Renormalization-Group Calculation of the Dependence on Gravity of the Surface Tension and Bending Rigidity of a Fluid Interface

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The surface tension and the bending rigidity of a planar liquid-vapor interface in the presence of vanishing gravity are analyzed using the renormalization group. Based on the density functional theory of inhomogeneous fluids, we show that a term, quartic in the density fluctuations, can be added to the classical capillary-wave model so that a renormalization-group calculation can be performed. By comparing the outcome of such a calculation with rigorous results relating the direct correlation function with surface tension and bending rigidity, we find the scaling dependence of the latter on gravity. The results agree with the expected fact that the interface should become unstable as gravity vanishes.

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The capillary-wave model of the liquid-vapor interface is one of the most striking and interesting theoretical results [1,2] in the study of the statistical mechanics of inhomogeneous fluids [3–5]. It was originally formulated in a phenomenological fashion by Buff, Lovett, and Stillinger [1] in order to describe the competition of gravity and surface tension, in the form of capillary-wave fluctuations of an otherwise planar intrinsic interface between two fluid phases. A significative prediction of the model is that the interfacial thermal fluctuations broaden the actual width of the interface and, in the limit of vanishing gravity, the width diverges (for a system infinite in size) [1,2]. Moreover, it can be shown that this broadening is the result of the fact that the transverse correlation length of the density fluctuations diverges as gravity vanishes [2,6]. Thus, an analogy with a critical phenomenon can be used with gravity playing the role of the distance to the critical point [7]. This roughening of the interfacial width has been clearly demonstrated in many similar models and in numerical calculations of Ising-like systems [8].

On the other hand, concentrating on a fluid interface and using density functional theory for inhomogeneous fluids, Romero-Rochín, Varea, and Robledo [9] showed that this model may be derived from a general expression for the cost in grand potential due to an arbitrary density fluctuation of the Gibbs dividing surface. Specializing to terms *quadratic* in the fluctuations of the surface, one obtains an expression for the energy cost that closely resembles the capillary-wave model but that actually includes higher order terms absent in the phenomenological model. In such a derivation use is made of exact rigorous results, namely, the relationship between the direct correlation function and the gradients of the external field, derived by Lovett, Mou, and Buff [10] and Wertheim [11] (LMBW), and of the expression for the surface tension in terms of the second transverse moment of the direct correlation function found by Yvon [12] and Triezenberg and Zwanzig [13] (YTZ). The higher order terms of the extended model are expressed in terms of higher derivatives of the deviation of the intrinsic surface, and they certainly have physical meaning [14]. The most notorious is the energy cost of bending the surface [15]. This term is proportional to the bending rigidity times the curvature of the surface, and the bending coefficient can be shown to be proportional to the fourth transverse moment of the direct correlation function (RRVR) [9,16]. The bending rigidity of fluid interfaces in the present context has been studied extensively [17–21].

Since the physics accompanying the long range development of the surface fluctuations indicate that a critical-like behavior is present, Weeks [7] proposed a scaling hypothesis of the corresponding correlation function in terms of the classical capillary length $L_c^2 = \gamma/\Delta\rho m g$; here γ is the (constant) surface tension, $\Delta\rho = \rho_l - \rho_g$ is the difference in liquid and vapor densities, m is the mass of the fluid particles, and g is the gravitational acceleration. This hypothesis is certainly obeyed by the original capillary-wave model and indicates that the correlation length of the system is the capillary length.

In this Letter, we introduce another point of view in the relationship between *exact* results pertaining to the interface, obtained from density functional theory, and the "critical" behavior of the interface as gravity vanishes. The idea is that instead of using density functional theory to build a capillary-wave model, we rather require those exact results to be satisfied by any phenomenological or otherwise theory of the surface fluctuations. This approach has already been used by several authors, in mean-field theories, to obtain expressions for surface properties [17–19,22]. Now, for gravity almost vanishing and assuming that we are facing a bona fide critical phenomenon, we propose that there exists a "bare" capillary-wave-like Hamiltonian, which includes *fourth order* surface fluctuations, as in any $\lambda\phi^4$ theory, that must be renormalized. The corresponding renormalized second order correlation function can thus be calculated, and the moments of this function are to be compared with the exact results: the LMBW expression yields the dependence of the actual correlation length on gravity (which differs from the classical capillary length), and with the use of the YTZ and RRVR expressions for the surface tension and the bending rigidity we find the dependence of those quantities in terms of gravity. Certainly, scaling is obeyed, not in terms of the mean-field fashion classical capillary length but in terms of an Ising-like correlation length with Ising critical exponents. We shall see that the existence of the analog of the η exponent yields, as gravity vanishes, a *diverging* surface tension and a *diverging* but *negative* bending rigidity. Although these results may appear not intuitive they are not unphysical [21,23,24]: while the surface tension opposes increase in area, the bending rigidity being negative favors curvature. As gravity vanishes, the rigidity diverges more strongly than the surface tension so that the surface ends up with large distortions that broaden the interfacial region. Our findings are also in agreement with independent results pertaining to the surface tension and the bending rigidity: Robert [24] argued that the second transverse moment of the direct correlation function diverges at zero gravity. And very recently, both by molecular dynamic simulations [21] and by experimental results [23], it has been found that the bending rigidity of a liquid-vapor interface is unequivocally negative.

Let us begin presenting the exact results of density functional theory [3–5,9–13]. Consider a fluid in a coexisting liquid-vapor state in the presence of gravity with an equilibrium density profile $\rho_0(z)$. The profile has the properties that $\rho(z \to \infty) = \rho_g, \rho(z \to -\infty) = \rho_l$ with an interfacial region of width w in the vicinity of $z = 0$. The change in grand potential due to an arbitrary density fluctuation, at given $\mu - V_{\text{ext}}(\vec{r})$ and T, with $V_{\text{ext}} = mgz$, is given by

$$\Delta\Omega = \Omega[\rho] - \Omega[\rho_0] = \frac{kT}{2}\int d\vec{r}\, d\vec{r}\,'\, C(\vec{r},\vec{r}\,')\delta\rho(\vec{r})\delta\rho(\vec{r}\,') + \frac{kT}{4!}\int d\vec{r}\, d\vec{r}\,'\, d\vec{r}\,''\, d\vec{r}\,'''\, C^{(4)}(\vec{r},\vec{r}\,',\vec{r}\,'',\vec{r}\,''')\delta\rho(\vec{r})\delta\rho(\vec{r}\,')\delta\rho(\vec{r})''\delta\rho(\vec{r}\,''') + \ldots, \quad (1)$$

where $\delta\rho(\vec{r}) = \rho(r) - \rho_0(z)$ and $\vec{R}$ is the projection of the d-dimensional vector $\vec{r} = (z, \vec{R})$ on the $z = 0$ plane. $C(\vec{r},\vec{r}\,')$ is the direct correlation function of the fluid, and $C^{(4)}(\vec{r},\vec{r}\,',\vec{r}\,'',\vec{r}\,''')$ is the next, fourth order correlation function. Following Triezenberg and Zwanzig [13], we consider the density fluctuation,

$$\delta\rho(\vec{r}) = \rho_0(z - \zeta(\vec{R})) - \rho_0(z) \approx -\zeta(\vec{R})\frac{d\rho_0}{dz}, \quad (2)$$

where $\zeta(\vec{R})$ is an arbitrary single-valued function that represents the "capillary-wave" fluctuation of the Gibbs dividing surface. Equation (1) becomes

$$\Delta\Omega = \frac{kT}{2}\int d\vec{R}\, d\vec{R}\,'\, C(|\vec{R} - \vec{R}\,'|)\zeta(\vec{R})\zeta(\vec{R}\,') + \frac{kT}{4!}\int d\vec{R}\, d\vec{R}\,'\, d\vec{R}\,''\, d\vec{R}\,'''\, C^{(4)}(\vec{R},\vec{R}\,',\vec{R}\,'',\vec{R}\,''')\zeta(\vec{R})\zeta(\vec{R}\,')\zeta(\vec{R}\,'')\zeta(\vec{R}\,''') + \ldots, \quad (3)$$

defining the *transverse* direct correlation function

$$C(|\vec{R} - \vec{R}\,'|) = \iint dz\, dz'\, \frac{d\rho_0}{dz}\frac{d\rho_0}{dz'}\, C(z, z'; |\vec{R} - \vec{R}\,'|), \quad (4)$$

and an analogous expression for $C^{(4)}(\vec{R},\vec{R}\,',\vec{R}\,'',\vec{R}\,''')$.

Lovett, Mou, and Buff [10] and Wertheim [11] derived the following exact result:

$$\nabla V_{\text{ext}}(\vec{r}) = -kT\int d\vec{r}\,'\, C(\vec{r},\vec{r}\,')\nabla'\rho_0(\vec{r}\,'). \quad (5)$$

In the present case, this expression can be written as

$$\int d^{d-1}\vec{R}\, C(\vec{R}) = \frac{\Delta\rho mg}{kT}. \quad (6)$$

Denoting by $\tilde{C}(\vec{Q})$ the $(d - 1)$-dimensional Fourier transform of $C(\vec{R})$, one may also write (LMBW)

$$\tilde{C}(0) = \frac{\Delta\rho mg}{kT}. \quad (7)$$

In a well-known paper, Triezenberg and Zwanzig [13] identified the surface tension of the interface as the cost in Ω due to an increase of area arising from the fluctuation $\zeta(\vec{R})$. They found (YTZ)

$$\gamma = \frac{kT}{2}\frac{\partial^2\tilde{C}(0)}{\partial\vec{Q}^2}. \quad (8)$$

Following the previous reasoning, Romero-Rochín, Varea, and Robledo [9,16] calculated the bending rigidity of the interface as the cost in Ω due to a change in curvature generated by the fluctuation $\zeta(\vec{R})$. The result is (RRVR)

$$\kappa = \frac{kT}{4!}\frac{\partial^4\tilde{C}(0)}{\partial\vec{Q}^4}. \quad (9)$$

Evidently, one may go to higher order terms in the expansion of $\tilde{C}(\vec{Q})$, and extend the capillary-wave model [9]. However, the relevant point now is that the results (7), (8), and (9) are exact and independent of any capillary-wave model. At the same time, those equations are simple statements of the relationship between measurable quantities and the direct correlation function $C(\vec{R})$. Without knowing anything about the latter, those relationships are empty as far as predicting actual dependences on thermodynamic quantities such μ and T and external variables such as g. Our purpose below is to show that with the use of the standard theory of critical phenomena and the renormalization group [25–27], adapted to the present case, one can fill the gap and obtain the dependence on gravity.

For vanishing gravity, the transverse direct correlation at zero momentum, $\tilde{C}(0)$, vanishes; cf. Eq. (7). This is the equivalent in usual critical phenomena of saying that the inverse susceptibility vanishes at the critical point [25,26]. The critical point is thus identified as the value $g = 0$. However, this does not imply that gravity is the equivalent of the temperature difference from the critical temperature $|T - T_c|$. The analogy is rather that gravity g, besides some constants, is equivalent to the inverse susceptibility χ^{-1}. This means that near the critical point $g = 0$, there exists a bare capillary-wave-like Hamiltonian of the form

$$H_{\mathrm{cw}} = \int d^{d-1}R\left[\frac{\gamma_0}{2}\,|\nabla\zeta(\vec{R})|^2 + \frac{a_0}{2}\,\zeta^2(\vec{R}) + \frac{\lambda}{4!}\,\zeta^4(\vec{R})\right], \tag{10}$$

with the partition function given by

$$\mathcal{Z} = \int \mathcal{D}[\zeta(\vec{R})]e^{-\beta H_{\mathrm{cw}}}. \tag{11}$$

Our main interest is to calculate, from Eq. (11), the correlation function

$$\mathcal{H}(|\vec{R} - \vec{R}'|) = \langle\zeta(\vec{R})\zeta(\vec{R}')\rangle, \tag{12}$$

whose inverse is the direct correlation function $C(\vec{R})$ (or the two-point vertex function in the renormalization-group language). In proposing the above form of the bare capillary-wave Hamiltonian, Eq. (10), we point out that there is no need to include quadratic terms beyond those already included [i.e., quadratic terms proportional to higher derivatives of $\zeta(\vec{R})$]: those terms in the Hamiltonian can be shown to be irrelevant, in the sense that do not modify the critical behavior [25]. What is very important, and the novelty of our proposal in the present problem, is the inclusion of the term $\lambda\zeta^4(\vec{R})$. This term in the Hamiltonian will give rise to terms of all orders in the correlation function $C(\vec{R})$. Clearly, if λ is zero, one recovers the Gaussian model, then $\gamma_0 = \gamma$ the actual surface tension, $a_0/2 = \Delta\rho m g$, and all the higher order terms such as κ vanish. Thus, it is the $\lambda\zeta^4(\vec{R})$ term which makes the calculation different. The physical motivation to include this contribution is the appearance of the fourth order term in the cost in grand potential due to a surface fluctuation, Eq. (1). In other words, the expression for the partition function, Eqs. (10) and (11), is the simplest one that follows from considering the lowest nontrivial contributions to $\Delta\Omega$. With this calculation we will find approximate expressions for the measurable quantities that necessarily depend on the parameters of the bare model, but as we shall see, the dependence on gravity will also be found, which is our goal here.

Using standard renormalization-group calculations [25,27] one can find, for arbitrary dimension, the *renormalized N-vertex functions*. Our interest now is the two-point function, which can be shown to be

$$\tilde{C}_R(\vec{Q}) \approx \gamma_0(k\xi)^{-2+\gamma_\phi(\lambda^*)}[k^2 + (k\xi)^2Q^2 - (k\xi)^4\kappa_b Q^4 + \ldots], \tag{13}$$

where ξ is the correlation length, and whose dependence on g is found below. k is the arbitrary renormalization scale. Up to two loops one can express $\gamma_\phi(\lambda^*)$, the anomalous dimension exponent evaluated at the fixed Ising point, as [27]

$$\gamma_\phi(\lambda^*) \approx \frac{(5 - d)^2}{54}. \tag{14}$$

For simplicity, and to follow the usual nomenclature, we shall now call the exponent $\eta = \gamma_\phi(\lambda^*)$. The fourth order coefficient κ_b can be calculated and yields

$$\kappa_b = \left(\frac{2}{27k^2\Gamma^2(\frac{5-d}{2})}\right)(4\pi)^{d-1}I_0, \tag{15}$$

where I_0 is the convergent, adimensional, integral

$$I_0 = \int d^{d-1}q\, d^{d-1}p\,\frac{1}{(p^2 + 1)(q^2 + 1)[(p + q)^2 + 1]^3}. \tag{16}$$

Again, if in the Hamiltonian λ is set equal to zero, one obtains $\kappa_b = 0$.

We wrote Eq. (13) in such a way to highlight the scaling form of the height-height correlation function. Namely, we find that, as expected [2,9], such a function scales as $C = C(\vec{R}/\xi)$. However, ξ does not equal the classical capillary length unless $\eta = 0$. The existence of the latter anomalous dimension is in agreement with the scaling hypothesis proposed by Romero-Rochín, Varea, and Robledo [9,20].

With the above results, we are now in a position to make contact with the exact results previously found. First, we make the main identification, by equating the renormalized vertex function $\tilde{C}_R(Q = 0)$, Eq. (13), with the *actual* transverse direct correlation function $\tilde{C}(Q = 0)$, Eq. (7). One obtains

$$\Delta\rho m g = \gamma_0(k\xi)^{-2+\eta}k^2. \tag{17}$$

The principal result here is that we find the dependence of the correlation length ξ on gravity. That is,

$$\xi \sim g^{-1/(2-\eta)}. \tag{18}$$

Needless to say, from Eq. (17) one sees that if $\eta = 0$, ξ equals the classical capillary length.

With the identification of the correlation length, Eq. (18), we can now predict the scaling dependence on gravity of the measured surface tension, Eq. (8), and the bending rigidity Eq. (9). The surface tension is

$$\gamma = \gamma_0(k\xi)^\eta \sim g^{-\eta/(2-\eta)}. \tag{19}$$

This result may appear quite surprising since it shows that as gravity vanishes the surface tension diverges [24], thus indicating that the free energy does not favor large undulations of the surface. However, the bending rigidity also diverges and it is negative [21],

$$\kappa = -\gamma_0 (k\xi)^{2+\eta} \kappa_b \sim -g^{-(2+\eta)/(2-\eta)}. \quad (20)$$

A negative bending rigidity favors large curvature of the interface. Moreover, as g vanishes, κ grows faster than γ such that large undulations of the surface may result. This is certainly a physical argument supporting the expected fact that as g vanishes the interface becomes wider and unstable, as the classical capillary-wave model suggests. However, as gravity becomes even smaller, the higher order terms in the transverse correlation function $\tilde{C}(Q)$ are more and more relevant, so that at $g = 0$, the renormalization-group calculation indicates the well-known singular behavior [25], $\tilde{C}(Q, g = 0) \sim Q^{2-\eta}$, that prevents the expansion in powers of Q and, therefore, the definition of γ and κ.

For small gravity the present results could be experimentally tested. It appears, however, that in the current microgravity experiments [28] the conditions are such that the liquid-vapor states obtained are in the form of drops of one phase on the other. To test these predictions the planar interface should remain pinned, while the size of the system should be made longer than the expected correlation length ξ at the given value of gravity, in order to simulate the infinite size of the system that this analysis requires. For $d = 3$ the surface is two dimensional and the exact Ising result predicts $\eta = 1/4$. Of course, this dependence may be tested only within the Ginzburg region; outside it, mean field is valid, then γ is constant, and κ, although finite, becomes an irrelevant quantity in determining the behavior of the interface at small values of gravity.

Finally, if as the classical capillary-wave model suggests [1], one identifies the square of the width of the interface as the value of the height-height correlation function at $\vec{R} = 0$, namely $w^2 = \mathcal{H}(0)$ [cf. Eq. (12)], the present scaling law predicts that the width diverges as $w^2 \sim \xi^{3-d-\eta}$ for $d < 3$. Since the correlation function $\mathcal{H}(0)$ appears finite for $d \geq 3$, one cannot conclude how the width of the interface diverges as gravity vanishes [9]. On the other hand, if the classical capillary-wave model is correct down to arbitrarily small values of g, then one finds for $d = 3$ the well-known logarithmic divergence in terms of the capillary length, $w \sim \ln(L_c)$ [1]. This would mean, however, that the critical behavior of the interface is always of the mean-field type, a result that should have to be experimentally verified.

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