Curvature corrections to the surface tension of fluid drops: Landau theory and a scaling hypothesis

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The leading curvature correction δ to the surface tension of a large spherical fluid drop at equilibrium is defined by $\sigma = \sigma_\infty(1 - 2\delta/R + \cdots)$, where R is the drop radius. When the two coexisting phases are symmetric, δ is shown to vanish exactly at all temperatures T. By using Landau theory and expanding in powers of $1/R$, we derive an explicit expression for δ in terms of the planar interfacial profile. In the presence of asymmetry and within Landau theory, $\delta(T)$ approaches a constant value δ_c (of the order of atomic dimensions), as $T \to T_c^-$. We propose a scaling hypothesis for the exact critical behavior of $\delta(T)$ beyond Landau theory, when fluctuations are important. There are two terms: One arises from field mixing and goes as $|t|^{1-\alpha-\beta-\nu}$, depending on bulk relevant exponents only $[t=(T-T_c)/T_c]$; the other arises from true, non-Ising asymmetry and goes as $|t|^{\theta_5-\nu}$, where θ_5 is the leading asymmetric correction-to-scaling exponent. Observation of the critical behavior of $\delta(T)$ would provide information about the irrelevant exponent θ_5.

I. INTRODUCTION

In recent years much progress has been made in understanding the statistical properties of planar fluid interfaces.[1-3] By contrast, the theory of curved interfaces, although given a solid thermodynamic base more than 30 years ago,[4-7] has received comparatively little attention. Here we address spherical fluid interfaces and focus in particular on the curvature correction δ to the surface tension, defined through

$$\sigma = \sigma_\infty[1 - 2(\delta/R) + \cdots], \quad R \to \infty \qquad (1.1)$$

where R is the radius of curvature and σ_∞ denotes the planar surface tension. We restrict our attention to one-component fluids.[8]

In Sec. II we recall briefly some standard thermodynamic results[1-3] for the surface tension of a spherical drop. We study a general Landau or square-gradient theory in Sec. III A and derive the expression

$$\delta = \frac{\int_{-\infty}^{\infty} dz\, z\rho_0'(z)}{\int_{-\infty}^{\infty} dz\, \rho_0'(z)} - \frac{\int_{-\infty}^{\infty} dz\, z\,[\rho_0'(z)]^2}{\int_{-\infty}^{\infty} dz\,[\rho_0'(z)]^2}, \qquad (1.2)$$

which involves only the derivative of the planar density profile $\rho_0(z)$. This and related Landau-theory results are found to be consistent with various thermodynamic expressions for δ.

It follows from (1.2), as discussed in Sec. III B, that within Landau theory δ vanishes identically for systems which are symmetric under interchange of the two phases (e.g., an Ising system, but not a real liquid-gas system). A description of real fluid drops consequently requires the retention of asymmetric terms in the Landau theory. As $T \to T_c^-$, the curvature correction $\delta(T)$ is then found to approach a constant value.

It is argued in Sec. IV that the vanishing of δ for symmetric systems is a general result and not merely an artifact of Landau theory. On this basis we propose in Sec. IV B a scaling hypothesis for the critical behavior of $\delta(T)$ beyond Landau theory, where fluctuations play an important role. There are two terms. One is associated with the asymmetry which at the Landau-theory level takes the form $\phi(\vec{\nabla}\phi)^2$. This leads to field mixing[9] and gives a contribution to δ of the form $|t|^{1-\alpha-\beta-\nu}$, which has a weak critical divergence in three dimensions. The other arises from the asymmetry which at the Landau-theory level is expressed in the ϕ^5 term of the free-energy density. This gives a contribution of the form $|t|^{\theta_5-\nu}$ near criticality, where θ_5 is the leading odd correction-to-scaling exponent. θ_5 has been computed[9,10] to order ϵ^3 (for dimensionality $d = 4 - \epsilon$), but the series is poorly convergent, so that it is not clear which of the two terms dominates the critical behavior of $\delta(T)$.

II. THERMODYNAMICS

It will prove helpful to review some of the standard thermodynamic results for spherical drops.[1-3] Consider a large spherical drop in the interior of a fixed volume V containing N particles at an overall temperature T and chemical potential μ. The conformation of the drop is fixed by N, V, etc.; however, on a microscopic level the density profile varies smoothly across the interface, and so the "radius" of the drop is only defined geometrically to within a distance of order the interfacial width and must, therefore, be fixed by convention. The usual approach is to introduce a spherical Gibbs dividing surface with a radius R which is deemed to separate the bulk phase within the drop from the external phase. The surface tension and other properties are defined with respect to the particular dividing surface chosen. For example, the surface tension

for the drop σ can be defined through the total Helmholtz free energy

$$F = -p^{\alpha}V^{\alpha} - p^{\beta}V^{\beta} + \mu N + 4\pi R^2 \sigma[R] , \qquad (2.1)$$

where p^{α}, p^{β} and V^{α}, V^{β} ($V^{\alpha} + V^{\beta} = V$) denote the pressures and volumes of the two bulk phases. The dividing surface is introduced strictly for computational convenience, and observable physical quantities such as F, p^{α}, p^{β}, and μ must be independent of its placement (for fixed N, V, and T). If these variables are to be independent of R, it is clear from (2.1) that the value of the surface tension must depend on the choice of the dividing surface. This dependence is normally denoted $\sigma[R]$, where the square brackets are used to stress that the variation of R is just that of the radius of the Gibbs surface and does not correspond to a change in the size of the physical drop.

Suppose we choose for reference that particular dividing surface (the "surface of tension") which makes the Laplace equation exact (α is the interior phase):

$$\Delta p = p^{\alpha} - p^{\beta} = \frac{2\sigma[R_s]}{R_s} . \qquad (2.2)$$

We are certainly free to hypothesize that, for large drops,[11]

$$\sigma_s \equiv \sigma[R_s] = \sigma_{\infty} \left[1 - \frac{2\delta}{R_s} + \frac{a}{R_s^2} + \cdots \right] , \qquad (2.3)$$

where σ_{∞} is the planar surface tension. The thermodynamic analysis[2,12] now allows us to make two statements. The first is that, for fixed N, V, and T (i.e., fixed R_s), $\sigma[R]$ has a minimum at R_s with

$$\sigma[R] = \sigma_s \left[1 + O\left[\left[\frac{R - R_s}{R_s} \right]^2 \right] \right] , \qquad (2.4)$$

so that, when R differs from R_s by a small distance such as the interfacial width, $\sigma[R]$ differs from σ_s by order $1/R_s^2$. This means that δ (but not, for example, the coefficient[11] a) should be independent of the choice of R. The second thermodynamic statement relates δ to the separation in the planar limit between the surface of tension R_s and the equimolar dividing surface R_e,[13]

$$\delta = \lim_{R_s \to \infty} (R_e - R_s) \equiv z_e - z_s . \qquad (2.5)$$

Here, the z axis is taken perpendicular to the interface, with positive z pointing away from the center of curvature. Assuming that the limit exists, Eq. (2.5) demonstrates explicitly the convention-independence of δ.

We note in passing that some doubts have been expressed about relation (2.5) and the quantities it contains. The issue is that certain quasithermodynamic arguments[14,15] have lead to apparent ambiguity in the evaluation of z_s, which would then infect δ via Eq. (2.5). Rowlinson and Widom[14] argue that the difficulty probably lies, not with the thermodynamic result, but rather with the mechanical definition used for z_s, which differs from Eq. (2.2). Recent numerical mean-field results for the penetrable sphere model[16] find consistent values of δ from (2.3) and (2.5) and tend to confirm this view. In the next section we calculate δ from (2.3) and, independently, z_e and z_s, all within the context of Landau theory. We find that the equality (2.5) is satisfied. Hence, within the approximations of Landau theory, there seems no reason to doubt the validity of (2.5) or the existence of the limit on which it rests.

III. LANDAU THEORY

A. General

In Landau theory one assumes the existence of a Helmholtz free-energy functional of the form

$$F[\rho(\vec{r})] = \int d^3r [m(\vec{\nabla}\rho)^2 + \tilde{f}(\rho)] , \qquad (3.1)$$

where $\rho(\vec{r})$ is the single-particle density. The Helmholtz free energy per unit volume for a fluid constrained to have uniform density ρ is denoted $\tilde{f}(\rho)$ and below criticality is assumed to have the usual double-well structure. The temperature dependence enters through m and $\tilde{f}(\rho)$. In the canonical prescription used here one must perform a functional minimization of F over $\rho(\vec{r})$ under the constraint that the total number of particles is fixed. This yields an equilibrium density profile and the corresponding Helmholtz free energy. With the free energy F in hand, one may use (2.1) to determine the surface tension.

Before using (3.1) to describe equilibrium spherical droplets, we briefly discuss the appropriate statistical ensemble needed to insure the formation of an equilibrium drop. In most problems in statistical mechanics the grand ensemble and the canonical ensemble give identical results; however, when dealing with two-phase coexistence, this is no longer true. As noted by Weeks[17,18] in his discussion of planar interfaces, the canonical ensemble is both more practical and more natural than the grand-canonical ensemble. Indeed, when a physical system is in contact with a particle bath of chemical potential μ, a stable equilibrium droplet will not form. The device of introducing a small gravitational field, often used when modeling a planar interface in the grand-canonical ensemble, has no convenient generalization for spherical drops. Even in the canonical ensemble it is impossible to stabilize a finite-size droplet in equilibrium after taking the thermodynamic limit. The free energy can always be reduced by spreading the excess density due to the droplet uniformly throughout space. In a system of finite volume with a fixed number of particles, however, one can have a spherical drop in stable equilibrium. It is important to realize that the difference between the two ensembles when discussing two-phase equilibria is not an artifact of statistical mechanics, but rather a reflection of the fact that the physics of a system in contact with a particle bath will indeed be different from that of one with fixed N.

In the canonical ensemble we look for solutions describing a spherically symmetric droplet which minimizes F while maintaining a fixed number of particles in the system. The method of Lagrange multipliers requires us to make stationary the functional

$$\Omega[\rho] = F[\rho] - \mu \int_V d^3r \, \rho(\vec{r}) , \qquad (3.2)$$

where μ is chosen so that the profile satisfies the canonical restriction. When the need arises, we shall assume the cell to be spherical in shape with $0 \leq |\vec{r}| \leq L$ and $V = (4\pi/3)L^3$. We require $L \gg R$ for all drops, so that the interface is always far from the cell boundary. Denoting the chemical potential required for formation of a planar interface between the two phases by μ_∞, and defining $f(\rho) \equiv \tilde{f}(\rho) - \rho\mu_\infty$ yields

$$\Omega[\rho] = \int d^3r [m(\vec{\nabla}\rho)^2 + f(\rho) - \Delta\mu\rho] , \qquad (3.3)$$

where $\Delta\mu = \mu - \mu_\infty$. The quantity

$$\omega(\rho) \equiv f(\rho) - \rho\,\Delta\mu \qquad (3.4)$$

is the grand free energy per unit volume, which for a uniform system equals the negative of the pressure. Assuming spherically symmetric solutions with the center of the droplet at the origin and setting $\delta\Omega/\delta\rho(r) = 0$ gives the Euler-Lagrange equation,

$$\rho''(r) + \frac{2\rho'(r)}{r} = \frac{1}{2m}\left[\frac{\partial f}{\partial\rho} - \Delta\mu\right] . \qquad (3.5)$$

To compute the free energy we must, in principle, solve for the density profile with appropriate boundary conditions and insert it into (3.1). Comparison of (3.1) with (2.1) then gives $\sigma[R]$, once the drop radius R has been related to $\Delta\mu$.

To find the curvature correction δ, it suffices to study large drops, which suggests treating $1/R$ as a small parameter. In this spirit we expand[19]

$$\rho(r) = \rho_0(r) + \frac{\rho_1(r)}{R} + \frac{\rho_2(r)}{R^2} + \cdots \qquad (3.6)$$

and

$$\Delta\mu = \frac{\Delta\mu_1}{R} + \frac{\Delta\mu_2}{R^2} + \cdots . \qquad (3.7)$$

The zero-order term $\rho_0(r)$ is the profile for an appropriately centered planar interface ($1/R = 0$). The zero-order term in $\Delta\mu$ vanishes, since Laplace's equation (2.2) shows that $\Delta p \sim 1/R \sim \Delta\mu$. Finally, we expect that, far from $r = R$ (the interface), $\rho(r)$ will be constant up to corrections of order $e^{-|r-R|/\xi}$. Thus, over the interesting region $r \sim R$ we may expand in the second term on the left-hand side of (3.5),

$$\frac{1}{r} = \frac{1}{R}\left[1 - \frac{r-R}{r} + \cdots\right] . \qquad (3.8)$$

Using Eqs. (3.6)–(3.8) in (3.5) and collecting powers of $1/R$, we find

$$\rho_0''(r) = \frac{1}{2m}\frac{\partial f}{\partial\rho_0} , \qquad (3.9)$$

$$\rho_1''(r) - \frac{1}{2m}\frac{\partial^2 f}{\partial\rho_0^2}\rho_1(r) = -2\rho_0'(r) - \frac{\Delta\mu_1}{2m} , \qquad (3.10)$$

$$\rho_2''(r) - \frac{1}{2m}\frac{\partial^2 f}{\partial\rho_0^2}\rho_2(r) = 2(r-R)\rho_0'(r) - 2\rho_1'(r)$$
$$+ \frac{1}{2m}\left[\frac{1}{2}\frac{\partial^3 f}{\partial\rho_0^3}[\rho_1(r)]^2 - \Delta\mu_2\right] . \qquad (3.11)$$

Notice that, although r is restricted in the original problem to $0 \leq r \leq L$, the functions $\rho_0(r)$, $\rho_1(r)$, and $\rho_2(r)$ have natural continuations to $-\infty < r < \infty$. In what follows we shall frequently use the extended boundaries $r \to \pm\infty$ in place of $r \to 0, L$, anticipating errors which are exponentially small for R and $L - R$ large.

Results for $R \to \infty$ follow directly from $\rho_0(r)$. Equation (3.9) shows that $m(\rho_0')^2 - f$ is independent of r. Substitution in (3.1) and comparison with the definition (2.1) gives the Landau-theory result for the planar surface tension,[20]

$$\sigma_\infty = 2m \int_{-\infty}^{\infty} dr [\rho_0'(r)]^2 . \qquad (3.12)$$

To obtain an expression for $\Delta\mu_1$, which is needed to compute δ, we multiply (3.10) by $\rho_0'(r)$ and integrate by parts twice to obtain

$$\int_{-\infty}^{\infty} dr\,\rho_1(r)\left[\frac{\partial^2}{\partial r^2} - \frac{1}{2m}\frac{\partial^2 f}{\partial\rho_0^2}\right]\rho_0'(r)$$
$$= -2\int_{-\infty}^{\infty} dr[\rho_0'(r)]^2 - \frac{\Delta\mu_1}{2m}\int_{-\infty}^{\infty} dr\,\rho_0'(r) . \qquad (3.13)$$

The contributions from the end points of integration vanish under the assumption that $\rho_1(\pm\infty)$ is finite. The left-hand side of (3.13) vanishes identically, since the bracketed part of the integrand is just the derivative of (3.9). Hence, using (3.12),

$$\Delta\mu_1 = -2\sigma_\infty \Big/ \int_{-\infty}^{\infty} dr\,\rho_0'(r) . \qquad (3.14)$$

Notice that a droplet of the dense phase has $\Delta\mu_1 > 0$, since $\rho_0'(r)$ is negative for all r; conversely, $\Delta\mu_1 < 0$ for a droplet of the less-dense phase.

Specializing to the case of an α-phase drop, we now express F in the form

$$F[\rho] = 4\pi \int_0^R dr\,r^2\{m[\rho'(r)]^2 + \omega(\rho) - \omega(\rho_\alpha)\}$$
$$+ 4\pi \int_R^L dr\,r^2\{m[\rho'(r)]^2 + \omega(\rho) - \omega(\rho_\beta)\}$$
$$+ V^\alpha\omega(\rho_\alpha) + V^\beta\omega(\rho_\beta) + \mu N , \qquad (3.15)$$

where $V^\alpha = \frac{4}{3}\pi R^3$, $V^\beta = \frac{4}{3}\pi(L^3 - R^3)$, and the integrands have been arranged to decay to zero far from the interface at $r = R$. The densities at the two minima of $\omega(\rho)$ [Eq. (3.4)] have been denoted ρ_α and ρ_β and satisfy $p^\alpha = -\omega(\rho_\alpha)$ and $p^\beta = -\omega(\rho_\beta)$. Comparison of (3.15) with (2.1) shows that the sum of the first two terms on the right-hand side must be identified with $4\pi R^2\sigma[R]$. In order to pick out δ, we now expand these terms in powers of $1/R$, using (3.6)–(3.8). We can then extend the limits of integration to $\pm\infty$, introducing an error which is only $O(e^{-R/\xi})$ and has no effect on the $1/R$ expansion.[19] The surface tension is finally found to be

$$\sigma[R] = \sigma_\infty\left[1 - \frac{2\delta}{R} + O(\xi^2/R^2) + O(e^{-R/\xi})\right] . \qquad (3.16)$$

σ_∞ is given by (3.11), and $\delta = I_1 + I_2 + I_3$ with

$$I_1 = -\frac{1}{2\sigma_\infty}\int_{-\infty}^{\infty} dr\left[\frac{\partial f}{\partial\rho_0}\rho_1(r) + 2m\rho_0'\rho_1'\right] , \qquad (3.17)$$

$$I_2 = \frac{\Delta\mu_1}{2\sigma_\infty} \left[\int_{-\infty}^{R} [\rho_0(r) - \rho_0(-\infty)]dr \right.$$

$$\left. + \int_{R}^{\infty} [\rho_0(r) - \rho_0(+\infty)]dr \right], \quad (3.18)$$

and

$$I_3 = -\int_{-\infty}^{\infty} dr(r-R)2m[\rho_0'(r)]^2/\sigma_\infty . \quad (3.19)$$

Expression I_1 is seen to vanish after integrating the second term by parts and using (3.9). Integrating I_2 by parts and using (3.14) for $\Delta\mu_1$ gives

$$I_2 = \frac{\int_{-\infty}^{\infty} dr(r-R)\rho_0'(r)}{\int_{-\infty}^{\infty} dr\rho_0'(r)} . \quad (3.20)$$

The apparent R dependence cancels between (3.19) and (3.20), and the result for δ reduces to Eq. (1.2), which is independent of choice of the Gibbs dividing surface, as expected from the thermodynamic arguments discussed in Sec. II.

Because of the controversy discussed in Sec. II, it is perhaps instructive to check directly, within Landau theory, the validity of the thermodynamic relation $\delta = z_e - z_s$ [Eq. (2.5)]. To this end we now obtain expressions for z_e and z_s. The equimolar dividing surface for a planar interface, z_e, is expressible in terms of the planar profile as

$$\int_{-\infty}^{z_e} dr[\rho_0(-\infty) - \rho_0(r)] = \int_{z_e}^{\infty} dr[\rho_0(r) - \rho_0(+\infty)] . \quad (3.21)$$

Integrating by parts on both sides and solving for z_e gives

$$z_e = \frac{\int_{-\infty}^{\infty} dr \, r\rho_0'(r)}{\int_{-\infty}^{\infty} dr \, \rho_0'(r)} . \quad (3.22)$$

To obtain an expression for z_s, the position of the surface of tension, we must compute the pressure difference Δp across the surface of the drop as a function of R and then choose the special radius R_s which satisfies (2.2). The analysis, presented in the Appendix, yields

$$\Delta p = \frac{2\sigma_\infty}{R} \left[1 + \frac{1}{R} \left[\frac{\int_{-\infty}^{\infty} dr(r-R)[\rho_0'(r)]^2}{\int_{-\infty}^{\infty} dr[\rho_0'(r)]^2} - \frac{2\int_{-\infty}^{\infty} dr(r-R)\rho_0'(r)}{\int_{-\infty}^{\infty} dr\rho_0'(r)} \right] + O(\xi^2/R^2) \right] . \quad (3.23)$$

Upon using (3.16) this can be rewritten,

$$\Delta p = \frac{2\sigma[R]}{R} - \frac{2\sigma_\infty}{R^2} \frac{\int_{-\infty}^{\infty} dr(r-R)[\rho_0'(r)]^2}{\int_{-\infty}^{\infty} dr[\rho_0'(r)]^2} + O(1/R^3) . \quad (3.24)$$

The radius R is then chosen such that the second term on the right-hand side vanishes, giving

$$R_s = \frac{\int_{-\infty}^{\infty} dr \, r[\rho_0'(r)]^2}{\int_{-\infty}^{\infty} dr[\rho_0'(r)]^2} + O(1/R_s) , \quad (3.25)$$

or, in the planar limit,

$$z_s = \frac{\int_{-\infty}^{\infty} dr \, r[\rho_0'(r)]^2}{\int_{-\infty}^{\infty} dr[\rho_0'(r)]^2} . \quad (3.26)$$

Using (3.22) and (3.26), we see immediately that the ther-

modynamic expression (2.5) reproduces our original result (1.2). This confirms within Landau theory the consistency of the thermodynamic results and gives us confidence in their more general validity.

It is shown in the Appendix that δ, given by (1.2), can alternatively be written

$$\delta = -\frac{2m}{\sigma_\infty} \int_0^\infty dr \, \rho_0'(r)\rho_1'(r) . \quad (3.27)$$

Upon insertion into (3.16), this gives

$$\sigma = 2m \int_0^\infty dr[\rho'(r)]^2 + O(\xi^2/R^2) , \quad (3.28)$$

where

$$\rho(r) = \rho_0(r) + \rho_1(r)/R + \cdots .$$

It is instructive to compare (3.28) with an exact expression for the interfacial tension of a curved interface recently derived by Hemingway et al.,[16] namely

$$\sigma = \frac{\pi kT}{2} \int_0^\infty dr_1 \int_0^\infty dr_2 \rho'(r_1)\rho'(r_2) \int_{|r_1-r_2|}^\infty dr_{12}r_{12}[r_{12}^2 - (r_1-r_2)^2]C(r_{12},r_1,r_2) + O(\sigma_\infty(r_0/R)^2) , \quad (3.29)$$

where $C(r_{12},r_1,r_2)$ is the direct correlation function for two points at radii r_1 and r_2 with respect to the center of the drop and at a separation r_{12}. In the error term, r_0 denotes the range of the direct correlation function. If we approximate (3.29) with a local kernel (precisely as done by Rowlinson and Widom[1] on the exact expression for the planar surface tension), it indeed reduces to the form (3.28) with m given, as in the planar theory, by the expression

$$m(\rho) = \frac{kT}{12} \int d^3r \, r^2 C(r;\rho) . \quad (3.30)$$

In the next section, (1.2) is used to determine the sign, magnitude, and, in particular, the critical temperature dependence of δ.

B. Critical properties

When studying critical behavior within the square-gradient Landau theory (3.1), it is usually argued that, as $T \rightarrow T_c^-$, it is sufficient to keep only quadratic and quartic terms in the expansion of $f(\rho)$ about the critical density ρ_c. Such a quartic double well satisfies

$$f(\rho - \rho_c) = f(-\rho + \rho_c) \tag{3.31}$$

and, hence, describes a two-phase system which is symmetric under interchange of phase. We now show that the presence of the special symmetry (3.31) causes δ to vanish identically within Landau theory. This symmetry manifests itself in the planar interfacial density profile as

$$\rho_0(z) = -\rho_0(2z_e - z) + \rho_0(+\infty) \quad \rho_0(-\infty) , \tag{3.32}$$

and so, consequently,

$$\rho_0'(z) = \rho_0'(2z_e - z) . \tag{3.33}$$

Inserting (3.33) into (1.2) and changing variables $z \to z' = 2z_e - z$ gives

$$\delta = -\frac{\int dz (z - 2z_e)\rho_0'(z)}{\int dz \rho_0'(z)} + \frac{\int dz (z - 2z_e)[\rho_0'(z)]^2}{\int dz [\rho_0'(z)]^2} . \tag{3.34}$$

The two terms containing z_e cancel, giving $\delta = -\delta$, i.e., $\delta = 0$. Real liquid-vapor systems do not, in general, possess the special symmetry (3.31). Consequently, a correct theory of δ near the critical point must include odd powers of $\rho - \rho_c$. It will be instructive to formulate such a theory here and to develop its consequences within Landau theory. This will set the stage for the scaling hypothesis of Sec. IV. Let us consider expanding the Helmholtz free-energy density about the critical density ρ_c and temperature T_c,

$$\tilde{f}(\tilde{\rho}, t) = \sum_{j=0}^{\infty} u_j(t)\tilde{\rho}^j \tag{3.35}$$

and

$$u_j(t) = u_j^0 + u_j^1 t + O(t^2) , \tag{3.36}$$

where $\tilde{\rho} = (\rho - \rho_c)/\rho_c$ and $t = (T - T_c)/T_c$. We shall require

$$u_2^0 = u_3^0 = 0, \quad u_2^1 > 0, \quad u_4^0 > 0 , \tag{3.37}$$

in order that the function $f = \tilde{f} - \mu_\infty \rho$ should have a unique minimum at $\tilde{\rho} = 0$ for $t = 0$ and exhibit the characteristic single- (double-) well form for $t > 0$ (<0). A simple linear shift in $\tilde{\rho}$,

$$\tilde{\rho} \to \tilde{\rho}' \equiv \tilde{\rho} - \frac{u_3^1}{4u_4^0} t + O(t^2) , \tag{3.38}$$

eliminates the cubic term in (3.35) and leaves all the other coefficients unchanged to leading order in t; hence, we may take $u_3 = 0$ without loss of generality. It is crucial, however, to include $u_5 \neq 0$, which is the leading odd-order term.

To obtain a planar interface we must choose the chemical potential such that the double well of $f = \tilde{f} - \mu \tilde{\rho}$ has both minima at the same depth (i.e., $\mu = \mu_\infty$). If

$$\mu_\infty = u_1(t) + u_5^0 \left[\frac{u_2^1}{2u_4^0} \right]^2 t^2 , \tag{3.39}$$

then $f(\tilde{\rho}, t)$ has two minima at

$$\tilde{\rho}^\pm = \pm \left[\frac{u_2^1}{2u_4^0} \right]^{1/2} (-t)^{1/2} + \frac{1}{4} \frac{u_5^0 u_2^1}{(u_4^0)^2} t + O(t^{3/2}) , \tag{3.40}$$

with

$$f(\tilde{\rho}^+, t) = f(\tilde{\rho}^-, t) + O(t^3) . \tag{3.41}$$

The change of variables,

$$\phi(z) = [\tilde{\rho}(z) - (\tilde{\rho}^+ + \tilde{\rho}^-)/2]/[(\tilde{\rho}^+ - \tilde{\rho}^-)/2] , \tag{3.42}$$

allows f to be factored,

$$f(\phi) = A + B(1 + \lambda\phi)(\phi^2 - 1)^2 + O(t^3) , \tag{3.43}$$

where A is a constant,

$$\lambda = u_5^0 \Delta\tilde{\rho}/u_4^0 , \tag{3.44}$$

$$B = u_4^0(\Delta\tilde{\rho})^4 , \tag{3.45}$$

and

$$\Delta\tilde{\rho} = [u_2^1/(2u_4^0)]^{1/2}(-t)^{1/2} . \tag{3.46}$$

This expresses $f(\phi)$ as a symmetric quartic well multiplied by a small asymmetric correction. It is precisely this small asymmetry which determines the sign and temperature dependence of δ near criticality.

To determine the planar interfacial density profile $\rho_0(z)$, we use the Euler equation (3.9), which in terms of $\phi(z)$ is given by

$$\phi''(z) = \frac{1}{2m (\rho_c \Delta\tilde{\rho})^2} \frac{\partial f}{\partial \phi} . \tag{3.47}$$

Multiplying by $\phi'(z)$ and integrating gives

$$[\phi'(z)]^2 = \frac{1}{\xi^2}(1 + \lambda\phi)(\phi^2 - 1)^2 , \tag{3.48}$$

where ξ is the Landau-theory correlation length,

$$\xi = \rho_c \left[\frac{2m}{u_2^1} \right]^{1/2} (-t)^{-1/2}, \quad t < 0 . \tag{3.49}$$

Since λ is of the order $t^{1/2}$, we solve (3.48) perturbatively, as an expansion in small λ. Introducing

$$\phi(z) = \phi_0(z) + \lambda\phi_1(z) + O(\lambda^2) \tag{3.50}$$

into (3.48) and comparing powers of λ gives

$$[\phi_0'(z)]^2 = \frac{1}{\xi^2}\{[\phi_0(z)]^2 - 1\}^2 \tag{3.51}$$

and

$$\phi_1'(z) - \left[\frac{2\phi_0\phi_0'}{\xi(\phi_0^2 - 1)} \right] \phi_1(z) = \frac{\phi_0\phi_0'}{2} . \tag{3.52}$$

Specializing to the dense droplet, whose planar limit has ϕ' negative, we find the analytic solutions

$$\phi_0(z) = -\tanh(z/\xi) \tag{3.53}$$

and

$$\phi_1(z) = \frac{\ln\cosh(z/\xi)}{2\cosh^2(z/\xi)} + \frac{k}{\cosh^2(z/\xi)} , \tag{3.54}$$

where k is a constant of integration. Since $\rho'(z)=(\rho_c\Delta\bar{\rho})\phi'(z)$, the $\rho'(z)$ appearing in expression (1.2) for δ can be replaced directly by $\phi'(z)$. Substituting the expansion for $\phi(z)$ into (1.2) and rescaling $z\rightarrow\xi z$ gives, for the denser phase drop,

$$\delta=\frac{5}{24}\left[\frac{u_2^1}{2(u_4^0)^3}\right]^{1/2}u_5^0\,|\,t\,|^{1/2}\xi+O(\,|\,t\,|\,\xi)\;. \qquad (3.55)$$

For a droplet of the less-dense phase, δ would take the same form but with opposite sign. Note for future reference that (3.55) is linear in both u_5^0 and ξ. Eliminating ξ using (3.49) gives, finally,

$$\delta=[(\tfrac{5}{24})\rho_c m^{1/2}(u_4^0)^{-3/2}]u_5^0,\quad t\rightarrow0^-\;. \qquad (3.56)$$

As the critical point is approached, δ tends to a finite nonzero value. Near criticality, the sign of δ is determined solely by the sign of u_5^0, the coefficient of the fifth-order term in the free-energy expansion.

We may compute a rough magnitude for δ at criticality by obtaining $\tilde{f}(\rho)$ from a Van der Waals theory.[21] The partition function for N classical particles is computed by treating the long-range intermolecular attraction in mean-field theory and approximating the hard-sphere configurational integral as an ideal gas with excluded volume Nb ($b=2\pi a^3/3$ with a the hard-sphere radius). The well-known result for the Helmholtz free-energy density is[21]

$$\tilde{f}(\rho)=\rho T\left[\ln\left[\frac{\rho\Lambda^3}{1-\rho b}\right]-1\right]-\rho^2\epsilon\;, \qquad (3.57)$$

where $\epsilon=2\pi\int_a^\infty dr\,r^2u(r)$ measures the strength of the attractive tail, and Λ is the thermal de Broglie wavelength. From this we deduce a critical density $\rho_c=(3b)^{-1}$ and a critical temperature $T_c=\frac{8}{27}(a/b)$. Expanding in a power series in $\tilde{\rho}$ leads to $u_4^0=\frac{1}{3}(a/b^2)$ and $u_5^0=-\frac{1}{3}(a/b^2)$. Inserting these expressions into (3.56) gives, for a dense-phase drop,

$$\delta\approx-0.02(r_0^5/a^3)^{1/2}\;, \qquad (3.58)$$

where m, defined in (3.30), has been approximated by $m\sim\frac{1}{10}r_0^5(a/b)$, with r_0 the range of the direct correlation function. Since $r_0\approx a$, δ within Van der Waals theory is negative and somewhat smaller than a hard-sphere radius. Of course, the magnitude of this number is irrelevant for real three-dimensional drops, where the critical behavior will differ from that found in Landau theory (see Sec. IV).

Notice, finally, that in addition to asymmetric terms in f (characterized by the coefficients u_3, u_5, etc.), asymmetry may also be introduced into the gradient term, via contributions such as $\bar{\rho}(\vec{\nabla}\bar{\rho})^2$. Landau-theory treatment of such gradient coupling would take us beyond the context of the free-energy functional (3.1) and therefore requires modification of the expression (1.2) for δ. Near criticality, it can be shown[22] that such a term produces, via a field-mixing[9] mechanism, an additional additive contribution to δ, which, like (3.56), goes to a constant as $t\rightarrow0^-$. We shall discuss this term further in Sec. IV B.

IV. BEYOND LANDAU THEORY

A. Symmetry considerations

In order to go beyond Landau theory, including fluctuations which are certainly important in three dimensions, we must show that the vanishing of δ for symmetric two-phase systems is a general result, not merely an artifact of Landau theory. The argument rests on the thermodynamic relation (2.5), linking δ to the separation between the equimolar dividing surface and the surface of tension. Imagine a planar interface separating two fluid phases α and β, which as yet have no special symmetry property (Fig. 1). In writing (2.5) we have already accepted the proposition that the positions z_e and z_s are well defined in the planar limit. z_e and z_s denote, respectively, the positons of the equimolar dividing surface and the surface of tension, as they intersect the z axis. The additional assumption here is that z_e and z_s vary *continuously* as the system moves smoothly between configurations A and C in Fig. 1, passing through the planar configuration B. For a system which is symmetric under phase interchange $\alpha\leftrightarrow\beta$ [e.g., (3.31)],

$$(z_e-z_s)_A=-(z_e-z_s)_C\;, \qquad (4.1)$$

where subscripts refer to the configurations shown in Fig. 1. In the limit $R_0\rightarrow\infty$, configurations A and C become planar and indistinguishable, and so, assuming continuity, Eq. (4.2) gives $\delta=0$. Of course, the argument fails if the limit (2.5) does not exist or if z_s jumps discontinuously from one side of z_e to the other in passing through configuration B. This symmetry property of the curvature correction does not appear to have been previously noted in the literature.[23]

B. Scaling of δ near criticality: asymmetry and field mixing

In $d=3$ (bulk) and more generally for $d<d^*=4$ (the upper critical dimension) fluctuations near criticality cannot be ignored and, in fact, are expected to modify the results of the Landau-theory analysis. Rigorous treatment awaits a full ϵ-expansion analysis of δ or some other nonperturbative treatment. We content ourselves here with formulation of a scaling hypothesis for the singular behavior of δ near criticality.
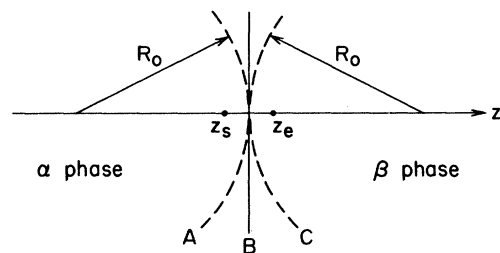

FIG. 1. Plane B is an interface between α and β phases. z_e and z_s denote, respectively, the positions of the equimolar dividing surface and the surface of tension, as they intersect the z axis. When the system is symmetric under phase interchange $\alpha\leftrightarrow\beta$, then $z_e=z_s$ in the planar limit by the continuity argument given in the text.

Landau theory suggests that there are two terms to consider: (a) the contributions (3.55) and (3.56), which arose from the *asymmetry* of the local free-energy density and which we now denote δ_a, and (b) the contribution arising from perturbations of the form $\tilde{\rho}(\vec{\nabla}\tilde{\rho})^2$ (as mentioned at the end of Sec. III), which we now call *field-mixing* effects and denote δ_f. Both δ_a and δ_f are constant at criticality within Landau theory; however, when fluctuations are included $(d < d^*)$, there are two separate effects, which scale differently.[24] What happens is that the three most important asymmetric perturbations, $\tilde{\rho}^3$, $\tilde{\rho}^5$, and $\tilde{\rho}(\vec{\nabla}\tilde{\rho})^2$, get mixed for $d < d^*$ in the formation of the odd eigenoperators. One of the resulting linear combinations (the analog of $u_3^0\tilde{\rho}^3$ in Landau theory) can be eliminated at the Hamiltonian level by a simple shift analogous to (3.38). A second [the analog of $\tilde{\rho}(\vec{\nabla}\tilde{\rho})^2$ in Landau theory] can also be eliminated to leading order, but only at the expense of a skewing of the (bulk) temperature (t) and chemical-potential $(\Delta\mu)$ directions. This "field-mixing" effect is well known in the discussion of bulk properties such as the asymmetry in the coexistence-curve diameter[25] and in that context has been treated in detail by Nicoll.[9] Inclusion of field mixing leads to a term in the curvature correction,[22]

$$\delta_f \sim |t|^{1-\alpha-\beta-\nu} \text{ as } t \to 0^-, \tag{4.2}$$

which involves the relevant (in the renormalization-group sense) bulk exponents only. The remaining (third) eigenoperator $\overline{O}_5$ cannot be eliminated by a rewriting of the Hamiltonian. $\overline{O}_5$ is irrelevant at bulk criticality and associated[9,26] with a corresponding scaling field $\bar{u}_5$, eigenvalue exponent λ_5, and correction-to-scaling exponent $\theta_5 = -\lambda_5\nu$. $\overline{O}_5$ is the leading source of true, non-Ising asymmetry in the problem, and its contribution to the curvature correction is the term δ_a. The scaling field $\bar{u}_5$ reduces to u_5^0 as $d \to d^*$ from below and enters into thermodynamic functions in the scaling combination $\bar{u}_5|t|^{\theta_5}$. With this background we are in a position to propose a scaling hypothesis which generalizes (3.55) in the presence of fluctuations. Our proposal is that[27]

$$\delta_a \sim \xi W(\bar{u}_5|t|^{\theta_5}), \tag{4.3}$$

with a scaling function $W(x)$ which varies linearly with x, as $x \to 0$, so that

$$\delta_a \sim \bar{u}_5|t|^{\theta_5-\nu} \text{ as } t \to 0^-. \tag{4.4}$$

The rationale for Eq. (4.3) is that δ_a (which is dimensionally a length) should scale as ξ, which is the only relevant length near criticality, but must vanish linearly with the asymmetry parameter $\bar{u}_5$ in accordance with the symmetry considerations of Sec. IV A. $\overline{O}_5$ is irrelevant, and so the effect of asymmetry shrinks as $t \to 0^-$ via the scaling combination $\bar{u}_5|t|^{\theta_5}$.

For $d > d^*$, $\alpha = 0$, $\beta = \frac{1}{2}$, $\nu = \frac{1}{2}$, and[28] $\theta_5 = \frac{1}{2}$, so that both (4.2) and (4.4) are constant at criticality in agreement with Landau theory. For $d = 3$, the bulk exponents are quite accurately known, and $1-\alpha-\beta-\nu \simeq -0.06$, indicating a weak divergence at criticality. On the other hand, for $d < 4$ we know of no analytic work on θ_5 beyond the ϵ-expansion $(\epsilon = 4-d)$, which gives[10]

$$\theta_5 = \frac{1}{2} + \epsilon - \frac{31}{36}\epsilon^2 + (3.20\ldots)\epsilon^3 + O(\epsilon^4). \tag{4.5}$$

The oscillatory behavior of this expansion makes it extremely difficult to obtain a reliable estimate for θ_5 for $d = 3$. If we take $\epsilon = 1$ in (4.5), the sequence of approximations at $O(\epsilon)$, $O(\epsilon^2)$, and $O(\epsilon^3)$ are, respectively, 1.5, 0.64, and 3.84. A simple (1,1) Padé approximant, on the other hand, gives 1.04, while (2,1) and (1,2) Padé approximants give 1.32 and 2.36. These numbers tend to suggest that for $d = 3$, $\theta_5 - \nu$ is positive; however, even the sign of $\theta_5 - \nu$ cannot be reliably determined.

In view of the uncertainty of θ_5, it is not clear which contribution to $\delta(T) = \delta_f(T) + \delta_a(T)$ will be dominant near criticality. Rowlinson[29] has reported a temperature dependence of the form (4.2) for the penetrable-sphere model. Contributions like (4.4) were not found; however, it seems likely that $\bar{u}_5 = 0$ because of the special symmetry of this model. We can, in any case, predict with some confidence that $\delta(T)$ will diverge at T_c. Perhaps this will encourage experimental interest in its measurement. Observation of a divergence stronger than (4.2) would demonstrate the dominance of δ_a and provide an experimental determination of θ_5 (which has not been possible up to now). If, on the other hand, observation confirms (4.4), then δ_f is dominant and the bound $\theta_5 \geq 1-\alpha-\beta$ is established.

APPENDIX

In this appendix an expression for the pressure difference Δp across the interface between a dense-phase droplet and the external phase is derived which to $O(\xi^3/R^3)$ depends only on the planar profile $\rho_0(r)$. Because $\omega(\rho) = -p$ in a uniform phase [see (3.4)],

$$\Delta p = \omega(\rho_\alpha) - \omega(\rho_\beta), \tag{A1}$$

where ρ_α and ρ_β are the densities at the two minima of $\omega(\rho)$. Expanding in inverse powers of R gives

$$\Delta p = \frac{1}{R}\left[\Delta\mu_1 + \frac{\Delta\mu_2}{R}\right](\rho_l - \rho_v)$$
$$+ \frac{(\Delta\mu_1)^2}{2R^2}\left[\frac{1}{K_l} - \frac{1}{K_v}\right] + O(1/R^3), \tag{A2}$$

with

$$K_{l\,(v)} = \frac{\partial^2 f}{\partial\rho^2}\bigg|_{\rho=\rho_{l\,(v)}}, \tag{A3}$$

where the densities at the two minima of $f(\rho)$ are denoted ρ_v and ρ_l. Recall that we obtained an expression for $\Delta\mu_1$ in terms of $\rho_0(r)$ by analyzing (3.10). Likewise, to relate $\Delta\mu_2$ to the profile, we study (3.11). Multiplying (3.11) by $\rho_0'(r)$ and integrating by parts twice on the first term gives

$$\int_{-\infty}^{\infty} dr\, \rho_2(r) \left[\frac{\partial^2}{\partial r^2} - \frac{1}{2m}\frac{\partial^2 f}{\partial \rho_0^2} \right] \rho_0'(r)$$

$$= 2\int_{-\infty}^{\infty} dr\, [(r-R)\rho_0'^2 - \rho_0'\rho_1']$$

$$+ \frac{1}{4m}\int_{-\infty}^{\infty} dr\, \rho_0' \frac{\partial^3 f}{\partial \rho_0^3}\rho_1^2 - \frac{\Delta\mu_2}{2m}(\rho_v - \rho_l) . \quad (A4)$$

The left-hand side vanishes by the same argument used after (3.13). The second term on the right-hand side can be rewritten and integrated by parts to give

$$\int_{-\infty}^{\infty} dr\, \frac{\partial}{\partial r}\left[\frac{\partial^2 f}{\partial \rho_0^2} \right]\rho_1^2 = \frac{\partial^2 f}{\partial \rho_0^2}\rho_1^2 \bigg|_{-\infty}^{+\infty} - 2\int_{-\infty}^{\infty} dr\, \frac{\partial^2 f}{\partial \rho_0^2}\rho_1\rho_1' , \quad (A5)$$

which, when inserted into (A4), yields

$$\Delta\mu_2(\rho_l - \rho_v) = 4m\int_{-\infty}^{\infty} dr\, [(r-R)(\rho_0')^2 - \rho_0'\rho_1']$$

$$+ \tfrac{1}{2}\{K_v[\rho_1(+\infty)]^2 - K_l[\rho_1(-\infty)]^2\}$$

$$- \int_{-\infty}^{\infty} dr\, \frac{\partial^2 f}{\partial \rho_0^2}\rho_1\rho_1' . \quad (A6)$$

To eliminate the explicit dependence on f, we multiply (3.10) by ρ_1' and integrate to obtain

$$\int_{-\infty}^{\infty} dr\, \frac{\partial^2 f}{\partial \rho_0^2}\rho_1\rho_1' = 4m\int_{-\infty}^{\infty} dr\, \rho_0'\rho_1'$$

$$+ \Delta\mu_1[\rho_1(+\infty) - \rho_1(-\infty)] , \quad (A7)$$

which can be used to eliminate the last term in (A6). After replacing $\rho_1(+\infty)$ by $\Delta\mu_1/K_v$ and $\rho_1(-\infty)$ by $\Delta\mu_1/K_l$ [which can be deduced from (3.10)] in (A6) and (A7), we find

$$\Delta\mu_2(\rho_v - \rho_l) = 4m\int_{-\infty}^{\infty} dr\, [(r-R)(\rho_0')^2 - 2\rho_0'\rho_1']$$

$$- \tfrac{1}{2}(\Delta\mu_1)^2\left[\frac{1}{K_v} - \frac{1}{K_l} \right] . \quad (A8)$$

Use of (A8) to eliminate $\Delta\mu_2$ from (A2) gives, for the pressure difference,

$$\Delta p = \frac{\Delta\mu_1(\rho_l - \rho_v)}{R}$$

$$- \frac{1}{R^2}\left[4m\int_{-\infty}^{\infty} dr\, [(r-R)(\rho_0')^2 - 2\rho_0'\rho_1'] \right]$$

$$+ O(1/R^3) . \quad (A9)$$

The final step is to eliminate all dependence on $\rho_1(r)$. Integrating by parts, we find

$$\int_{-\infty}^{\infty} dr\, \rho_0'\rho_1' = -\int_{-\infty}^{\infty} dr\, r\,(\rho_0''\rho_1' + \rho_0'\rho_1'') , \quad (A10)$$

which can be rewritten using (3.9) and (3.10) as

$$\int_{-\infty}^{\infty} dr\, \rho_0'\rho_1' = 2\int_{-\infty}^{\infty} dr\, r\,(\rho_0')^2$$

$$+ \int_{-\infty}^{\infty} dr\, \rho_0''\rho_1 + \frac{\Delta\mu_1}{2m}\int_{-\infty}^{\infty} dr\, r\rho_0' . \quad (A11)$$

The second term, after a partial integration, can be combined with the left-hand side, and, after eliminating $\Delta\mu_1$ with (3.14), finally yields

$$\int_{-\infty}^{\infty} dr\, \rho_0'\rho_1' = \frac{-\delta}{2m}\sigma_\infty , \quad (A12)$$

where σ_∞ and δ are defined in terms of $\rho_0(r)$ in (3.12) and (1.2), respectively. Substituting (A12) into (A9) gives the desired formula for the pressure difference, namely,

$$\Delta p = \frac{2\sigma_\infty}{R}\left[1 + \frac{1}{R}\left[\frac{\int_{-\infty}^{\infty} dr\,(r-R)(\rho_0')^2}{\int_{-\infty}^{\infty} dr\,(\rho_0')^2} \right.\right.$$

$$\left.\left. - \frac{2\int_{-\infty}^{\infty} dr\,(r-R)\rho_0'}{\int_{-\infty}^{\infty} dr\,\rho_0'} \right]\right] + O(1/R^3) . \quad (A13)$$

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[1]J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982). This excellent book contains extensive discussion and references to the literature.

[2]G. Navascues, Rep. Prog. Phys. **42**, 1131 (1979), and references contained therein.

[3]R. B. Griffiths, in *Phase Transitions in Surface Films*, edited by J. G. Dash and J. Ruvalds (Plenum, New York, 1972), p. 1.

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[8]In multicomponent systems, δ is not unique and the discussion requires modification. We thank J. S. Rowlinson for bringing this to our attention.

[9]J. F. Nicoll, Phys. Rev. A **24**, 2203 (1981); J. F. Nicoll and R. K. P. Zia, Phys. Rev. B **23**, 6157 (1981).

[10]F. C. Zhang and R. K. P. Zia, J. Phys. A **15**, 3303 (1982).

[11]The overall free energy F is believed to have the form ($d = 3$)

$$F = C_3 R^3 + C_2 R^2 + C_1 R + C_l \ln R + C_0 + \cdots ,$$

with appropriate coefficients. C_2 is associated with the surface tension and C_1 with the curvature correction. The presence of the logarithmic term has been discussed in a somewhat different context by M. E. Fisher [Physics (N.Y.) **3**, 255

(1967)] and N. J. Günther, D. A. Nicole, and D. J. Wallace [J. Phys. A <u>13</u>, 1755 (1980)]. Such a term has been demonstrated numerically by G. Jacucci *et al.* [(unpublished)]. Its existence suggests that a/R^2 corrections to surface tension are not meaningful.

[12]J. S. Rowlinson and B. Widom, in *Molecular Theory of Capillarity*, Ref. 1, p. 40.

[13]The equimolar dividing surface is the Gibbs surface that divides an N-particle system with two bulk phases having densities ρ_α and ρ_β into two volumes, denoted V^α and V^β, such that $N = \rho_\alpha V^\alpha + \rho_\beta V^\beta$.

[14]A general discussion is given in J. S. Rowlinson and B. Widom, in *Molecular Theory of Capillarity*, Ref. 1, Chap. 4. See particularly p. 113.

[15]P. Schofield and J. R. Henderson, Proc. R. Soc. London, Ser. A <u>379</u>, 231 (1982).

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[17]J. D. Weeks, J. Chem. Phys. <u>67</u>, 3106, (1977).

[18]Also see H. Furukawa and K. Binder, Phys. Rev. A <u>26</u>, 556 (1982).

[19]Here, as in Ref. 11, one may legitimately worry about the character of the expansion in the "small parameter" $1/R$. In Landau theory there is no evidence of problems at the order to which we work.

[20]J. S. Rowlinson and B. Widom, in *Molecular Theory of Capillarity*, Ref. 1, p. 56.

[21]G. Navascues, Rep. Prog. Phys. <u>42</u>, 1131 (1979), p. 1170.

[22]M. P. A. Fisher (unpublished).

[23]An analogous statement for the *unstable* drop has been noted in another context (Goldstone modes in vacuum decay) by Günther, Nicole, and Wallace (Ref. 11), in their discussion after Eq. (15a).

[24]There is a close parallel here with the theory of the asymmetry of the coexistence-curve diameter (Ref. 9) in which two terms $|t|^{1-\alpha}$ and $|t|^{\beta+\theta_5}$ occur.

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[26]See, for example, F. J. Wegner, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1976), Vol. 6, pp. 7ff.

[27]The assumption here is that the dominant asymmetric operator for the interface problem is the same as that of the bulk. This is plausible, but certainly not required.

[28]J. F. Nicoll, Phys. Lett. <u>76A</u>, 112 (1980).

[29]J. S. Rowlinson (private communication).