STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

COLLEGE OF
ENGINEERING

Report No. 133

THE FREE-ENERGY DENSITY NEAR THE CRITICAL POINT

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ABSTRACT

We show how both the "classical" expression for the free-energy density and Widom's alternative expression can be modified so as to be consistent with known and expected critical behavior in all dimensions. In so doing, we postulate that an increase in the effective range of interaction due to an increase in dimensionality will tend to inhibit density fluctuations.

I. INTRODUCTION

Widom has shown[1] how the square gradient theory of surface tension and critical opalescence can be modified so as to be consistent with known results for the two-dimensional lattice gas. However, as Widom[1] and others[2,3] have pointed out, his modified theory may itself break down in higher dimensions when applied to a continuum fluid or the Ising model. Moreover, for the spherical model with a short-ranged interaction potential it can easily be verified that certain of the relationships between critical exponents implied by Widom's theory -- our Eq. (15a) with $p=o$ is one of them -- do not hold when the dimensionality d is greater than four[4].

In this note we show a way in which the "classical" free-energy expansion that is assumed in the square-gradient theory can be modified so as to be consistent with both the known two-dimensional Ising results and the expected continuum and Ising results for higher dimensionality. A key point of our argument is the assumption that an increase in the effective volume of interaction will tend to inhibit density fluctuations.

II. THE SQUARE-GRADIENT THEORY REANALYSED

According to the square-gradient theory, the Helmholtz free energy ϕ associated with a density inhomogeneity Δn occurring over a volume v small compared to a total volume of the fluid is given by $\phi_1 + \phi_2$ where

$$\phi_1 = Bv(\Delta n)^2/\rho^2 K_T, \qquad \phi_2 = Av(\Delta n/L)^2 \tag{1}$$

with B assumed constant and A assumed to be a slowly varying positive function of the mean density ρ and temperature T. Here K_T is the isothermal compressibility and $v=L^d$, and hence L is the linear size of the volume v over which the inhomgeneity is being considered. In using (1), Widom identifies L with a correlation length κ^{-1}, which becomes infinite at the critical point. In Widom's treatment this length appears as both the interface thickness separating two phases and the range of the two-point correlation function $h(\underset{\sim}{r})$, and in its former role it appears in an expression for the surface tension σ that is similar to (1) and is based on the same assumptions (σ is Widom's γ):

$$\sigma = BL(\Delta\rho)^2/\rho^2K_T + AL(\Delta\rho/L)^2 \quad (2)$$

where $\Delta\rho$ is the difference between the dinsities of the two phases. Minimizing this σ with respect to L leads to the relation

$$B/\rho^2K_T = A/L^2 \quad . \quad (3)$$

The justification for (1) lies in an expansion[5,6] for a local free-energy density $F(\underset{\sim}{r})$ associated with any deviation of the local density $n(\underset{\sim}{r})$ from ρ. Expanding $F(\underset{\sim}{r})$ about its mean value over the volume Ω of the whole system, $\overline{F}$, yields

$$\Delta F(\underset{\sim}{r}) = F(\underset{\sim}{r}) - \overline{F} = \tfrac{1}{2}a(\Delta n)^2 + \ldots + \tfrac{1}{2}b(\nabla n)^2 + \ldots \quad , \quad (4)$$

where $\Delta n = n(\underset{\sim}{r})-\rho$ and ∇n is the gradient of $n(\underset{\sim}{r})$.

The free energy ϕ associated with the density fluctuation in a volume v is then obtained by integration over that volume:

$$\phi = \int_V \Delta F(\underset{\sim}{r}) d\underset{\sim}{r} \tag{5}$$

As can be seen from the treatments of $F(\underset{\sim}{r})$ given by Landau and Lifshitz[5] and by Fisher[6,7] the constants a and b are proportional to the zeroth and second moments of $\hat{c}(\underset{\sim}{r})$, the "modified" direct correlation function. It follows that the constant a is inversely proportional to the zeroth moment of $\hat{h}(\underset{\sim}{r}) = h(\underset{\sim}{r}) + \delta(\underset{\sim}{r})/\rho$, where $\delta(\underset{\sim}{r})$ is the Dirac delta function (or the Kronecker delta, in the lattice-gas case):

$$\begin{aligned} BK_T^{-1} &\sim a \sim \int_\Omega \hat{c}(\underset{\sim}{r}) d\underset{\sim}{r} \sim [\int_\Omega \hat{h}(\underset{\sim}{r}) d\underset{\sim}{r}]^{-1} \\ A &\sim b \sim \int_\Omega r^2 \hat{c}(\underset{\sim}{r}) d\underset{\sim}{r} \quad . \end{aligned} \tag{6}$$

Here $r = |\underset{\sim}{r}|$ and $\hat{c}(\underset{\sim}{r}) + \delta(\underset{\sim}{r})/\rho$ is the direct correlation function $c(\underset{\sim}{r})$. From (6) and $kT\rho K_T = \rho \int_\Omega \hat{h}(\underset{\sim}{r}) d\underset{\sim}{r}$ where k is Boltzman's constant, one sees that if unexhibited terms in (4) can be neglected, one indeed has B equal to a constant. On the other hand we would expect[2] that near the critical point

$$\int_\Omega r^2 \hat{c}(\underset{\sim}{r}) d\underset{\sim}{r} \sim \kappa^{-\eta} \tag{7}$$

if

$$\hat{h}(\underset{\sim}{r}) \sim f(\kappa r)/r^{d-2+\eta}, \; r >> R \quad , \tag{8}$$

where R is the range of the interaction potential and $f(x) \sim$ constant for $x \sim 0$, yielding the relation

$$\hat{h}(\underset{\sim}{r}) \sim 1/r^{d-2+\eta} \tag{9}$$

for $R << r << \kappa^{-1}$ near the critical point.

From (6) and (8), $A \sim b \sim \kappa^{-\eta}$ near the critical point. Despite this very sensitive and singular dependence of b on κ, Eqs. (1) through (4) still make sense and lead to expressions that are consistent without knowledge of the lattice gas when $d=2$. For example, finding L by minimizing σ still leads to (3) and yields

$$\gamma' = (2-\eta)\nu' \quad ,$$

as well as

$$\mu = 2\beta - \nu' + \gamma' \quad ,$$

$$\mu = 2\beta + (1-\eta)\nu' \quad .$$

Here we are using Fisher's notation[2] for critical exponents supplemented by the use of μ to describe the temperature variation of σ on the coexistence curve, i.e., we are assuming that along the coexistence curve near the critical point (T_c,ρ_c)

$$|\rho-\rho_c| \sim |T-T_c|^{\beta}, \; \kappa \sim |T-T_c|^{\nu'} \quad ,$$

$$K_T \sim |T-T_c|^{-\gamma'}, \; \sigma \sim |T-T_c|^{\mu} \quad .$$

We remark that out result $b \sim \kappa^{-\eta}$ duplicates a relation derived by Josephson[8] in connection with the use of a variant of (4) that is appropriate to the consideration of a superfluid, and (6) and (7) provide a basis for Josephson's result that is somewhat different from Josephson's original argument.

Although the use of (4) with (6) leads to results that are consistent with the known behavior of the two-dimensional lattice gas, these results in themselves do not appear to imply a relation between η and the exponent δ that describes the shape of the critical isotherm. This is in contrast to the results of the modification of the square-gradient theory proposed by

Widom, who assumed that density fluctuations in the vicinity of the critical point manifest themselves with high probability as the appearance of microdomains of conjugate phase and volume $v \sim \kappa^{-d}$. Widom's assumption implies both that the expected free energy associated with density fluctuations over the volume v is a constant of order unity times kT, and that the expected value of $(\Delta n)^2$ over the volume v is proportional to the square of the difference $\Delta\rho$ between the mean density ρ of the dominant phase and the mean density $\rho_{conj.}$ of the conjugate phase (which in turn is proportional to $(\rho-\rho_c)^2$). Here we shall retain the first of these conclusions but not the second, on the following grounds:

We might anticipate the appearance of microdomains of conjugate phase to become less and less likely as the dimensionality increases, since the number of molecules caught within the range of each other's interaction potential will increase if the linear interaction range remains constant, and the effects of this average decrease in the freedom of a molecule to move uninhibited by neighboring molecules will presumably include a decrease of average fluctuation amplitude as d increases. Thus, over a volume $\sim\kappa^{-d}$, $\Delta\rho$ will no longer represent the order of magnitude of the largest likely fluctuation amplitude for all d but instead will represent only an upper estimate of that quantity, which may or may not be realized by the actual fluctuation amplitude with appreciable frequency, depending upon whether d is small or large. Hypothesizing that the mean-square fluctuation over a volume $\sim\kappa^{-d}$ can still be expressed as a power of $\Delta\rho$, we conclude that instead of

$$\langle(\Delta n)^2\rangle_v \simeq C(\Delta\rho)^2 \qquad , \qquad (10)$$

with C of order $(\Delta\rho)^0$, we shall find along the coexistence curve

$$\langle (\Delta n)^2 \rangle_v \sim (\Delta\rho)^{2+p} \tag{11}$$

where $p \geq 0$ and where we anticipate $p>0$ for large d. From (8) and

$$\langle (\Delta n)^2 \rangle_v = \rho^2 \int_v h(\underset{\sim}{r}) d\underset{\sim}{r}/v \quad , \tag{12}$$

we have

$$\langle (\Delta n)^2 \rangle_v \sim \kappa^{d-2+\eta} \quad . \tag{13}$$

Assuming that

$$\kappa \sim |\rho - \rho_c|^{\varepsilon} \tag{14}$$

along the coexistence curve, our two different assessments of $\langle (\Delta n)^2 \rangle_v$ yield

$$\varepsilon(d-2+\eta) = 2 + p \quad , \tag{15a}$$

and

$$2/\varepsilon \leq d-2+\eta \quad . \tag{15b}$$

This is equivalent to the Gunton-Buckingham inequality[9] $2d(d-2+\eta)^{-1} \leq \delta+1$ if we accept the relation $(2-\eta)\varepsilon = \delta-1$, which follows from the use of (6), (8) and the assumption that (14) holds on the critical isotherm as well as on the coexistence curve. We note that we have not arrived at a relationship that determines η given d and ε, as we would have on the basis of Widom's argument. Instead we have derived a result that can be written as an equality only after the introduction of p, which is a measure of the extent to which density fluctuations have been inhibited by the interaction potential. Our argument implies that $p \geq 0$, and also that p is nondecreasing as d increases, but it provides no quantitative means for assessing p

independent of the use of (15a). However, we can gain further insight into the nature of p by viewing (15) in a somewhat different way. If the probability of a fluctuation of amplitude $\sim|\Delta\rho|$ appearing over a volume $v \sim \kappa^{-d}$ is negligible for a given d, one can consider shrinking the volume one is sampling until one comes to a smaller volume $\omega \sim \kappa^{-\theta d}$, $0 \leq \theta \leq 1$, over which the probability of such a fluctuation has become appreciable, so that

$$\langle(\Delta n)^2\rangle_\omega \sim C_\omega (\Delta\rho)^2 \quad \text{as} \quad \Delta\rho \to 0 \quad ,$$

where C_ω is of order one. For such ω, it is also reasonable, on the basis of (9) and (12), to expect

$$\langle(\Delta n)^2\rangle_\omega \sim \omega^{\langle(2-\eta)/d\rangle - 1} \sim \eta^{\omega(d-2+\eta)} \quad ,$$

so that

$$(\Delta\rho)^2 \sim \kappa^{\theta(d-2+\eta)} \quad ,$$

or

$$2/\varepsilon = \theta(d-2+\eta) \quad , \tag{16}$$

which is another way of writing (15).

Using a relation suggested by considerations discussed by us elsewhere[10] we can relate θ to the exponent s that we expect[3] to appear in the direct correlation function for large r:

$$\hat{c}(\underset{\sim}{r}) \sim f_b(\kappa r)/r^{d+s}, \; r \gg R, \quad s \geq 2-\eta \quad .$$

The relation[10] is

$$2/\varepsilon = d-s \quad , \tag{17}$$

implying through (16) that

$$\theta = (d-s)/(d-2+\eta) \; . \tag{18}$$

Since s is the exponent associated with the "singular part"[11] of the

Fourier transform $\hat{c}(\underset{\sim}{k})$ of $\hat{c}(\underset{\sim}{r})$, (18) can be interpreted to mean that the length $\kappa^{-\theta}$ appears in the problem whenever the regular part of $\hat{c}(\underset{\sim}{k})$ dominates the singular part. As noted elsewhere[3], if the regular part of $\hat{c}(\underset{\sim}{k})$ (which reflects the immediate presence of the pair potential) were suppressed, one would have

$$\hat{h}(\underset{\sim}{r}) \sim f(\kappa \underset{\sim}{r})/r^{d-s}, \quad r \gg R,$$

instead of (8). Hence one would expect

$$\langle (\Delta n)^2 \rangle_v \sim \kappa^{d-s}$$

instead of (13). Thus the inhibitory effect of the pair potential changes $\langle (\Delta n)^2 \rangle_v$ in a way that enters both of the assessments of that quantity that we make in relating ε to η. Ignoring the effect in both assessments yields (17), which we believe is in fact correct, but further implies that $s=2-\eta$, which we believe becomes incorrect as $d\to\infty$.

In conclusion, we consider the relation

$$\langle F(\underset{\sim}{r})-\overline{F} \rangle_v \sim kT/v \quad . \qquad (19)$$

If we apply $\langle \quad \rangle_v$ to (4), using the estimates $a \sim \kappa^{2-\eta}$, $b \sim \kappa^{-\eta}$, and assuming, as is plausible, that $\langle (\nabla n)^2 \rangle_v \sim \langle (\Delta n)^2/v^{2/d} \rangle_v$, we then find from (13) that

$$\langle F(\underset{\sim}{r})-\overline{F} \rangle_v \sim O(\kappa^d) \quad .$$

Thus we are not forced by our arguments to modify (19). It is perhaps noteworthy and surprising that our picture of the fluctuation-inhibiting effect of the pair potential has led us to abandon (10) rather than (19), since Widom has suggested[1] that (19) rather than (10) is the hypothesis most open to suspicion in the square-gradient theory.

Acknowledgments

The author is indebted to Prof. M.E. Fisher for a very helpful discussion concerning this work.

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7. See in particular footnote 53 of ref. 6.

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10. To appear, Molecular Physics (1969).

11. See ref. 2 for a discussion of the way one relates exponents to the singular part of a function. In the notation of Fisher, we could write $s=2-\eta_s$.