Scaling Relations between Correlations in the Liquid-Vapor Interface and the Interface Width

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Long-ranged density correlations, varying on the scale of the capillary length L_c, exist in the liquid-vapor interface in a weak gravitational field. A scaling hypothesis, similar to that made near the bulk critical point, predicts that in dimensions $d < 3$, the interface width $W \rightarrow \infty$ as $L_c \rightarrow \infty$. For $d > 3$, W can remain finite provided there is power-law decay of correlations for separations less than L_c. These results are consistent with capillary-wave theory.

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As first pointed out by Wertheim,[1] one can establish the existence of very long-ranged density correlations parallel to the planar interface of a liquid in equilibrium with its vapor in an (arbitrarily weak) gravitational field[2] $\phi_{ex}(z) = mgz$. The range of these correlations at very large horizontal separations is given by the *capillary length*

$$L_c = [\sigma / mg(\rho_l - \rho_v)]^{1/2}. \tag{1}$$

L_c is about 1 mm for argon at its triple point in earth normal gravity; in principle we can imagine the gravitational constant g arbitrarily small and hence L_c arbitrarily large.[3] Here σ is the surface tension, ρ_l and ρ_v are the number densities of the coexisting bulk liquid and vapor phases, and m is the particle's mass. We require always that $L_c >> \xi_B$, the bulk correlation length. These anomalous correlations exist only in the interfacial region, whose width W is determined by the approach of the density profile $\rho(z)$ to its limiting values ρ_l and ρ_v. For convenience we choose the chemical potential so that the Gibbs dividing surface is at the $z = 0$ plane.[3]

The behavior of the interface width W has been the subject of much discussion recently. Classical ideas,[3-5] generalized by Widom[3,4] to give relations between the critical behavior of the surface tension and bulk thermodynamic properties, assume the existence of an "intrinsic" profile whose width W is essentially independent of g as $g \rightarrow 0^+$. Wertheim made such an assumption in his discussion[1] of the long-ranged interface correlations. On the other hand, exact results for various lattice models in two and three dimensions[6,7] strongly suggest that no limiting profile should exist. Weeks[8] offered a resolution based on capillary-wave theory[9] for these two seemingly contradictory pictures but this too has been questioned.[3,5]

Here I show that very simple scaling ideas imply that there is an intimate connection between the nature of the long-ranged correlations and the behavior of the interface width that allows us to deduce new properties of each. If the scaling hypothesis is correct, then in bulk dimensions $d < 3$, the interface width W must itself diverge as $L_c \rightarrow \infty$: The existence of the long-ranged correlations *requires* the divergence of the interface width.

For $d > 3$, the interface width W can remain finite as $g \rightarrow 0^+$ in accord with the classical picture; in that case correlations parallel to the interface must decay as $r^{-(d-3)}$ for $r << L_c$. Here $\vec{r}$ is a $d-1$ dimensional vector in the interface "plane." As noted below, this behavior is completely consistent with the predictions of capillary-wave theory[8,9] and these results give additional support to the physical picture of the long-ranged interfacial correlations that it provides.[8]

The analysis begins from the definition in the grand ensemble of the pair correlation function of a fluid in an external field $\phi_{ex}(\vec{R})$ [10]:

$$H(\vec{R}_1, \vec{R}_2) = \delta\rho(\vec{R}_1)/\delta[\beta\mu - \beta\phi_{ex}(\vec{R}_2)]. \tag{2}$$

Here $\rho(\vec{R}_1)$ is the probability density for finding a particle at $\vec{R}_1$, μ is the chemical potential, and $\beta = (k_B T)^{-1}$ with T the temperature. Specializing to the case of an external field $\phi_{ex}(z)$ depending on z only, H has the form $H(z_1, z_2, r_{12})$, where $r_{12} = |\vec{r}_1 - \vec{r}_2|$, and $\vec{r}_i$ is the projection of $\vec{R}_i$ in the $(d-1)$-dimensional interface plane. Further, for an isotropic fluid a displaced field $\phi_{ex}(z+\epsilon)$ implies exactly the same displacement $\rho(z+\epsilon)$ in the singlet density since ϕ_{ex} is the only field inducing inhomogeneities in the fluid. As $\epsilon \rightarrow 0$ we have then from Eq. (2) and the definition of the functional derivative the exact result[1,3,11]

$$\rho'(z_1) = -\int dz_2 \int d^{d-1}r\, H(z_1, z_2, r)\beta\phi'_{ex}(z_2), \tag{3}$$

valid for all d and for one- as well as two-phase systems. Here $\rho'(z)=d\rho(z)/dz$.

In order to insure that the field has only a very small effect on the bulk phases, we choose a "truncated" graviational potential $\phi_{\rm ex}(z)=mgz$, $-z_W \le z \le z_W$, and $\phi_{\rm ex}(z)=\mathrm{sgn}(z)mgz_W$ otherwise. Here $z_W>0$ is some (large) value of z chosen so that $\lim gz_W \to 0$ as $g\to 0$. Using this in (3) and integrating over z_1, we obtain the basic equation

$$\rho(-\infty)-\rho(\infty)=\beta mg\int_{-\infty}^{\infty}dz_1\int_{-z_W}^{z_W}dz_2\int d^{d-1}r\, H(z_1,z_2,r). \tag{4}$$

In a one-phase system with average number density ρ, note that the right-hand side of (4) approaches $2mgz_W\rho^2\kappa$, where use has been made of the fluctuation definition[3] of the isothermal compressibility κ. Thus $\Delta\rho=\rho(-\infty)-\rho(\infty)$ vanishes as $g\to 0^+$, as one would expect.

In contrast, if $\mu=\mu_{\rm eq}$ appropriate for liquid-vapor coexistence, then an arbitrarily weak field will induce macroscopic phase separation. Hence the left-hand side of (4) approaches the *finite* value $\Delta\rho\equiv\rho_l-\rho_v$ as $g\to 0^+$. As recognized by Wertheim,[1] Eq. (4) can continue to hold for arbitrarily small g only if there are long-ranged correlations in H which increase as g decreases.[1,3]

To examine this point more quantitatively, we make a scaling hypothesis for the large-distance behavior of the correlation function H in analogy to the scaling theory for the pair correlation function near the bulk critical temperature T_c.[3,12] The two problems are very similar: As $T\to T_c$, bulk critical fluctuations are driven by the diverging correlation length ξ_B, and in the interface as $g\to 0^+$, long-ranged correlations arise from the diverging capillarly length L_c.

For horizontal separations $r \gg \xi_B$, the bulk correlations are exponentially small and only the anomalous interface correlations remain. We assume that H then has the form

$$H(z_1,z_2,r)\sim r^{-\theta}H_I\left(\frac{z_1}{W},\frac{z_2}{W},\frac{r}{L_c}\right), \tag{5}$$

where $\theta\ge 0$ is an exponent to be determined later giving the decay of correlations for $\xi_{\rm B} \ll r \ll L_c$, and H_I is a scaling function of order unity which tends to zero for large values of its arguments. The dependence of H_I on z/W in (5) insures that the anomalous correlations, scaling with L_c, are confined to the interfacial region. However, we assume no necessary connection between the behavior of L_c and of W.

We take $z_W=\alpha W$, where α is some constant. Substituting Eq. (5) into Eq. (4) (thus assuming the divergent contribution to the integral comes at large r), we find after changing variables that as $g\to 0^+$

$$\rho_l-\rho_v\sim\beta mgL_c^{d-1-\theta}W^2\int d^{d-1}x\int_{-\infty}^{\infty}dt_1\int_{-\alpha}^{\alpha}dt_2\, x^{-\theta}H_I(t_1,t_2,x). \tag{6}$$

The integral is a constant independent of g, and so from Eq. (1) we have the final result, valid as $g\to 0^+$:

$$W^2L_c^{d-3-\theta}\sim\text{const.} \tag{7}$$

Since θ must be nonnegative [otherwise correlations in Eq. (5) would grow for $\xi_B \ll r \ll L_c$], one concludes from Eq. (7) that for $d<3$, W must *diverge* as $L_c\to\infty$. This scaling argument alone does not allow us to deduce the value of θ (just as η is undetermined in ordinary critical-point scaling) but capillary-wave theory[8,9] and exact results for various lattice models[6,7] agree that $\theta=0$ and that for $d=3$, W^2 varies as $\ln L_c$. It follows that $gz_W\to 0$ as $g=0$, so that the field is indeed weak as assumed.

On the other hand, W can remain *finite* for $d>3$ as $g\to 0^+$ if $\theta=d-3$. Thus the existence of *algebraic* decay of interface correlations for $r \ll L_c$ is predicted in interfaces of higher dimensions if the interface width W remains finite. This is the interface analog of the $r^{-(d-2+\eta)}$ decay of the bulk pair correlation function[3,12] near T_c for $r \ll \xi_B$.

The derivation of the scaling relation (7) is directly analogous to that leading to the bulk critical-exponent relation $(2-\eta)/\nu=\gamma$.[3,12] Given the plausibility of the basic scaling hypothesis, I expect both results to be valid in all dimensions.

It is interesting to compare these general predictions to those arising from capillary-wave theory.[3,8,9] At wavelengths much greater than ξ_B, the work, ΔF, required for small distortions of the Gibbs dividing surface can be estimated from thermodynamics and consists of two parts: work against the gravitational field and work given by the (macroscopic) surface tension times the change in area. Representing the vertical displacement of the distorted surface at position $\vec{r}$ by the Fourier series

$$z(\vec{r})=\sum_{\vec{q}}\tilde{h}(\vec{q})e^{i\vec{q}\cdot\vec{r}}, \tag{8}$$

we have

$$\Delta F = \tfrac{1}{2}\sigma L^{d-1} \sum_{\vec{q}} \tilde{h}(\vec{q})\tilde{h}(-\vec{q})(L_c^{-2}+q^2), \quad (9)$$

where L^d is the system's volume which will tend to infinity. As argued in detail by Weeks,[8] the sums over $\vec{q}$ should be cut off at $q_{\max} \approx \pi/\xi_B$, since only long-wavelength distortions are properly described by Eq. (9) with σ the *macroscopic* surface tension. Capillary-wave theory assumes that the long-wavelength fluctuations integrated over in the *equilibrium* partition function[8] can also be described with use of (9) as the proper weight in the Boltzmann factor.

One measure[8,9] of the interface width involves the mean-squared fluctuation in $z(\vec{r})$; when fluctuations are large this will dominate any "intrinsic" contribution[13] in determining the decay at large z of $\rho(z)$. We can compute this and other measures of the width in terms of the height-difference correlation function,[8]

$$G(r) \equiv \frac{1}{2L^{d-1}} \int d^{d-1}s \langle [z(\vec{r}+\vec{s}) - z(\vec{s})]^2 \rangle \approx \frac{1}{\beta\sigma(2\pi)^{d-1}} \int_{|\vec{q}| \le \pi/\xi_B} d^{d-1}q \frac{1-e^{i\vec{q}\cdot\vec{r}}}{L_c^{-2}+q^2}, \quad (10)$$

by using (8), taking the large system limit, and noting that the quadratic nature of (9) implies that $\langle \tilde{h}(\vec{q})\tilde{h}(-\vec{q})\rangle = [\beta\sigma L^{d-1}(L_c^{-2}+q^2)]^{-1}$. Integrals similar to (10) arise in the Ornstein-Zernike theory of the bulk pair correlation function near T_c,[3,12] so that the discussion can be brief.

We define the fluctuation width $W_\infty^2 \equiv G(\infty)$ from Eq. (10) in terms of the mean-squared height difference between widely separated parts of the interface. For $d < 3$, the value of W_∞ from (10) is dominated by the small-q behavior and the restriction on $q_{\max}$ can be ignored. Equation (10) then implies the scaling law

$$W_\infty^2 \propto L_c^{-(d-3)} \quad (d<3) \quad (11)$$

consistent with (7) for $\theta = 0$. A more careful treatment gives $W_\infty^2 \propto \ln L_c$ for $d = 3$.[8,9] Clearly these divergent contributions dominate any intrinsic part of W.

For $d > 3$, the cutoff at $|\vec{q}| \approx \pi/\xi_B$ cannot be ignored in computing W_∞, but there is no longer a divergence at small q, so that the $g \to 0$ limit can be taken. Scaling out the ξ_B dependence we then find a *finite* value for W_∞:

$$W_\infty^2 \propto \frac{1}{\beta\sigma\xi_B^{d-3}} = \frac{\xi_B^2}{\beta\sigma\xi_B^{d-1}} \quad (d>3). \quad (12)$$

Equation (12) is consistent with the classical picture of an interface whose width varies as ξ_B as $T \to T_c$ (but with $\xi_B \ll L_c$ as always) if we make use of the Widom hyperscaling relation $\beta\sigma\xi_B^{d-1} \approx \text{const}$.[3,14]

However, this happy state of affairs holds only for $3 < d < 4$, since hyperscaling is incorrect[3] for $d > 4$. For $d > 4$ as $T \to T_c$, the interface becomes increasingly stiff and the long-wavelength interface fluctuations measured by W_∞ make a negligible contribution to the interface width, which is dominated by "intrinsic" contributions. This of course does not imply a failure in high dimensions of capillary-wave theory to describe long-wavelength fluctuations, and in particular to describe the long-ranged correlations in $H(z_1,z_2,r_{12})$, but merely reflects the negligible contribution of W_∞ to the true interface width near T_c.

For $d < 3$, the classical picture of an intrinsic profile fails because of fluctuations between widely separated regions of the interface as measured by W_∞. However, as argued by Widom,[4,14] it is fluctuations between regions of the interface separated by distances of the order ξ_B which represent the elementary density fluctuations of importance near T_c. Indeed one can verify for all $d < 4$ that the *local width*[8] $W_{\xi_B}^2 \equiv G(\xi_B)$ is independent of g as $g \to 0^+$; and that W_{ξ_B} is proportional to ξ_B near T_c. Unfortunately W_{ξ_B} is not what is measured from the profile $\rho(z)$ and a more precise and unambiguous definition of an intrinsic width has yet to be given.[13,15]

Finally we note that capillary-wave theory can be used to estimate the pair correlation function H.[8] It predicts that $H(z_1,z_2,r)$ with fixed z_1,z_2 in the interfacial region varies as $1 - G(r)/G(\infty)$ for $r \gg \xi_B$.[8,16] Equation (10) then shows that H decays as $\exp(-r/L_c)$ for $r \gg L_c$ in all d. For $\xi_B \ll r \ll L_c$ we find $H \propto (L_c^{3-d} - r^{3-d})/(L_c^{3-d} - 1)$. This gives the $r^{-(d-3)}$ decay for $d > 3$ already deduced from Eq. (7) for finite W. For $d = 3$, there is a crossover logarithmic form,[8] and finally behavior consistent with $\theta = 0$ for $d < 3$.[17] (Note that capillary-wave theory predicts the absence of a clustering property for the interface pair correlation function for $d \le 3$ as well as the divergence of the interface width.) Thus capillary-wave theory agrees with all scaling predictions and provides us with a physical picture which shows why correlations parallel and perpendicular to the interface are coupled together. Further discussions of these results and implications for the direct correlation function in the interfacial region will be given in a sepearate publication.[16]

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[1]M. S. Wertheim, J. Chem. Phys. **65**, 2377 (1976); J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).

[2]We consider an infinite system and choose a nonzero field so that the relative amounts of the bulk liquid and vapor phases and the location of the Gibbs dividing surface are well defined in the grand ensemble. In a finite system of volume L^d, appropriate fields at the system's boundaries {the analog of the $(+-)$ boundary conditions for Ising systems [G. Gallavotti, Riv. Nuovo Cimento **2**, 133 (1972); D. B. Abraham and P. Reed, Phys. Rev. Lett. **33**, 377 (1974); for results on a continuum system in $d=2$, see M. Requardt, J. Stat. Phys. **31**, 679 (1983)]} can also fix the overall density. Results similar to those given here should apply to this finite system if L_c is replaced by L.

[3]For a recent review, see Rowlinson and Widom, Ref. 1.

[4]An excellent discussion of the conceptual issues involved is given by B. Widom, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2, p. 79.

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[13]A useful picture models the interface as a thick drumhead in thermal equilibrium. The average profile $\rho(z)$ will be determined both by the "intrinsic" width—the thickness of the drumhead itself—and by averages over the long-wavelength normal-mode fluctuations in the positions of the center of the drumhead as determined by the $z(\vec{r})$. Thus there are "fluctuation" and "intrinsic" contributions to W as determined from $\rho(z)$. See Refs. 3, 4, and 8. It seems likely that the density profile $\rho(z, \vec{r}; \{n_i\})$ in the *constrained* ensemble introduced by Weeks (Ref. 8) (where the volume is divided into columns whose width is the order ξ_B, each of which contains a fixed number of particles as given by the $\{n_i\}$) could be used to give a more precise definition of these quantities.

[14]B. Widom, J. Chem. Phys. **43**, 3892 (1965).

[15]Some progress has been made for lattice systems. See. D. B. Abraham, Phys. Rev. B **29**, 525 (1984).

[16]D. Bedeaux and J. D. Weeks, to be published.

[17]Similar results have been obtained by R. Lipowsky, to be published, at interface depinning transitions.