressions given by Eqs. (2.3) to (2.8) can be particularized to the special case of a planar interface described by the local free energy functional[7]

$$\Omega[\rho] = \int d\mathbf{r}\{f_0[\rho] - (\mu - \varphi)\,\rho + \tfrac{1}{2}A[\rho]\,|\nabla\rho|^2 - \tfrac{1}{4}B[\rho]\,|\nabla^2\rho|^2\}, \quad (3.3)$$

where the quantities f_0, A and B, are found to be (for sufficiently short-ranged interactions)[12, 7]

$$f_0[\rho(\mathbf{r})] = kT\{\rho(\mathbf{r})[\ln(\lambda^3\rho(\mathbf{r})) - 1] - \frac{1}{2}[\rho(\mathbf{r})]^2 \int d\mathbf{r}'\, c(\mathbf{r}'; \rho(\mathbf{r}))\}, \quad (3.4)$$

$$A[\rho(\mathbf{r})] = \frac{1}{3!}kT \int d\mathbf{r}'\, |\mathbf{r}'|^2\, c(\mathbf{r}'; \rho(\mathbf{r})) \quad (3.5)$$

and

$$B[\rho(\mathbf{r})] = \frac{2}{5!}kT \int d\mathbf{r}'\, |\mathbf{r}'|^4\, c(\mathbf{r}'; \rho(\mathbf{r})). \quad (3.6)$$

In the above, λ is the de Broglie thermal length, $c(\mathbf{r}'; \rho(\mathbf{r}))$ is the direct correlation function of a uniform and isotropic fluid of density $\rho(\mathbf{r})$; f_0 is the free energy density of that uniform fluid (i.e. the reference fluid state changes from point to point). And A and B are the second and fourth moments, respectively, of the reference $c(\mathbf{r}'; \rho(\mathbf{r}))$. We apply the functional expansion given originally by Yang *et al.*[12] to the nonlocal $\delta\Omega$ in Eq. (2.8) and find[9]

$$\gamma_T(z) = A[\rho]\left(\frac{d\rho}{dz}\right)^2 - B[\rho]\left(\frac{d^2\rho}{dz^2}\right)^2, \quad (3.7)$$

$$\gamma_N(z) = A[\rho]\left(\frac{d\rho}{dz}\right)^2 - 3B[\rho]\left(\frac{d^2\rho}{dz^2}\right)^2 + 2\frac{d}{dz}B[\rho]\left(\frac{d\rho}{dz}\right)\left(\frac{d^2\rho}{dz^2}\right), \quad (3.8)$$

and

$$\kappa_T(z) = \frac{1}{2}\kappa_{TN}(z) = \kappa_N(z) = -\frac{1}{4}B[\rho]\left(\frac{d\rho}{dz}\right)^2. \quad (3.9)$$

The same expressions are found by making a nonrigid density fluctuation directly on Eq. (3.3). Interestingly, we observe that both tensions γ_T and γ_N are of the same order of magnitude, their leading square-gradient contributions are equal, while the three rigidities $\kappa_T(z)$, $\frac{1}{2}\kappa_{TN}(z)$ and $\kappa_N(z)$ are all equal too.

4. GENERALIZED CAPILLARY-WAVE MODEL

The quadratic form for the change in grand potential $\delta\Omega$ given by Eq. (2.1) can be used immediately to obtain expressions for the height–height correlations $\langle \zeta(\mathbf{R}, z_1)\, \zeta(\mathbf{R}', z_2)\rangle$, and the same-site or mean-square fluctuation $W^2 \equiv \langle \zeta(\mathbf{R}, z)\, \zeta(\mathbf{R}, z)\rangle$, where the brackets indicate averages evaluated from the gaussian distribution $\exp(-\delta\Omega)$. These expressions are the density functional theory counterparts of those generated by a capillary-wave model generalized to incorporate nonrigid fluctuations $\zeta(\mathbf{R}, z)$. Use of the definitions for $\mathscr{C}(|\mathbf{R}|, \bar{z}, \delta z)$ and $\zeta(\mathbf{R}, z)$ into Eq. (2.1) and replacement of the real space integrations by summations in Fourier space, yield

$$\delta\Omega = \frac{1}{L^{d+1}} \sum_{\mathbf{Q}} \sum_{\bar{q}, q} \tilde{\mathscr{C}}(Q, \bar{q}, q)\, \tilde{\zeta}(\mathbf{Q}, \bar{q}+q)\, \tilde{\zeta}(-\mathbf{Q}, \bar{q}-q), \tag{4.1}$$

where $\tilde{\mathscr{C}}(Q, \bar{q}, q)$ and $\tilde{\zeta}(\mathbf{Q}, q_i)$ are, respectively, the Fourier transforms of $\mathscr{C}(|\mathbf{R}|, \bar{z}, \delta z)$ and $\zeta(\mathbf{R}, z_i)$, $i = 1, 2$, $\bar{q} = (q_1 + q_2)/2$ and $q = (q_1 - q_2)/2$. There are difficulties in obtaining W^2 from the inverse of $\tilde{\mathscr{C}}(Q, \bar{q}, q)$, as it is the usual procedure,[6] because of the dependence on $\bar{q}$ in both $\tilde{\mathscr{C}}$ and $\tilde{\zeta}$, while we notice too that $\tilde{\mathscr{C}}(Q, q_1 + q_2, q_1 - q_2)$ is not diagonal in (q_1, q_2). There are two limiting situations for which these complications are circumvented. The first one corresponds to the restriction to rigid fluctuations, in which case $\tilde{\zeta}(\mathbf{Q}, q_i) = \tilde{\zeta}_0(\mathbf{Q})\, \delta_{q_i, 0}$ and we are lead to the standard result[6]

$$W^2 = \frac{kT}{l^{d-1}} \sum_{\mathbf{Q}} \frac{1}{\tilde{\mathscr{C}}(Q, 0, 0)}, \tag{4.2}$$

where $\tilde{\mathscr{C}}(Q, 0, 0) = \Delta\rho mg + \gamma Q^2 + \kappa Q^4 + \cdots$, and $\Delta\rho = \rho_l - \rho_v$ is the density difference between the coexisting phases. A second limit is that of a wide interfacial region due to, say, a diverging correlation length ξ. In this case the density profile can be approximated by

$$\rho_0(z) = \begin{cases} \rho_l, & z < -\xi/2 \\ (\rho_l + \rho_v)/2 - \Delta\rho z/\xi, & -\xi/2 < z < \xi/2 \\ \rho_v, & z > \xi/2, \end{cases} \tag{4.3}$$

so that the fluctuations can be taken to have the form $\zeta^*(\mathbf{R}, z) = \zeta(\mathbf{R}, z)$, $-\xi/2 < z < \xi/2$, and zero otherwise. Then we obtain, when $C(\mathbf{r}_1, \mathbf{r}_2) = C(|\mathbf{r}_r - \mathbf{r}_2|)$,

$$W^2 = \frac{kT}{L^d} \sum_{\mathbf{Q}} \sum_{q} \frac{1}{\tilde{\mathscr{C}}^*(Q, q)}, \tag{4.4}$$

where $\tilde{\mathscr{C}}^*(Q, q)$ is the Fourier transform of

$$\mathscr{C}^*(|\mathbf{R}|, z_2 - z_1) \equiv (kT/2)(\Delta\rho/\xi)\, C(|\mathbf{R}|, z_2 - z_1)(\Delta\rho/\xi). \tag{4.5}$$

For small q (and Q) we have

$$\tilde{\mathscr{C}}^*(Q, q) \simeq (\Delta\rho/\xi)\, mg + \gamma_T Q^2 + \gamma_N q^2 + \kappa_T Q^4 + \kappa_{TN} Q^2 q^2 + \kappa_N q^4, \tag{4.6}$$

where the interfacial coefficients turn out independent of the local height $\bar{z} = (z_1 + z_2)/2$. If for simplicity we consider the case in which the only two nonvanishing coefficients are γ_T and γ_N, and assume $\gamma_T = \gamma_N$, as is found in Eq. (3.8) with $B = 0$, the expression for W^2 in Eq. (4.4) corresponds to that given by the ordinary capillary-wave model but for a system dimension $D = d + 1$. Therefore, when $d = 3$ we obtain a vanishing W in the absence of gravity (recall that $W^2 \sim L_c^{3-d}$ where L_c is the capillary length) indicating that capillary-waves do not broaden $\rho(z)$. The finite, but large (because ξ has been assumed to be large), interfacial width in the limit when $L \to \infty$ and $g \to 0$ would be given (see below) by other measures not based on the mean-square height fluctuation W^2. As it is known, the ordinary capillary-wave model provides a quantitative account of ellipsometric studies of liquid-vapor interfaces away from bulk criticality where rigid interfacial fluctuations provide a good description, but fails when close to it, where simple "intrinsic" interfacial models succeed by treating the interface in terms only of width fluctuations.[5] We suggest that the density functional expressions associated to nonrigid fluctuations provide a comprehensive description for interfacial fluctuations, including the crossover to behavior close to bulk criticality where local width fluctuations intensify and couple with shape distortions.

If as assumed $\rho(z)$ is the exact (or, in the capillary-wave model language, the already fluctuation-broadened profile) we require that the average $\langle \rho(\mathbf{R}, z) \rangle$ of $\rho(\mathbf{R}, z) \equiv \rho(z - \zeta(\mathbf{R}, z))$ with respect to the fluctuations $\zeta(\mathbf{R}, z)$ reproduces $\rho(z)$, that is $\langle \rho(\mathbf{R}, z) \rangle \simeq \rho(z)$. An expansion of $\langle \rho(\mathbf{R}, z) \rangle$ in the powers $\langle [\zeta(\mathbf{R}, z)]^{2n} \rangle$, leads, to second order, to

$$\langle \rho(\mathbf{R}, z) \rangle = \rho(z) + \frac{1}{2} \frac{d^2\rho(z)}{dz^2} W^2, \tag{4.7}$$

therefore we need $(d^2\rho(z)/dz^2)\, W^2$ to be small. The requirement in Eq. (4.7) can be checked for the case of the ordinary capillary-wave model (rigid fluctuations $\zeta(\mathbf{R})$ together with $\mathscr{C}(Q, 0, 0) = \Delta\rho m g + \gamma Q^2$ and $d\rho(z)/dz = (\Delta\rho/W)\exp(-z^2/W^2)$),[4] for which we obtain

$$\langle \rho(\mathbf{R}, z)\rangle = \rho(z) - \frac{z\,\Delta\rho}{W}\exp\left(-\frac{z^2}{W^2}\right). \tag{4.8}$$

Both, in dimensions $d \leqslant 3$, when the width W diverges, and $d > 3$ when the width W vanishes in the abscence of gravity the requirement is satisfied. It is also interesting to compare W with another measure for the width of $\rho(z)$, w, given by

$$w^2 = \frac{1}{\Delta\rho}\int dz\, z^2 \frac{d\rho(z)}{dz}. \tag{4.9}$$

It is easy to show that $w^2 = W^2 \int dx\, x^2 \exp(-x^2) \simeq W^2$, $L_c < \infty$, for the ordinary capillary-wave model when $d \leqslant 3$. However, for the profile $\rho_0(z)$ that leads to Eq. (4.4) when $d = 3$ we have $w^2 = \xi^2/12 > W^2$.

5. PARRY-BOULTER EFFECTIVE BENDING RIGIDITY

Recently,[13] some properties of interfacial fluctuation theories have been explored by considering a specific type of nonrigid density fluctuation. An expansion of $\delta\Omega$ in Fourier space equivalent to that given by Eq. (4.1) has been analysed for the case in which the distortions $\zeta(\mathbf{R}, z)$ obey the particular form consisting of a rigid term ζ_0 plus a nonrigid contribution proportional to the laplacian of ζ_0 and linear in z, that is, $\zeta(\mathbf{R}, z) = \zeta_0(\mathbf{R}) - (z\xi/2)\,\nabla^2_{\mathbf{R}}\zeta_0(\mathbf{R})$.[13] For this type of fluctuation only those terms with $n = 0$ and $n = 1$ contribute to $\delta\Omega$ in Eq. (2.3), which can therefore be written, after performing the integration over $\bar{z}$, as

$$\begin{aligned}\delta\Omega = \int d\mathbf{R} \sum_m \Big\{ &|\nabla^m_{\mathbf{R}}\zeta_0(\mathbf{R})|^2 L^{(0)}_{m0} + 2\,|\nabla^{m+1}_{\mathbf{R}}\zeta_0(\mathbf{R})|^2 L^{(1)}_{m0} \\ &+ |\nabla^{m+2}_{\mathbf{R}}\zeta_0(\mathbf{R})|^2 L^{(2)}_{m0} + |\nabla^{m+2}_{\mathbf{R}}\zeta_0(\mathbf{R})|^2 L^{(0)}_{m1} \Big\},\end{aligned} \tag{5.1}$$

where

$$L^{(k)}_{mn} = \int d\bar{z}(\bar{z}\xi/2)^k\,(\xi/2)^{2n}\,K_{mn}(\bar{z}). \tag{5.2}$$

Since $\delta\Omega$ above has been expressed only in terms of the rigid contribution ζ_0 contained in the original nonrigid fluctuation, the coefficients $L_{mn}^{(k)}$ become necessarily associated to the tangential interfacial coefficients. Thus, by collecting terms proportional to $(\nabla_{\mathbf{R}}^2 \zeta_0)^2$ we note that in Eq. (5.1) appear other contributions proportional to the mean curvature in addition to the bending rigidity term $\kappa = L_{20}^{(0)}$. We obtain an effective bending rigidity

$$\kappa_{eff} = \kappa + 2L_{10}^{(1)} + L_{00}^{(2)} + L_{01}^{(0)}, \tag{5.3}$$

which is identical to Eq. (22) of ref. 13. It should be noted that the treatment in ref. 13 given to this type of nonrigid fluctuation assumes a given response of the interfacial width to the curvature of the dividing surface ζ_0. In contrast, our analysis here considers both width and capillary-wave fluctuations on the same footing and of the same order.

6. SUMMARY

In summary, by considering general nonrigid fluctuations of a planar interface we have derived formal sum rules for a set of interfacial coefficients in terms of the density gradient and the moments, in the transverse and normal directions, of the direct correlation function. These coefficients refer, locally across the interface, to the free energy changes due to deformations that have components tangential and normal to the plane. These coefficients include surface tension and bending rigidity per unit length and also novel quantities that refer to interfacial width extensions or contractions and higher-order deformations of the density profile that preserve width. When the distortions are rigid, $\zeta(\mathbf{R})$, we recover the known expressions for the surface tension and the bending rigidity. On the other hand, when the distortions are purely normal, $\zeta(z)$, the free energy change is given in terms of the width coefficients. These two limiting behaviors are mirrored by a capillary-wave model for the $\zeta(\mathbf{R}, z)$. As discussed, one manifestation of the physical existence of the width coefficients described here is the crossover from capillary-wave to pure-width fluctuation behavior observed in ellipsometric studies of interfaces as bulk criticality is approached. Other situations in which interfacial width fluctuations are conspicuous (and provide circumstances in which to study the new coefficients) are those of the non-critical interface at a critical end point and the unbinding interface at complete wetting when bulk coexistence is approached. As we have seen, when fluctuations are restricted to be rigid the known results for the interfacial tension and the bending rigidity are recovered, and we observed that the density functional approach leads to the same results of the ordinary capillary-wave model but without need of the costumary reference to the "broadening" of a "bare" interface.

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