Absence of Phase Separation for Fluids in Three Dimensions

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It is demonstrated that for short-range forces the density profile of the planar interface between fluid phases in three dimensions does not exist in the absence of a macroscopic external field such as gravity. This result holds for all nonzero values of the temperature and implies the absence of a roughening transition in continuous fluid interfaces in three dimensions, in contrast to the existence of such a transition in interfaces of three-dimensional lattice gases.

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A fundamental open problem in the theory of spatially nonuniform classical fluids is that of determining from first principles the structure of the interface between two coexisting phases in equilibrium.[1] Intimately related to this problem is the question of the possibility of spatial separation for two coexisting fluid phases in three dimensions in the absence of a macroscopic external field such as gravity.[2]

This basic question has been answered differently by the two phenomenological theories of fluid interfaces, to wit the theory of the "intrinsic" structure of the interface and the theory of the capillary-wave-like structure of the interface. In the theory of the "intrinsic" interface,[3] one postulates the existence of an interfacial structure which can be defined without reference either to the actual area of the interface or to an external field such as gravity. But these assumptions are contradicted by the prediction of the capillary-wave theory[4] of interfacial structure according to which the density profile of the liquid-vapor interface of a d-dimensional continuous fluid with $d \leqslant 3$ is eroded at the thermodynamic limit in the absence of gravity.

For lattice-gas models with short-range forces,[5] it is known from rigorous studies that a self-maintained interface does not exist[6] for $d=2$, while for $d=3$ such an interface does exist[7] provided the temperature is low enough, but ceases to exist when the temperature is high enough. The temperature at which this qualitative change occurs in the structure of the interface is called the roughening temperature.[8] At low enough temperatures, the density profile does vary on the scale of the lattice spacing, while it does not at high enough subcritical temperatures.

For continuous fluids, it has more recently been established[9] that self-maintained planar interfaces do not exist for $d=2$. However, the methods used for the case $d=2$ do not allow any conclusions to be drawn for the interesting case $d=3$.

In this Letter we use exact methods to study the possibility of a self-maintained interface between fluid phases in three dimensions. By analysis of the recently derived[10] form of the asymptotic decay at infinity of the direct correlation function of Ornstein and Zernike, it is found that the transverse second moment of this function does not exist for $d \leqslant 3$. When combined with the exact Buff-Lovett formula for the surface tension of a planar interface, this result implies that no self-maintained planar interfacial structure can exist in $d \leqslant 3$. This method does not enable us to draw any conclusions for $d > 3$ and test the prediction of capillary-wave theory according to which self-maintained planar interfaces do exist when $d > 3$.

I now sketch the derivation of my results, the details of which will appear elsewhere. Let us consider the two-phase equilibrium of a liquid in coexistence with its vapor or, equivalently, the phase equilibrium of a binary mixture in its coexistence region.

The interface between the two fluid phases is taken to be planar. In the absence of a macroscopic external field such as gravity, planarity can be ensured by local or microscopic external fields acting on the boundaries of the fluid; such boundary fields play an essential role in rigorous studies of spontaneous symmetry breaking in lattice systems.[5a] Or, equivalently,[5b] planarity results from suppression of a global or macroscopic external field (such as gravity) after the thermodynamic limit has been taken. This is the procedure I shall adopt here. It enables us to study the problem of the existence of self-maintained planar interfaces in continuous fluids in the explicit absence of external fields.

In a spatially nonuniform three-dimensional continuous fluid, the direct correlation function $c_2(\mathbf{r},\mathbf{r}')$ between two molecules located at $\mathbf{r}$ and $\mathbf{r}'$, with $\mathbf{r}$ and $\mathbf{r}' \in R^3$, is related to the total correlation function $h_2(\mathbf{r},\mathbf{r}')$ by the generalized Ornstein-Zernike definition:

$$h_2(\mathbf{r},\mathbf{r}')=c_2(\mathbf{r},\mathbf{r}')+\int d^3r''\, c_2(\mathbf{r},\mathbf{r}'')\rho(\mathbf{r}'')\,h_2(\mathbf{r}'',\mathbf{r}'),$$

where $\rho(\mathbf{r}'')$ is the mean local density of the spatially nonuniform fluid at $\mathbf{r}'' \in R^3$. For the planar fluid interface in which the vertical coordinate z is that along which the density $\rho(\mathbf{r})=\rho(z)$ is assumed to vary, the correlation functions h_2 and c_2 are translationally invariant in the transverse directions x and y, and we write

$$h_2(\mathbf{r},\mathbf{r}') = h_2(z,z',|\mathbf{x}^\perp|)$$

and

$$c_2(\mathbf{r},\mathbf{r}') = c_2(z,z',|\mathbf{x}^\perp|),$$

where $|\mathbf{x}^\perp| = [(x-x')^2+(y-y')^2]^{1/2}$ is the transverse separation for the points $\mathbf{r}=(x,y,z)$ and $\mathbf{r}'=(x',y',z')$.

The proof is based on a *reductio ad absurdum*: We assume that a self-maintained interface does exist and then show that this assumption leads to a contradiction.

I have recently shown[10] that if there exists, in the absence of a macroscopic external field, a nonconstant planar density profile $\rho(\mathbf{r})=\rho(z)$, then the direct correlation function $c_2(\mathbf{r},\mathbf{r}')=c_2(z,z',|\mathbf{x}^\perp|)$ decays at infinity like

$$c_2(z,z',|\mathbf{x}^\perp|) \underset{|\mathbf{x}^\perp|\to\infty}{\sim} \frac{m(z,z')}{|\mathbf{x}^\perp|^{3+\lambda}}, \tag{1}$$

where $0\le\lambda<1$ and where $m(z,z')$ is proportional to $[d\rho(z)/dz\, d\rho(z')/dz']$.[11] This result holds independently of the ensemble used. Result (1) follows[10] from combining a rigorous bound on the decay of the pair correlation function h_2,[9,10] obtainable from the Bogoliubov inequality for potentials ϕ such that their second derivative has a finite second moment, with the generalized Ornstein-Zernike definition of c_2 given above. The bound $\lambda<1$ is a direct consequence of the clustering requirement that h_2 vanish at infinity if a self-maintained density profile exists.

This last point is most readily understood by considering the transverse Fourier transforms $\hat{C}$ and $\hat{H}$ of the functions

$$C(z,z',|\mathbf{x}^\perp|) = \rho^{-1}(z)\rho(\mathbf{r}-\mathbf{r}') - c_2(z,z',|\mathbf{x}^\perp|)$$

and

$$H(z,z',|\mathbf{x}^\perp|) = \rho(z)\rho(z')h_2(z,z',|\mathbf{x}^\perp|) + \rho(z)\delta(\mathbf{r}-\mathbf{r}').$$

We have[1,10]

$$\hat{H}\hat{C} = \mathbf{1},$$

where the caret denotes Fourier transform with respect to transverse distance, and both $\hat{H}$ and $\hat{C}$ are nonanalytic at the origin for all $T<T_c$. Assuming incorrectly, as do all previous authors,[12] that $\hat{C}$ is analytic at the origin, i.e., that c_2 decays exponentially in the transverse directions, leads, for $d\le 3$, to an h_2 which no longer vanishes at infinity, in violation of the assumed extremal property of the equilibrium state.

Equation (1) is a mere reflection of Goldstone's theorem in classical statistical mechanics. That it does not hold for lattice models[7] expresses the inapplicability of Bogoliubov's inequality, from which this form of Goldstone's theorem follows,[13] to systems in which the spontaneously broken symmetry (here, that of spatial translations) is discrete rather than continuous.

We note that result (1) holds for all subcritical values of the temperature. We also observe that the quantity $1-\lambda$ plays a role similar to that of the exponent η measuring the departure from the Ornstein-Zernike behavior $\eta=0$ of the correlation functions of a uniform fluid at its critical point. In the interface problem for $d\le 3$, the necessary condition $\lambda<1$ is the exact analog of the equally necessary condition $\eta>0$ in the problem of light scattering by a fluid at the critical point for $d\le 2$. But while $\eta>0$ is only necessary to $T=T_c$, $\lambda<1$ is required for *all* $T<T_c$.

Consider the transverse second moment of the direct correlation function, i.e., the function

$$\int d^2x^\perp\, |\mathbf{x}^\perp|^2 c_2(z,z',|\mathbf{x}^\perp|). \tag{2}$$

Result (1) implies that the integrand of (2) behaves at infinity like

$$|\mathbf{x}^\perp|^3 c_2(z,z',|\mathbf{x}^\perp|) \sim m(z,z')|\mathbf{x}^\perp|^{-\lambda},$$

and because $0\le\lambda<1$, this decay at infinity is nonintegrable, so that the transverse second moment (2) diverges for all subcritical values of the temperature. This is in constrast to the behavior of the second moment of the direct correlation function of a pure fluid phase which only diverges at the critical point (if the critical behavior is nonclassical).

Consider next the exact formula[14] expressing the surface tension σ of a planar interface in terms of the direct correlation function and the density profile:

$$\sigma = \tfrac{1}{4}kT\int dz[d\rho(z)/dz]\int dz'[d\rho(z')/dz'] \times\int d^2x^\perp|\mathbf{x}^\perp|^2 c_2(z,z',|\mathbf{x}^\perp|), \tag{3}$$

with k Boltzmann's constant and T the absolute temperature. The surface tension σ is clearly finite for all subcritical values of the temperature, and because we have seen from (1) that the integral (2) diverges, we conclude from the finiteness of the left-hand side of (3), assuming either a ρ' of constant sign or an absolutely integrable integrand in (3), that (3) implies $d\rho(z)/dz=0$ for all z.

We have therefore shown that the initial assumption of a self-maintained planar interface with $d\rho(z)/dz\ne 0$ leads to a contradiction, and we are left with the solution $d\rho(z)/dz=0$. This result confirms the prediction of capillary-wave theory.[4]

The above proof was explicitly described for the interesting case $d=3$, but it obviously applies to all $d\le 3$; in particular we recapture earlier results[9] for the case $d=2$. Unfortunately, the present method does not enable us to discuss the possibility of self-maintained planar interfaces in $d>3$. This is because the value $\lambda = 1$ cannot be excluded[10] when $d > 3$, and for $\lambda = 1$ the direct correlation function decays exponentially in the transverse directions[10] so that the transverse second moment

$$\int d^{d-1}x^{\perp} |\mathbf{x}^{\perp}|^2 c_2(z,z', |\mathbf{x}^{\perp}|)$$

is bounded for all values of the temperature.

For real $d > 3$, capillary-wave theory predicts that the interfacial density profile is maintained in the absence of a macroscopic external field such as gravity, and we recall that when $d > 4$, mean-field theory, on which the "intrinsic" structure theory is based, is presumably correct; therefore, when $d = 4$ the identical prediction of the two phenomenological theories of the continuous fluid interface is likely to be correct as well.

The above result, which holds for all nonzero values of the temperature, implies the absence of a roughening transition in continuous fluids for $d < 3$. This is in strong contrast to the case of lattice-gas models in which the interface is known[8] to exhibit a roughening transition in $d = 3$, as described above.

Finally, when the intermolecular forces decay sufficiently slowly at infinity, the Bogoliubov inequality becomes inconclusive and the above proof is inapplicable. While several arguments indicate that the roughening transition in *lattice* models is suppressed when the interactions decay sufficiently slowly at infinity,[15] it is not quite so clear whether long-range forces can stabilize interfaces in *continuous* fluids, as they do in the mean-field limit. Precisely the same situation prevails in the better known problem of crystalline or isotropic ferromagnetic order in two dimensions: Such order is absent for short-range forces[16] and while ferromagnetic order is restored in the presence of long-range forces which decay sufficiently slowly at infinity,[17] it is not known whether the same will occur for crystalline order.

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