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Unstable modes of a quenched fluid interface

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It is shown that the flat interface separating two coexisting phases of a binary liquid is unstable under nonequilibrium conditions corresponding to quenching the system deeper into the two-phase region. For given quench depth the instability persists out to a finite wave number k_0; for larger wave numbers surface tension renders the interface stable. As a by-product of the calculation, the effect of diffusive relaxation on the ordinary capillary-wave dispersion relation and power spectrum is evaluated. Results indicate that previous experiments were conducted in a regime in which diffusive effects do not affect the extraction of the surface tension from the power spectrum.

I. INTRODUCTION

A recent experiment by Schwartz *et al.*[1] raised the possibility that the interface separating the two coexisting phases in a critical binary mixture may become unstable as the system is rapidly quenched deeper into the two-phase region. The situation is depicted in Fig. 1. The system is initially in equilibrium at temperature T_i, and it is quenched to final temperature

$$T_f = T_c(1-\epsilon) \tag{1.1}$$

with final miscibility gap ΔC as shown.[2] When the system was quenched, a certain amount of structure was observed in the vicinity of the interface, but none was observed in the bulk. Thus the quench was not sufficiently deep to induce homogeneous nucleation in the bulk material.

As pointed out by Cahn[3] the usual phenomenological assumptions of local equilibrium suggest that ordinary nucleation should be suppressed in the vicinity of the sharp interface and should not give rise to observable structure. Under these assumptions particle transfer occurs very rapidly across the interface and there the system reaches the final equilibrium compositions characterized by T_f. Hence one is led to consider the possibility of a special interface instability.

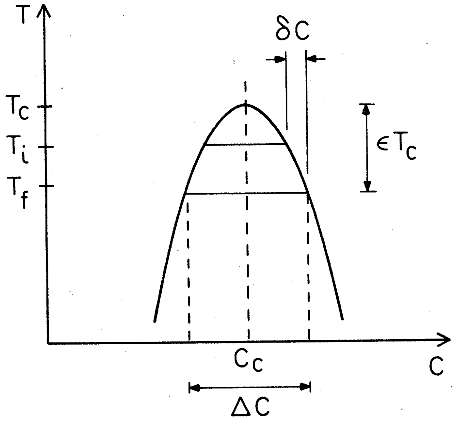

FIG. 1. Coexistence curve for a typical binary fluid showing the miscibility gap ΔC and the reduced temperature ϵ.

It is not clear at this stage whether the initial experimental results were caused by such an instability. A more systematic series of experiments is in progress.[1] The purpose of this short paper is to point out that, in principle at least, such a surface instability exists and to suggest that the preliminary experimental observations may have been related to the phenomenon.

The instability is related to one well known in metallurgy, the Mullins-Sekerka instability,[4] which is driven by supercooling. The boundary between stable and unstable domains (of parameters) is essentially due to a competition between diffusion and surface tension. In the case of a fluid the shear viscosity plays an important role. However, as we shall see, at sufficiently long wavelengths the instability is not removed.

Our calculation is based completely on macroscopic hydrodynamics in which the interface is considered sharp. Near the critical point of a simple fluid or typical binary fluid the characteristic width of the interface is experimentally on the order of the bulk correlation length,[5,6] although there is strong evidence[7] that there is a nonuniversal dependence on the gravitational acceleration which plays a stablizing role. We shall in any event assume the interface is stabilized and of strictly finite width L. A hydrodynamic analysis in the regime $kL \ll 1$ can effectively neglect the finite interface width. This is the usual phenomenological assumption which we adopt while recognizing that a complete microscopic analysis for its justification is not yet available.

Our primary interest is in the character and characteristic length scale of any instability. Thus we make several simplifying assumptions of symmetry between the two phases. As a by-product we shall also evaluate the contribution of diffusive relaxation to the capillary-wave spectrum as analyzed by Wu and Webb[5] and Huang and Webb.[6] Under the experimental circumstances it appears that such contributions do not affect the extraction of the surface tension from the ordinary capillary-wave power spectrum.

The remainder of the paper is divided as follows. In Sec. II we briefly review the surface instability that occurs when velocity fields are completely neglected. In Sec. III we include the Navier-Stokes equations to obtain the full dispersion relation for the surface modes. Analysis of the result is contained in Secs. IV–VI, while concluding remarks and a brief summary appear in Sec. VII.

II. INTERFACE INSTABILITY: NO VELOCITY FIELDS

This model neglects any velocity fields and is thought to be applicable to the situation in solid alloys. This case has been treated by Langer and Turski[8]; however, for completeness and to introduce notation we sketch briefly the analysis.

Before the system is quenched we have the situation depicted in Fig. 2(a); that is, there are two coexisting phases, α and β of compositions[9] C_α^0 and C_β^0 in equilibrium. The interface separating the phases is sharp and planar. A short time after the quench the situation is depicted schematically in Fig. 2(b). At the planar interface the concentrations rapidly reach the final equilibrium values C_α^{eq} and C_β^{eq} appropriate to the final temperature T_f as shown in Fig. 1. However, in the bulk of the material the compositions have not yet adjusted as a finite time is required for matter diffusion, in contrast to temperature equilibration which is taken to be infinitely rapid. Since we are only interested in the instability or stability of the planar interface we characterize the non-equilibrium situation by the initial slopes at the interface. Hence following Langer and Turski[8] we replace the solid-line shape in Fig. 2(b) by the dashed straight lines, the slope of which characterizes the degree of supercooling.

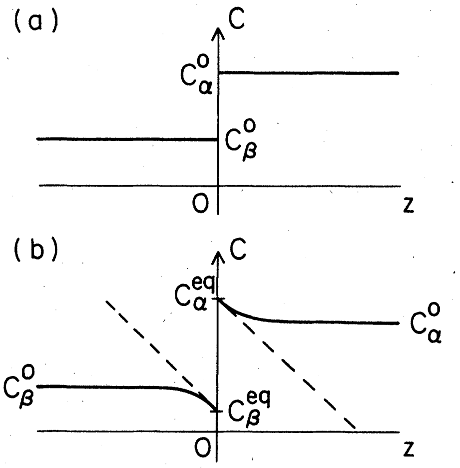

FIG. 2. The interfacial shape assumed in the macroscopic analysis. (a) Prior to the quench, showing the initial compositions. (b) A short time after the quench, showing that at the boundary the compositions have adjusted to the final equilibrium values. The dashed lines show the profile in the kinetic model.

The equation which governs the relaxation is the diffusion equation

$$D\nabla^2 C = \frac{\partial C}{\partial t}, \tag{2.1}$$

where we have assumed for simplicity symmetry in the coefficients

$$D_\alpha = D_\beta = D. \tag{2.2}$$

The diffusion equation must be supplemented by appropriate boundary conditions. At some instant the configuration of the surface is shown schematically in Fig. 3. The interface is specified by the function $z = \zeta(\vec{x}, t)$ where $\vec{x}$ is a two-dimensional vector in the plane perpendicular to the z axis. Because of the curvature, at the interface, C_α and C_β are no longer the coexisting equilibrium values of the composition. Rather, a Gibbs-Thompson relation[10] requires

$$\begin{aligned} u_\alpha &= C_\alpha - C_\alpha^{\text{eq}} = -(\Delta C) l_c K, \\ u_\beta &= C_\beta - C_\beta^{\text{eq}} = -(\Delta C) l_c K, \end{aligned} \tag{2.3}$$

where K is the local curvature which we can take for small displacements as

$$K = -\nabla^2 \zeta, \tag{2.4}$$

and as noted $\Delta C = C_\alpha^{\text{eq}} - C_\beta^{\text{eq}}$ is the final miscibility gap. The parameter l_c is a capillary length. We

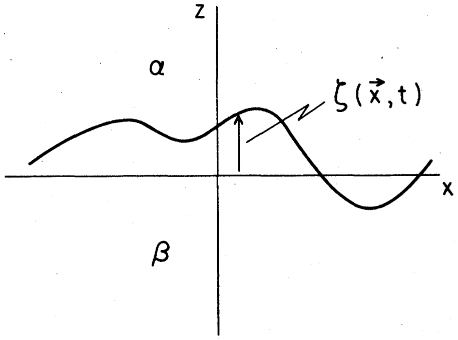

FIG. 3. Schematic indication of a perturbation of the flat interface $z = 0$. The instantaneous interface is described by $z = \zeta(\vec{x}, t)$.

have chosen the same value for this parameter in both phases consistent with our assumption of a symmetric binary system with

$$\left(\frac{\partial C}{\partial \mu}\right)_\alpha = \left(\frac{\partial C}{\partial \mu}\right)_\beta \tag{2.5}$$

along with equal molar volumes. Under these conditions,

$$l_c = \left(\frac{\partial C}{\partial \mu}\right)\bar{v}\,\frac{\sigma}{(\Delta C)^2}\,, \tag{2.6}$$

where σ is the surface tension and $\bar{v}$ is the volume per unit mass. Note that C is the mass fraction of type A molecules. We note for future applications that (in our notation) near the critical point l_c is proportional to the bulk correlation length ξ since $\partial C/\partial \mu \sim |\epsilon|^{-\gamma}$, $\sigma \sim |\epsilon|^{(d-1)\nu}$, and $(\Delta C) \sim |\epsilon|^{\beta}$ in the usual notation.[11] From (2.6), l_c is given by $l_c \sim |\epsilon|^{-\gamma+(d-1)\nu-2\beta} \sim |\epsilon|^{-\nu} \sim \xi$.

In addition to (2.3) one further boundary condition is required. Namely, if $(dC/dz)_{z\to\zeta\pm}$ do not match, there will be an imbalance of diffusion fluxes which will cause the interface to move. The appropriate condition is[8]

$$-D[(\vec{\nabla} u)_\alpha - (\vec{\nabla} u)_\beta]\cdot d\vec{S} = (\Delta C)\frac{d\zeta}{dt}\,d^2x\,, \tag{2.7}$$

where $d\vec{S}$ is the surface normal (oriented toward the α phase). For small displacements $d\vec{S}$ becomes parallel to the z direction.

To study the linear stability of the planar interface, one makes an harmonic analysis. One writes

$$C_\alpha = C_\alpha^{\mathrm{eq}} - \frac{(\Delta C)}{l}\,z + u_1\,, \tag{2.8}$$

which embodies the "ramp" shown in Fig. 2(b), and assumes

$$u_1 = \hat{u}_1 e^{ikx - i\omega t} e^{-pz}, \quad \mathrm{Re}\,p > 0 \tag{2.9}$$

along with a similar form for the β phase. The interface is also assumed to oscillate according to

$$\zeta = \hat{\zeta} e^{ikx - i\omega t}\,. \tag{2.10}$$

Matching the boundary conditions (recalling that $\hat{u}_1$, $\hat{\zeta}$ are considered to be small parameters), one obtains

$$-2Dp\left(\frac{1}{l} - l_c k^2\right)\hat{\zeta} + i\omega\hat{\zeta} = 0 \tag{2.11a}$$

with

$$p = (k^2 - i\omega/D)_+^{1/2}\,, \tag{2.11b}$$

where + indicates the positive real part. Equation (2.11a) yields the dispersion relation

$$y_M(1+\mathfrak{z})_+^{1/2} + \mathfrak{z} = 0\,, \tag{2.12}$$

where the dimensionless parameters y_M and $\mathfrak{z}$ are given by

$$\mathfrak{z} = -i\omega/Dk^2\,,$$

$$y_M = -\frac{2}{kl}\,(1-\kappa^2)\,, \tag{2.13a}$$

with

$$\kappa = k/k_c, \quad k_c^2 = 1/ll_c\,. \tag{2.13b}$$

The signature of an instability is a solution to (2.13) with $\mathrm{Re}\,\mathfrak{z} > 0$ corresponding to $\mathrm{Re}(-i\omega) > 0$. It is easy to see that for $k < k_c$ there is always such a solution[12]: The planar interface is unstable at long enough wavelengths.

The situation is easily understood. The boundary between instability and stability is due to competition between surface tension and diffusion. At $k = 0$, where surface tension plays no role (there being no curvature), the interface is always unstable. Consider the solid lines in Fig. 2(b). If the flat interface were shifted to the right, the values of the composition at the new position would remain at their equilibrium values (the local equilibrium assumption). But the α phase would have a larger composition gradient at the interface. The difference is such as to displace the interface further to the right. At finite wave vector k, surface tension resists the displacement. At $k > k_c$ there are only damped-wave solutions. We now turn to the case of a binary fluid mixture. As we shall see the inclusion of velocity fields (mass transport instead of merely composition) reduces the domain of instability.

III. INCLUSION OF VELOCITY FIELDS

Here we generalize the analysis of Bouchiat and Meunier and Wu[13] of the capillary-wave spectrum in a single-component fluid. In addition to the diffusion equation (2.1) we have the equations for the velocity fields

$$\vec{\nabla}\cdot\vec{V} = 0\,,$$

$$\frac{\partial \vec{V}}{\partial t} = \bar{\nu}\,\nabla^2\vec{V} - \frac{1}{\rho}\vec{\nabla}P\,. \tag{3.1}$$

Here $\bar{\nu} = \eta/\rho$ is the kinematic viscosity (η being the shear viscosity and ρ the mass density) and P is the pressure. We assume incompressible flow as is reasonable for typical binary fluids.

The boundary conditions at the α-β interface are modified as follows[14]:

$$\vec{V}_\alpha = \vec{V}_\beta\,,$$

$$\eta_\beta\left(\frac{\partial V_x}{\partial z} + \frac{\partial V_z}{\partial x}\right)_\beta = \eta_\alpha\left(\frac{\partial V_x}{\partial z} + \frac{\partial V_z}{\partial x}\right)_\alpha\,, \tag{3.2}$$

$$\left(-P + 2\eta_\beta\frac{\partial V_z}{\partial z}\right)_\beta = \left(-P + 2\eta_\alpha\frac{\partial V_z}{\partial z}\right)_\alpha + \sigma\frac{d^2\zeta}{dx^2}\,,$$

where the second and third lines express the equality of the tangential and normal parts of the stress tensor. The normal part includes the extra contribution due to the curvature; σ is the surface tension as above. Because of the velocity-field coupling the diffusion equation (2.1) becomes

$$D\nabla^2 C = \frac{\partial C}{\partial t} + \vec{\mathrm{V}} \cdot \vec{\nabla} C \,. \tag{3.3}$$

The second term is usually of higher order, but here because of the composition ramp in (2.9) we have, to lowest order,

$$D\nabla^2 u = \frac{\partial u}{\partial t} - \frac{V_z}{l}(\Delta C) \,. \tag{3.4}$$

The conservation condition (2.8) is modified to read

$$-D[(\vec{\nabla} u)_\alpha - (\vec{\nabla} u)_\beta] \cdot d\vec{\mathrm{s}} = (\Delta C)\left(\frac{d\zeta}{dt} - V_z\right), \tag{3.5}$$

where again we have assumed symmetry in the diffusion coefficients. Finally, we must take account of the statement of local equilibrium analogous to the Gibbs-Thompson relation. When there are velocity fields and curvature of the interface, the pressure is discontinuous across the interface $P_\alpha \neq P_\beta$, which means that the compositions C_α and C_β no longer take their bulk equilibrium values. One finds a modification of (2.3). The thermodynamic boundary condition for this binary system becomes

$$\left[\tilde{v}_\alpha - (\Delta C)\left(\frac{\partial \mu}{\partial P}\right)^\alpha_{C,\,T}\right]\delta P_\alpha - \tilde{v}_\beta\, \delta P_\beta = (\Delta C)\left(\frac{\partial \mu}{\partial C}\right)^\alpha_{P,\,T} u_\alpha \,,$$

where $\delta P_{\alpha,\beta} = P_{\alpha,\beta} - P^{\mathrm{eq}}$ are the pressure fluctuations and $u_\alpha = C_\alpha - C_\alpha^{\mathrm{eq}}$; the designation "eq", as usual, refers to the final flat-interface situation. For ease in analysis we assume complete symmetry of the coexisting liquid phases. (We shall return to this point in the discussion below.) We take $\rho_\alpha = \rho_\beta = \rho$ and further we assume[15] $\eta_\alpha = \eta_\beta = \eta$. Under these conditions the form (2.3) is recovered.

A somewhat tedious but straightforward analysis yields the dispersion relation

$$\mathfrak{z} + \frac{2ra}{\kappa \mathfrak{z}}\left(1 - \frac{1}{(1+\mathfrak{z}/a)_+^{1/2}}\right) - \frac{2}{k_c l \kappa}\left\{(1+\mathfrak{z})_+^{1/2}(1-\kappa^2) - \frac{2ar\,(1+\mathfrak{z})_+^{1/2}}{\mathfrak{z}^2 \kappa}\left[\frac{1}{(1+\mathfrak{z}/a)_+^{1/2}}\left(\frac{a}{a-1}\right) - 1\right] + \frac{2ra}{\mathfrak{z}^2 \kappa}\left(\frac{1}{a-1}\right)\right\} = 0 \,, \tag{3.6}$$

where κ, k_c, l, l_c, and the complex frequency $\mathfrak{z} = -i\omega/Dk^2$ have been defined in (2.13), and where

$$a \equiv \bar{v}/D \tag{3.7}$$

and

$$r \equiv \frac{\sigma}{4Dk_c\eta} \tag{3.8}$$

are dimensionless constants. All square roots are understood to have positive real part.

The dispersion relation has been presented in full detail to comment on its limits. Below we shall mainly be concerned with the *scaling limit* of (3.6). Note that (3.6) reproduces the earlier dispersion relation (2.12) in which velocity fields were neglected in the limit $\bar{v} \to \infty$ (or $a \to \infty$) for fixed k. Furthermore, if diffusion is neglected, $D \to 0$, (3.6) reproduces the ordinary capillary-wave dispersion relation[13,16] (in the somewhat unusual case of two fluids of equal density and viscosity but nonvanishing surface tension). If such a symmetric system has an instability, it will appear as a solution $\omega = \omega(k)$ of (3.6) with $\mathrm{Re}[-i\omega(k)] > 0$.

One can determine the power spectrum of the interface fluctuations as follows.[17] Suppose a surface force $\pi(\vec{\mathrm{x}}, t)$ (of dimensions force per area) were applied to the interface; such force would be added to the third boundary condition in (3.2). One then determines the linear response

$$\hat{\zeta}(k, \omega) = \chi(k, \omega)\hat{\pi}(k\omega) \,, \tag{3.9}$$

and according to usual fluctuation-dissipation relations the power spectrum is given by[13]

$$P_k(\omega) = \frac{k_B T}{\pi \omega}\, \mathrm{Im}\chi(k\omega) \,. \tag{3.10}$$

The analysis is once again straightforward; however, the general result is quite lengthy. Our main interest *here* is in the effect of diffusion in the absence of supercooling ($l \to \infty$). In that (equilibrium) case it is convenient to express the result in terms of the dimensionless frequency variable

$$\begin{aligned} f &= \mathfrak{z}/a = -i\omega/\bar{v}k^2 \\ &\equiv -i\omega\tau \,. \end{aligned} \tag{3.11}$$

The reduced response function Φ_{eq} is given by

$$\Phi_{\mathrm{eq}} = \frac{2\rho}{\tau^2 k}\chi = \frac{1 + w\gamma(f)}{\mathfrak{D}(f)} \,, \tag{3.12}$$

where

$$\gamma(f) \equiv (1+f)^{1/2}[1+(1+f)^{1/2}] \tag{3.13}$$

and

$$\mathfrak{D}(f) = y_{\text{eq}}\gamma(f)(1+af)^{1/2} + f\gamma(f) + x\,. \tag{3.14}$$

In these equations all roots have positive real parts. The parameters w, x, and y_{eq} are determined by the physical conditions and fluid characteristics according to

$$x \equiv 2r/\kappa a = \sigma/2\bar{\nu}^2\rho k$$

$$\equiv 2(kl_c)/aw\,, \tag{3.15a}$$

$$y_{\text{eq}} = 2(kl_c)/a\,. \tag{3.15b}$$

Note that in the limit of vanishing diffusion coefficient $D \to 0$ we have $a \to \infty$ so that $y_{\text{eq}} \to 0$ and $w \to 0$. In that case (3.12) reduces to the ordinary capillary-wave response function. The dispersion relation (3.6) and the response function (3.12) constitute our final results. Before turning to a discussion of the dispersion relation we comment on the magnitudes of various parameters which have been introduced, in regimes of experimental interest.

IV. EVALUATION OF PARAMETERS IN THE KINETIC MODEL

For realistic comparison with experiment we must identify the "supercooling length" l used in the kinetic model to simulate the nonequilibrium state. In an experiment the system requires an "intermediate" time on the order of $t_0 \sim \xi^2/D$ to respond to the quench, this being the time for material to diffuse across the (finite) interface thickness which for practical purposes is of the order ξ, the bulk correlation length. From the macroscopic point of view a concentration adjustment is required at the boundary to establish local equilibrium after an infinitely rapid quench (see Fig. 2). The adjustment is

$$\delta C = C_\alpha^{\text{eq}} - C_\alpha^0 \equiv \Theta(\Delta C)\,, \tag{4.1}$$

so that δC is a measure of the supercooling; Θ measures it as a proportion of the final miscibility gap. Hence an estimate for the gradient that can be established on time scales of the order t_0 ("zero time" for the macroscopic analysis) is $(dC/dz) \sim \Theta(\Delta C)/\xi$. This leads to an estimate of the supercooling length

$$l = \frac{\xi}{\Theta}\,. \tag{4.2}$$

A consistent identification arises from solution of the diffusion equation in the halfspace $z > 0$,[18] when such macroscopic analysis is continued to intermediate times of order t_0.

The identification (4.2) yields k_c from (2.13),

$$k_c^2 = \Theta/\xi^2\,. \tag{4.3}$$

Hence for sufficiently small supercooling Θ, one can consider wave numbers up to and greater than k_c and remain in the hydrodynamic regime. Note also that l is at least several times the correlation length ξ which suggests that the macroscopic analysis is valid.

In Table I the physical parameters in the scaling limit of a typical binary fluid are shown. Note that in the scaling regime

$$r \approx 6\pi/4\Theta^{1/2} \equiv (d_1\Theta^{1/2})^{-1}\,, \tag{4.4}$$

where the form of D from Table I has been used. The convenient abbreviation d_1 has been introduced since *formally* the limit $d_1 \to 0$ corresponds to neglecting diffusion. Other useful combinations which will appear below are

$$\frac{r}{\kappa} = \frac{\sigma}{4\eta Dk} \approx (d_1 k\xi)^{-1} \gg 1\,, \tag{4.5}$$

$$k_c l \approx \Theta^{-1/2}\,, \tag{4.6}$$

$$w \approx d_1(k\xi)^2 \ll 1\,. \tag{4.7}$$

Note that $w \to 0$, $r \to \infty$ when diffusion is neglected. However, the parameter x introduced in (3.15a) remains finite.

V. DISPERSION RELATION

We return to an analysis of the dispersion relation (3.6). The ordinary capillary-wave dispersion relation [neglecting the entire third term of (3.6)] is a fourth-order equation. The situation with supercooling is much more complicated. Diffusion alone, with no supercooling, raises it to an eighth-order equation. In the ex-

TABLE I. Numerical parameters for typical binary fluids near criticality.

Symbol	Name	ϵ dependence	Values used
ξ	Correlation length	$\xi_0\lvert\epsilon\rvert^{-\nu}$	$\xi_0 \simeq 2$ Å $\nu \simeq 0.62$
ΔC	Miscibility gap	$B\lvert\epsilon\rvert^{\beta}$	$B \simeq 1$ $\beta \simeq \frac{1}{3}$
σ	Surface tension	$\sigma_0\epsilon^{2\nu}$	$\sim k_B T_c/\xi^2$
$\bar{\nu}$	Kinematic viscosity		$\bar{\nu} \sim 0.02$ cm²/s
ρ_c	Fluid density		$\rho \sim 1$ gm/cm³
D	Diffusion coefficient	$D_0\epsilon^{\nu}$	$\sim k_B T_c/6\pi\bar{\nu}\rho\xi$

perimental regime of interest (near but below the phase separation critical point) the diffusion coefficient is very small and the parameter a is very large (10^6–10^8). This causes computational problems which can be circumvented in the scaling limit (see below). The terms of (3.6) which involve the combination $\mathfrak{z}^2\kappa$ arise from the $\vec{\nabla}\cdot\vec{V}$ coupling.

The characteristic feature of the interface instability discussed in Sec. II is that as $k\to 0$, $-i\omega$ approaches a real positive quantity $[-i\omega \to 4D(\Delta C)/l^2]$ as is easily seen from (2.11). This feature persists with the inclusion of velocity fields; as $k\to 0$, there is a solution of (3.6) with $\mathrm{Re}(-i\omega)>0$. The question of principle is resolved as expected—at sufficiently long wavelength the quenched-fluid interface is unstable. One finds once again as $k\to 0$, $-i\omega\to 4D(\Delta C)/l^2$ so that the (finite) shear viscosity does not make itself felt in leading order. The question of the *domain* of instability, that is, the upper limit k_0 for which the system is unstable, can be answered numerically. A complete interpretation of the preliminary experiments of Schwartz *et al.*[1] requires an estimate of such a scale.

Fortunately it is possible to reduce (3.6) to manageable proportions by going to the scaling limit. Near the critical point the diffusion coefficient is small so that $a\gg 1$. Frequencies of interest are in the domain $|\mathfrak{z}|\sim\omega/Dk^2=O(1)$, which means that we may treat $\mathfrak{z}/a$ as a small parameter. We shall show that we can make a self-consistent approximation especially valid in the boundary region between stability and instability where $\mathrm{Re}\,\mathfrak{z}$ goes through zero.

Hence we replace (3.6) by the scaling-limit form

$$D_s(\mathfrak{z})=\mathfrak{z}+\frac{r}{\kappa}-\frac{2\Theta^{1/2}}{\kappa}\left[(1+\mathfrak{z})_+^{1/2}\left((1-\kappa^2)-\frac{2r}{\kappa\mathfrak{z}^2}\left(1-\tfrac{1}{2}\mathfrak{z}\right)\right)+\frac{2r}{\kappa\mathfrak{z}^2}\right]=0. \tag{5.1}$$

In this form the values of r (depending only on the degree of supercooling) and $\kappa=k/k_c$ specify everything. The equation becomes fourth order, and solutions are easily obtained. The condition $\mathrm{Re}[(1+\mathfrak{z})^{1/2}]>0$ eliminates spurious roots. For $\kappa<\kappa_0\simeq 0.49$ the solution has $\mathrm{Re}\,\mathfrak{z}>0$ (unstable) while for $\kappa>\kappa_0$ the system is stable. In the vicinity of the crossing the root is purely real; on the stable side the capillary waves are overdamped as is the case close to the critical point when diffusion is neglected.

Numerically the $\omega(k)$ relation is quite flat below k_0 so there does not appear a "most unstable" wave number, in contrast to the situation described in Sec. II. Translating the scale k_0 to a length scale d_0 one finds

$$d_0\sim\frac{2\pi}{k_0}=\frac{2\pi}{\kappa_0 k_c}\sim\frac{4\pi}{\Theta^{1/2}}\xi\sim 40\xi, \tag{5.2}$$

which is quite compatible with microscope observations of fine structure.[1]

One further point is worth noting here. In equilibrium (no quench, $\Theta=0$, $l=\infty$) the scaling-limit dispersion relation (5.1) becomes

$$\mathfrak{z}+\frac{\sigma}{4\eta Dk}+2(k\xi)(1+\mathfrak{z})_+^{1/2}=0. \tag{5.3}$$

Recalling from (4.5) that $\sigma/4\eta Dk\approx 1/d_1 k\xi$, one easily verifies that this equation has no solution on the physical sheet determined by $\mathrm{Re}[(1+\mathfrak{z})^{1/2}]>0$. This may indicate interesting analytic properties for correlations in the system. We comment further in Sec. VI below.

VI. POWER SPECTRUM

In the stable regime the response function for the surface involves the dispersion relation (3.6) as denominator. We have not included the general expressions as they are lengthy; the response function for the *equilibrium fluid* (no quench, $\Theta=0$, $l=\infty$) has been given in equations (3.12)–(3.14). The power spectrum of surface fluctuations is essentially the space-time Fourier transform of the surface displacement autocorrelation

$$G(\vec{x},t)=\langle\zeta(0,0)\zeta(\vec{x},t)\rangle \tag{6.1}$$

and is directly measurable. In light scattering experiments the value of k is determined by the wavelength and by the scattering geometry.[16] Values of k in the approximate range 200 to 2000 cm^{-1} were reported by Wu and Webb,[5] while in the earlier experiments of Huang and Webb[6] somewhat smaller values of k were achieved. We shall concentrate on the binary-liquid experiments of Huang and Webb since the comparison with the present calculation is most direct.[19] We have used $k=200\ \mathrm{cm}^{-1}$ as a representative low value of k. The power spectrum $P_k(\omega)$ is plotted in Fig. 4 for a frequency range ~ 0.1 to $\sim 10^3$ Hz corresponding to $0.001\lesssim|f|\lesssim 10$. This frequency range is fairly typical although in an experiment the window would be adjusted as parameters were varied.

The first feature to notice in Fig. 4 is the (expected) increase in intensity as T_c is approached. At $\epsilon=10^{-4}$ the effect of diffusion would not be

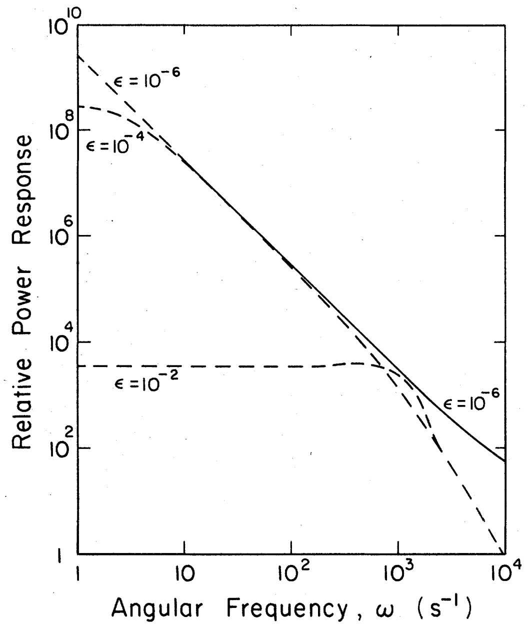

FIG. 4. The power spectrum $P_k(\omega)$ of interface displacements under equilibrium conditions (zero quench) at $k = 200$ cm^{-1}. The dashed lines are the pure capillary-wave power spectrum. At $\epsilon = 10^{-2}$ and 10^{-4} the inclusion of diffusive relaxation produces no distinguishable change in the frequency range shown. At $\epsilon = 10^{-6}$ the solid line indicates the new spectrum including diffusive effects which deviates from the pure capillary-wave spectrum above $\omega \approx 20$ s^{-1}.

observable at $\omega \sim 10^4$ s^{-1} where it produces a $\frac{1}{2}\%$ effect (over the pure capillary-wave power spectrum). At $\epsilon = 10^{-6}$ and above 1000 s^{-1} the difference is at least a factor of 2 (3dB).

In the experiments of Huang and Webb[6] a reduced temperature of $\epsilon = 10^{-5}$ was reached. Our numerical analysis indicates that at $k = 200$ cm^{-1} and $\epsilon = 10^{-5}$ diffusive effects (or at least a clear deviation from the pure capillary-wave spectrum) would have been observable at $\omega \gtrsim 5 \times 10^3$ s^{-1}. At *frequencies* greater than about 1 kHz the deviations would have been at least a factor of 2 (3 dB). Our numerical analysis further indicates that there would have been ample intensity out at such frequencies.

The experiment of Huang and Webb[6] directly determined the surface autocorrelation function. At temperatures close to critical and for small k relaxation times were on the order of 20 s. For these measurements low frequencies were the primary concern. By converting their analyses to equivalent frequency windows,[20] we conclude that diffusive relaxation was probably unobservable in those experiments. Hence the extraction of such quantities as the surface tension from the experiments should have been unaffected. At higher frequencies, or more precisely, at higher values of $|f|$, if one can separate out the interface contributions from bulk scattering, apparently the effects of diffusive relaxation can be detected.

One further point should be made on the analytic structure of the results. As first pointed out by Bouchiat and Meunier,[13] the power spectrum in the case of pure capillary waves [see (3.12) to (3.14) with $w = y_{\mathrm{eq}} \equiv 0$] contains a branch cut which makes the analytic structure somewhat more complicated than for an harmonic system exhibiting only simple poles. There are, in addition to the cut, poles corresponding to the solution $\mathfrak{D}(f) = 0$. These poles are on the physical sheet determined by $\mathrm{Re}[(1 + af)^{1/2}] > 0$. On the other hand, when $y_{\mathrm{eq}} \neq 0$, so that D is no longer neglected, we have already noted that $\mathfrak{D}_s(\mathfrak{z}) = 0$ (or equivalently setting $\mathfrak{D}(f) = 0$ in the scaling regime) has no such solution on the physical sheet [see (5.3) *et seq.*]. Hence, while in most regions the effect of diffusive relaxation on the correlations may be *numerically* small, there may be interesting analytic effects. This prospect has not been fully examined at this stage.

VII. CONCLUDING REMARKS

The standard hydrodyanmic analysis we have reported indicates that the flat interface separating two coexisting phases is unstable to long wavelength perturbations when the system is quenched. The question of the existence of an instability was addressed using a generalization of the nonequilibrium model introduced by Langer and Turski[8] in which the evolving composition profile is replaced by a *time-independent* supercooling length l (see Fig. 2). Such analysis is probably sufficient to demonstrate the existence of an instability and to estimate the cutoff wave number k_0, but it may need modification at long experimental times. When the system is stable to the quench, the power spectrum of surface distortions will evolve in time; at very long times it must become characteristic of the final equilibrium state ($l \to \infty$). This evolution is not included in our analysis. The present analysis is expected to hold for times $t \gtrsim \xi^2/D$ following an infinitely rapid quench. In practice a rapid quench may take several milliseconds so that the results are expected to hold as soon as the final temperature is reached.

As noted above, Schwartz *et al.*[1] have reported observation of structure near the interface of a quenched sample. Their experiment was not originally designed for the study of a (potential) instability, but the size of the structures these calculations suggest are in the appropriate range. As a biproduct of the calculation we have allowed for diffusive relaxation in the ordinary capillary-wave spectrum. Such relaxation makes an observable contribution at sufficiently high frequencies; fortunately the experiments of Huang and Webb[6] were effectively restricted in frequency so that the contribution was negligible. This allowed proper extraction of the surface tension from the ordinary capillary-wave power spectrum.

We have made a number of simplifying symmetry assumptions to reduce the algebraic complexity. It is not too difficult to break the complete symmetry by allowing the two coexisting fluids to have slightly differing densities. One expects

$$\Delta\rho/\rho_c \approx B'|\epsilon|^{\beta}. \tag{7.1}$$

The magnitude of the correction on the power spectrum is typically very small and for our purposes can be neglected. The effect on the dispersion relation is computationally serious in that the small perturbation due to $\Delta\rho \neq 0$ raises the order of the characteristic equation. We have not attempted to allow for differences in the kinematic viscosities of the two phases. Finally we have noted the possibility of interesting analytic consequences due to the singularity structure of the power spectrum when diffusion fields are allowed to couple with the ordinary velocity fields.

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[1] A. J. Schwartz, S. Krishnamurthy, and W. I. Goldburg, Phys. Rev. A 21, 1331 (1980); W. I. Goldburg (private communication).

[2] In the actual experiment the system has an inverted coexistence curve, so the system is *heated* to go deeper into the ordered phase. Our analysis will be phrased in terms of a normal coexistence curve as shown in Fig. 1.

[3] J. Cahn (private communication).

[4] W. W. Mullins and R. F. Sekerka, J. Appl. Phys. 34, 323 (1963); 35, 444 (1964).

[5] E. S. Wu and W. W. Webb, Phys. Rev. A 8, 2065 (1973); 8, 2077 (1973).

[6] J. S. Huang and W. W. Webb, J. Chem. Phys. 50, 3677 (1969).

[7] D. Jasnow and J. Rudnick, Phys. Rev. Lett. 41, 698 (1978).

[8] J. S. Langer and L. A. Turski, Acta Metall. 25, 1113 (1977).

[9] The compositions are dimensionless corresponding to mass fractions.

[10] The derivation is similar in spirit to that for the condensation of a liquid drop. See, e.g., J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946) or A. B. Pippard, *Classical Thermodynamics* (Cambridge University Press, London, 1957).

[11] See, e.g., H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, London and New York, 1971). For discussion relating to surface tension see B. Widom, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2 and references cited therein.

[12] We assume $l > 0$ corresponding to supercooling. If $l < 0$, Eq. (2.12) shows that $-i\omega$ is real and negative leading to stability.

[13] E. S. Wu, Ph.D. thesis, Cornell University, 1973 (unpublished); M. A. Bouchiat and J. Meunier, J. Phys. (Paris) 32, 561 (1971); 33, C1-141 (1972).

[14] We have neglected the gravitational term $g\Delta\rho$ due to our symmetry assumption. In any event this term is usually negligible for near-critical binary liquids.

[15] We neglect the weak anomaly believed to be present in the shear viscosity near the critical point. Our symmetry assumptions are for ease in determining the linear stability of the system and are not too serious for typical binary fluids near T_c.

[16] J. S. Huang, Ph.D. thesis, Cornell University, 1969 (unpublished).

[17] Experiments [see, e.g., Refs. 5, 7, and Wu's thesis (Ref. 13)] typically measure the *intensity* autocorrelation function of light scattered from the interface. Such correlation is related to the displacement autocorrelation $\langle \zeta_k(t)\zeta_{-k}(t+\tau)\rangle$ or its time Fourier transform, the displacement power spectrum.

[18] L. D. Landau and I. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959), Sec. 52.

[19] The experiments of Ref. 5 were on the single component fluid SF_6, so that heat conduction would play the role analogous to mutual diffusion discussed here.

[20] J. S. Huang (private communication).