

## Some Considerations of Fluid Interfaces in Two Dimensions

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Basic assumptions of the capillary wave theory of fluid interfaces are examined critically as a function of space dimensionality  $d$ . When the predictions of capillary wave theory are compared with those of the nonclassical Maxwell–van der Waals theory, agreement is found in  $d=3$  and 4, but strong disagreement occurs in  $d=2$ . It is shown that the total effective mass density obtained from the Hamiltonian describing the collective capillary wave excitations has a logarithmic divergence in  $d=2$ . This result suggests the possibility of anomalous behavior for fluid interfaces in  $d=2$ .

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**KEY WORDS:** Fluid interfaces; critical phenomena; capillary wave theory.

### 1. INTRODUCTION

When two fluid phases coexist in the presence of gravity, they are separated by a planar diffuse interface of finite thickness. In three or fewer dimensions of space, a macroscopic external field is essential to maintain a finite interfacial thickness.<sup>(1a,b)</sup> Gravity is explicitly taken into account in the capillary wave theory of fluid interfaces, while it is ignored in conventional theories of the Maxwell<sup>(2a)</sup>–van der Waals type<sup>(2b)</sup> in order to simplify the analysis.<sup>4</sup>

Capillary wave theory requires a density of modes, an upper cutoff on allowable wave vectors and an effective mass. Designed for low temperatures,<sup>(3)</sup> this theory can be extrapolated into the near-critical region,<sup>(1a)</sup> although not strictly up to the critical point itself.<sup>(4)</sup>

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<sup>4</sup> The formulation including an external field is available in Ref. 2c.

**Table I. Critical Exponent of Interfacial Thickness**  
 $\langle z^2 \rangle^{1/2} \propto (T_c - T)^{-\omega}$   
 as a Function of Dimensionality  $d$

$d$	2	3	4
$\omega_c^a$	9/32	$\sim 0.64$	1/2
$\omega_{\text{MW}}^b$	1	$\sim 0.64$	1/2

<sup>a</sup>  $\omega_c$  denotes prediction of capillary wave theory.

<sup>b</sup>  $\omega_{\text{MW}}$  denotes prediction of nonclassical Maxwell-van der Waals theory.

It has recently been observed<sup>(5)</sup> that in two dimensions of space, capillary wave theory predicts a critical behavior of the interfacial thickness which differs significantly from that predicted by the nonclassical<sup>(6)</sup> Maxwell-van der Waals theory. In three dimensions or more, these theories make identical predictions,<sup>(5)</sup> expressing the insensitivity of critical behavior to macroscopic external fields such as normal gravity. For general dimension  $d$ , their predictions are compared in Table I, where  $\omega$  is the critical exponent describing the divergence of the interfacial thickness as the critical temperature is approached. Note the nonmonotonic behavior of  $\omega_c$ , the value of  $\omega$  predicted by capillary wave theory, as a function of  $d$ .

In this paper, we discuss critically basic assumptions of capillary wave theory such as density of modes, cutoff, and effective mass density. The analysis confirms earlier agreements between the predictions of capillary wave and nonclassical Maxwell-van der Waals theories in  $d=3$  and 4, but suggests that the behavior of fluid interfaces may be anomalous in  $d=2$ .

## 2. DERIVATION OF RESULTS

### 2.1. Analysis of Basic Assumptions of Capillary Wave Theory

In capillary wave theory, one considers a microscopically sharp interface which undergoes thermal fluctuations restored by gravity and surface tension. These thermal modes are characterized by: a wave vector  $\mathbf{k} \in R^{d-1}$ , a density of modes  $g(k)$ , a cutoff  $k_{\text{max}}$ , a dispersion relation  $\omega(k)$ , and an effective mass  $m(k)$ .

With  $L$  the edge length of the system assumed for simplicity to be hypercubic, a Rayleigh-Weyl enumeration gives

$$g(k) \propto L^{d-1} k^{d-2} \quad (1)$$

so that the total number  $N$  of modes of wave number  $k$  smaller or equal to  $k_{\max}$  is

$$\begin{aligned}
 N &\propto \int_0^{k_{\max}} g(k) dk \\
 &\propto L^{d-1} k_{\max}^{d-1}
 \end{aligned}
 \tag{2}$$

At low temperatures,  $k_{\max}$  may reasonably be chosen as  $k_{\max} \propto \pi/a$ , with  $a$  some atomic distance. But more generally, when the theory is extrapolated into the neighborhood of the critical temperature  $T_c$ , where the interface disappears, one clearly must have  $N \rightarrow 0$ , so that, according to (2),  $k_{\max}$  must vanish in that limit. A dimensional argument<sup>(1a)</sup> yields

$$k_{\max} \propto \frac{\pi}{\text{interfacial thickness}}
 \tag{3}$$

For  $d \geq 3$ , interfacial thickness and bulk correlation length are proportional to each other.<sup>(5)</sup> Result (3) can be interpreted as expressing the fact that capillary waves, as collective modes, are ill defined when their wavelength is smaller than the interfacial thickness or, for  $d \geq 3$ , the bulk correlation length. This cutoff  $k_{\max}$  is similar to the high-frequency cutoff used by Debye in his theory of specific heat of solids and has been used in other applications of capillary wave concepts.<sup>(7)</sup>

It should be stressed that it is only with the choice (3) that capillary wave theory yields,<sup>(5)</sup> for  $d \geq 3$ , the hyperscaling-like relation  $\mu = 1 + r = (d - 1)\omega$ , where  $\mu$  is the critical exponent describing the vanishing of the surface tension as  $T \rightarrow T_c$  and  $r$  is Guggenheim's exponent. According to the simplified version of the Maxwell-van der Waals theory, which ignores the effect of gravity,  $\omega = \nu$  for all  $d$ , with  $\nu$  the critical exponent describing the divergence of the bulk correlation length as  $T \rightarrow T_c$ .

It is interesting to observe that interfacial theories give the correct values of the critical exponents when  $d = 4$ . This follows from the well-known results<sup>(8)</sup>  $r = \nu = 1/2$  of mean-field theory.

### 2.2. Effective Mass of Capillary Waves

Conventionally, capillary wave theory takes as its starting point the work of deformation  $W$  of a single-valued distortion  $z(\mathbf{x})$  of the interface. Decomposing  $z$  into its elementary excitations  $z(\mathbf{x}) = \sum_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k}\mathbf{x}}$  gives in the linearized theory<sup>(1a)</sup>

$$W(z) \propto \frac{1}{2} L^{d-1} \sum_{\mathbf{k}} [(\rho_{\alpha} - \rho_{\beta}) g + \gamma_0 k^2] a_{\mathbf{k}}^2
 \tag{4}$$

with  $\rho_\alpha$  and  $\rho_\beta$  the mass densities of the coexisting phases  $\alpha$  and  $\beta$ ,  $g$  the acceleration of gravity, and  $\gamma_0$  the bare surface tension.

It is however more useful for our purpose to consider the Hamiltonian which describes capillary waves as collective modes. This Hamiltonian assumes the form<sup>(9a)</sup>

$$H = \frac{1}{2} \sum_{\mathbf{k}} \left[ \frac{p_{\mathbf{k}}^2}{m(k)} + m(k) \omega^2(k) a_{\mathbf{k}}^2 \right] \tag{5}$$

where the effective mass is given by

$$m(k) \propto \frac{\rho_\alpha + \rho_\beta}{k} L^{d-1} \tag{6}$$

and where, according to the classical dispersion relation,<sup>(10)</sup>

$$\omega^2(k) = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta} gk + \frac{\gamma k^3}{\rho_\alpha + \rho_\beta} \tag{7}$$

Hamiltonian (5) is required for the theory of quantum interfaces.<sup>(9b)</sup>

The first term in (5), which yields  $m(k)$  as given by (6), arises from a classical hydrodynamic calculation of the kinetic energy,<sup>(11)</sup> where  $m(k)$  represents the effective inertia of a surface wave of wave number  $k$ .<sup>(12)</sup>

The potential energy term in (5) reduces to the conventional work term given by Eq. (4):

$$W = \frac{1}{2} \sum_{\mathbf{k}} m(k) \omega^2(k) a_{\mathbf{k}}^2 \tag{8}$$

In terms of the effective mass, the optically observed mean-square displacement of the interface,  $\langle z^2 \rangle$ , is proportional to

$$\int_0^{k_{\max}} \frac{g(k)}{m(k) \omega^2(k)} dk$$

For the total effective mass density per unit interfacial area,  $\bar{m}$ , we have from (1) and (6)

$$\bar{m} = \frac{\int_0^{k_{\max}} m(k) g(k) dk}{L^{d-1} \int_0^{k_{\max}} g(k) dk} \tag{9}$$

$$\propto (\rho_\alpha + \rho_\beta) \begin{cases} \frac{1}{k_{\max}}, & d > 2 \\ \frac{1}{k_{\max}} \ln k \Big|_0^{k_{\max}}, & d = 2 \end{cases}$$

It is seen that the case  $d=2$  is anomalous in that the total effective mass density per unit interfacial area,  $\bar{m}$ , is regular for all  $d > 2$ , while it is logarithmically divergent for  $d=2$ .

This divergence of the total effective mass density in  $d=2$  occurs for all subcritical values of the temperature, and is induced by the modes of small wave numbers. We note that while the capillary wave prediction  $\omega \neq \nu$  holds for  $d < 3$ , the total effective mass density only diverges for  $d \leq 2$ .

The effective mass is, from equipartition, directly proportional to the fluctuation in momentum and inversely proportional to the fluctuation in position. It is not directly measurable but does determine, as seen above, the optically observable quantity  $\langle z^2 \rangle$ .

### 2.3. Surface Tension

The optically observable quantity  $\langle z^2 \rangle$  is related in an exact way to the measured surface tension  $\gamma$  in a gravitational field. We have indeed<sup>(14)</sup>

$$\gamma = \int_{-\infty}^{+\infty} (\sigma_T - \sigma_N) dz + \frac{mg}{2} \int_{-\infty}^{+\infty} z^2 \frac{\partial \rho}{\partial z} dz \tag{10}$$

where  $\sigma_{T(N)}$  denotes the tangential (normal) component of the stress tensor,  $m$  the mass of a molecule, and  $z$  the vertical distance across the interface (to be distinguished from the instantaneous location  $z(\mathbf{x})$  of the interface introduced above). The second term in the right-hand side of (10) is proportional to  $\langle \dot{z}^2 \rangle$ .<sup>(15)</sup>

In terms of the capillary length  $a = (2\gamma/\Delta\rho g)^{1/2}$ , (10) can be rewritten as:

$$\gamma = \left( \int_{-\infty}^{+\infty} (\sigma_T - \sigma_N) dz \right) / (1 + \langle z^2 \rangle / a^2) \tag{11}$$

Note that in the right-hand side of (11) the external field, explicitly present in the denominator, is implicitly contained in the numerator, which is given by the exact version of density gradient theory.<sup>(16)</sup>

Result (11) leads, for  $a^2 \gg \langle z^2 \rangle$ , to the following extended scale form:

$$\frac{\gamma \langle z^2 \rangle^{(d-1)/2}}{kT} = \left( \frac{a^2}{\langle z^2 \rangle} \right)^{\zeta(d)} f \left( \frac{a^2}{\langle z^2 \rangle} \right) \tag{12}$$

For  $d \geq 3$ , we have  $\zeta(d) = 0$ . For  $d = 2$ , we find, using the exact values<sup>(17a,b)</sup>  $\mu = 1$  and  $\beta = 1/8$  of the critical exponents of surface tension<sup>(17a)</sup> and order parameter<sup>(17b)</sup> of the lattice gas:

$$\zeta(2) = \frac{1 - \omega}{2\omega + 7/8} \quad (13)$$

suggesting  $0 \leq \zeta(2) \leq 1/2$ , with  $1/2$  the value given by the linearized capillary wave theory, for which  $\omega = 9/32$ .<sup>(5)</sup> It may be noted that the exact form<sup>(13)</sup> of the interfacial density profile of the infinite two-dimensional lattice gas in the absence of a macroscopic external field, but with distances rescaled on the scale of the fluctuations, yields<sup>(13a)</sup>  $\omega = 1/2$  and therefore, from Eq. (13),  $\zeta(2) = 4/15$ ; this value does lie within the above suggested range. The same result obtains<sup>(13b)</sup> for another definition of the interfacial thickness in the same model, which however remains finite on the scale of the lattice spacing, diverging only at the critical point.

The Maxwell–van der Waals theory implies

$$\frac{\gamma \zeta^{d-1}}{kT} = \text{const} \quad (14)$$

satisfying (12) with  $\zeta = 0$  and  $f = \text{const}$ . However this theory explicitly ignores any external field such as gravity, while such a macroscopic field is essential to obtain nontrivial equilibrium interfaces in  $d \leq 3$ . Relation (12) therefore appears more general and suitable to describe the equilibrium properties of fluid interfaces in the presence of external fields: the effect of the macroscopic external field, hidden in  $d > 3$ , manifests itself strikingly in  $d = 2$ .

### 3. DISCUSSION

The above analysis confirms the earlier observation<sup>(5)</sup> that in  $d = 3$  and 4, the predictions of capillary wave and nonclassical Maxwell–van der Waals theories are concordant. It suggests that the behavior of fluid interfaces in  $d = 2$  may be anomalous. Although the exact value of  $\omega$ , the exponent describing the divergence of the interfacial thickness at the critical point, is not known, this work does suggest the following behavior of near-critical interfaces between fluid phases in two dimensions: near the critical point in  $d = 2$ , the predictions of capillary wave theory may be qualitatively valid; but very close to the critical point, there may be, because of the very weak singularity in the total effective mass density, a crossover from the singular capillary wave behavior of the interfacial thickness to a different singular behavior.

This view is supported by the observation that in  $d=2$ , the diverging total effective mass density  $\bar{m}$  corresponds, in a hydrodynamic description, to a diverging mean generalized inertia:  $\bar{m}$  is proportional to the mean generalized inertia of a fluid in which a surface wave of wavelength  $k^{-1}$  carries with it a layer of fluid of depth approximately equal to  $m(k)$ .<sup>(12)</sup> Consequently, this diverging inertia inhibits the surface's excitations, making the interface less diffuse and yielding a weaker divergence of the interfacial thickness in  $d=2$ .

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## NOTE ADDED IN PROOF

It may be mentioned that the predictions of capillary wave theory, originally derived on the basis of phenomenological concepts (Ref. 1a) and recently proved from first principles (Ref. 1b), have also been verified numerically in two dimensions of space by machine simulations (J. H. Sikkenk, H. J. Hilhorst and A. F. Bakker, *Physica* **131A**; 587 (1985)).

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