

## Dynamics of a diffuse liquid-vapor interface

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As a sequel to our previous discussion of a hydrodynamic model for the condensation of a near-critical fluid, we describe the dynamics of a diffuse planar liquid-vapor interface. We show that inclusion of the thermal mode and its coupling to the density mode is essential in deriving the dispersion relation for capillary waves, and the isothermal approach based either on hydrodynamic or mean-field kinetic theory must lead to a nonphysical description of excitations of the diffuse interface. The problem of the rate of growth of a critical liquid droplet in a supersaturated vapor is reconsidered, and a corrected expression for this rate is shown to have the expected scaling behavior.

### I. INTRODUCTION

An essential ingredient of any systematic theory of first-order phase transitions is an analysis of the dynamics of the interface which separates the phases. In conventional hydrodynamic problems, these dynamics can be described by use of the Euler or Navier-Stokes equations together with phenomenological boundary conditions imposed at a supposedly sharp bounding surface. In phase-transition problems, however, one must use models in which material is allowed to cross the interface. That is, the interface must be diffuse, and the applicability of conventional boundary conditions is not obvious. This problem arose in our earlier theory<sup>1</sup> of the nucleation of a droplet during condensation of a near-critical fluid. (Our previous paper<sup>1</sup> is hereafter referred to as I.) It was argued in I that, although the equilibrium properties of the interface—its energy, the density profile, etc.,—can be described by means of an isothermal free-energy functional, the dynamics of the interface require a full adiabatic description. Indeed, the rate of growth for the critical liquid drop is determined by heat dissipation in the vicinity of the growing embryo of the new phase, and the isothermal calculations give rise to an incorrect rate of growth.

In I, we developed a generalized hydrodynamic model for the description of a diffuse liquid-vapor interface. That model is used in the current work in which we address the problems of the dynamics of a planar interface separating the bulk of the liquid from the bulk of the vapor. This classical van der Waals problem has previously been studied in the literature<sup>2,3</sup>; but we feel that these earlier attempts are not completely satisfactory, especially near the critical point. In fact, both of these calculations are isothermal; and the more recent one,<sup>3</sup> based upon kinetic theory, leads to an

expression for the spectrum of capillary waves in which the temperature dependence is nonphysical.

The plan for this paper is as follows. In Sec. II we shall recall the basic assumptions of our hydrodynamic model from I and discuss in detail the formulation of our problem. In Sec. III we apply the model to the problem of capillary waves on a diffuse interface. We prove that inclusion of the slow thermal mode is essential in restoring the validity of the Laplace boundary condition for the velocity field on the interface. The correct expression for the spectrum of capillary waves is also derived in that section. In Sec. IV we rederive our expression for the rate of growth of a critical nucleus of the new (liquid) phase growing in the supersaturated vapor. Our corrected expression now agrees with the prediction of dynamical scaling laws and with explicit calculations of Kawasaki.<sup>4</sup> Section V contains final comments and conclusions.

### II. THE HYDRODYNAMIC MODEL

The basic quantity which enters our model is the coarse-grained free-energy functional  $F$  discussed in detail in I. [See also Ref. (5).] Here  $F$  is a functional of the fluid density  $n(\vec{r})$ , the local velocity  $\vec{u}(\vec{r})$ , and equivalently, the temperature  $T$  or the internal energy density per unit volume  $e(\vec{r})$ .

As in I, we hypothesize that  $F$  consists of two parts:

$$F = F_K + F_U, \quad (2.1)$$

where  $F_K$  is the fluid kinetic energy

$$F_K = \frac{1}{2} m \int d^3r n(\vec{r}) u^2(\vec{r}); \quad (2.2)$$

and  $F_U$  is the thermodynamic potential. For pres-

ent purposes we write

$$F_V = \int d^3r [e(\vec{r}) + \frac{1}{2} K(\nabla n)^2 - \mu n - Ts(e, n)]. \quad (2.3)$$

The second term on the right-hand side of  $F_V$  is the van der Waals-Cahn-Hilliard gradient energy term,  $\mu$  is the chemical potential, and  $s$  is the entropy per unit volume. The states of the system for which  $F$  is stationary include the homogeneous liquid and vapor phases and also states in which a critical liquid drop is immersed in a supersaturated vapor. Yet another stationary state is one in which there is a unidirectional change of the density. In that case the conditions

$$\frac{\delta F}{\delta n(\vec{r})} = 0, \quad \frac{\delta F}{\delta \vec{u}(\vec{r})} = 0, \quad \frac{\delta F}{\delta e(\vec{r})} = 0, \quad (2.4)$$

reduce to the one-dimensional version of Eq. (4.1) from I. This equation is just a generalization of the van der Waals equation for the density profile and therefore describes the van der Waals "soliton," that is, the hyperbolic-tangentlike density profile.

In the following section we shall investigate the stability of the one-dimensional solution of the stationarity conditions (2.4). It is convenient in this analysis to use the local temperature rather than the energy density as the basic thermal variable. Linearizing the full set of hydrodynamic equations around the stationary solution  $\bar{n} = n(z)$ ,  $\bar{\vec{u}} = 0$ , and  $T = \text{constant}$ , we obtain

$$\frac{\partial \nu}{\partial t} = -\kappa \nu = -\vec{\nabla} \cdot (\bar{n} \vec{u}), \quad (2.5)$$

$$\frac{\partial \vec{u}}{\partial t} = -\kappa \vec{u} = -\frac{1}{m} \vec{\nabla} \frac{\delta^2 F}{\delta \bar{n}^2} \nu - \frac{1}{m \bar{n}} \vec{\nabla} \frac{\partial \bar{P}}{\partial T} \theta, \quad (2.6)$$

$$\frac{\partial \theta}{\partial t} = -\kappa \theta = -\frac{T}{\bar{n} C_v} \frac{\partial \bar{P}}{\partial T} \vec{\nabla} \cdot \vec{u} + \frac{\lambda}{\bar{n} C_v} \nabla^2 \theta. \quad (2.7)$$

In the above  $\nu$ ,  $\vec{u}$ ,  $\theta$  are the deviations from their stationary values of the density, velocity, and temperature, respectively;  $\delta^2 F / \delta \bar{n}^2$  is the differential operator discussed in I;  $P$ ,  $C_v$ , and  $\lambda$  denote the pressure, the specific heat at constant volume, and the thermal conductivity, respectively. Barred quantities are functions of the density and the temperature evaluated at the values corresponding to the stationary solution. These quantities are position dependent and, away from the interfacial region, they become equal to their constant values in the corresponding phases.

The stability analysis of the van der Waals soliton is equivalent to computing the eigenvalue  $\kappa$  in Eqs. (2.5)–(2.7). In contrast to the conventional theory of capillary waves (see Landau and Lifshitz),<sup>6</sup> we do not have at our disposal the boundary conditions for the velocity, density, and tem-

perature fields at a sharp interface between the phases. These conditions must be inferred from the solutions of Eqs. (2.5) and (2.7). It turns out that the Laplace condition for the velocity field is the most important of these conditions and, as we shall see in the next section, inclusion of the heat mode into our analysis effectively brings that condition into our calculations.

It is possible to see on physical grounds why the thermal mode is essential in determination of the eigenvalue  $\kappa$ . Consider a small bulge in the stationary density profile. This bulge may be due either to a hydrodynamic deformation of the interface or it may result from excess condensation of the vapor. The latter mechanism, however, involves the generation and dissipation of latent heat. For systems of the kind we are considering, the thermal modes are generally much slower than the hydrodynamic modes; thus thermal effects impose important constraints on the kinds of motion that can occur at the interface. In the following section we shall see how this picture emerges from the mathematics of Eqs. (2.5)–(2.7).

The model described above is quite simplified. We have neglected two factors which are important in the description of real experimental situations, namely, viscosity and gravity. One can, if one wishes, include both of these in the calculations; however, these additional effects do not contribute to the main results and tend to make an already involved calculation quite complicated.

### III. CAPILLARY WAVES

Equations (2.5)–(2.7) form a set of linear differential equations with position-dependent coefficients. We shall solve them for the eigenvalue  $\kappa$  by analyzing them separately in the interfacial region and in the bulk of both phases and then matching the solutions at the boundaries of these three regions. In the process of doing this we shall consider only those perturbations of the interface whose wavelengths are larger than the only characteristic length in our problem, that is, the thickness of the interface. Specifically, we assume that  $k\xi \ll 1$ , where the wave vector  $\vec{k}$  lies in the plane parallel to the unperturbed interface and  $\xi$  is the interface thickness, equal essentially to the critical correlation length.

Our first observation is that the velocity field  $\vec{u}(\vec{r}, t)$  determined by Eq. (2.6) can be written in terms of potentials  $\Phi$  and  $\Psi$  defined as follows:

$$\vec{u}(\vec{r}, t) = -\vec{\nabla} \Phi - \frac{1}{\bar{n}} \vec{\nabla} \Psi, \quad (3.1)$$

where

$$\Phi = -\frac{1}{m\kappa} \frac{\delta^2 F}{\delta \bar{n}^2} \nu, \quad \Psi = -\frac{1}{m\kappa} \frac{\partial \bar{P}}{\partial T} \theta. \quad (3.2)$$

Equation (3.1) tells us that the velocity field  $\bar{\mathbf{u}}$  is generally rotational but that its vorticity is localized in the vicinity of the interface and is essentially due to the coupling between the temperature variation and the stationary interface profile:

$$\bar{\nabla} \times \bar{\mathbf{u}} = (1/\bar{n}^2) \bar{\nabla} \bar{n} \times \bar{\nabla} \Psi. \quad (3.3)$$

Outside the interface the velocity field is potential, and one can define velocity potentials:

$$\bar{\Phi}_\alpha = \Phi_\alpha + \frac{1}{n_\alpha} \Psi_\alpha, \quad (3.4)$$

where the subscript  $\alpha$  ( $\alpha = l, v$ ) denotes either liquid or vapor.

We now look for solutions of our equations by Fourier transforming in the directions parallel to the unperturbed interface; thus

$$\begin{aligned} \Phi_\alpha &= \bar{\Phi}_\alpha(z) \exp(i\bar{\mathbf{k}} \cdot \bar{\mathbf{x}} - \kappa t), \\ \Psi_\alpha &= \psi_\alpha(z) \exp(i\bar{\mathbf{k}} \cdot \bar{\mathbf{x}} - \kappa t), \end{aligned} \quad (3.5)$$

where  $\bar{\mathbf{k}}$  is a two-dimensional wave vector. In each of the bulk phases we are looking for solutions which decay when we move away from the interfacial region. (We assume that the interface is located near  $z = 0$ .) We assume therefore that

$$\phi_\alpha(z), \psi_\alpha(z) \propto \exp(-q|z|). \quad (3.6)$$

Using Eqs. (3.5) and (3.6), we can simplify our basic equations considerably. Recall from I that  $\delta^2 F / \delta \bar{n}^2$  in either of the bulk phases becomes equal to  $1/(n_\alpha^2 K_{T\alpha})$  where  $K_{T\alpha}$  is the isothermal compressibility of the  $\alpha$ th phase. The resulting equations for the amplitudes  $\nu_\alpha$  and  $\theta_\alpha$  are

$$m\kappa^2 \nu_\alpha = (n_\alpha K_{T\alpha})^{-1} (q^2 - k^2) \nu_\alpha + \Gamma_\alpha (q^2 - k^2) \theta_\alpha, \quad (3.7)$$

$$\kappa \theta_\alpha (\kappa T / n_\alpha^2 C_{V\alpha}) \Gamma_\alpha \nu_\alpha - D_\alpha (q^2 - k^2) \theta_\alpha, \quad (3.8)$$

where we have used the notation  $D_\alpha \equiv (\lambda / n_\alpha C_{V\alpha})$ ,  $\Gamma_\alpha \equiv (\partial P / \partial T)_{n_\alpha}$ .

The condition for nontrivial solutions of the above equations gives us an expression for the wave number  $q$  as a function of  $k^2$ ,  $\kappa$ , and the system parameters. This expression simplifies if one keeps only the lowest order terms in  $k^2$ ; but this approximation is not essential to our argument. The two solutions for  $q^2$  are

$$q_1^2 \cong -\kappa \gamma_\alpha / D_\alpha, \quad q_2^2 \cong k^2 + O(k^4), \quad (3.9)$$

where  $\gamma_\alpha = C_{P\alpha} / C_{V\alpha}$ . The first of these solutions would describe thermal diffusion in a homogeneous compressible fluid. The second is the hydrodynamic mode. For small  $k$ , we expect  $|q_1| \gg |q_2|$ .

Let the amplitudes of the density  $\nu_\alpha(z)$  corresponding to the solutions (3.9) be denoted by  $N_{1\alpha}$  and  $N_{2\alpha}$ , respectively. Thus,

$$\nu_\alpha(z) = N_{1\alpha} \exp(-q_1|z|) + N_{2\alpha} \exp(-q_2|z|). \quad (3.10)$$

The analogous amplitudes of the temperature deviations  $\theta_\alpha$  turn out to be

$$\frac{\Theta_{1\alpha}}{N_{1\alpha}} = \left( \frac{\partial n_\alpha}{\partial T} \right)_P^{-1}, \quad (3.11)$$

$$\frac{\Theta_{2\alpha}}{N_{2\alpha}} = T \left( \frac{\partial P}{\partial T} \right)_{n_\alpha} / (n_\alpha^2 C_{V\alpha}). \quad (3.12)$$

Inserting the above expressions into the definition for the velocity potential (3.4) away from the interface, we obtain

$$\begin{aligned} \bar{\phi}_\alpha(z) &\equiv \phi_\alpha(z) + \frac{1}{n_\alpha} \psi_\alpha(z) \\ &= \bar{\phi}_\alpha \exp(-q_2|z|), \end{aligned} \quad (3.13)$$

where the symbol  $\bar{\phi}_\alpha$  (without the argument  $z$ ) denotes the value of the velocity potential at the interface and is given in terms of the previously defined amplitudes  $N$  by the ratio  $(-N_{2\alpha} \gamma_\alpha / m\kappa n_\alpha^2 K_{T\alpha})$ . Note that the  $q_1$  terms have canceled out so that only the long-range hydrodynamic mode remains in this expression. Finally, we can write the  $z$  components of the velocities at the interface ( $z = 0$ ) in the form

$$u_i = -q_2 \bar{\phi}_i, \quad u_v = q_2 \bar{\phi}_v. \quad (3.14)$$

Having derived the important relations (3.14), we turn to an investigation of our equations within the interfacial region. Our first step here is to solve Eq. (3.2) for the density field. This requires inversion of the operator  $\delta^2 F / \delta \bar{n}^2$ . Following the discussion in I, we use the approximate form of that operator, namely,

$$\left( \frac{\delta^2 F}{\delta \bar{n}^2} \right)^{-1} \cong \frac{1}{\sigma k^2} \frac{d\bar{n}}{dz} \frac{d\bar{n}}{dz'}, \quad (3.15)$$

where  $\sigma$  is the van der Waals surface tension:  $\sigma = K \int (d\bar{n}/dz)^2 dz$ . Using Eq. (3.15) we can relate the potential  $\phi(z)$  to the interfacial displacement  $A$  defined by the relation  $\nu(z) = -A d\bar{n}/dz$ . Solving (3.2) we obtain

$$\nu(z) \cong \frac{m\kappa}{\sigma k^2} \frac{d\bar{n}}{dz} \int_{-\infty}^{\infty} dz' \phi(z') \frac{d\bar{n}}{dz'}, \quad (3.16)$$

and therefore

$$A = -\frac{m\kappa}{\sigma k^2} \int_{-\infty}^{\infty} dz' \phi(z') \frac{d\bar{n}}{dz'}. \quad (3.17)$$

The use of this approximate form of the operator  $(\delta^2 F / \delta \bar{n}^2)^{-1}$  is in agreement with our basic assumption that  $k\xi \ll 1$ . With the same accuracy we conclude from the heat balance equation (3.7)

that  $\theta$  is nearly constant over the interfacial region, and therefore we write

$$\theta(\vec{x}, z) = \theta_0 \exp(i\vec{k} \cdot \vec{x}); \quad (3.18)$$

thus the potential  $\psi$  is equal to

$$\psi \cong -\frac{\theta_0}{m\kappa} \frac{\partial \bar{P}}{\partial T}. \quad (3.19)$$

Our next step is similar to that in Eq. (6.23) of I. We integrate (2.7) across the interface and identify the quantity  $Q$ :

$$Q = -T \int_{-\infty}^{\infty} \frac{\partial \bar{P}}{\partial T} \vec{\nabla} \cdot \vec{u} dz \cong \frac{m\kappa}{\theta_0} T \int_{-\infty}^{\infty} \psi(z) (\vec{\nabla} \cdot \vec{u}) dz \quad (3.20)$$

as the rate at which latent heat is generated per unit area at the interface. Our evaluation of this integral in I was incorrect; and a correct argument is as follows. Suppose that the interface moves with velocity  $V$ . Integrating the continuity equation across the interface we obtain the first of the so-called Kotchine conditions from continuous media mechanics,<sup>7</sup> that is,

$$n_1 u_1 - n_v u_v = (\Delta n) V, \quad (3.21)$$

where  $\Delta n = n_1 - n_v$  and, as previously,  $u_\alpha$  is the limiting value of the  $z$  component of the velocity field when  $z$  approaches the interfacial region. (Notice that this makes sense only if  $k\xi \ll 1$ .) The rate of evaporation  $\chi$  (in molecules per unit area) is  $n_v(u_v - V)$ ; therefore the heat generated at the interface in the process of condensation is  $Q = -l\chi$ . Solving (3.21) for  $\chi$  we obtain

$$Q = l n_1 n_v (u_1 - u_v) / (\Delta n), \quad (3.22)$$

which gives us the value of the integral in (3.20).

We turn now to the continuity equation. To lowest order in  $k\xi$  we can write  $\vec{\nabla} \cdot \vec{u} \cong du_x/dz$ . Then the continuity equation becomes

$$\frac{d}{dz} (\bar{n} u_x) \cong \kappa v \cong \kappa A \frac{d\bar{n}}{dz}, \quad (3.23)$$

where we have used Eqs. (3.16) and (3.17). Because the interface velocity  $V$  is just the time derivative of the interface displacement,  $V = \kappa A$ , we obtain from (3.22)

$$\frac{d}{dz} (\bar{n} u_x) \cong V \frac{d\bar{n}}{dz}, \quad (3.24)$$

and after integration

$$\bar{n}(z) u_x(z) = \bar{n}(z) V + n_1 (u_1 - V). \quad (3.25)$$

It follows that the derivative of the velocity field is equal to

$$\frac{du_x}{dz} = -\frac{1}{\bar{n}^2} \frac{d\bar{n}}{dz} n_1 (u_1 - V) = \frac{n_1 n_v}{\bar{n}^2 \Delta n} (u_1 - u_v) \frac{d\bar{n}}{dz}, \quad (3.26)$$

where we have used again the condition (3.21). We now can use Eq. (3.26) in the evaluation of the integral in (3.20):

$$\begin{aligned} \int_{-\infty}^{\infty} \psi(z) (\vec{\nabla} \cdot \vec{u}) dz &\cong \int_{-\infty}^{\infty} \psi(z) \frac{du_x}{dz} dz \\ &\cong \int_{-\infty}^{\infty} \psi(z) \frac{1}{\bar{n}^2} \frac{d\bar{n}}{dz} dz \left( \frac{n_1 n_v (u_1 - u_v)}{\Delta n} \right); \end{aligned}$$

and by virtue of (3.22)

$$\int_{-\infty}^{\infty} \psi(z) \frac{1}{\bar{n}^2} \frac{d\bar{n}}{dz} dz = \frac{\theta_0 l}{m\kappa T}. \quad (3.27)$$

Because the velocity field  $u_x(z)$  given by (3.25) is finite in the interfacial region, we conclude that, to lowest order in  $k\xi$ , we have

$$\int_{\text{interface}} \bar{n}(z) u_x(z) dz \cong 0. \quad (3.28)$$

Recalling Eqs. (3.1) and (3.4), we rewrite (3.28) in the form

$$-\int_{-\infty}^{\infty} dz \left( \bar{n} \frac{d\phi}{dz} + \frac{d\psi}{dz} \right) = [\bar{n}\phi + \psi] + \int_{-\infty}^{\infty} \phi(z) \frac{d\bar{n}}{dz} dz, \quad (3.29)$$

where the square bracket denotes the jump of the bracketed quantity across the interface, viz.,  $[M] = M_1 - M_v$ . From Eqs. (3.29) and (3.17) it follows that

$$[\bar{n}\phi + \psi] = \sigma k^2 A / m\kappa. \quad (3.30)$$

Similarly, integrating the velocity field  $u_x$  across the interface, we obtain

$$\begin{aligned} 0 &\cong \int_{\text{interface}} u_x(z) dz = -\int dz \left( \frac{d\phi}{dz} + \frac{1}{\bar{n}} \frac{d\psi}{dz} \right) \\ &= \left[ \phi + \frac{1}{\bar{n}} \psi \right] - \int \psi \frac{1}{\bar{n}^2} \frac{d\bar{n}}{dz} dz. \end{aligned}$$

Using Eq. (3.27), we obtain:

$$\left[ \phi + \frac{1}{\bar{n}} \psi \right] = \frac{\theta_0 l}{m\kappa T}. \quad (3.31)$$

Equations (3.30), (3.31), and (3.14) are the conditions that we need for final derivation of the dispersion relation for capillary waves.

From the jump condition (3.21) and the definition of the interface displacement, as well as from the conditions (3.14), we have

$$\kappa A (\Delta n) = -q_2 (n_1 \phi_1 + n_v \phi_v + \psi_1 + \psi_v). \quad (3.32)$$

Eliminating  $A$  via Eq. (3.30) we obtain

$$\kappa^2 = -\frac{\sigma k^2 q_2 (n_1 \phi_1 + \psi_1 + n_v \phi_v + \psi_v)}{m(\Delta n) (n_1 \phi_1 + \psi_1 - n_v \phi_v - \psi_v)}, \quad (3.33)$$

which can be converted easily into an expression which will be specially convenient for the following

discussion:

$$\kappa^2 = -\frac{\sigma k^2 q_2}{m(\Delta n)} \left( \frac{n_1 u_1 - n_v u_v}{n_1 u_1 + n_v u_v} \right). \quad (3.34)$$

Equation (3.34) is our main result in this section.

Before showing how the correct dispersion relation for capillary waves follows from (3.34), let us observe what goes wrong with this formula when the thermal effect is neglected. In the isothermal case the potential  $\psi$  vanishes,  $\theta_0 = 0$ , and Eq. (3.31) asserts that  $\phi_1 = \phi_v$ , that is, the velocity potential is continuous across the interface. From (3.32) it follows that

$$\kappa_{\text{isothermal}}^2 = -\frac{\sigma k^2 q_2}{m(\Delta n)^2} (n_1 + n_v). \quad (3.35)$$

This is a nonclassical expression for the capillary spectrum which has questionable scaling properties in the vicinity of the critical point. Experimental results<sup>8,9</sup> leave little room for doubt that the capillary spectrum is classical even very close to  $T_c$ . One should notice that, away from the critical point, Eq. (3.35) gives results numerically similar to those of the normal dispersion relation. Since the incorrect expression (3.35) follows from a theory in which the heat mode was neglected, it is not surprising that recent mean-field kinetic theory calculations<sup>3</sup> also give a dispersion relation for capillary waves which differs from the correct one.

The final step in obtaining a correct dispersion relation from Eq. (3.34) is based upon thermal balance in the interfacial region. Using heat conservation and Eq. (3.22), we can write

$$u_1 - u_v = -\frac{\lambda(\Delta n)}{ln_1 n_v} \left[ \frac{d\theta}{dz} \right]. \quad (3.36)$$

Equation (3.36) plays the role in our theory of the Laplace condition for the velocity field in the conventional (sharp interface) theory of capillary waves. In order to estimate the jump in the heat current we recall that the interfacial temperature is almost constant [see Eq. (3.18)]. The main contribution to the jump in  $d\theta/dz$  comes then, in the limit  $k\xi \ll 1$ , from the short-range solution in Eq. (3.8), that is, from  $q_1$ . Because  $q_1$  is proportional to  $\kappa$  [see Eqs. (3.11) and (3.31)], it follows that the right-hand side of Eq. (3.36) is proportional to  $\kappa^{3/2}$ . In the long wavelength limit we expect that  $\kappa$  will vary as  $k^{3/2}$  and therefore, in that limit,  $u_1 \cong u_v$ . This means that the velocity field is continuous across the interfacial region while the velocity potential  $\phi$  is not.

Substituting  $u_1 = u_v$  into Eq. (3.34) we obtain

$$\kappa^2 = -\sigma k^2 q_2 / m(n_1 + n_v). \quad (3.37)$$

The fact that  $\kappa^2$  is less than zero implies that the

van der Waals soliton is stable against small deformations even in the presence of heat conduction. Setting  $\kappa = i\omega$  and recalling that, according to (3.8),  $q_2^2 = k^2 + O(k^4)$ , we obtain the conventional dispersion relation for capillary waves:

$$\omega^2 = \sigma k^3 / m(n_1 + n_v). \quad (3.38)$$

We want to emphasize again the role played by the thermal mode in our derivation of Eq. (3.38). Without the thermal mode the basic relation (3.33) would be different and the velocity field would be discontinuous at the interface. Because the Laplace condition for the velocity follows from heat conservation, we conclude that it is impossible to obtain the correct capillary spectrum in an isothermal theory without making inconsistent assumptions about the continuity of the velocity field.<sup>2</sup>

#### IV. THE GROWING DROPLET

The main part of the analysis in Sec. III was devoted to the derivation of three conditions which have to be satisfied at the interface by velocity potentials and the density and temperature fields. These calculations were necessary to prove that it is legitimate to use jump conditions such as (3.30), (3.31), and the Laplace condition in studying the dynamics of a diffuse interface. The main result is that, for excitations whose wavelengths are long compared to the interfacial thickness, it is entirely possible to use such jump conditions. The most general versions of these conditions are called Kotchine relations in the theory of continuous media, and these relations are ordinarily derived by integrating the conservation laws for fluid mechanics in regions containing singular surfaces.<sup>7</sup> In what follows we shall write the Kotchine conditions for the specific problem of a spherically growing droplet of liquid, and shall use them in a rederivation of the expression for the rate of growth of a critical droplet from I. In contrast to the planar problem where recovery of the Laplace condition was crucial to the derivation of the capillary-wave dispersion relation, the spherically symmetric growth mode in the droplet case is one in which matter does cross the interface. We shall see that the correct growth rate, the rate which scales properly, comes out naturally from the full adiabatic treatment. Again, coupling to the thermal mode is essential.

The Kotchine conditions for a spherical droplet have the form:

$$[nu_R] = [n] V_R, \quad (4.1)$$

$$[P] = -2\sigma \bar{K}, \quad (4.2)$$

$$[\mu] = 0, \quad (4.3)$$

$$\ln_1 n_v [u_R] / (\Delta n) = -\lambda [(\nabla T)_R]. \quad (4.4)$$

Here  $P$  is the pressure,  $\mu$  is the chemical potential,  $\sigma$  is the surface tension,  $\bar{K}$  is the curvature of the interface, and the subscript  $R$  denotes the component of a vector normal to the interface. In our spherical case, this is always the radial component; and  $\bar{K} = 1/R$  where  $R$  is the radius of the droplet.

It is slightly more convenient to linearize the basic hydrodynamic equations using not the density but the excess pressure in either phase as the independent variable. Let  $P_{\alpha}$  be the pressure for two-phase equilibrium at temperature  $T$ , and then write, for phase  $\alpha$ ,

$$p_{\alpha} \equiv P_{\alpha} - P_{\alpha} \cong \frac{1}{n_{\alpha} K_{T\alpha}} \nu_{\alpha} + \Gamma_{\alpha} \theta_{\alpha}. \quad (4.5)$$

The velocity field  $\vec{u}$  may be eliminated in the equations of motion (2.5) through (2.7) by means of the continuity equation. The resulting equations for the pressure and temperature fields are

$$m n_{\alpha} K_{T\alpha} \frac{\partial^2 p_{\alpha}}{\partial t^2} - \nabla^2 p_{\alpha} = m \Gamma_{\alpha} n_{\alpha} K_{T\alpha} \frac{\partial^2 \theta_{\alpha}}{\partial t^2}, \quad (4.6)$$

$$\frac{\partial \theta_{\alpha}}{\partial t} - \frac{\lambda}{n_{\alpha} C_{P\alpha}} \nabla^2 \theta_{\alpha} = \left( \frac{C_{P\alpha}}{C_{P\alpha} - C_{V\alpha}} \right) \frac{1}{\Gamma_{\alpha}} \frac{\partial p_{\alpha}}{\partial t}. \quad (4.7)$$

For present purposes, however, it is adequate to use a quasistationary approximation in which these equations reduce simply to

$$\nabla^2 p_{\alpha} \cong \nabla^2 \theta_{\alpha} \cong 0. \quad (4.8)$$

Moreover, because neither phase can support a pressure gradient in the slow mode of interest here, we can assume that the quantities  $p_{\alpha} = p_i$ ,  $p_v$  are constants, that is, independent of position. The thermal field does depend on the radius  $r$  measured from the center of the droplet:

$$\theta_i = \theta_0 = \text{constant}, \quad r < R \quad (4.9)$$

$$\theta_v = \theta_0 R/r, \quad r > R.$$

We now apply the Kotchine conditions to evaluate  $p_v$ ,  $p_i$ , and  $\theta_0$ . Continuity of the chemical potential, Eq. (4.3), leads *via* standard thermodynamic manipulations to the relation

$$\frac{p_i}{n_i} - \frac{p_v}{n_v} = -\frac{l\theta_0}{T}, \quad (4.10)$$

where  $l$  is again the latent heat per molecule. Using (4.2) to eliminate  $p_i$ , we find

$$p_v = \frac{n_v}{(\Delta n)} \left( \frac{2\sigma}{R} + \frac{l\theta_0 n_i}{T} \right). \quad (4.11)$$

It is useful to rewrite (4.11) in terms of the critical radius  $R^*$  instead of the excess pressure  $p_v$ . At exactly  $R^*$  the critical droplet is neither growing

nor diminishing. It is not generating latent heat, therefore  $\theta_0$  must vanish, and

$$p_v = \frac{2n_v \sigma}{(\Delta n) R^*}. \quad (4.12)$$

The resulting expression for  $\theta_0$  is

$$\theta_0 = \frac{2T\sigma}{ln_1} \left( \frac{1}{R^*} - \frac{1}{R} \right). \quad (4.13)$$

The remaining two conditions, (4.1) and (4.4), now provide an equation of motion for  $R$ . We have

$$(\Delta n) \frac{dR}{dt} = -n_v u_v = -\frac{\lambda(\Delta n)}{ln_1} \left( \frac{d\theta_v}{dr} \right)_{r=R} = \frac{\lambda(\Delta n)\theta_0}{ln_1 R}. \quad (4.14)$$

With (4.13), this becomes

$$\frac{dR}{dt} = \frac{2\lambda\sigma T}{l^2 n_1} \left( \frac{R - R^*}{R^* R^2} \right), \quad (4.15)$$

which is our basic equation of motion for  $R$ . Linearizing (4.15) around  $R^*$  and looking for solutions of the form  $R - R^* \propto \exp(\kappa t)$ , we find

$$\kappa = \frac{2\lambda\sigma T}{l^2 n_1 (R^*)^3}. \quad (4.16)$$

Equation (4.16) is the Kawasaki result<sup>4</sup> and should be used instead of Eq. (6.34) from I in the calculation of critical supersaturations. It turns out that the numerical error brought about by use of the improper expression for  $\kappa$  is less than 2%. The physical difference, however, is more profound. The rate of growth from I does not scale properly while the above expression for  $\kappa$  leads to the following scaling law:

$$\kappa \propto \xi^{-3} (\xi/R)^3. \quad (4.17)$$

This is precisely the critical behavior of  $\kappa$  that one should expect on the basis of dynamical scaling laws, which predict that  $\kappa$  should have the form  $\xi^{-3} f(R/\xi)$  with an undetermined function  $f(x)$ . Here, as usual,  $\xi$  is the interface thickness, i.e., the critical correlation length. Essentially the same technique, with additional algebraic complications, can be used in the theory of capillary waves on the surface of a growing droplet. As expected, one obtains the classical result of Lamb for the spectrum of waves which adjust themselves adiabatically to the instantaneous droplet radius.

## V. FINAL COMMENTS AND CONCLUSIONS

We have investigated dynamical effects associated with planar and spherical interfaces separating two phases of a one-component fluid. We have shown that the dynamical theory of such an interfacial region must include coupling between the density and heat modes. This is particularly crucial close to

the critical point of a fluid where the heat mode becomes the slowest mode in the system. We have shown with examples of capillary waves and the growth of a liquid droplet that omitting this coupling leads to wrong and inconsistent results.

Although our theory was purely hydrodynamic, we feel that it illuminates certain points in recent kinetic theories of inhomogeneous fluid systems. The liquid-vapor interface is certainly the simplest example of a unidirectional density inhomogeneity, and the microscopic as well as phenomenological theory of such a system was recently discussed in a review paper.<sup>10</sup> No systematic kinetic theory of such a system exists and the mean-field theory developed in Ref. 3 suffers from the same difficulties as the hydrodynamic isothermal approach. We infer from our phenomenological theory that any future microscopic theory should include the mode-coupling terms. The coupling between the density and heat mode would be described essentially by the same procedure as in this paper. One notices that there also will be an

additional coupling between the shear modes and the thermal mode. This fact follows from the expression for the fluid velocity field vorticity in Eq. (3.3).

There are many possible extensions of our work. One should look more closely at the surface excitations close to the critical point of a binary mixture. Various hydrodynamic instabilities associated with the surface effects should also be reexamined. Finally, it would be very interesting to repeat all the calculations for the case of a quantum system where a first-order phase transition of the form of the liquid-vapor phase transition is observed, namely in the theory of the electron-hole liquid.

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