International Journal of Thermophysics, Vol. 10, No. 2, 1989

External Field Effect on the Critical Behavior of the Interface Between Fluid Phases[1]

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The equilibrium structure of the interface between fluid phases in d dimensions in the presence of an external field is investigated. The equilibrium interface is assumed to consist of an intrinsic interface which undergoes capillary-wave fluctuations. It is found that in two dimensions the interfacial thickness is very sensitive to the choice of external field and intrinsic interface. For an intrinsic interface of a thickness proportional to ξ, the bulk correlation length, the exponent ω, which describes the divergence of the interfacial thickness as the critical point is approached, depends on the scale of the external field relative to ξ and ranges from $\omega = 9/32$ to $\omega = 17/32$, in contrast to the prediction $\omega = 1$ of scaling theory. When an intrinsic interface of vanishing thickness is chosen, $\omega = 9/32$ for any external field. This is in strong contrast to the results in three or more dimensions, where ω is found to be independent of both the external field and the intrinsic interface and satisfies $\mu = (d-1)\omega$, with μ the critical exponent of the surface tension, in accord with scaling theory.

KEY WORDS: capillary waves; critical point; external field; interfacial thickness.

1. INTRODUCTION

It has long been believed that close to the critical point, the properties of fluid interfaces are directly related to those of the coexisting bulk phases and correspondingly share the universal critical properties the latter are well known to exhibit. Such a belief originated with van der Waals [1] and culminates in the modern generalizations and extensions [2, 3] of van der Waals' original ideas, in particular in Widom's scaling theory [3]

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[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

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of the interface. A characteristic prediction of scaling theory is that close to the critical point the interfacial thickness is proportional to the correlation length of the spontaneous density (composition) fluctuations in either bulk phase [4] and is, thus, independent of the size of the system and the presence of an external field such as gravity.

A different approach to the problem of fluid interfacial structure was developed by Buff et al. [5], who advocated capillary waves, which have no analogue in the bulk, as the proper modes of the interfacial fluctuations. In capillary-wave theory, the interfacial thickness depends on both the size of the system and the presence of an external field, in contrast to the assumptions of the van der Waals theory.

In accord with more recent ideas [6], these two apparently conflicting approaches of the van der Waals and capillary-wave theories should be combined into a single picture in which their contradictions are resolved. In this unified picture, the fluctuating bare interface of zero thickness of Buff et al. [5] is replaced by an interface of nonzero thickness proportional to the bulk correlation length. This interface, called the intrinsic interface, undergoes capillary-wave fluctuations as it does in the original study by Buff et al. This new treatment enables one to describe the complete interfacial structure without losing any aspects of the two originally conflicting capillary-wave and van der Waals theories. It is hoped, in such an amalgamation, to recapture from a single model the capillary-wave aspects at large distances on the one hand and the traditional critical behavior of van der Waals (scaling) theory on the other hand. As will be seen, such a hope is fullfilled in three or more dimensions but not in two dimensions.

In Section 2, we study the planar fluid interface in an arbitrary dimension of space. In Section 3 we analyze the case of fluids in two dimensions, and in Section 4, that of fluids in three and four dimensions. Our results are briefly discussed in Section 5 and summarized in Fig. 1.

2. THERMAL BROADENING OF THE INTRINSIC INTERFACE IN AN ARBITRARY DIMENSION

In the capillary-wave theory of the planar fluid interface [5] in d dimensions, the probability $p(\zeta)$ of a distortion ζ of an infinitely sharp interface separating two incompressible fluid phases is given by

$$p[\zeta(\mathbf{x})] \cong \exp\{-\beta W[\zeta(\mathbf{x})]\} \tag{1}$$

where $W[\zeta(\mathbf{x})]$ is the work necessary to distort the infinitely sharp interface from z to $z-\zeta(\mathbf{x})$, $\mathbf{x}$ is a $(d-1)$-dimensional vector describing position in the transverse directions parallel to the equilibrium interfacial plane, and $\beta = 1/kT$, with T the absolute temperature and k Boltzmann's constant.

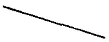
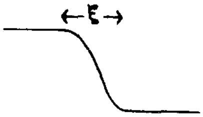
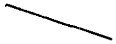
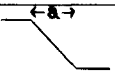
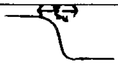
ρ_{int}	u_{ext}	ω
		undefined [11]
		9/32 [8]
	arbitrary with $u'_{ext}(0) < \infty$	9/32
		17/32 [11]
		9/32 [11]
		9/32 ($a \gg \xi$) 17/32 ($a \ll \xi$)
		9/32 ($\xi_u \gg \xi$) 17/32 ($\xi_u \ll \xi$)

Fig. 1. Values of ω in $d = 2$.

More generally, the infinitely sharp interface of the original capillary-wave theory can and indeed, according to current ideas described above, should be replaced by a diffuse interface of nonzero thickness, the intrinsic interface.

We consider for simplicity, but with no loss of generality, a single-component liquid–vapor phase equilibrium and denote by $\rho_I(z)$ the equilibrium density profile of the intrinsic interface. Following Percus [7], we write the energy change due to capillary-wave fluctuations in the form

$$W[\zeta(\mathbf{x})] = \gamma_0 \cdot \int [1 + |\nabla\zeta(\mathbf{x})|^2]^{1/2} \, d\mathbf{x} - \gamma_0 \cdot \int d\mathbf{x}$$
$$+ \int \rho_I[z - \zeta(\mathbf{x})] \cdot u_{\text{ext}}(z) \, d\mathbf{r} - \int \rho_I(z) \, u_{\text{ext}}(z) \, d\mathbf{r} \tag{2}$$

where γ_0 is the bare surface tension [5], i.e., the surface tension of the intrinsic interface, and u_{ext} is the external field taken to depend on the coordinate z only. The distorted intrinsic profile $\rho_I[z - \zeta(\mathbf{x})]$ is illustrated in Fig. 2.

Expanding the distorted profile $\rho_I[z - \zeta(\mathbf{x})]$ to second order in $\zeta(\mathbf{x})$, assuming $\int \zeta(\mathbf{x}) \, d\mathbf{x} = 0$ to preserve the average position of the profile and expanding $[1 + |\nabla\zeta(\mathbf{x})|^2]^{1/2}$ to second order in $|\nabla\zeta(\mathbf{x})|^2$ turns Eq. (2) into

$$W[\zeta(\mathbf{x})] = \frac{\gamma_0}{2} \int |\nabla\zeta(\mathbf{x})|^2 \, d\mathbf{x} + \frac{1}{2} \iint \rho_I''(z) \, u_{\text{ext}}(z) \, \zeta^2(\mathbf{x}) \, dz \, d\mathbf{x} \tag{3}$$

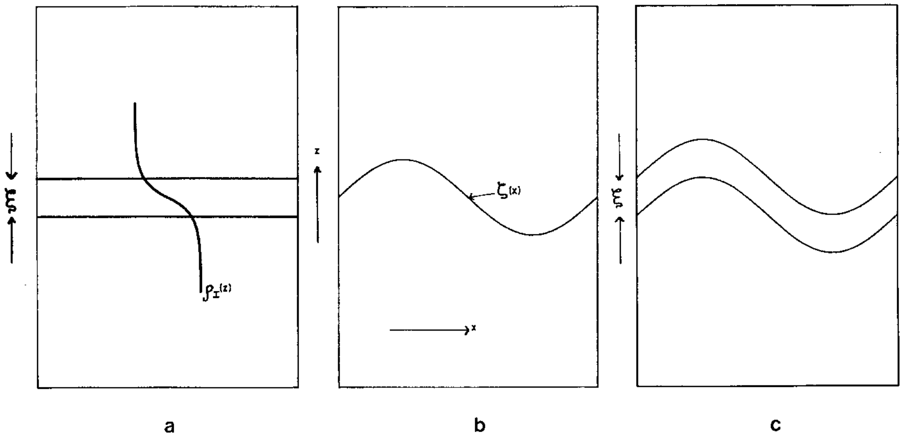


Fig. 2. (a) Intrinsic profile $\rho_{\mathrm{I}}(z)$ from van der Waals (scaling) theory. (b) Capillary wave $\zeta(x)$. (c) Intrinsic profile $\rho_{\mathrm{I}}(z)$ shown in (a) distorted by capillary wave ζ shown in (b).

Integrating by parts the second term in Eq. (3) yields

$$W[\zeta(\mathbf{x})]=\frac{\gamma_0}{2}\int|\nabla\zeta(\mathbf{x})|^2\,d\mathbf{x}-\frac{1}{2}\int\rho_{\mathrm{I}}'(z)\,u_{\mathrm{ext}}'(z)\,dz\int\zeta^2(\mathbf{x})\,d\mathbf{x} \tag{4}$$

Assuming the fluctuations of the intrinsic interface as a whole to be capillary-wave-like enables one to decompose these into sums of decoupled surface waves: $\zeta(\mathbf{x})=\sum_{\mathbf{k}}a_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{x}}$. As shown by Percus [7], Eq. (4) then assumes the form

$$W(a_{\mathbf{k}})=\frac{\gamma_0\mathscr{L}^{d-1}}{2}\sum_{\mathbf{k}}a_{\mathbf{k}}^2\,|\mathbf{k}|^2+\frac{KL^{d-1}}{2}\sum_{\mathbf{k}}a_{\mathbf{k}}^2 \tag{5}$$

with $\mathscr{L}$ the transverse edge length of the system and

$$K\equiv-\int_{-\infty}^{+\infty}\rho_{\mathrm{I}}'(z)\,u_{\mathrm{ext}}'(z)\,dz \tag{6}$$

Note that K is positive since the two derivatives in the integrand are of opposite signs.

We define a generalized capillary length l by

$$l\equiv\sqrt{\frac{2\gamma_0}{K}} \tag{7}$$

and so rewrite Eq. (5) as

$$W(a_{\mathbf{k}})=\frac{K\mathscr{L}^{d-1}}{2}\sum_{\mathbf{k}}a_{\mathbf{k}}^2\left(1+\frac{1}{2}l^2\cdot|\mathbf{k}|^2\right) \tag{8}$$

And we note that if, following Buff et al. [5], we choose the intrinsic interface to be a step function, i.e., $\rho_\mathrm{I}(z) = \rho_\mathrm{L} - \Delta\rho \cdot \theta(z)$, with $\theta(z)$ the unit step function, and the external field to be that of gravity, i.e., $u_\mathrm{ext}(z) = mgz$, then the quantity K of Eq. (6) is given by

$$\begin{aligned} K &= \int \Delta\rho\, \delta(z)\, mg\, dz \\ &= mg\, \Delta\rho \end{aligned} \tag{9}$$

with $\Delta\rho$ the difference $\rho_\mathrm{L} - \rho_\mathrm{V}$ between the bulk liquid and the bulk vapor phase densities ρ_L and ρ_V, so that l reduces to the ordinary capillary length $l = \sqrt{2\gamma_0/mg\,\Delta\rho}$, in accord with Ref. 5.

The equilibrium average of $a_\mathbf{k}^2$ is readily found, from Eqs. (1) and (8), to be

$$\begin{aligned} \langle a_\mathbf{k}^2 \rangle &\equiv \frac{\int_0^\infty a_\mathbf{k}^2 \exp[-W(a_k)]\, da_\mathbf{k}}{\int_0^\infty \exp[-W(a_\mathbf{k})]\, da_\mathbf{k}} \\ &= \frac{1}{\beta K \mathscr{L}^{d-1}(1 + \frac{1}{2} l^2 \cdot |\mathbf{k}|^2)} \end{aligned} \tag{10}$$

leading to the mean-squared thickness of the interface

$$\begin{aligned} \langle Z^2 \rangle &= \sum_{\mathbf{k}=0}^{\mathbf{k}_\mathrm{max}} \langle a_\mathbf{k}^2 \rangle \\ &= \frac{1}{\beta K \mathscr{L}^{d-1}} \sum_\mathbf{k} \frac{1}{1 + \frac{1}{2} l^2 \cdot |\mathbf{k}|^2} \end{aligned} \tag{11}$$

Result (11) enables one to determine the behavior of the interfacial thickness for several model intrinsic interfaces and several choices of the external field in any dimension of space. The case of an intrinsic interface of vanishing thickness and of a gravitational external field has already been treated [5, 8] for $d = 3$ as well as for general d.

3. FLUIDS IN TWO DIMENSIONS

In the two-dimensional version of the generalized capillary-wave theory, we have a fluctuating intrinsic interface separating two-dimensional bulk phases, the wave vector $\mathbf{k}$ being now simply a one-dimensional vector the length of which may assume the values $|\mathbf{k}| = 2\pi n/\mathscr{L}$, $n = 1, 2, \ldots$.

Evaluating the sum in Eq. (11) as an integral (thermodynamic limit $\mathcal{L} \to \infty$), we find for the square of the total interfacial thickness,

$$\langle Z^2 \rangle = \frac{1}{2\pi\beta K} \int_0^{|\mathbf{k}_{\max}|} \frac{d\,|\mathbf{k}|}{1 + \frac{1}{2} l^2 \cdot |\mathbf{k}^2|}$$

$$= \frac{1}{2\sqrt{2}\pi\beta K l} \cdot \arctan\left(\frac{l \cdot |\mathbf{k}_{\max}|}{\sqrt{2}}\right) \tag{12}$$

where K is given by Eq. (6), and $|\mathbf{k}_{\max}|$ is of the order of the inverse interfacial thickness [5].

Two limiting cases can occur: one for $l \cdot |\mathbf{k}_{\max}| \gg 1$ and another for $l \cdot |\mathbf{k}_{\max}| \ll 1$. In three-dimensional fluids [9], the former case corresponds to $10^{-3}\,°\mathrm{C} < T_c - T < 10°\mathrm{C}$, while the latter holds for $T_c - T \ll 10^{-5}\,°\mathrm{C}$. The original capillary-wave theory is essentially a low-temperature theory which can be extrapolated into the critical region, and the latter case corresponds to a region where the approximations of this theory can no longer be considered realistic [10], lying, moreover, in an experimentally inaccessible temperature range. We therefore consider only the regime $l \cdot |\mathbf{k}_{\max}| \gg 1$.

For large k, $\arctan(k) \cong \pi/2 - 1/k$, implying from Eq. (12), and the above definition (7) of the generalized capillary length l:

$$\langle Z^2 \rangle \cong \frac{1}{\beta K l}$$

$$= \frac{1}{\beta\sqrt{2\gamma_0 K}} \tag{13}$$

3.1. Step-like Intrinsic Profile

The first intrinsic density profile chosen was the step-like profile of Buff et al. [5], that is,

$$\rho_{\mathrm{I}}(z) = \rho_{\mathrm{L}} - \Delta\rho\, \theta(z) \tag{14}$$

where $\theta(z)$ is the unit step function. For this infinitely sharp intrinsic profile, one finds from Eq. (6)

$$K = \Delta\rho\, u'_{\mathrm{ext}}(0) \tag{15}$$

Assuming that $u'_{\mathrm{ext}}(0)$ is finite (an infinite $u'_{\mathrm{ext}}(0)$ would lead to a vanishing interfacial thickness [11]) we find, from Eq. (13),

$$\langle Z^2 \rangle \sim \frac{1}{\sqrt{\gamma_0\, \Delta\rho}} \sim (T_c - T)^{-(\mu + \beta)/2} \tag{16}$$

where μ and β are the critical exponents describing the vanishing of the density difference $\Delta\rho$ and the surface tension, respectively, at the critical point. From the known exact values $\beta=\frac{1}{8}$ and $\mu=1$ we find that the interfacial thickness $L \equiv \langle Z^2 \rangle^{1/2}$ diverges like

$$L \sim (T_c - T)^{-9/32} \tag{17}$$

It is assumed in deriving Eq. (17) that γ_0 vanishes at the critical point like the true surface tension and that the values of the critical exponents are not affected by the external field; in particular, it is assumed that $\mu(u_{\text{ext}} \neq 0) = \mu(u_{\text{ext}} = 0) = 1$, which has not been proven but is most likely to be correct, at least for $|u_{\text{ext}}|$ small. Thus, for *any* external field satisfying $u'_{\text{ext}}(0) < \infty$, when an intrinsic profile of vanishing thickness is chosen, as it is in the original capillary wave theory of Buff et al., one finds $\omega = 9/32$ in two dimensions. This generalizes the result of Ref. 8, which was restricted to the case of gravity.

3.2. Diffuse Intrinsic Profile

When one chooses the intrinsic profile given by the van der Waals (scaling) theory, which for simplicity, we take to be described by an exponential (Fermi) profile with a decay length equal to the bulk correlation length ξ (see Fig. 2a), K becomes

$$K = \frac{\Delta\rho}{2\xi} \int_{-\infty}^{+\infty} \exp\left(\frac{-|z|}{\xi}\right) u'_{\text{ext}}(z)\, dz \tag{18a}$$

In a recent study [11], it was found that for a step-like external field of amplitude c, for which K reduces to

$$K = \frac{c\,\Delta\rho}{2\xi} \tag{18b}$$

the value of the interfacial thickness exponent is $\omega = 17/32$. However, when a linear external field was chosen with the same intrinsic density profile, the interfacial thickness exponent was found in that same study to be 9/32. These unexpected results prompted us to investigate more general external fields.

As an example of a more general external field, we first choose

$$u_{\text{ext}}(z) = \begin{cases} -g_0 & z < a \\ \dfrac{g_0}{a} z & -a < z < a \\ g_0 & z > a \end{cases} \tag{19}$$

For this external field, K, from Eq. (18a), is given by

$$K = \frac{\Delta\rho\, g_0}{\xi a} \int_0^{+a} \exp\left(\frac{-z}{\xi}\right) dz \tag{20}$$

The critical behavior of K is readily evaluated for two limiting cases: one when $a \ll \xi$ and the second when $a \gg \xi$. The former corresponds to the case where the change in u_{ext} occurs over a scale much smaller than that of the bulk correlation length, while the latter treats the case where the change in u_{ext} occurs more gradually, over a distance much greater than the bulk correlation length.

In the first case, the integrand in Eq. (20) can be expanded about $z = 0$ and K thus becomes

$$K = \frac{\Delta\rho\, g_0}{\xi} \tag{21}$$

from which the interfacial thickness L is found to diverge like

$$\begin{aligned} L &\sim (T_c - T)^{-(\mu + \beta + \nu)/4} \\ &= (T_c - T)^{-17/32} \end{aligned} \tag{22}$$

where the exact value $\nu = 1$ of the critical exponent of the bulk correlation length has been used.

For the regime where $a \gg \xi$, K is simply

$$K = \frac{\Delta\rho\, g_0}{a} \tag{23}$$

and L is readily found to diverge like

$$\begin{aligned} L &\sim (T_c - T)^{-(\mu + \beta)/4} \\ &= (T_c - T)^{-9/32} \end{aligned} \tag{24}$$

A second choice of a general external field is the exponential form

$$u_{\mathrm{ext}}(z) = g_0 \operatorname{sgn}(z) \left[1 - \exp\left[\frac{-|z|}{\xi_u} \right] \right] \tag{25}$$

where ξ_u, similar to the length scale a introduced in Eq. (19), is a measure of the distance over which the external field varies. For the external field (25), K is given by

$$K = \frac{\Delta\rho\, g_0}{\xi + \xi_u} \tag{26}$$

For small ξ_u, i.e., $\xi_u \ll \xi$, we find that the interfacial thickness can be described in power-law form by

$$L \sim (T_c - T)^{-17/32} \tag{27}$$

whereas in the regime $\xi_u \gg \xi$, we find that L is described by

$$L \sim (T_c - T)^{-9/32} \tag{28}$$

The results for $d = 2$, summarized in Fig. 1, show that when one chooses a diffuse intrinsic density profile rather than the infinitely sharp intrinsic density profile of the original capillary-wave theory, the exponent ω describing the divergence of the interfacial thickness is strongly dependent on the choice of external field. Moreover, the distance over which the external field varies is found to affect the value of the critical exponent ω [compare Eqs. (22) and (24) and Eqs. (27) and (28)].

It should be noted that both values of the exponent ω given above, namely, 9/32 and 17/32, disagree severely with the prediction of the generalized van der Waals (scaling) theory, according to which $\omega \equiv \nu$, in any d, independently of any external field, so that, in $d = 2$, using the exact value of ν quoted above,

$$L \sim (T_c - T)^{-1} \tag{29}$$

4. FLUIDS IN THREE AND FOUR DIMENSIONS

The nonuniversal critical behavior of the interfacial thickness in two dimensions expressed by Eqs. (27) and (28) strongly suggests considering an arbitrary external field in both three and four dimensions. We find from Eq. (11)

$$\langle Z^2 \rangle \cong \frac{1}{2\pi\beta K} \int \frac{|\mathbf{k}|^{d-2}\, d\,|\mathbf{k}|}{1 + \frac{1}{2} l^2 \cdot |\mathbf{k}|^2} \tag{30}$$

In $d = 3$, this equation yields

$$\begin{aligned}\langle Z^2 \rangle &= \frac{1}{2\pi\beta K l^2} \ln\left(1 + \frac{1}{2} l^2 \cdot |\mathbf{k}_{\max}|^2\right)\\ &\sim \frac{1}{\gamma_0}\end{aligned} \tag{31}$$

while for $d=4$,

$$\begin{aligned}\langle Z^2\rangle &= \frac{1}{2\pi\beta K l^2}\left[2\,|\mathbf{k}_{\max}| - \frac{2\sqrt{2}}{l}\arctan\left(\frac{|\mathbf{k}_{\max}|\cdot l}{\sqrt{2}}\right)\right]\\ &\sim \frac{|\mathbf{k}_{\max}|}{\gamma_0}\\ &\sim \frac{1}{L\gamma_0}\end{aligned} \tag{32}$$

From Eqs. (31) and (32) it is seen at once that

$$\begin{aligned}\omega &= \mu/2 \qquad \text{for} \quad d=3\\ \omega &= \mu/3 \qquad \text{for} \quad d=4\end{aligned} \tag{33}$$

in full agreement with the predictions $\mu=(d-1)\cdot\omega$ of capillary-wave theory for the case of a gravitational field [8], as well as with the identical prediction [3] of the generalized van der Waals (scaling) theory. We observe that in strong contrast to the case of fluids in two dimensions, Eq. (33) holds for an *arbitrary* intrinsic profile as well as for an *arbitrary* external field.

5. CONCLUSION

Assuming the equilibrium structure of the fluid interface to result from averaging capillary-wave excitations on an intrinsic interface, we have studied the effect of temperature on the thickness of the interface in the presence of an external field.

The main result is that while the external field does not affect the divergence of the interfacial thickness in the critical region of fluids in three or more dimensions (except of course, as already mentioned, extremely close to the critical point [4]), its effect is dramatic in two dimensions, where the critical behavior is found to be *nonuniversal*, depending on the scale of the external field relative to the bulk correlation length. Consequently, the relation $\mu=(d-1)\omega$, which links the critical exponents of surface tension and interfacial thickness to the dimension of space and which is most probably correct in $d\geqslant 3$, appears to be incorrect in $d=2$, since in that case ω, unlike μ, is strongly field dependent.

ACKNOWLEDGMENTS

This work was supported by the Welch Foundation, the National Science Foundation, and the Donors of the Petroleum Research Fund administered by the American Chemical Society.

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