Intrinsic Structure of the Critical Liquid-Gas Interface

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A new theory is presented to determine the structure of the intrinsic density profile of the liquid-gas interface near the critical point. A nonlinear integral equation for this profile is derived and it is shown that a nontrivial solution branches off at the critical temperature. The scaling form and the asymptotic behavior of this solution are derived exactly: The wings of the intrinsic density profile decay exponentially with an exponent proportional to the inverse correlation length, confirming the conjectures of Widom.

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There is considerable modern work in the statistical thermodynamics and statistical mechanics of nonuniform systems,[1] and the foundation for much of this work has been van der Waals's theory[2] of the critical liquid-gas interface. However, this theory, as well as its various rederivations[3] or extensions,[4] is open to criticism at a fundamental level.[5]

A basic assumption of the van der Waals theory is that there exists an intrinsic structure of the interface definable without reference either to the actual interfacial area or to an external field such as gravity. According to the scaling ideas of Widom[6] the thickness of the critical intrinsic interface is proportional to the correlation length of the density fluctuations in either bulk liquid or gas phase. Other intrinsic interfacial structures which are not of this form have recently been proposed.[7]

The very idea of a density profile is contradicted by the capillary-wave model,[8,9] according to which the thickness of the interface of a d-dimensional fluid ($d \leq 3$) diverges at the thermodynamic limit as the external field (gravity) tends to zero.[9] In spite of these divergences induced by the capillary waves, it is nevertheless reasonable to believe that there is some structure of the interface which is an intrinsic property of the phase equilibrium: This intrinsic structure manifests itself, for example, in the surface tension, to which capillary waves contribute very little.[10]

This Letter describes a new microscopic approach to the problem of the structure of the critical liquid-gas interface. Contrary to the theory of van der Waals and its rederivations or extensions, no use is made here of the metastable and unstable portions of the Andrews-Thompson isotherm[11] or of the equivalent mean-field approximation[12]; moreover, no use is made of scaling and homogeneity conjectures[6,13] or of local thermodynamic[14] or local density[15] arguments.

We first derive a nonlinear integral equation for the structure of the intrinsic density profile near the critical point. This equation brings in the direct correlation functions of a uniform fluid, which are related to those of the bulk liquid and gas phases. We then show that for any value of the temperature, the associated linearized equation admits only the trivial solution describing a spatially uniform phase. It is therefore necessary to study the effect of the first nonlinear terms of the integral equation.

A study of the nonlinear equation shows that a nontrivial solution bifurcates, at the critical temperature, from the trivial solution. In the Ornstein-Zernike approximation for the direct correlation functions of the uniform fluid, both the scaling form and the asymptotic behavior of the intrinsic density profile can be derived analytically.

We now sketch the derivation of our results. To be consistent with the lattice-gas symmetry, the mean global density $\bar{\rho}$, which is fixed, is chosen to be equal to $\frac{1}{2}(\rho_L + \rho_G)$. It is convenient to introduce the dimensionless quantity $\Psi(z) \equiv [\rho(z) - \bar{\rho}]/\bar{\rho}$; Ψ vanishes when only one phase is present; and, provided $\bar{\rho}$ is equal to the critical density of the fluid, Ψ is small when liquid and gas coexist at a temperature T slightly below the critical temperature T_c. Considering the free energy F as a functional $F[\Psi]$ of Ψ, the latter can be expanded, in the critical region, in powers of Ψ. Making then $F[\Psi]$ extremal with respect to Ψ gives, up to terms in Ψ^3, our basic equation:

$$\Psi(z)=\bar{\rho}\int_{-\infty}^{+\infty}\mathcal{C}_2(z,z')\Psi(z')dz'-\tfrac{1}{3}\Psi^3(z)$$
$$+\tfrac{1}{6}\bar{\rho}^3\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\mathcal{C}_4(z,z',z'',z''')\Psi(z')\Psi(z'')\Psi(z''')dz'dz''dz'''. \tag{1}$$

The functions $\mathcal{C}_2$ and $\mathcal{C}_4$ are the two- and four-point direct correlation functions C_2 and C_4 of a uniform d-dimensional fluid of density $\bar{\rho}$, integrated over the transverse coordinates; e.g., $\mathcal{C}_2(z)=\int_{-\infty}^{+\infty}dx_1\int_{-\infty}^{+\infty}dx_2\cdots\int_{-\infty}^{+\infty}dx_{d-1}\,C_2(\underline{r})$, with $\underline{r}=(x_1,x_2,\ldots,x_{d-1},z)$. These functions are invariant under translations of all their arguments and vanish when the distance between any two of their arguments tends to infinity.[16] Terms even in Ψ do not appear in equation (1): Their presence would prevent Eq. (1) from admitting odd solutions Ψ consistent with the lattice-gas symmetry.

Equation (1) can also be derived from an exact relation[17] which links the one-point distribution function to the two-point direct correlation function.

No use is made of the loop of the Andrews-Thompson subcritical isotherm; but when the lattice-gas symmetry is taken into account and F is chosen to be, in the two-phase region, the convex linear combination of the free energies of the bulk phases, the function C_2 is expressible in terms of the direct correlation functions of the bulk phases and is identical to the one which is obtained by a smooth extension from the pure phase.

The intrinsic density profile is given by that solution Ψ of Eq. (1) which satisfies the two boundary conditions $\lim_{z\to\pm\infty}\Psi(z)=\mp(\rho_L-\rho_G)/(\rho_L+\rho_G)$. The linearization of Eq. (1) reads $\Psi(z)=\bar{\rho}(\mathcal{C}_2*\Psi)(z)$, where the asterisk denotes convolution. For $T\neq T_c$, this equation does not admit a nontrivial solution satisfying the boundary conditions. It is therefore necessary to take the nonlinear terms of Eq. (1) into account.

The unknown Ψ is now split into $w+h$, where $h(z)\equiv-\operatorname{sgn}(z)(\rho_L-\rho_G)/(\rho_L+\rho_G)$. $w(z)$ denotes the wings of the density profile; under the assumption that the temperature dependence of $\rho_L-\rho_G$ is given, w is then the unknown to be determined. We define the quantities

$$t=(T_c-T)^y,\quad \rho_L-\rho_G=\Lambda t^b,\quad 1-\bar{\rho}\hat{\mathcal{C}}_2(0)=At^c,$$
$$S=\int_{-\infty}^{+\infty}dz\,z^2\mathcal{C}_2(z),$$

with constants y, Λ, b, A, c, and $S>0$. The caret denotes the Fourier transform.

The next step is to define new unknowns u_t and a by $u_t(z)=t^{-a}w(z/t)$, with $a>0$. If one considers t small and assumes Ornstein-Zernike forms for $\mathcal{C}_2$ and $\mathcal{C}_4$, the nonlinear integral equation (1) for Ψ is turned into a nonlinear differential equation for u_t.[18] For $z>0$ this equation reads

$$\bar{\rho}\frac{S}{2}u_t''(z)=\left(\frac{\Lambda^2}{4\bar{\rho}^2}t^{2b-2}+At^{c-2}\right)u_t(z)-\left(\frac{\Lambda}{2\bar{\rho}}t^{a+b-2}\right)u_t^2(z)+(\tfrac{1}{3}t^{2a-2})u_t^3(z)$$
$$+\text{higher order terms in } t. \tag{2}$$

The details of the derivation will be given elsewhere. In the limit as $t\to0$ under the conditions $a=b=c/2=1$ which are the only ones appropriate for a nontrivial limiting equation and allow our bifurcation approach to be used, Eq. (2) becomes

$$\bar{\rho}(S/2)u_0''(z)=(\Lambda^2/4\bar{\rho}^2+A)u_0(z)-(\Lambda/2\bar{\rho})u_0^2(z)+\tfrac{1}{3}u_0^3(z). \tag{3}$$

For small values t the wings of the intrinsic profile are given by

$$w(z)=t^a u_0(tz). \tag{4}$$

The condition $a=b$ gives

$$t^a\sim\rho_L-\rho_G \tag{5}$$

with $a=1$; the condition $c/2=1$ gives

$$t\sim\xi^{-1}. \tag{6}$$

Result (6) follows from the fact that in the Ornstein-Zernike approximation $\gamma/2=\nu$, with γ and ν the critical exponents of the compressibility and the correlation length, respectively. Furthermore when β, the exponent of the order parameter $\rho_L-\rho_G$, assumes its classical value of $\frac{1}{2}$, Eqs. (5) and (6) show that ν is also equal to its classical value of $\frac{1}{2}$.

Now Eq. (3) admits the exact solution

$$u_0(z)=\frac{\delta K\exp(-\Gamma^{1/2}z)}{\delta-[\Lambda/2\bar{\rho}+K\exp(-\Gamma^{1/2}z)]^2}, \tag{7}$$

where

$$\delta = 24(\Lambda^2/4\bar{\rho}^2 + A),$$

$$K = \frac{2\bar{\rho}}{\Lambda}\left\{3\left[\frac{\delta}{12}\left(\frac{\delta}{3} - \frac{\Lambda^2}{\bar{\rho}^2}\right)\right]^{1/2} + \left(\frac{\Lambda^2}{\bar{\rho}^2} - \frac{\delta}{2}\right)\right\},$$

and

$$\Gamma = \delta/12\bar{\rho}S. \tag{8}$$

For $z > 0$, $u_0(z)$ is positive and monotone decreasing. Also $u_0(-z) = -u_0(z)$. Thus for $|z|$ large we get, combining Eqs. (4)–(7),

$$w(z) \sim (\rho_L - \rho_G)\,\mathrm{sgn}(z)\exp(-\Gamma^{1/2}|z|/\xi). \tag{9}$$

The results (4)–(9) confirm the equations proposed by Widom.

Some remarks are in order. Firstly, according to (9), the decay length of $w(z)$ is equal to the correlation length up to the temperature-independent factor, $\sqrt{\Gamma}$, which is not present in Ref. 13; moreover there is experimental uncertainty[19] as to whether the decay length of the wings of the critical profile is proportional to the correlation length rather than equal to it. Next, our results, which have been derived with use of the Ornstein-Zernike approximation for the direct correlation functions of the uniform fluid, are expected[13] not to be restricted to that approximation.

As regards the suppression of capillary waves in this theory, it may be mentioned that whereas the structure of the *global* interface of a d-dimensional fluid ($d \leq 3$) is generally believed to be washed out at the thermodynamic limit as the external field vanishes, yielding isotropic and nonclustering correlation functions, it is assumed here in (1) that the functions $\mathfrak{C}_k$ do vanish at infinity, giving rise through functional expansion to an anisotropic direct correlation function for the *intrinsic* profile which also vanishes at infinity. It is these assumptions which amount to suppression of the capillary waves in this theory.

Finally, with u_0 given by (7), the predicted profile (4) differs both from the classical hyperbolic-tangent profile implicit in van der Waals's work[2] and from the nonclassical profile which is obtained when in van der Waals's original derivation the mean-field equation of state is replaced by one that reproduces more accurately the known thermodynamic singularities at the critical point[13]; unfortunately neither the existing optical reflectivity measurements of Webb and his coworkers in binary mixtures of cyclohexane and methanol[20] and in sulphur hexafluoride,[21] together with their reinterpretation by Meunier,[22] nor the reflectivity and ellipsometry measurements of Beaglehole in the binary mixture of cyclohexane and aniline[23] can discriminate between the shapes of the density profile predicted here and those proposed in earlier works.[9,13] Webb (private communication) has suggested that absolute reflected- and scattered-power measurements can distinguish the capillary-wave model[8,9] from the present model and that of Ref. 13 but not between the latter two cases.

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