

Renormalization Group Approach to the Interfacial Order Parameter Profile near the Critical Point

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(Received February 10, 1977)

The interfacial order parameter profile near the critical point is studied using the renormalization group method. The equation for the order parameter profile is derived up to first order in $\varepsilon=4-d$ where d is the spatial dimensionality of the system. This equation consists of two parts. One is related to the equation of state with a slight modification. The other comes from the spatial inhomogeneity of the order parameter. Our result is compared with that of Fisk and Widom in which the form of the equation of state has been postulated. An explicit solution of the equation which describes the order parameter profile is obtained. The universal amplitude of the surface tension is also evaluated using the ε -expansion technique.

§ 1. Introduction

Several years ago Fisk and Widom^{1a)} generalized the theory of Cahn and Hilliard²⁾ for the structure and free energy of the interface between fluid phases by using the equation of state which is based on the scaling hypothesis. Although the main features of the interface have been clarified by their theory, the determination of the order parameter profile requires the explicit form of the free energy density in the nonuniform fluid. In their theory the profile and the associated quantities, such as the surface tension, have been obtained by assuming a simple form of the equation of state. The theory was then criticized by Widom himself.^{1b)} The main issues besides the fundamental question of the proper definition of the profile are: (1) What is the proper equation of state or the free energy to use for homogeneous states with the values of the order parameter lying between those of the coexisting phases below the critical point T_c ? In particular, can one use the free energy analytically continued from that of the coexisting phases? (2) Is the square gradient form of the local free energy adequate? Although indirect evidences support affirmative answers to these questions, the situation clearly leaves a plenty of room for further theoretical study.

In this paper we apply the renormalization group theory^{3),4)} to investigate the structure of the interface. The order parameter profile through the interface is derived by the technique of the $\varepsilon(=4-d)$ expansion, d being the dimensionality of space. In § 2 the free energy functional for given spatially nonuniform average order parameter $M(\mathbf{x})$ is formally obtained in terms of the Ginzburg-Landau-Wilson (G-L-W) Hamiltonian for the local order parameter $S(\mathbf{x})$. For simplicity we

regard the interface as flat. (Suppose a sufficiently large droplet.) In § 3 the equilibrium state of the system is found by the extremal condition on the free energy functional. After eliminating the divergent integrals characteristic of the G-L-W Hamiltonian we obtain the equation for the order parameter profile, which is correct up to first order in ε . This equation is compared with that of Fisk and Widom and is solved exactly in § 4. The surface tension is also evaluated up to first order in ε and is compared with the experiments. The final section is devoted to a short summary and discussion.

§ 2. Local free energy in the nonuniform fluid

The earlier theories of the interface between two coexisting phases have made use of the properly chosen local Helmholtz free energy in the inhomogeneous system. Cahn and Hilliard used the classical Van der Waals free energy in their theory of interfaces.²⁾ Fisk and Widom have extended the theory of Cahn and Hilliard by assuming a non-classical free energy.¹⁾

Here we derive the free energy functional in the two-phase region starting with the G-L-W Hamiltonian for the renormalized local order parameter $S(\mathbf{x})$:^{4), 5)}

$$\mathcal{H}(S) = \int d^d \mathbf{x} \left\{ \frac{1}{2} Z (\nabla S(\mathbf{x}))^2 + \frac{1}{2} \tau Z_2 S(\mathbf{x})^2 + \frac{1}{2} \delta \tau S(\mathbf{x})^2 + \frac{g}{4!} Z_4 S(\mathbf{x})^4 \right\}, \quad (2.1)$$

where Z , Z_2 , Z_4 and $\delta \tau$ are the renormalization constants. Here τ is chosen to be negative and g is the renormalized coupling constant.*) The local order parameter is chosen so that it vanishes at the critical point. For example, for a simple fluid,

$$S(\mathbf{x}) = \rho(\mathbf{x}) - \rho_c, \quad (2.2)$$

where $\rho(\mathbf{x})$ and ρ_c are the local density and its critical value, respectively. The formalism we use is the field theoretical formulation due to Brezin et al.^{4), 5)} where we start with the free energy functional $W\{h\}$ in the presence of an arbitrary external field $h(\mathbf{x})$ defined by (we choose a normalization slightly different than that of Ref. 4)

$$W\{h\} = \ln \int d\{S\} \exp \left[-\mathcal{H}\{S\} + \int S(\mathbf{x}) h(\mathbf{x}) d\mathbf{x} \right]. \quad (2.3)$$

The vertex functional $\Gamma\{m\}$ is defined through the following Legendre transformation:

$$\Gamma\{m\} = \int d\mathbf{x} m(\mathbf{x}) h(\mathbf{x}) - W\{h\} \quad (2.4)$$

with

*) Here in fact g is the dimensionless renormalized coupling constant where the reference wavenumber was chosen to be unity. See below.

$$m(\mathbf{x}) = \delta W\{h\} / \delta h(\mathbf{x}). \tag{2.5}$$

Consequently, we also have

$$h(\mathbf{x}) = \delta \Gamma\{m\} / \delta m(\mathbf{x}). \tag{2.6}$$

In the absence of an external field, the order parameter profile $M(\mathbf{x})$ is determined by

$$\delta \Gamma\{M\} / \delta M(\mathbf{x}) = 0 \tag{2.7}$$

and the free energy Ψ by

$$\Psi = \Gamma\{M\}. \tag{2.8}$$

Let us now expand \mathcal{H} in powers of $\psi(\mathbf{x}) = S(\mathbf{x}) - m(\mathbf{x})$ as

$$\mathcal{H}\{S\} = \sum_{n=0}^{\infty} \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_n \frac{1}{n!} \mathcal{H}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n) \psi(\mathbf{x}_1) \cdots \psi(\mathbf{x}_n), \tag{2.9}$$

where

$$\mathcal{H}^{[n]}(\mathbf{x}_1, \dots, \mathbf{x}_n) = \left. \frac{\delta^n \mathcal{H}\{S\}}{\delta S(\mathbf{x}_1) \cdots \delta S(\mathbf{x}_n)} \right|_{\{S\} = \{m\}}. \tag{2.10}$$

Explicitly the $\mathcal{H}^{[n]}$ s are given by

$$\mathcal{H}^{[0]} = \int d\mathbf{x} \left\{ \frac{1}{2} Z(\nabla m(\mathbf{x}))^2 + \frac{1}{2} \tau Z_2 m(\mathbf{x})^2 + \frac{1}{2} \delta \tau m(\mathbf{x})^2 + \frac{g}{4!} Z_4 m(\mathbf{x})^4 \right\}, \tag{2.11}$$

$$\mathcal{H}^{[1]} = -Z\nabla^2 m(\mathbf{x}) + \delta \tau m(\mathbf{x}) + \frac{g}{6} Z_4 m(\mathbf{x})^3 + \tau Z_2 m(\mathbf{x}), \tag{2.12}$$

$$\mathcal{H}^{[2]}(\mathbf{x}_1, \mathbf{x}_2) = \left\{ -Z\nabla_1^2 + \delta \tau + \tau Z_2 + \frac{g}{2} Z_4 m(\mathbf{x}_1)^2 \right\} \delta(\mathbf{x}_1 - \mathbf{x}_2), \tag{2.13}$$

etc. ...

The vertex functional $\Gamma\{m\}$ is calculated in the loop expansion.⁴⁾ It should be noted that the equation $\mathcal{H}^{[1]}(\mathbf{x}) = h(\mathbf{x})$ with $Z = Z_2 = Z_4 = 1$ and $\delta \tau = 0$ is nothing but the equation for the classical order parameter profile in the presence of a field $h(\mathbf{x})$. Hence the contributions from $\mathcal{H}^{[1]}$ to the vertex functional $\Gamma\{m\}$ are at most of second order in g . Note that $gm^2(\mathbf{x})$ should be taken to be of the order unity in general. By taking these into account, the vertex functional is given in the one loop approximation by

$$\Gamma(m) = \int d\mathbf{x} \left\{ \frac{1}{2} Z(\nabla m(\mathbf{x}))^2 + \frac{1}{2} \delta \tau m(\mathbf{x})^2 + \frac{\tau}{2} Z_2 m(\mathbf{x})^2 + \frac{g}{4!} Z_4 m(\mathbf{x})^4 \right\} + \frac{1}{2} \text{Tr} \ln \mathcal{H}^{[2]}, \tag{2.14}$$

where $\mathcal{H}^{[2]}$ is an operator with matrix elements $\mathcal{H}^{[2]}(\mathbf{x}_1, \mathbf{x}_2)$ in the coordinate

representation, and we have used the operator formula:

$$\text{Det } A = \exp(\text{Tr } \ln A). \tag{2.15}$$

The explicit form of the last term in (2.14) will be derived in the next section where divergences will be also eliminated.

§ 3. Equation for the order parameter profile

Minimization of the free energy functional with respect to $\{M\}$ gives the equilibrium value for $M(r)$. By (2.7) and (2.14) we obtain the equation

$$\begin{aligned} Z \frac{d^2}{dr^2} M(r) = & \tau Z_2 M(r) + \delta \tau M(r) + \frac{g}{6} Z_4 M(r)^3 \\ & + \frac{1}{2V_{d-1}} \text{Tr} \{ [\mathcal{H}^{[2]}]^{-1} \delta(r-s) \}_{s=r} g M(r), \end{aligned} \tag{3.1}$$

where r is the coordinate in the direction perpendicular to the interface and

$$\mathbf{x} = (\bar{\mathbf{x}}, r), \tag{3.2}$$

$\bar{\mathbf{x}}$ being the $d-1$ dimensional vector, and $V_{d-1} \equiv \int d^{d-1} \mathbf{x}$. The equation (3.1) is to be solved under the following boundary condition:

$$M(r) = \begin{cases} M_e > 0 & \text{for } r \rightarrow \infty \\ -M_e & \text{for } r \rightarrow -\infty, \end{cases} \tag{3.3}$$

where M_e is the finite uniform solution of (3.1), that is, the equilibrium value of the order parameter in one of the coexisting phases. The renormalization constants have been evaluated as⁵⁾

$$\begin{aligned} Z = 1 + O(g^2), \quad \delta \tau = -\frac{g}{2} \int_q \frac{1}{q^2}, \\ Z_2 = 1 + \frac{g}{2} J + O(g^2), \quad Z_4 = 1 + \frac{3}{2} g J + O(g^2), \end{aligned} \tag{3.4}$$

where

$$\int_q \equiv \left(\frac{1}{2\pi} \right)^d \int d\mathbf{q} \tag{3.5}$$

and

$$J = \int_q \frac{1}{(q^2 + 1)^2} = \frac{S_{d-\varepsilon}}{\varepsilon} \left(1 - \frac{\varepsilon}{2} + O(\varepsilon^2) \right) \tag{3.6}$$

with

$$S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} \frac{1}{(2\pi)^d}. \tag{3.7}$$

In (3.4) the reference wavenumber in the normalization conditions for the Z 's has been equated to unity.

The method of the spectral decomposition can be used in order to evaluate the last term in (3.1) explicitly. Namely, let us consider the Schrödinger equation

$$\left(-\frac{d^2}{ds^2} + \tau + \frac{g}{2}M(s)^2\right)f(s) = \lambda f(s), \tag{3.8}$$

where $M(s)$ is the lowest order solution of (3.1), i.e., the classical order parameter profile given by

$$M(s) = (6|\tau|/g)^{1/2} \tanh(\kappa s/2) \tag{3.9}$$

with

$$\kappa = \sqrt{2|\tau|}. \tag{3.10}$$

The solution of (3.8) is easily obtained. The normalized eigenfunctions $f_0(s)$ and $f_1(s)$ for the two bound states with the eigenvalues $\lambda_0=0$ and $\lambda_1=3|\tau|/2$, respectively, are given by

$$f_0(s) = (3\kappa/8)^{1/2} \text{sech}^2(\kappa s/2) \tag{3.11}$$

and

$$f_1(s) = (3\kappa/4)^{1/2} \text{sech}(\kappa s/2) \tanh(\kappa s/2). \tag{3.12}$$

The eigenfunction with the continuum spectrum

$$\lambda_p = p^2 + 2|\tau|, \quad (-\infty < p < \infty) \tag{3.13}$$

is given by

$$f_p(s) = \frac{1}{\omega_p} e^{ips} \{2p^2 + |\tau| - 3|\tau| \tanh^2(\kappa s/2) + 3\kappa p i \tanh(\kappa s/2)\}, \tag{3.14}$$

where

$$\omega_p^2 = 2(p^2 + 2|\tau|)(2p^2 + |\tau|). \tag{3.15}$$

The normalization of (3.14) has been chosen as

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} ds f_p(s) f_q^*(s) = \delta(p-g). \tag{3.16}$$

Expression (3.14) is essentially equivalent to the one derived by Rajaraman.⁶⁾ By the use of these eigenfunctions the delta function can be expressed as

$$\delta(x-y) = \sum_n f_n^*(x) f_n(y) + \frac{1}{2\pi} \int dp f_p^*(x) f_p(y). \tag{3.17}$$

Thus the last term of (3.1) becomes

$$\begin{aligned} \frac{gM(r)}{2V_{d-1}} \text{Tr} \{ (\mathcal{H}^{[2]})^{-1} \delta(r-s) \}_{s=r} &= \frac{gM(r)}{2} \int_{\bar{q}} \left(\bar{q}^2 - \frac{d^2}{ds^2} + \tau + \frac{g}{2} M(s)^2 \right)^{-1} \delta(r-s) \Big|_{s=r} \\ &= \frac{gM(r)}{2} \left\{ \int_{\bar{q}} \sum_n \frac{|f_n(r)|^2}{\bar{q}^2 + \lambda_n} + \int_{\bar{q}, p} \frac{|f_p(r)|^2}{\bar{q}^2 + p^2 + 2|\tau|} \right\}, \end{aligned} \quad (3.18)$$

where the integration on \bar{q} is performed in the $d-1=3-\varepsilon$ dimensional vector space parallel to the interface. Substitution of (3.4) and (3.18) into (3.1) yields

$$\frac{d^2 M(r)}{dr^2} = \tau M(r) + \frac{g}{6} M(r)^3 + \frac{g}{2} M(r) \left(\tau + \frac{g}{2} M(r)^2 \right) J + \frac{g}{2} M(r) Q(r), \quad (3.19)$$

where $Q(r)$ is a function free of divergences for $d < 4$ and is given by

$$\begin{aligned} Q(r) &= -2|\tau| \int_{\bar{q}} \frac{1}{q^2(q^2 + 2|\tau|)} - \int_{\bar{q}} \sum_n \frac{\lambda_n |f_n(r)|^2}{\bar{q}^2(\bar{q}^2 + \lambda_n)} \\ &\quad - \int_{\bar{q}, p} \frac{(p^2 + 2|\tau|)(|f_p(r)|^2 - 1)}{\bar{q}^2(\bar{q}^2 + p^2 + 2|\tau|)}. \end{aligned} \quad (3.20)$$

In deriving (3.20) we have again used the identity (3.17). After performing the integrations which will be described in Appendix A, $Q(r)$ is given for small ε by

$$\begin{aligned} Q(r) &= (2|\tau|)^{-\varepsilon/2} \frac{S_{4-\varepsilon}}{\varepsilon} \{ |\tau| - 3|\tau| \tanh^2(\kappa r/2) \} \\ &\quad + \frac{3}{2} |\tau| S_4 \text{sech}^2(\kappa r/2) - \frac{\sqrt{3}}{16\pi} |\tau| \text{sech}^2(\kappa r/2) \tanh^2(\kappa r/2). \end{aligned} \quad (3.21)$$

From (3.19) and (3.21) we have

$$\begin{aligned} \frac{d^2 M(r)}{dr^2} &= \tau M(r) + \frac{g}{6} M(r)^3 + \frac{\varepsilon}{6} M(r) \left(\tau + \frac{g}{2} M(r)^2 \right) (\ln(2|\tau|) - 1) \\ &\quad - \frac{\varepsilon}{6} \tau M(r) \left\{ 3 - \frac{g}{6|\tau|} (3 + \sqrt{3}\pi) M(r)^2 + \sqrt{3}\pi \left(\frac{g}{6|\tau|} \right)^2 M(r)^4 \right\}, \end{aligned} \quad (3.22)$$

where we have used the fixed point value of g :⁴⁾

$$gS_{4-\varepsilon} = \frac{2}{3} \varepsilon + O(\varepsilon^2). \quad (3.23)$$

In (3.22) we have used (3.9) in terms of $O(\varepsilon)$, which is allowed in the spirit of the ε -expansion.

The equation (3.22) without the term in curly bracket^{*)} should be compared with the equation of state with the uniform external field H :⁴⁾

$$H = \tau M + \frac{g}{6} M^3 + \frac{\varepsilon}{6} M \left(\tau + \frac{g}{2} M^2 \right) \left\{ \ln \left(\tau + \frac{g}{2} M^2 \right) - 1 \right\}. \quad (3.24)$$

^{*)} Note that the quantity in the curly bracket vanishes for $M(r) \rightarrow \pm M_e$ with $M_e = (6|\tau|/g)^{1/2}$ in the lowest order. Hence this term arises from the spatial inhomogeneity of $M(r)$.

Of course (3.24) cannot be applicable in the unstable region inside the mean field spinodal curve where $\tau + (g/2)M^2$ becomes negative. It should be noted that (3.22) is free from this difficulty.*)

§ 4. Order parameter profile and surface free energy

Before solving Eq. (3.22) we compare it with the work of Fisk and Widom.^{1a)} First, let us introduce the scaled quantity by

$$\mu(r)^\beta = \left(\frac{g}{6}\right)^{1/2} \frac{|M(r)|}{|\tau|^\beta}. \tag{4.1}$$

Then (3.22) is written as

$$\begin{aligned} \frac{d^2 M(r)}{dr^2} = |\tau|^\gamma M(r) & \left\{ -1 + \mu(r)^{2\beta} + \frac{\varepsilon}{6} (-1 + 3\mu(r)^{2\beta}) (\ln 2 - 1) \right. \\ & \left. + \frac{\varepsilon}{6} (3 - 3\mu(r)^{2\beta} - \sqrt{3}\pi\mu(r)^{2\beta} + \sqrt{3}\pi\mu(r)^{4\beta}) \right\}, \end{aligned} \tag{4.2}$$

where

$$\gamma = 1 + \frac{\varepsilon}{6} + O(\varepsilon^2), \quad \beta = \frac{1}{2} - \frac{\varepsilon}{6} + O(\varepsilon^2). \tag{4.3}$$

Next we normalize $\mu(r)$ by**)

$$\mu(r)^\beta = cz(r)^\beta \tag{4.4}$$

so that the right-hand side of (4.2) vanishes for $z(r)^\beta = 1$. The constant c is then given by

$$c^\beta = 1 + \frac{1}{3}\varepsilon(1 - \ln 2) + O(\varepsilon^2). \tag{4.5}$$

Thus Eq. (4.2) takes the following scaling form postulated by Fisk and Widom:¹⁾

$$\frac{d^2 M(r)}{dr^2} = -j(1)|\tau|^\gamma M(r) (1 - z(r)) \frac{j(z)}{j(1)}, \tag{4.6}$$

where, however,

$$(1 - z)j(z)/j(1) = \frac{1 - a}{2\beta} (1 - z^{2\beta}) (1 + az^{2\beta}) \tag{4.7}$$

$$\approx \frac{1}{2\beta(1 + a)} (1 - z^{2\beta}) (1 + az^{2\beta}) \tag{4.7'}$$

*¹⁾ Since we have used the solution of the Schrödinger equation (3.8) with (3.9), Eq. (3.22) does not reduce to the equation of state even in the spatially uniform limit.

**²⁾ The variable z is equal to $(T_c - \tau(\rho))/(T_c - T)$ of Fisk and Widom,^{1a)} and to ω of Sarkies and Frankel.⁷⁾

with

$$a = \frac{\sqrt{3}}{6} \pi \varepsilon \approx 0.91 \quad \text{for } \varepsilon = 1. \quad (4.8)$$

The value $j(1)$ is given by

$$j(1)/\beta = 2 + \frac{\varepsilon}{3} (\sqrt{3}\pi - 4 + \ln 2) + O(\varepsilon^2). \quad (4.9)$$

Furthermore, $j(z)$ is positive for $0 \leq z \leq 1$ and $j'(1)/j(1) = (1+2a)\beta - 1/2$ which is also finite. Thus our function j satisfies the requirements of Fisk and Widom¹⁾ (see Appendix B also).

Expression (4.7) should be compared with that adopted by Fisk and Widom^{1a)}

$$(1-z)j(z)/j(1) = \frac{3}{4}(1-z^{4/3}). \quad (4.10)$$

If we put $a=1$ and $\beta=1/3$ in (4.7') it coincides with (4.10). On the other hand, the choice $a=1$ in (4.7') yields

$$(1-z)j(z)/j(1) = (1-z^{4\beta})/4\beta, \quad (4.10')$$

which is the form used by Sarkies and Frankel.⁷⁾ It should be noted, however, that the $z^{4\beta}$ term in (4.7) originated from the nonuniformity of the order parameter, which does not exist in the equation of state in the one phase region.*⁸⁾ In Appendix B we discuss the properties of the function $j(z)$ and the function $h(z)$ which corresponds to the equation of state (3.24). In particular, we will see that $j(1)$ and $h(1)$ differ by a small amount contradicting the continuity assumption of Fisk and Widom¹⁾ up to $O(\varepsilon)$.

Following Fisk and Widom,^{1a)} we obtain the solution of Eq. (4.6) in the form

$$|M(r)| = A|\tau|^\beta [\theta(|r|/L)]^\beta, \quad (4.11)$$

where

$$A = (6/g)^{1/2} c^{\beta/2}, \quad (4.12)$$

$$L = (\beta|\tau|^{-\tau}/j(1))^{1/2}. \quad (4.13)$$

$\theta(s)$ is defined through

$$s = \int_0^{\theta(s)} t^{\beta-1} [\omega(t)]^{-1/2} dt, \quad (4.14)$$

where

$$\omega(t) = 2 \int_t^1 z^{2\beta-1} (1-z)j(z)/j(1) dz. \quad (4.15)$$

Substitution of (4.7) into (4.15) yields

* See the footnote after Eq. (3.23).

$$\omega(t) = \frac{1}{6\beta^2} a(1-a) (1-t^{2\beta})^2 \left(t^{2\beta} + \frac{3}{2a} + \frac{1}{2} \right). \tag{4.16}$$

From (4.11), (4.14) and (4.16) we easily obtain the following result for the order parameter profile:

$$M(r) = A|\tau|^\beta \frac{\tanh(r/(2L))}{\{1 + 2a/(3+a) \operatorname{sech}^2(r/(2L))\}^{1/2}}. \tag{4.17}$$

If we take the limit $\varepsilon \rightarrow 0$ ($d \rightarrow 4$) in (4.17), it reduces to the classical order parameter profile:

$$M(r) = (6/g)^{1/2} |\tau|^{1/2} \tanh(\sqrt{|\tau|} r / \sqrt{2}). \tag{4.18}$$

Next we evaluate the surface free energy density σ . In our nonlocal theory we must start with the definition of σ :

$$\sigma = \int dr (\Gamma \{M(r)\} - \Gamma \{M_c\}). \tag{4.19}$$

By the procedure similar to that in § 3 (see Appendix C) we obtain

$$\sigma = C_0 (2A|\tau|^\beta)^2 / L, \tag{4.20}$$

where the universal constant C_0 [= $\beta^2 c$ of Ref. 1a)] is found to be given by

$$C_0 = \frac{1}{6} \left\{ 1 + \varepsilon \left(\frac{1}{2} - \frac{\sqrt{3}}{9} \pi \right) + O(\varepsilon^2) \right\}. \tag{4.21}^*)$$

In (4.20) the constant A of Fisk and Widom^{1a)} (which should not be confused with our A) has been equated to unity up to $O(g)$. The surface tension critical

Table I. The universal constant C_0 of the surface tension.

Classical theory		0.167	(Ref. 2))
Fisk and Widom		0.142	(Ref. 1a))
First order ε -expansion		0.149	
Experimental values	SF ₆	0.093 ± 0.011	(Ref. 8))
	CO ₂	$\left\{ \begin{array}{l} 0.110 \\ 0.123 \\ 0.146 \end{array} \right.$	(Ref. 8), 9)) ^{a)}
			(Ref. 10)) ^{a)}
			(Ref. 10)) ^{a)}
Xe	0.100 ± 0.012	(Ref. 11)) ^{a)}	

a) The original values quoted in these references are 0.115, 0.129 and 0.153 for CO₂ and 0.105 ± 0.012 for Xe, which are obtained by equating L with ξ , the correlation range of critical fluctuations deduced from light scattering. However, in view of (B.7) we should have $L/\xi = [j(1)/h(1)]^{1/2}$. Hence the values of C_0 obtained in these references ought to be multiplied by $[j(1)/h(1)]^{1/2} \approx 1 - 0.047\varepsilon$, although the corrections appear to be very small.

*) If we used the expression $C_0 = (\beta^2/2) \int_0^1 t^{\beta-1} (\omega(t))^{1/2} dt$ which is derived under the square gradient approximation of the free energy density,^{1a)} we would obtain $C_0 = (1/6)(1 - (2\sqrt{3}/45)\pi\varepsilon + O(\varepsilon^2))$, which gives, $C_0 = 0.126$ in three dimensions.

exponent $\mu^* = 2\beta + \gamma/2$ is equal to $\gamma + 2\beta - \nu$ by the scaling law.¹⁾ Incidentally, note that the first order value of the surface tension critical exponent $\mu^* = 1.5 - \varepsilon/4 = 1.25$ for $\varepsilon = 1$ is close to the experimental values $1.28 \sim 1.29$.¹⁾ From (4.21) we have $C_0 = 0.149$ in three dimensions. This value is a bit smaller than the classical value $C_0 = 0.167$ and is comparable to Fisk and Widom's value $C_0 = 0.142$. In Table I we summarize the values C_0 obtained by various theories and experiments.^{9)~11)} Our first order result definitely improves agreement with experiments over the classical value, but is not better than that of Fisk and Widom. It seems that the second order calculation is necessary for further improvement.

§ 5. Summary and discussion

In the preceding sections we have obtained the order parameter profile in equilibrium (4.17) by the ε expansion technique without any *ad hoc* assumptions. The equation for $\varepsilon = 1$ which describes the order parameter profile in three dimensions is found to be very close numerically to that found by Fisk and Widom.^{1a)} It should be noted, however, that the equation (3.22) cannot be obtained by continuing the equation of state (3.24) into the thermodynamically metastable or unstable regions. In particular, the compressibility (or the susceptibility) on the two sides of the coexistence curve differ by a small amount.^{*)}

A typical difference with the classical order parameter profile is found in the maximum value of the gradient $\Delta M = (dM/dr)_{\max}$ in the interface, which is given from (4.17) by

$$\Delta M = \left(1 - \frac{\sqrt{3}\pi\varepsilon}{18}\right) A |\tau|^\beta / (2L). \quad (5.1)$$

The ratio of this with its classical one $(\Delta M)_c = (3/g)^{1/2} |\tau|$ is given by

$$\begin{aligned} (\Delta M) / (\Delta M)_c &= |\tau|^{-\varepsilon/12} \left\{ 1 - \frac{\varepsilon}{36} (6 + 3 \ln 2 - \sqrt{3}\pi) \right\} \\ &= (1 - 0.073\varepsilon) |\tau|^{-\varepsilon/12}. \end{aligned} \quad (5.2)$$

The surface tension has been also calculated and compared with the experiments.

Acknowledgements

One of the authors (T.O.) would like to thank H. Shigematsu for valuable discussions.

Appendix A

Here the derivation of (3.21) is described. The first term of (3.20) is

*) See note added (1).

easily integrated to give

$$-2|\tau| \int_{\mathbf{q}} \frac{1}{q^2(q^2+2|\tau|)} = -2|\tau| (2|\tau|)^{-\varepsilon/2} \frac{S_{4-\varepsilon}}{\varepsilon} (1 + O(\varepsilon^2)). \tag{A.1}$$

By the use of the discrete eigenvalues with their associated eigenfunctions obtained in § 3 the second term of (3.20) is obtained after carrying out three-dimensional integration

$$- \int_{\mathbf{q}} \sum_n \frac{\lambda_n |f_n(r)|^2}{\bar{q}^2(\bar{q}^2 + \lambda_n)} = -\frac{3\sqrt{3}}{16\pi} |\tau| \operatorname{sech}^2(\kappa r/2) \tanh^2(\kappa r/2). \tag{A.2}$$

In order to evaluate the third term of (3.20) we note the following formulae:

$$\begin{aligned} \int_{\bar{q}, p} \frac{1}{\bar{q}^2(\bar{q}^2 + p^2 + a)} &= a^{-\varepsilon/2} S_{3-\varepsilon} \frac{1}{\pi} \int_0^\infty dx x^{-\varepsilon} \int_0^\infty dy \frac{1}{x^2 + y^2 + 1} \\ &= a^{-\varepsilon/2} S_{3-\varepsilon} \frac{\Gamma(\varepsilon/2) \Gamma(1/2 - \varepsilon/2)}{4\Gamma(1/2)} \\ &= a^{-\varepsilon/2} S_{4-\varepsilon} \frac{1 - (\varepsilon/2)}{1 - \varepsilon} \Gamma\left(1 - \frac{\varepsilon}{2}\right) \Gamma\left(\frac{\varepsilon}{2}\right) \\ &= a^{-\varepsilon/2} S_{4-\varepsilon} \frac{2}{\varepsilon} \left(1 + \frac{\varepsilon}{2} + O(\varepsilon^2)\right) \end{aligned} \tag{A.3}$$

and

$$\begin{aligned} \int_{\bar{q}, p} \frac{1}{\bar{q}^2(\bar{q}^2 + p^2 + a)(2p^2 + (a/2))} &= \left(\frac{a}{2}\right)^{-1} S_3 \frac{1}{\pi} \int_0^\infty dx \int_0^\infty dy \frac{1}{(x^2 + y^2 + 1)(4y^2 + 1)} \\ &= \left(\frac{a}{2}\right)^{-1} \frac{\sqrt{3}}{36\pi} \end{aligned} \tag{A.4}$$

for $a > 0$. With (3.14) the third term of (3.20) is written as

$$\begin{aligned} & - \int_{\bar{q}, p} \frac{(p^2 + 2|\tau|) (|f_p(r)|^2 - 1)}{\bar{q}^2(\bar{q}^2 + p^2 + 2|\tau|)} \\ &= \frac{3}{2} |\tau| \operatorname{sech}^2(\kappa r/2) \int_{\bar{q}, p} \frac{1}{\bar{q}^2(\bar{q}^2 + p^2 + 2|\tau|)} \\ &+ \frac{9}{2} |\tau|^2 \operatorname{sech}^2(\kappa r/2) \tanh^2(\kappa r/2) \int_{\bar{q}, p} \frac{1}{\bar{q}^2(\bar{q}^2 + p^2 + 2|\tau|)(2p^2 + |\tau|)}. \end{aligned} \tag{A.5}$$

Using the formulae (A.3) and (A.4) we obtain

$$\begin{aligned} \text{(A.5)} &= 3|\tau| S_{4-\varepsilon} (2|\tau|)^{-\varepsilon/2} \frac{1}{\varepsilon} \left(1 + \frac{\varepsilon}{2} + O(\varepsilon^2)\right) \operatorname{sech}^2(\kappa r/2) \\ &+ \frac{\sqrt{3}}{8\pi} |\tau| \operatorname{sech}^2(\kappa r/2) \tanh^2(\kappa r/2). \end{aligned} \tag{A.6}$$

Putting together (A.1), (A.2) and (A.6) we find (3.21).

Appendix B

Widom¹²⁾ postulated the scaling form of the equation of state as^{*)}

$$H = -M|\tau|^r(1-z)h(z) \quad (\text{B}\cdot 1)$$

with

$$z \equiv [T_c - T_s(M)] / (T_c - T) \quad (\text{B}\cdot 2)$$

which coincides with z introduced through (4.1) and (4.4) near the critical point where the coexistence curve is written as $T = T_s(M)$. Then, for the equation of state (3.24) we obtain using (4.3) and (4.5) the following which is correct to $O(\varepsilon)$:

$$(1-z)h(z) = -\left(c^\beta - \frac{\varepsilon}{2}\right)(z^{2\beta} - 1) - \frac{\varepsilon}{6}\{(3z^{2\beta} - 1)\ln(3z^{2\beta} - 1) - 2\ln 2\}. \quad (\text{B}\cdot 3)$$

From a general consideration Widom¹¹⁾ assumed for $h(z)$ the following properties:

- (a) $h(z)/z^{r-1}$ is regular in $1/z$ at $z = \infty$ (critical isotherm),
- (b) $(1-z)h(z)$ is regular in $z^{2\beta}$ at $z = 0$ (critical isochore),
- (c) $\lim_{z \rightarrow 1} (1-z)h'(z) = 0$ (coexistence curve).

The result (B.3) satisfies the properties (b) and (c). On the other hand, for large z (B.3) yields $h(z)/z^{r-1} \simeq (c^\beta - (\varepsilon/2))z^{2\beta-r}(1 + (\varepsilon/2)\ln z) + O(\varepsilon^2)$. Using (4.3) we have $z^{2\beta-r}(1 + (\varepsilon/2)\ln z) \simeq z^{-\varepsilon/2}(1 + (\varepsilon/2)\ln z) \simeq z^0$. Hence $h(z)$ is expected to satisfy (a) as well. See also Ref. 4) in this regard.

One can also consider the properties (a'), (b') and (c') corresponding to (a), (b) and (c), respectively, for the function $j(z)$, for which we can write by (4.7) as

$$(1-z)j(z) = B(1-z^{2\beta})(1+az^{2\beta}) \quad (\text{B}\cdot 4)$$

with

$$B = j(1)/2\beta(1+a) = 1 - \frac{2}{3}\varepsilon + \frac{\varepsilon}{6}\ln 2 + O(\varepsilon^2). \quad (\text{B}\cdot 5)$$

This function $j(z)$ does satisfy (b') and (c'), but not (a') which is not relevant here.

On the other hand, we obtain from (B.3)

$$h(1)/\beta = 2 + \frac{\varepsilon}{3}(2 + \ln 2). \quad (\text{B}\cdot 6)$$

Thus, on the contrary to the assumption of Fisk and Widom,¹³⁾ $j(1)$ and $h(1)$ are different to first order in ε :

$$j(1)/h(1) = \chi_-/\chi_* = 1 + \frac{\varepsilon}{6}(\sqrt{3}\pi - 6) \simeq 1 - 0.093\varepsilon, \quad (\text{B}\cdot 7)$$

^{*)} This function $h(z)$ should not be confused with the external field h introduced in § 2.

where χ_- and χ_* are the compressibilities (or the susceptibilities) on the coexistence curve in the equilibrium and metastable states, respectively.

Appendix C

By making use of the spectral decomposition of § 3 the surface free energy is written up to $O(g)$ as

$$\begin{aligned}
 g\sigma = & \int dr \left\{ \frac{1}{2} \left(\frac{dm(r)}{dr} \right)^2 + \frac{1}{2} \tau (m(r)^2 - m_e^2) + \frac{1}{4!} (m(r)^4 - m_e^4) \right. \\
 & + \frac{\delta\tau}{2} (m(r)^2 - m_e^2) + \frac{1}{2} (Z_2 - 1) \tau (m(r)^2 - m_e^2) \\
 & \left. + \frac{1}{4!} (Z_4 - 1) (m(r)^4 - m_e^4) \right\} + g\sigma_b + g\Delta\sigma_s, \tag{C.1}
 \end{aligned}$$

where

$$\begin{aligned}
 m^2 &= gM^2, \\
 g\sigma_b &= \frac{g}{2} \int_{\bar{q}} \{ \ln(\bar{q}^2) + \ln(\bar{q}^2 + 3|\tau|/2) \}, \tag{C.2}
 \end{aligned}$$

$$g\Delta\sigma_s = \frac{g}{2} \int_{\bar{q}, p} \ln(\bar{q}^2 + p^2 + 2|\tau|) \int dr (|f_p(r)|^2 - 1). \tag{C.3}$$

After some manipulations we have

$$\begin{aligned}
 g\sigma_b + g\Delta\sigma_s = & -3\sqrt{2|\tau|}g \int_{\bar{q}} \frac{1}{q^2 + 2|\tau|} - \frac{3(2|\tau|)^{3/2}}{2}g \int_{\bar{q}} \frac{1}{(q^2 + 2|\tau|)^2} \\
 & - (2|\tau|)^{3/2}gS_4 \frac{\sqrt{3}}{12}\pi. \tag{C.4}
 \end{aligned}$$

$m(r)$ is given from (4.17) by

$$m(r) = \tilde{A} \tanh\left(\frac{r}{2L}\right) \left\{ 1 - \frac{a}{3} \operatorname{sech}^2\left(\frac{r}{2L}\right) \right\}, \tag{C.5}$$

where

$$\tilde{A}^2 = 6c^\beta |\tau|^{2\beta}. \tag{C.6}$$

Substitution of (C.5) into the first three terms in (C.1) yields

$$\frac{1}{2} \int dr \left(\frac{dm(r)}{dr} \right)^2 = \frac{2\tilde{A}^2}{3L} \left(\frac{1}{2} - \frac{2}{15}a \right), \tag{C.7}$$

$$\frac{\tau}{2} \int dr (m(r)^2 - m_e^2) = \frac{2\tilde{A}^2}{3L} 3L^2 |\tau| \left(1 + \frac{2}{9}a \right), \tag{C.8}$$

$$\frac{1}{4!} \int dr (m(r)^4 - m_e^4) = \frac{2\tilde{A}^2}{3L} \left(-\frac{L^2 \tilde{A}^2}{3} \right) \left(1 + \frac{1}{5}a \right). \tag{C.9}$$

The remaining terms in (C·1) are of first order in g . Hence we can use the lowest order expressions for $m(r)$, \tilde{A} and L . Thus we have

$$\frac{\delta\tau}{2} \int dr (m(r)^2 - m_e^2) = 3\sqrt{2|\tau|}g \int_q \frac{1}{q^2}, \quad (\text{C}\cdot 10)$$

$$\frac{\tau}{2} (Z_2 - 1) \int dr (m(r)^2 - m_e^2) = \frac{3}{2} (2|\tau|)^{3/2} gJ, \quad (\text{C}\cdot 11)$$

$$\frac{1}{4!} (Z_4 - 1) \int dr (m(r)^4 - m_e^4) = -3(2|\tau|)^{3/2} gJ, \quad (\text{C}\cdot 12)$$

where J has been defined in (3·6). With (C·10)~(C·12) and (C·4) all the divergences that emerge as $\varepsilon \rightarrow 0$ can be eliminated. Namely we have

$$\begin{aligned} & (\text{C}\cdot 4) + (\text{C}\cdot 10) + (\text{C}\cdot 11) + (\text{C}\cdot 12) \\ &= \frac{2\tilde{A}^2}{3L} \varepsilon \left\{ -\frac{1}{4} \ln(2|\tau|) + \frac{1}{2} - \frac{\sqrt{3}}{36} \pi \right\} + O(\varepsilon^2). \end{aligned} \quad (\text{C}\cdot 13)$$

From (C·7)~(C·9) and (C·13) we finally obtain (4·20) with (4·21).

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Note added:

(1) The fact that (3·24) extrapolated within the coexistence region does not show any singularity until the mean field spinodal curve $\tau + (g/2)M^2 = 0$ is reached seems to imply the continuity of the equation of state (3·24) into the metastable phase. We thus tend to ascribe the discrepancy between $j(1)$ and $h(1)$ found here to the nonlocal nature of the free energy functional $F\{M\}$.

In order to verify this let us replace (3·18) by its *local* form:

$$\frac{gM(r)}{2} \int_{\bar{q}} \left(\bar{q}^2 - \frac{d^2}{ds^2} + \tau + \frac{g}{2} M(r)^2 \right)^{-1} \delta(r-s)_{s=r} = \frac{gM(r)}{2} \int_{\bar{q}} \left(q^2 + \tau + \frac{g}{2} M(r)^2 \right)^{-1}$$

since the differential operator has only plane wave eigenfunctions. Adding to this the counter term involving $\delta\tau$ this expression becomes $R(M(r))$ where

$$R(M) = \frac{gM}{2} \int_{\bar{q}} \left(\frac{1}{q^2 + \tau + (g/2)M^2} - \frac{1}{q^2} \right) = -\frac{gM}{2} \left(\tau + \frac{g}{2} M^2 \right) F \left(\tau + \frac{g}{2} M^2 \right).$$

Here

$$F(x) = \int_{\mathbf{q}} \frac{1}{q^2(q^2+x)}$$

For small $\varepsilon=4-d$, we can show that

$$F(x) \cong \frac{1}{\varepsilon} S_{4-\varepsilon} \left[1 - \frac{\varepsilon}{2} \ln|x| + O(\varepsilon^2) \right]$$

In this way we obtain the following equation for $M(r)$ in the local approximation which replaces (3.22):

$$\frac{d^2M}{dr^2} = \tau M + \frac{g}{6} M^3 + \frac{gS_4}{4} M \left(\tau + \frac{g}{2} M^2 \right) \left[\ln \left| \tau + \frac{g}{2} M^2 \right| - 1 \right]$$

The right-hand side also follows from the equation of state (3.24) by analytical continuation into the unstable region. The change of the variable from M to z as given by (4.1), (4.4) and (4.5) is still valid here with the right-hand side of the above equation vanishing at $z=1$, and we finally obtain

$$\frac{d^2M}{dr^2} = -|\tau|^\gamma M(r) [1-z(r)] j_i(z(r)),$$

where

$$(1-z) j_i(z) = 1 - c^2 z^{2\beta} - \frac{\varepsilon}{6} (3z-1) [\ln|3z-1| - 1] + O(\varepsilon^2)$$

This yields

$$j_i(1)/\beta = 2 + \frac{\varepsilon}{3} (2 + \ln 2) = h(1)/\beta$$

Thus, as is anticipated, validity of the use of the analytically continued equation of state is verified only in the local approximation up to $O(\varepsilon)$.

(2) If we extrapolate the calculation to three dimensions, $\varepsilon=1$, we encounter the following infrared divergence in the first term of (3.18) associated with $n=0$:

$$\left[\frac{d^2M(r)}{dr^2} \right]_D = \frac{g}{2} M(r) |f_0(r)|^2 \frac{1}{2\pi} \ln \left(\frac{k_m}{k_l} \right), \tag{1}$$

where k_l and k_m are the lower and upper cutoffs, respectively (the ultraviolet divergence at $k_m \rightarrow \infty$ cancels out with the counter terms and need not be considered). The interpretation that the eigenmode $n=0$ corresponds to a displacement of the interface as a whole suggests that the infrared divergence in (1) is caused by capillary waves.⁽¹⁾ This can be studied by considering a model of the interface with the rigid profile $M_0(r') = (6|\tau|/g)^{1/2} \tanh(r'/2L)$, but with fluctuating positions, $r' = r - \delta r(\bar{x})$. We take the actual profile to be the average $\bar{M}(r) = \langle M_0(r') \rangle$ over the distribution of δr . We then obtain

$$\frac{d^2\bar{M}(r)}{dr^2} = \tau \bar{M}(r) + \frac{g}{6} \langle M_0 [r - \delta r(\bar{x})]^3 \rangle \cong \tau \bar{M}(r) + \frac{g}{6} M_0(r)^3 + \frac{g}{2} M_0(r) \left[\frac{dM_0(r)}{dr} \right]^2 \langle \delta r(\bar{x})^2 \rangle. \tag{2}$$

Using $\langle \delta r(\bar{x})^2 \rangle = (2\pi\sigma)^{-1} \ln(k_m/k_l)$ ⁽¹⁾ with $\sigma = 2\kappa^3/g$ and $(dM_0/dr)/f_0(r) = (2/g)^{1/2} \kappa^{3/2}$ we indeed verify that the last term of (2) coincides with (1) with $M(r) = M_0(r)$. If we adopt the view that the capillary wave contributions are not intrinsic to the properties of the interface and should be excluded (see Ref. 1b) of the text), we should add the counter term

$$-\frac{g}{2} M_0(r)^2 f_0(r)^2 \ln \frac{k_m}{k_l} \tag{3}$$

to the right-hand side of (3.19) or (3.22) where $k_m = \alpha/L$ (we expect α to be sufficiently smaller than 1). The effects of the counter term are (i) a of (4.8) is changed to $a = (\sqrt{3}/6)\pi\varepsilon - 6\alpha$ (ii) C_0 of the surface free energy (4.20) has a small temperature-dependent additional contribution $(4/9)\alpha^2\varepsilon(\frac{1}{3} - \ln(\alpha/L))$ which is, however, negligible for sufficiently small values of α .

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