

## Sound propagation in phase-separating fluids

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We examine sound propagation in two-phase states of one- and two-component fluids by taking into account heat and mass transport between the two phases. For the sake of simplicity, detailed calculations are performed on near-critical fluids undergoing nucleation or spinodal decomposition, which exhibit very large acoustic anomalies at relatively low frequencies. As a universal relation the zero-frequency sound speed is reduced to 82% of the sound speed without domains in near-critical pure fluids. However, our predictions can be applied even to fluids far from criticality. One of our main findings is that, when droplets are sparsely distributed, sounds can induce latent-heat generation or absorption at the interfaces and produce long-range temperature gradients extending far from the droplets. The sounds are then anomalously attenuated at low frequencies, and the effect may be used to detect onset of nucleation. We also calculate a frequency-dependent adiabatic compressibility in two-phase states, which is valid even far from criticality and is applicable to bubbly fluids. It reproduces the effective-medium theory at relatively high frequencies and a Landau-Lifshitz result in the zero-frequency limit. The mechanism investigated is general and is not limited to fluids.

### I. INTRODUCTION

When systems are composed of finely divided domains, increased sound attenuation has been observed in a number of materials. Examples are polycrystals,<sup>1,2</sup> fluids of emulsions,<sup>3-8</sup> solids undergoing martensitic transitions,<sup>9</sup> polymer solutions undergoing spinodal decomposition,<sup>10</sup> and so on. As an analogous effect a strong increase of the second-sound damping was recently observed in a phase-separating <sup>3</sup>He-<sup>4</sup>He mixture near the tricritical point.<sup>11</sup> Many years ago Zener and Isakovich independently predicted that acoustic attenuation at relatively low frequencies should be enhanced by small-scale heat currents between adjacent crystallites or two phases.<sup>1,3</sup> In this paper I will examine this problem particularly in phase-separating near-critical fluids, which will turn out to be an ideal system to confirm the original idea of Zener and Isakovich. Near-critical fluids are known to be suitable for both unambiguous theoretical studies and definite experiments on various fundamental effects of phase transitions.<sup>12-15</sup> We should then generalize our results to other more complicated systems.

It seems necessary to explain the essence of Zener and Isakovich's sound-attenuation mechanism.<sup>1-3</sup> Although the idea is general and applicable to a wide range of two-phase states, the effect has not drawn enough attention and systematic experimental confirmation has been lacking. To make simple order estimations we assume that physical properties, such as thermodynamic derivatives and transport coefficients, are of the same order in the two phases. In systems such as a liquid suspended with gas bubbles physical properties are very different in the two phases and more careful analysis will be required. We send a sound wave into a two-phase, one-component material with small-scale domains whose size  $R$  is much shorter than the sound wavelength. While the pressure

variation  $\delta p$  itself changes slowly in space, it causes small-scale temperature inhomogeneities if the adiabatic coefficient  $(\partial T/\partial p)_s$  is different in the two phases, 1, and 2. The inhomogeneities are of the following order:

$$(\delta T)_{\text{inh}} = \left[ \left( \frac{\partial T}{\partial p} \right)_s^{(1)} - \left( \frac{\partial T}{\partial p} \right)_s^{(2)} \right] \delta p. \quad (1.1)$$

The  $\delta T$  changes by the above amount near the interface on the spatial scale of the thermal diffusion length,

$$l_D = (D/\omega)^{1/2}, \quad (1.2)$$

where  $D$  is the thermal diffusivity and  $\omega$  is the acoustic frequency. Here we assume that  $l_D$  is shorter than the domain size  $R$  and this condition amounts to  $\omega > DR^{-2}$ . Then the volume fraction of the inhomogeneous region is of order  $Al_D$ ,  $A$  being the surface area per unit volume, and the heat production rate per unit volume is estimated as<sup>6</sup>

$$\int d\tau \frac{\lambda}{T} |\nabla T|^2 \simeq \frac{\lambda}{T} |(\delta T)_{\text{inh}}|^2 Al_D^{-1}, \quad (1.3)$$

where  $\lambda$  is the thermal conductivity and the integral is over a unit volume. The above quantity is expressed in terms of the sound attenuation  $\alpha_{D\lambda}$  per wavelength due to domains as  $(\omega\alpha_{D\lambda}/\pi\rho c^2)|\delta p|^2$ , where  $\rho$  is the mass density and  $c$  is the sound velocity (see Sec. II for more details). Thus, for  $\omega > DR^{-2}$ , we obtain

$$\begin{aligned} \alpha_{D\lambda} &\simeq \frac{1}{T\rho c^2\lambda} \left[ \left( \frac{\partial T}{\partial p} \right)_s^{(1)} - \left( \frac{\partial T}{\partial p} \right)_s^{(2)} \right]^2 A (\omega l_D)^{-1} \\ &\simeq A_0 (D/\omega R^2)^{1/2}, \end{aligned} \quad (1.4)$$

where the coefficient  $A_0$  on the second line is independent of  $R$ . We shall see that  $A_0 \sim \phi$  for pure fluids and

$A_0 \sim \phi(1 - T/T_c)^\alpha$  with  $\alpha \approx 0.1$  for binary mixtures near criticality, where  $\phi$  is the volume fraction of the minority phase.

On the other hand, if  $l_D > R$  or  $\omega < DR^{-2}$ , Zener and Isakovich found that the attenuation becomes weak as

$$\alpha_{D\lambda} \approx A_0(\omega R^2/D). \quad (1.5)$$

Therefore,  $\alpha_{D\lambda}$  was concluded to have a broad peak at  $\omega \approx DR^{-2}$  in accord with experiments on polycrystals.<sup>1</sup> The above result is based on the picture that thermal relaxation in domains can follow the temperal change of sounds in the low-frequency limit. Zener stated that sounds are nearly adiabatic for  $\omega \gg DR^{-2}$  and nearly isothermal for  $\omega \ll DR^{-2}$ . However, a crucial process is missed in the derivation of (1.5), which makes (1.5) invalid in many important systems including two-phase fluids. That is, mass conversion can take place through the interface from one phase to the other periodically in time, and the latent heat thus generated produces a temperature gradient extending over  $l_D$ . If the volume fraction  $\phi$  of the minority phase is very small and domains are far from one another, thermal equilibration cannot be achieved even for  $l_D \gg R$  or for  $\omega \ll DR^{-2}$  outside domains. This leads to anomalous low-frequency damping in nucleation processes. Such a latent-heat generation is, however, nonexistent for polycrystals and emulsions, which were systems treated by Zener<sup>1</sup> and Isakovich.<sup>3</sup> In the former case domains with an identical crystal structure are separated by grain boundaries and domain motion releases no latent heat, but inhomogeneous temperatures arise from elastic anisotropy of individual domains. In the latter case immiscible fluids cannot pass through membranes on the acoustic time scale. The role of latent heat has hence remained unnoticed.

Because of its simplicity we here give a formula for attenuation by spherical domains with a small volume fraction  $\phi$ . The temperature deviation and the pressure deviation due to sounds are related by  $\delta T = (\partial T / \partial p)_{\text{coex}} \delta p$  at the interface position from the continuity of the chemical potential  $\mu$  (see Sec. II), where  $(\partial T / \partial p)_{\text{coex}}$  is the derivative along the coexistence curve. The temperature is inhomogeneous outside the domain as

$$\delta T - \left[ \frac{\partial T}{\partial p} \right]_s \delta p = \left[ \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} - \left[ \frac{\partial T}{\partial p} \right]_s \right] \delta p G(r). \quad (1.6)$$

Since  $G(r)$  obeys a thermal diffusion equation, it tends to  $R/r$ , a solution of  $\nabla^2 G = 0$ , as  $\omega R^2/D \rightarrow 0$ . For  $\omega \ll DR^{-2}$  the temperature is nearly homogeneous inside the domain, so that the heat current is discontinuous at the interface and is balanced by latent-heat release or absorption. By calculating the heat production around each domain, we readily obtain for small  $\omega$

$$\alpha_{D\lambda} = 3\pi\phi(\gamma_s - 1) \left[ \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \left[ \frac{\partial p}{\partial T} \right]_s - 1 \right]^2 (D/R^2\omega), \quad (1.7)$$

where use has been made of the thermodynamic identity

$\rho^2 c^2 C_v = T(\partial p / \partial T)_s^2 (1 - 1/\gamma_s)$ ,  $\gamma_s = C_p/C_v$  being the specific-heat ratio, and the quantities on the right-hand side of (1.7) are those in the phase outside domains. We shall see that this expression can be used in the region  $\phi \lesssim \omega R^2/D \lesssim 1$  in Sec. II. For  $\omega > DR^{-2}$ ,  $\alpha_{D\lambda}$  is given by (1.4). The behavior  $\alpha_{D\lambda} \propto 1/\omega$  in (1.7) is markedly different from the usual low-frequency behavior  $\alpha_\lambda \propto \omega$  in one-phase states.<sup>2</sup>

There are a great number of papers on the sound velocity in bubbly fluids,<sup>16-19</sup> in which the gas and liquid phases have very different densities and compressibilities in contrast to the case near criticality. In bubbly fluids the sound velocity is known to be much decreased in the presence of a small fraction of gas bubbles. Its behavior is fairly well described by the effective-medium theory,<sup>16,20</sup> which is a mean-field theory for the compressibility of composite materials neglecting heat conduction. However, the two phases in near-critical fluids have nearly the same compressibilities, and the effective-medium theory predicts no appreciable change due to domains in the sound velocity. See Sec. III for more discussions.

In anisotropic solids, scattering of sounds at interfaces can be the dominant sound attenuation mechanism.<sup>21,22</sup> The resultant attenuation  $\alpha_{\text{scat}}$  per unit length is known to be proportional to  $\omega^4$  and become small at low frequencies if the domain size is much shorter than the sound wavelength.<sup>8</sup> On the other hand, in near-critical fluids, the density difference between the two phases is very small and the scattering mechanism can be completely neglected. Remarkably, the critical divergence<sup>11</sup> of the thermal conductivity  $\lambda$  enhances the dissipation of sounds. As a result, the attenuation due to domains dominates over the attenuation due to critical fluctuations at low frequencies.<sup>23-25</sup> We will also show in Sec. IID that the viscous damping due to velocity gradients is much smaller than the heat-flow damping at most by the factor of  $(\xi/R)^2$ ,  $\xi$  being the interface thickness.

The organization of this paper is as follows. In Sec. II we will discuss the problem in near-critical pure fluids to avoid unnecessary complications at the starting point. Their thermodynamics is now well understood and the temperature obeys a simple diffusion equation at long wavelengths. In Sec. III we will derive a general expression for the effective adiabatic compressibility in two-phase states for pure fluids by taking into account heat conduction. It can be used even away from the critical point and constitutes a generalization of the effective-medium theory for bubbly fluids. In Sec. IV we will treat binary mixtures, whose thermodynamics and hydrodynamics are much more complicated unfortunately. However, experiments are much easier in binary mixtures than in pure fluids.<sup>14</sup> Hence, we need to show that almost the same effect exists in binary mixtures. Readers who are not interested in the theoretical details of binary mixtures may read only the first and last paragraphs of Sec. IV. As a by-product, we will derive some thermodynamic relations which show asymptotic critical behavior and leading corrections of thermodynamic derivatives, such as  $(\partial T / \partial p)_s$  or  $(\partial T / \partial p)_{sX}$ , for pure fluids in Appendix A and for binary mixtures in Appendix D.

## II. PURE FLUIDS

### A. Adiabatic heating in two-phase states

We first consider a one-component fluid near the gas-liquid critical point in a two-phase state in the course of nucleation or spinodal decomposition.<sup>14</sup> We assume that the characteristic size  $R$  of domains is much longer than the thermal correlation length  $\xi$  (of the order of the interfacial thickness) and then the fluid is nearly on the coexistence curve. Namely, the pressure difference  $p - p_c$  and the temperature difference  $T - T_c$  are linearly related by

$$p - p_c \cong \left[ \frac{\partial p}{\partial T} \right]_{\text{coex}} (T - T_c), \quad (2.1)$$

where  $p_c$  and  $T_c$  are the critical pressure and temperature and  $(\partial p / \partial T)_{\text{coex}}$  is the derivative on the coexistence curve and may be equated to its critical point value.

We then send a sound wave into the fluid. In most realistic conditions the acoustic wavelength  $2\pi c / \omega$  is much longer than the domain size  $R$  and the pressure inhomogeneity is very weak compared to that of the domain structure. The acoustic frequency  $\omega$  is assumed to be much faster than the growth rate  $\gamma_R$  of domains but much slower than the relaxation rate  $\Gamma_\xi = (k_B T / 6\pi\eta)\xi^{-3}$  of the critical fluctuations, where  $\eta$  is the shear viscosity.<sup>13,23-25,26</sup> Namely,

$$\gamma_R \ll \omega \ll \Gamma_\xi. \quad (2.2)$$

Under these conditions we may regard the domain structure as stationary on the acoustic time scale  $2\pi / \omega$  and may use the usual linear hydrodynamic equations to describe the relaxation processes under consideration. We are also allowed to regard the interface as infinitesimally thin.

Far from the interface the temperature  $T$  is adiabatically disturbed as

$$\delta T = \left[ \frac{\partial T}{\partial p} \right]_s \delta p, \quad (2.3)$$

where  $\delta p$  is the pressure variation associated with the sound. We can show that the coefficient  $(\partial T / \partial p)_s$  is slightly different between the gas and liquid phases and the temperature is more perturbed in the gas phase than in the liquid phase. To show this let us consider two infinitesimally separated thermodynamic states on the liquid (or gas) phase side of the coexistence curve. From  $dT = (\partial T / \partial p)_s dp + (\partial T / \partial s)_p ds$ , we obtain

$$\begin{aligned} \left[ \frac{\partial T}{\partial p} \right]_s \left[ \frac{\partial p}{\partial T} \right]_{\text{coex}} &= 1 - \frac{T}{C_p} \left[ \frac{\partial s}{\partial T} \right]_{\text{coex}} \\ &\cong 1 + [\beta \Delta s / (2\epsilon C_p)] \theta. \end{aligned} \quad (2.4)$$

Hereafter  $\theta = 1$  in the gas phase and  $\theta = -1$  in the liquid phase. The dominant contribution to  $(\partial s / \partial T)_{\text{coex}}$  arises from the derivative of  $s_0 \epsilon^\beta \theta$ , where  $s_0$  is constant,  $\epsilon = 1 - T / T_c > 0$ , and  $\Delta s = 2s_0 \epsilon^\beta$ . Hereafter  $\beta \cong 0.33$ ,  $\alpha \cong 0.1$ , and  $\gamma \cong 1.24$  are the usual critical exponents. They satisfy  $\gamma + 2\beta + \alpha = 2$ . On the coexistence curve the

asymptotic critical power laws are as follows:<sup>12,27,28</sup>

$$\Delta v \cong \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \Delta s \cong 2B \epsilon^\beta, \quad (2.5)$$

$$K_T \cong \frac{\rho}{T} \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}}^2 C_p \cong \rho T \Gamma' \epsilon^{-\gamma}, \quad (2.6)$$

$$C_v \cong \frac{A'}{\alpha} \epsilon^{-\alpha}, \quad (2.7)$$

where  $v = 1 / \rho$  is the volume per unit mass and  $K_T$  is the isothermal compressibility. The  $B$ ,  $\Gamma'$ , and  $A'$  are coefficients dependent on fluids. However, it is known that the combination  $B^2 / A' \Gamma'$  is a universal number and is estimated to be 44.6 for the three-dimensional Ising model.<sup>27,29</sup> It is then convenient to rewrite (2.4) as

$$\left[ \frac{\partial T}{\partial p} \right]_s \left[ \frac{\partial p}{\partial T} \right]_{\text{coex}} = 1 + \gamma_s^{-1/2} a_c \theta + \dots, \quad (2.8)$$

where  $a_c$  is a universal positive number determined by

$$a_c^2 = (\beta \Delta s / 2\epsilon)^2 / C_p C_v = \alpha \beta^2 B^2 / A' \Gamma' \cong 0.485, \quad (2.9)$$

so  $a_c \cong 0.70$ . The  $\gamma_s$  is the specific-heat ratio growing as

$$\gamma_c = C_p / C_v \sim \epsilon^{-\gamma + \alpha}. \quad (2.10)$$

See Appendix A for more details. Thus, due to domains, the temperature becomes inhomogeneous near the interface by the following amount:

$$(\delta T)_{\text{inh}} \cong \gamma_s^{-1/2} \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \delta p \cong \gamma_s^{-1/2} \delta T. \quad (2.11)$$

Recently (2.11) was used to explain slow thermal relaxation in two-phase states of pure fluids realized in  $C_v$  measurements.<sup>30-32</sup> That is, if a cell has a fixed volume, a small change of the boundary temperature instantaneously gives rise to a small homogeneous change in the pressure which induces a latent-heat flow through the interface due to the temperature difference given by (2.11). We expect that this exchange of latent heat much slows down thermal equilibration throughout the cell.

### B. Extra dissipation due to heat currents

At the interface we assume the continuity of the acoustically induced variations  $\delta T$ ,  $\delta p$ , and  $\delta \mu$ , where  $\mu$  is the chemical potential (the Kotchine conditions).<sup>33</sup> From the Gibbs-Duhem relation  $\delta \mu = -s \delta T + v \delta p$ , we find at the interface

$$-(\Delta s) \delta T + (\Delta v) \delta p = 0, \quad (2.12)$$

where  $\Delta s = s_g - s_l$  and  $\Delta v = v_g - v_l$  are the differences of the entropy  $s$  per unit mass and the volume  $v$  per unit mass between the gas and liquid phases. Using the Clapeyron-Clausius relation we thus obtain

$$\delta T = \left[ \frac{\Delta v}{\Delta s} \right] \delta p = \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \delta p, \quad (2.13)$$

where  $(\partial T / \partial p)_{\text{coex}}$  represents the derivative along the

coexistence curve. This means that the fluid stays on the coexistence curve at the interface. Note that the pressure inside droplets is higher than that outside them by  $2\sigma/R$ ,  $\sigma$  being the surface tension. We assume that the acoustic variation  $\delta p$ , which is superposed on the above unperturbed pressure, is continuous at the interface. We will discuss the validity of this assumption further in Sec. III D. On the other hand, in the emulsion case<sup>3-6</sup> the continuity of the heat current was assumed at the interface instead of (2.12).

The temperature deviation  $\delta T$  obeys<sup>30</sup>

$$\frac{\partial}{\partial t}\delta T = \left[ \frac{\partial T}{\partial p} \right]_s \frac{\partial}{\partial t}\delta p + D\nabla^2\delta T, \quad (2.14)$$

where the first term on the right-hand side represents the adiabatic heating and the coefficient  $(\partial T/\partial p)_s$  is slightly different in the two phases. The diffusion constant  $D$  becomes small near criticality and is excellently approximated by the Kawasaki-Stokes formula,<sup>13,23</sup>

$$D = k_B T_c / 6\pi\eta\xi. \quad (2.15)$$

The viscosity  $\eta$  has a very weak singularity and may be regarded as a constant for qualitative analysis. In the following we solve (2.14) under the two boundary conditions (2.3) and (2.13) with the adiabatic coefficient given by (2.8). We are interested in temperature variations on spatial scales much longer than the interface thickness  $\xi$  but much shorter than the sound wavelength  $2\pi c/\omega$ . It is convenient to introduce a dimensionless temperature variation  $F$  by the following definition:

$$\begin{aligned} \delta T - \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \delta p \\ = \left[ \left[ \frac{\partial T}{\partial p} \right]_s - \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \right] (\delta p) F \\ \cong \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} (\gamma_s^{-1/2} a_c \theta \delta p) F, \end{aligned} \quad (2.16)$$

where use has been made of (2.8) on the second line. From (2.11) the typical value of  $F$  is of order 1. We have  $F=0$  at the interface from (2.13) and would have  $F=1$  in one-phase states from (2.3). In (2.14) we neglect the weak spatial dependence of  $\delta p$  and replace  $\partial/\partial t$  by  $i\omega$  to obtain

$$i\omega F = i\omega + D\nabla^2 F, \quad (2.17)$$

which should be solved by letting

$$F=0 \quad \text{at the interface.} \quad (2.18)$$

It goes without saying that  $F$  is meaningful only on spatial scales much longer than  $\xi$ .

The sound attenuation  $\alpha_D$  per unit length due to domains is related to the effective (frequency-dependent) bulk viscosity  $\zeta_D$  (Refs. 8, 23, and 34) due to domains by  $2\alpha_D = \zeta_D \omega^2 / \rho c^3$ . The heat production per unit volume should have the form

$$\zeta_D k^2 u^2 \cong \zeta_D \omega^2 |\delta p / \rho|^2 \cong \zeta_D \omega^2 |\delta p|^2 / c^4 \rho^2,$$

where  $k = \omega/c$  and  $u$  are the wave number and the veloci-

ty field, respectively, associated with the sound. Therefore we find

$$2(\alpha_D / \rho c) |\delta p|^2 = \frac{1}{T} \int d\mathbf{r} \lambda |\nabla \delta T|^2, \quad (2.19)$$

where the spatial integral is over a unit volume and  $\lambda$  is the thermal conductivity related to  $D$  by

$$\lambda = \rho C_p D \propto \xi. \quad (2.20)$$

Then the specific heat  $C_p$  arises from  $\lambda$  [if the right-hand side of (2.19) is rewritten in terms of  $D$ ] and cancels  $1/C_p$  arising from  $1/\gamma_s \cong |(\delta T)_{\text{inh}}/\delta T|^2$  [see (2.11)]. In fact, substitution of (2.16) into (2.19) yields

$$2c\alpha_D = a_c^2 D \int d\mathbf{r} |\nabla F|^2, \quad (2.21)$$

where further use has been made of  $\nabla(\theta F) = \theta \nabla F$  due to (2.18) and the following thermodynamic relation:

$$C_p \rho^2 c^2 = T \left[ \frac{\partial p}{\partial T} \right]_s \left[ \frac{\partial p}{\partial T} \right]_\rho \cong T \left[ \frac{\partial p}{\partial T} \right]_{\text{coex}}^2. \quad (2.22)$$

Furthermore, we notice the following relation:

$$i\omega \int d\mathbf{r} |F|^2 = i\omega \int d\mathbf{r} F^* - D \int d\mathbf{r} |\nabla F|^2, \quad (2.23)$$

which follows from multiplication of (2.17) by  $F^*$  and integration over space. The real part of (2.23) is

$$D \int d\mathbf{r} |\nabla F|^2 = \omega \int d\mathbf{r} (\text{Im} F), \quad (2.24)$$

where  $\text{Im} F$  is the imaginary part of  $F$ . Now we obtain a very simple expression for the attenuation  $\alpha_{D\lambda}$  per wavelength,

$$\alpha_{D\lambda} = (2\pi c / \omega) \alpha_D = \pi a_c^2 (\text{Im} F), \quad (2.25)$$

where  $\langle \rangle$  denotes taking the spatial average over many domains.

So far we have neglected a small difference in  $D$  in (2.14) and that in  $\lambda$  in (2.19) between the two phases. They give rise to higher-order corrections to  $\alpha_D$  as  $\epsilon \rightarrow 0$ . We only take into account the small difference in  $(\partial T/\partial p)_s$  between the two phases.

### C. Nearly flat interfaces

It is very easy to solve (2.17) when the interface is nearly flat as compared to the diffusion length  $l_D = (D/\omega)^{1/2}$ . This means that the domain size  $R$  is much larger than  $l_D$ , so

$$\omega \gg DR^{-2}. \quad (2.26)$$

Then the problem is nearly one-dimensional and the solution to (2.17) is

$$F \cong 1 - \exp(-\kappa|x|), \quad (2.27)$$

where  $|x|$  is the distance from the interface and

$$\kappa = (i\omega/D)^{1/2} = (1+i)(\omega/2D)^{1/2}, \quad (2.28)$$

$\omega$  being taken to be positive. The spatial average of  $F$  is

$$\langle F \rangle \cong 1 - A \int_{-\infty}^{\infty} dx e^{-\kappa|x|} = 1 - 2A/\kappa, \quad (2.29)$$

where  $A$  is the interface area per unit volume and is of order  $\phi/R$ ,  $\phi$  being the volume fraction of the minority phase. Therefore (2.25) leads to

$$\alpha_{D\lambda} \cong \pi a_c^2 (2D/\omega)^{1/2} A \quad \text{for } DR^{-2} \ll \omega \ll D\xi^{-2}. \quad (2.30)$$

It is convenient to define a dimensionless frequency  $\hat{\omega}$  by

$$\hat{\omega} = \omega R^2/D = \omega^*(R/\xi)^2, \quad (2.31)$$

where  $\omega^*$  is the usually defined scaled frequency,<sup>23-25</sup>

$$\omega^* = \omega \xi^2/D = \omega/\Gamma_\xi. \quad (2.32)$$

Then,

$$\alpha_{D\lambda} \cong \phi/\sqrt{\hat{\omega}}. \quad (2.33)$$

Recall that the attenuation per wavelength  $\alpha_\lambda$  in the one-phase region arises from the critical fluctuations and is of order  $\omega^*$  for  $\omega^* \lesssim 1$ .<sup>23-25</sup> Hence  $\alpha_{D\lambda}$  exceeds  $\alpha_\lambda$  at low frequencies  $\omega \lesssim \omega_X$  and (2.30) yields

$$\omega_X \cong D(\phi/R\xi^2)^{2/3}. \quad (2.34)$$

If  $\phi \sim \frac{1}{2}$ ,  $\omega_X$  is surely larger than  $DR^{-2}$  and smaller than  $D\xi^{-2}$ . For small  $\phi$  this expression for  $\omega_X$  holds for  $\phi(R/\xi)^2 > 1$  from the initial assumption (2.26). Note that  $\omega_X$  shifts to lower frequencies as the coarsening proceeds.

In Appendix C we shall see that the mass flow is negligible for nearly planar interfaces near criticality. In accord with this (2.30) is consistent with results for the emulsion case<sup>3,6</sup> in the region  $\omega \gg DR^{-2}$ .

#### D. Spherical droplets

Let us consider a dilute assembly of spherical droplets in the nucleation process. Their slow evolution will be neglected and their size distribution will be treated as monodisperse for simplicity. We first solve (2.17) for a single droplet assuming  $F \rightarrow 1$  far from it and  $F = 0$  at  $r = R$ ,  $r$  being the radius from the droplet center. The solution reads

$$F = \begin{cases} 1 - (R/r)\sinh(\kappa r)/\sinh(\kappa R) & \text{for } r < R \\ 1 - (R/r)\exp(\kappa R - \kappa r) & \text{for } r > R \end{cases} \quad (2.35a)$$

$$(2.35b)$$

For  $\hat{\omega} \ll 1$  we have  $F \cong 1 - R/r$  outside the sphere and  $F \cong 0$  inside it. As a result  $\nabla T$  is nonvanishing outside the sphere even in the limit  $\hat{\omega} \rightarrow 0$ ,

$$|\nabla T| \cong a_c \gamma_s^{-1/2} |\delta T| R/r^2, \quad (2.36)$$

where use has been made of (2.16) and  $\delta T \cong (\partial T/\partial p)_{\text{coex}} \delta p$ . Then (2.19) or (2.21) suggests  $\alpha_D \cong DR^{-2} \phi/c$  or  $\alpha_{D\lambda} \cong \phi/\hat{\omega}$ ,  $\phi$  being the volume fraction of droplets.

More precisely, we calculate  $\alpha_{D\lambda}$  using (2.25) in the following. First we neglect interference among droplets to obtain

$$\begin{aligned} \langle F \rangle &\cong 1 + n_D \int d\mathbf{r} (F - 1) \\ &\cong 1 - 3\phi [1 + \coth(i\hat{\omega})^{1/2}]/(i\hat{\omega})^{1/2}. \end{aligned} \quad (2.37)$$

Here  $n_D$  is the droplet density and  $\phi = \frac{4}{3}\pi R^3 n_D$ . Therefore  $\alpha_{D\lambda}$  becomes

$$\alpha_{D\lambda} = \frac{6\pi a_c^2 \phi [1 + e^{-z}(\sin z - \cos z)]}{z(1 + e^{-2z} - 2e^{-z} \cos z)}, \quad (2.38)$$

where  $z \equiv (2\hat{\omega})^{1/2}$ . The right-hand side  $\cos z$  of (2.38) is complicated, so that we propose the following approximate expression:

$$\alpha_{D\lambda} \cong 3\pi a_c^2 \phi \left[ \frac{1}{\hat{\omega}} + \frac{2}{(2\hat{\omega})^{1/2}} \right]. \quad (2.39)$$

The right-hand sides of (2.38) and (2.39) behave in the same manner both for  $\hat{\omega} \ll 1$  and  $\hat{\omega} \gg 1$  and the difference is within 20%. For  $\hat{\omega} \gg 1$  we have  $\alpha_{D\lambda} \sim \phi/\sqrt{\hat{\omega}}$  in accord with (2.24). Surprisingly, however, we have  $\alpha_{D\lambda} \cong \phi/\hat{\omega}$  for  $\hat{\omega} < 1$ , which indeed grows up to order 1 for  $\hat{\omega} \cong \phi$ .

In Appendix B we shall see that interference among droplets suppresses the above growth at very low frequencies  $\hat{\omega} \lesssim \phi$ . We propose the following approximate expressions which describe the overall behavior of  $\langle F \rangle$ :

$$\langle F \rangle \cong 1 / \{ 1 + 3\phi [1 + \coth(i\hat{\omega})^{1/2}] / (i\hat{\omega})^{1/2} \} \quad (2.40a)$$

$$\cong 1 / \left[ 1 + 3\phi \left[ \frac{1}{i\hat{\omega}} + \frac{2}{(i\hat{\omega})^{1/2}} \right] \right]. \quad (2.40b)$$

The first line is an interpolation of (2.37) and (B7), while the second line is a further approximation of the first line and reduces to (2.39) for  $\hat{\omega} \gg \phi$ . If  $\hat{\omega} \ll \phi$ , we obtain

$$\langle F \rangle \cong \frac{1}{3\phi} i\hat{\omega}, \quad (2.41)$$

$$\alpha_{D\lambda} \cong \frac{\pi}{3\phi} a_c^2 \hat{\omega}. \quad (2.42)$$

The relation (2.38) or (2.39) holds in the region  $\phi \lesssim \hat{\omega} \ll 1$ . The crossover at  $\hat{\omega} = \phi$  occurs when the diffusion length  $l_D$  is of the order of the so-called screening length  $l_s$  introduced in previous theories of nucleation,<sup>35</sup>

$$l_s = (4\pi R n_D)^{-1/2} = (3\phi)^{-1/2} R. \quad (2.43)$$

Thus Zener's isothermal limit is attained only for  $\hat{\omega} < \phi$  or  $l_D > l_s$  in the dilute case. In Fig. 1 we plot  $\alpha_{D\lambda}$  on the basis of (2.40a) for  $\phi = 0.1$  and 0.2.

What is the origin of the anomalous attention  $\alpha_{D\lambda} \cong \phi/\hat{\omega}$  in the region  $\phi < \hat{\omega} < 1$ ? It is due to the dissipation of latent heat periodically generated or absorbed by oscillating droplets. Appendix C will show that the sound induces a small oscillating variation  $\delta R$  of the droplet radius. For  $\hat{\omega} < 1$  it is given by

$$\delta R = -\frac{1}{2} \beta D (i\omega R)^{-1} \delta p / (p_c - p). \quad (2.44)$$

We require  $|\delta R| \ll R$  to find another lower bound of  $\hat{\omega}$  as

$$\hat{\omega} \gg |\delta p| / (p_c - p). \quad (2.45)$$

The mass conversion rate per droplet is

$$4\pi \rho R^2 \left[ \frac{\partial}{\partial t} \delta R \right] \cong -2\pi \beta \rho D R \delta p / (p_c - p). \quad (2.46)$$

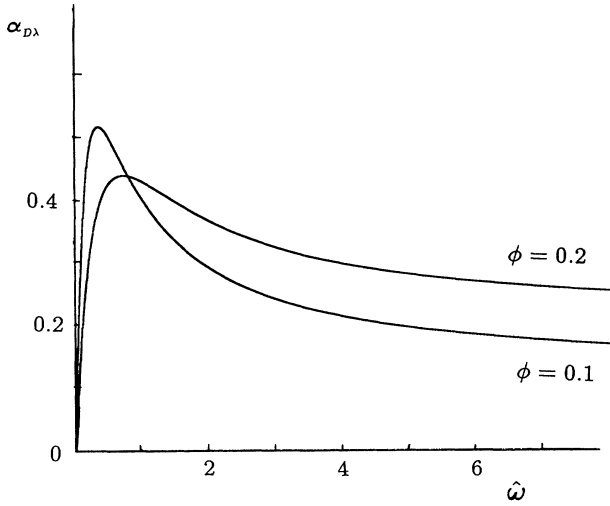


FIG. 1. The attenuation  $\alpha_{D\lambda}$  per wavelength due to domains vs  $\hat{\omega} = \omega R^2/D$  in near-critical pure fluids at  $\phi = 0.1$  and  $0.2$  on a linear scale. Use has been made of (2.40a).

The latent-heat production rate at the interface is equal to (2.46) multiplied by  $\Delta s$ . We should note here that the acoustic pressure variation can be slightly discontinuous at the interface by  $(2\sigma/R^2)\delta R$ . Its effect is, however, negligible even at low frequencies as long as  $\hat{\omega} > \phi R_c/R$ ,  $R_c$  being the critical radius of nucleation. See the last paragraph of Appendix C for its justification.

However, we should note that, even without sounds, the latent-heat generation (or absorption) of a growing droplet in a metastable medium induces a temperature deviation decaying as  $1/r$  at long distances.<sup>33</sup> The heat dissipation of growing droplets is much greater than that induced by sounds by the factor of  $[(p - p_{cx})/\delta p]^2$  (see Appendix C). Therefore ambiguity remains in separating the small dissipation of sounds from that of growing droplets at very low frequencies. By this reason (2.39) and (2.42) are still not well established for  $\hat{\omega} \ll 1$ , which requires us to construct a more systematic theory.

Here we also estimate the order of magnitude of the viscous damping using the results in Appendix C. For  $\hat{\omega} < 1$  the acoustically induced velocity field immediately outside a gas droplet is

$$\delta v_l = (1 - \rho_g/\rho_l) \frac{\partial}{\partial t} \delta R, \quad (2.47)$$

where we have used (C1) assuming  $v_g = 0$  inside the gas droplet. The velocity gradient outside the droplet is of order  $\delta v_l/R$ , so that the heat product rate  $\dot{Q}_{\text{vis}}$  is estimated as

$$\dot{Q}_{\text{vis}} \sim \phi \eta (1 - \rho_g/\rho_l)^2 \left[ \frac{\partial}{\partial t} \delta R \right]^2 R^{-2}. \quad (2.48)$$

This should be compared with the heat production rate (2.19) due to heat conduction, which will be written as  $\dot{Q}_{\text{heat}}$  here. Using (2.15) and (2.44) we find

$$\dot{Q}_{\text{vis}}/\dot{Q}_{\text{heat}} \sim (1 - \rho_g/\rho_l)^2 (\xi/R)^2. \quad (2.49)$$

The above ratio is very small and the viscous damping is obviously negligible.

### E. Attenuation in spinodal decomposition

We suppose spinodally decomposing fluids at  $\phi \simeq \frac{1}{2}$ . The relatively high-frequency behavior (2.30) remains valid. The low-frequency regime  $\hat{\omega} < 1$  has a sizable width only when  $\gamma_R \ll DR^{-2}$ . If  $\hat{\omega} < 1$ , the heat current extends over distances longer than  $R$ . If  $\phi$  is not small, the distances between domains are of order  $R$  and the temperature equilibration can be nearly achieved even on the acoustic time scale. Here (2.17) suggests  $F \sim \omega$  and we may set  $F \equiv (i\omega/D)F_1$ , where  $F_1$  is real and satisfies

$$\nabla^2 F_1 = -1, \quad (2.50)$$

in the bulk region and  $F_1 = 0$  at the interface. For  $\phi \simeq \frac{1}{2}$ ,  $R$  is the unique length of the domains and  $\langle F_1 \rangle \simeq R^2$ , so that we find for  $\hat{\omega} < 1$ ,

$$\alpha_{D\lambda} \sim a_c^2 \omega R^2/D \simeq a_c^2 \hat{\omega}. \quad (2.51)$$

## III. SOUND VELOCITY AND ADIABATIC COMPRESSIBILITY IN TWO-PHASE STATES

### A. Kramers-Kronig relation

It is known that the complex sound velocity  $c_D(\omega)$  is a causal response function and is analytic for  $\text{Re}(i\omega) > 0$ . Here we suppose

$$\langle \delta p \rangle \propto \exp[i\omega(-x/c_D + t)]. \quad (3.1)$$

Therefore, due to the Kramers-Kronig relation,<sup>25</sup> once we know the  $\omega$ -dependent attenuation, we can find the  $\omega$ -dependent dispersion without going into details of the dynamics. Notice that our derivation of  $\alpha_{D\lambda}$  is a perturbation theory, where we have assumed that the sound velocity is nearly equal to the thermodynamic value  $c = [(\delta p/\delta p)_s]^{1/2}$  and  $|\alpha_{D\lambda}| \ll 1$ . Our theory is valid only to first order in the domain contribution, so that

$$c_D/c - 1 \simeq \frac{1}{2} a_c^2 (\langle F \rangle - 1), \quad (3.2)$$

where  $F$  is defined by (2.16) and use has been made of  $c_D \rightarrow c$  for  $\hat{\omega} \gg 1$ . The sound velocity is the real part of  $c_D$  and is an increasing function of  $\omega$  from (2.29) and (2.40) as

$$1 - \text{Re}(c_D/c) \simeq \begin{cases} a_c^2 (D/2\omega)^{1/2} A & \text{for } \hat{\omega} \gg \phi \\ \frac{1}{2} a_c^2 & \text{for } \hat{\omega} \ll \phi, \end{cases} \quad (3.3a)$$

$$(3.3b)$$

which holds for any  $\phi$ . We notice that the right-hand side of (3.3b) is remarkably of order 1 but is inconsistent with the assumption  $|c_D/c - 1| \ll 1$ .

### B. Effective adiabatic compressibility

To remove the above defect in (3.3b) we here devise a formula for a frequency-dependent (complex) compressi-

bility  $K_D(\omega)$  in two-phase states, taking into account heat conduction. The following discussions can be used generally at low frequencies even away from criticality. In bubbly fluids, if  $\omega$  is much smaller than the so-called bubble resonance frequency,<sup>18,19,36</sup> the droplet motion is governed by heat conduction<sup>37</sup> and the attenuation due to scattering is expected to be much smaller than that due to heat conduction. The complex sound velocity  $c_D(\omega)$  defined by (3.1) is expressed as

$$1/\bar{\rho}c_D(\omega)^2 = K_D(\omega), \quad (3.4)$$

where  $\bar{\rho}$  is the average mass density given by

$$\bar{\rho} = \phi_g \rho_g + \phi_l \rho_l. \quad (3.5)$$

The  $\phi_g$  (or  $\phi_l = 1 - \phi_g$ ) is the volume fraction of the gas (or liquid) phase, while  $\rho_g$  and  $\rho_l$  are the mass densities in the two phases. We rewrite (3.1) as

$$\langle \delta p \rangle \propto \exp(-i\omega x/c_{\text{eff}} - \alpha_D x + i\omega t). \quad (3.6)$$

The effective sound velocity  $c_{\text{eff}}$  and the attenuation  $\alpha_D$  per unit length are expressed as

$$1/c_{\text{eff}} = \text{Re}[\bar{\rho}K_D(\omega)]^{1/2}, \quad (3.7)$$

$$\alpha_D = -\omega \text{Im}[\bar{\rho}K_D(\omega)]^{1/2}. \quad (3.8)$$

The attenuation per wavelength is of the form,

$$\alpha_{D\lambda} = -2\pi \text{Im}[K_D(\omega)^{1/2}]/\text{Re}[K_D(\omega)^{1/2}]. \quad (3.9)$$

We consider a small volume element containing many domains in the fluid. Its linear dimension is much shorter than the sound wavelength. Its volume in the absence of the sound is denoted by  $V$  and its small change due to the sound by  $\delta V$ . Then the change of the average density  $\delta\bar{\rho}$  is related to  $\delta V$  and  $\delta p$  by

$$\delta\bar{\rho}/\bar{\rho} \cong -\delta V/V \quad (3.10a)$$

$$\cong K_D(\omega)\delta p. \quad (3.10b)$$

The second line is the definition of  $K_D(\omega)$ . Now the task is to calculate  $\delta V$  in two-phase states. Within a domain the specific volume  $v$  changes as

$$\begin{aligned} \delta v &= \left[ \frac{\partial v}{\partial p} \right]_T \delta p + \left[ \frac{\partial v}{\partial T} \right]_p \delta T \\ &= \left[ \frac{\partial v}{\partial p} \right]_s \delta p + \left[ \frac{\partial v}{\partial T} \right]_p \left[ \delta T - \left[ \frac{\partial T}{\partial p} \right]_s \delta p \right]. \end{aligned} \quad (3.11)$$

At the interface, however, there can be mass conversion. Let  $w$  be the mass flux through the interface from liquid to gas; then, due to the difference  $\Delta v = v_g - v_l$  of the specific volume, a volume increase takes place at the interface at the rate  $(\Delta v)w$  per unit area. Therefore, the rate of the total volume change consists of two parts,

$$\frac{\partial}{\partial t}(\delta V) = \int d\mathbf{r} \frac{1}{v} \frac{\partial}{\partial t}(\delta v) + \int dS (\Delta v)w, \quad (3.12)$$

where the integral in the first term is within the volume element and that in the second term is over the interfaces contained in it. In Appendix C we will derive the follow-

ing expression for  $w$ :

$$w = \frac{1}{T(s_g - s_l)} [\lambda_g \nabla T_g - \lambda_l \nabla T_l] \cdot \mathbf{n}, \quad (3.13)$$

where  $\nabla T_g$  and  $\nabla T_l$  are the temperature gradients at the interface in the gas and liquid sides, respectively,  $\lambda_g$  and  $\lambda_l$  are the thermal conductivities in the two phases, and  $\mathbf{n}$  is the normal unit vector from liquid to gas.

The surface integral in the second term of (3.12) may be transformed into a volume integral using the Gauss theorem. Integration of (3.12) over time yields

$$\delta V = \int d\mathbf{r} \frac{1}{v} \delta v - \frac{1}{i\omega T} \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \int d\mathbf{r} \lambda \nabla^2 \delta T. \quad (3.14)$$

The second term on the second line of (3.11) and the second term in (3.14) will take a simple form if added and expressed in terms of  $F$ , (2.16). Here we use

$$\begin{aligned} \lambda \nabla^2 \delta T &= i\omega \rho C_p \left[ \delta T - \left[ \frac{\partial T}{\partial p} \right]_s \delta p \right] \\ &= i\omega \rho C_p \left[ \left[ \frac{\partial T}{\partial p} \right]_s - \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \right] \delta p (F - 1). \end{aligned} \quad (3.15)$$

The  $F$  obeys (2.17) and (2.18); however,  $D$  takes different values,  $D_g$  and  $D_l$ , in the two phases. Some manipulations lead to

$$\delta V/V = \delta p \int d\mathbf{r} \frac{1}{v} \left[ \frac{\partial v}{\partial p} \right]_s [1 + Z(1 - F)]. \quad (3.16)$$

The coefficient  $Z$  is simply of the form

$$Z = (\gamma_s - 1) \left[ \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \left[ \frac{\partial p}{\partial T} \right]_s - 1 \right]^2, \quad (3.17)$$

$\gamma_s$  being the specific-heat ratio. We have used the identity stated below (1.7), (2.22), and  $(\partial v/\partial T)_p / (\partial s/\partial T)_p = (\partial v/\partial s)_p = (\partial T/\partial p)_s$ . Recall that the same factor appeared in (1.7). Near criticality we simply have  $Z \cong a_c^2$  from (2.8). It will also be useful to express  $Z$  in terms of the derivative of the specific entropy along the coexistence curve,

$$Z = \rho^2 c^2 T C_p^{-1} \left[ \frac{\partial s}{\partial T} \right]_{\text{coex}}^2 \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}}^2. \quad (3.18)$$

Use has been made of the formula written on the first line of (2.4). For gases  $Z = Z_g$  is typically of order 1, but it can vanish at a particular temperature. This is because the specific heat  $T(\partial s/\partial T)_{\text{coex}}$  of saturated vapor is known to change its sign from positive to negative with lowering of  $T$ .<sup>38</sup> For liquids we expect that  $Z = Z_l$  grows as  $(\partial T/\partial p)_{\text{coex}}^2 \propto v_g^2$  with increasing  $v_g/v_l$ , where the other factors in (3.18) are assumed to change more slowly.

Thus from (3.10) we arrive at the desired result,

$$\begin{aligned} K_D(\omega) &= (\phi_g/\rho_g c_g^2) [1 + Z_g \langle 1 - F \rangle_g] \\ &\quad + (\phi_l/\rho_l c_l^2) [1 + Z_l \langle 1 - F \rangle_l], \end{aligned} \quad (3.19)$$

where  $c_g$  and  $c_l$  are the sound velocities of the gas and the liquid,  $Z_g$  and  $Z_l$  are the values of  $Z$  defined by (3.17) in the two phases, and  $\langle \rangle_g$  and  $\langle \rangle_l$  are the spatial averages in the gas region and the liquid region, respectively.

### C. Near-critical fluids

Near criticality we have  $\rho_g \cong \rho_l$ ,  $c_g \cong c_l$ , and  $Z_g \cong Z_l \cong a_c^2$ , so that

$$K_D(\omega) \cong \frac{1}{\rho c^2} (1 + a_c^2 \langle 1 - F \rangle), \quad (3.20)$$

where  $\langle \rangle = \phi_g \langle \rangle_g + \phi_l \langle \rangle_l$ . Therefore,

$$c^2/c_D(\omega)^2 \cong 1 + a_c^2 \langle 1 - F \rangle. \quad (3.21)$$

The sound velocity  $c_{\text{eff}}$  tends to the following value in the low-frequency limit (or in the isothermal limit):<sup>2</sup>

$$c_{\text{eff}} = c_D(0) = c / (1 + a_c^2)^{1/2} \cong 0.82c, \quad (3.22)$$

irrespective of the volume fraction  $\phi$ . The expression (3.21) is consistent with (2.25) and (3.2) only when  $a_c^2 \langle 1 - F \rangle$  is small compared to 1. Particularly, when one phase is dilute with a small volume fraction  $\phi$ , (2.40b) [or (2.40a)] gives an overall approximate expression in the region  $\hat{\omega} = \omega R^2/D < (R/\xi)^2$ ,

$$c^2/c_D(\omega)^2 \cong 1 + 3a_c^2 \phi (1 + 2\sqrt{i\hat{\omega}}) / [i\hat{\omega} + 3\phi(1 + 2\sqrt{i\hat{\omega}})]. \quad (3.23)$$

In Fig. 2 we plot  $1 - c_{\text{eff}}/c$  and  $\alpha_{D\lambda}$  defined (3.8) and (3.9) on the basis of (3.23). The limiting sound velocity (3.22) is attained only at very low frequencies,  $\omega < \phi DR^{-2}$ . The maximum of  $\alpha_{D\lambda}$  is of order 1 at  $\omega \cong 3\phi DR^{-2}$ .

The result  $K_D(0) \cong (1 + a_c^2)/\rho c^2$  means that the zero-frequency adiabatic compressibility in two-phase coexistence is larger than that of pure phases on the coexistence curve by the factor  $1 + a_c^2$ . Interestingly Bailey and Cannell<sup>39</sup> have recently found that the specific heat  $(C_v)_{\text{coex}}$  in two-phase coexistence is larger than that of pure phases  $C_v$  on the coexistence curve by the same factor  $1 + a_c^2$ , as  $\epsilon \rightarrow 0$ , owing to mass conversion between the two phases.

### D. Fluids far from criticality

In Sec. II we have seen that  $F \propto \omega$  and  $\langle F \rangle \rightarrow 0$  as  $\omega \rightarrow 0$ . More generally we have  $\langle F \rangle_g \rightarrow 0$  and  $\langle F \rangle_l \rightarrow 0$  as  $\omega \rightarrow 0$ , so that the zero-frequency sound velocity becomes

$$1/c_D(0)^2 = (\phi_g \rho_g + \phi_l \rho_l) \times \left[ \frac{\phi_g}{\rho_g c_g^2} (1 + Z_g) + \frac{\phi_l}{\rho_l c_l^2} (1 + Z_l) \right]. \quad (3.24)$$

The  $Z_g$  and  $Z_l$  have arisen from heat conduction. It is interesting here to mention a work by Landau and Lifshitz.<sup>40</sup> They calculated the sound velocity in two-phase states by assuming that the fluid stays on the coex-

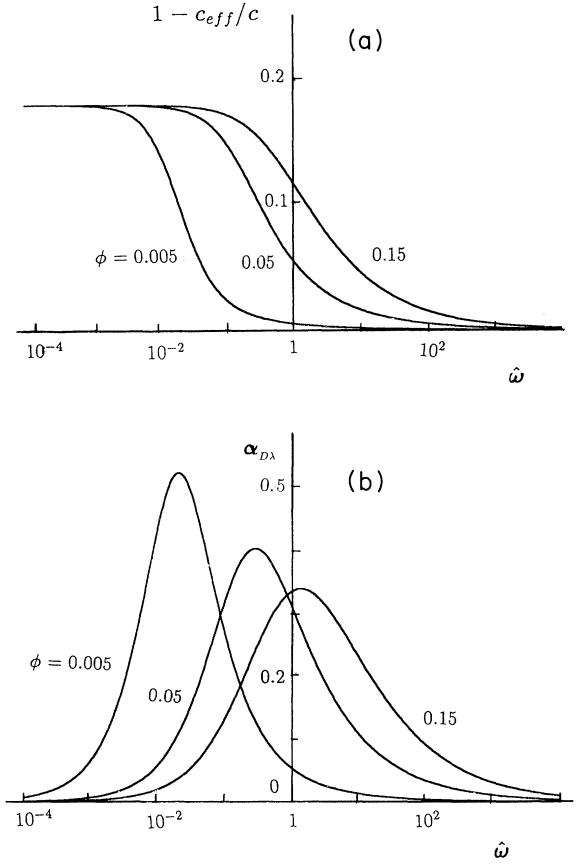


FIG. 2. (a)  $1 - c_{\text{eff}}/c$  vs  $\hat{\omega} = \omega R^2/D$  on a semilog scale at  $\phi = 0.005, 0.05,$  and  $0.15$ . Here  $c_{\text{eff}}$  and  $c$  are the sound velocities in two-phase states and in one-phase states, respectively. (b) The attenuation  $\alpha_{D\lambda}$  per wavelength vs  $\hat{\omega}$  on a semilog scale at  $\phi = 0.005, 0.05,$  and  $0.15$ . The peak height becomes smaller than that from (2.40).

istence curve as  $\omega \rightarrow 0$  or, in our notation,  $\delta T = (\partial T / \partial p)_{\text{coex}} \delta p$  throughout the fluid as  $\omega \rightarrow 0$ . Their expression can be shown to be equivalent to (3.24). If the gas phase is dilute, (3.24) holds only when

$$\omega \ll D_g R^{-2}, \quad \omega \ll \phi_g D_l R^{-2}. \quad (3.25)$$

The first condition ensures thermal equilibration within gas bubbles, while the second ensures thermal equilibration in the liquid region as can be found from (2.40). If  $\phi_g \ll 1$ , the second condition requires extremely low frequencies. We notice that  $c_D(0)$  tends to  $c_l / \sqrt{1 + Z_l}$  as  $\phi_g \rightarrow 0$ . This is not a contradiction because  $c_D(\omega) \rightarrow c_l$  as  $\phi_g \rightarrow 0$  if  $\omega$  is fixed at a nonzero value. If the liquid phase is dilute, the conditions for (3.24) are obtained by exchange of the subscripts,  $g$  and  $l$ , in (3.25).

On the other hand, at relatively high frequencies

$$\omega \gg D_g R^{-2}, \quad \omega \gg D_l R^{-2}, \quad (3.26)$$

the thermal diffusion lengths in the two phases are much shorter than  $R$  and (2.29) indicates



$$\begin{aligned}\phi_g \langle 1-F \rangle_g &\cong A(D_g/i\omega)^{1/2}, \\ \phi_l \langle 1-F \rangle_l &\cong A(D_l/i\omega)^{1/2},\end{aligned}\quad (3.27)$$

where  $A$  is the surface area per unit volume. Then

$$K_D(\omega) \cong \frac{1}{\bar{\rho}c_{EM}^2} + \left[ \frac{Z_g D_g^{1/2}}{\rho_g c_g^2} + \frac{Z_l D_l^{1/2}}{\rho_l c_l^2} \right] A(i\omega)^{-1/2}, \quad (3.28)$$

where  $c_{EM}$  is the sound velocity in Wood's theory,<sup>16,20</sup>

$$\frac{1}{c_{EM}^2} = \bar{\rho} \left[ \frac{\phi_g}{\rho_g c_g^2} + \frac{\phi_l}{\rho_l c_l^2} \right], \quad (3.29)$$

$\bar{\rho}$  being given by (3.5). Note that the above result is consistent with the effective-medium theory.<sup>16,20</sup> It neglects heat conduction and predicts the sound velocity  $c_{EM}$  determined by (3.29).<sup>41</sup> Obviously the effective-medium theory is valid in the frequency region (3.26). In the experiment of Coste, Laroche, and Fauve,<sup>18</sup> the radius of gas bubbles was 0.5 mm and (3.26) was satisfied. In accord with this, their data on the sound velocity were explained by the effective-medium theory rather than by the Landau-Lifshitz's theory. Notice also that the second term in (3.28) gives the attenuation  $\alpha_{D\lambda}$  proportional to  $\omega^{-1/2}$ .

We then examine the anomalous low-frequency attenuation due to latent-heat generation. For liquids with gas bubbles, we may readily generalize (3.23) for  $\omega \ll D_g R^{-2}$  as

$$K_D(\omega) = \frac{1}{\bar{\rho}c_{EM}^2} + \frac{3\phi_g(Z_l/\rho_l c_l^2)(1+\sqrt{i\hat{\omega}})}{i\hat{\omega} + 3\phi_g(1+\sqrt{i\hat{\omega}})}, \quad (3.30)$$

where  $\hat{\omega} \equiv \omega R^2/D_l$  and  $\phi_g \ll 1$ . We have retained  $(i\hat{\omega})^{1/2}$  in case of  $D_l \ll D_g$  and have multiplied the factor of  $\frac{1}{2}$  because the gas-phase side has a homogeneous temperature. The attenuation  $\alpha_{D\lambda}$  grows as  $1/\omega$  in the region  $\phi_g < \hat{\omega} < 1$ , surprisingly, and becomes weak as  $\omega$  in the region  $\hat{\omega} < \phi_g$ . It goes without saying that when liquid droplets are suspended in a gas, the corresponding expression for  $K_D(\omega)$  can be obtained by exchange of  $l$  and  $g$  in (3.30).

## IV. BINARY MIXTURES

### A. Coupled diffusion equations

In binary mixtures the entropy and the concentration obey coupled diffusion equations and the calculations are very complicated.<sup>42,43</sup> Nevertheless our final result is very simple: the previous formulas for near-critical pure fluids can be used asymptotically even for near-critical binary mixtures if the coefficient  $a_c^2$  for pure fluids is replaced by a weakly temperature-dependent coefficient  $A_b$  defined by (4.43) below. This is because a diffusive mode undergoing critical slowing-down dominantly dissipates sounds owing to a strong increase of the Onsager kinetic coefficients.<sup>13,23</sup> For simplicity we exclude exceptional cases such as critical azeotropy, which arise when the

thermodynamic coordinate axes bear a special relationship to the coexistence surface or the critical line.<sup>44</sup>

The thermodynamic state of binary mixtures will be represented by the three independent field variables,  $T$ ,  $p$ , and the chemical potential difference  $\Delta = \mu_1 - \mu_2$  per particle.<sup>44,45</sup> The corresponding potential is  $\mu_2$  (the chemical potential of the second component per particle) and the Gibbs-Duhem relation is

$$d\mu_2 = -sdT - Xd\Delta + vdp. \quad (4.1)$$

We slightly changed the definitions of  $s$  and  $v$  in the previous sections; they are now the entropy and the volume per particle, respectively. Then  $n = 1/v$  is the number density and  $X$  is the (molar) concentration. Following Ref. 43 we define dimensionless deviations,

$$m_1(\mathbf{r}, t) = k_B^{-1} \delta s(\mathbf{r}, t), \quad m_2(\mathbf{r}, t) = \delta X(\mathbf{r}, t), \quad (4.2)$$

$$h_1(\mathbf{r}, t) = \frac{1}{T_c} \delta T(\mathbf{r}, t), \quad h_2(\mathbf{r}, t) = \frac{1}{k_B T_c} \delta \Delta(\mathbf{r}, t). \quad (4.3)$$

Neglecting the velocity field we write the linear hydrodynamic equations as

$$\frac{\partial}{\partial t} m_i = -\nabla \cdot \mathbf{J}_i = \sum_{j=1}^2 K_{ij} \nabla^2 h_j, \quad (4.4)$$

where  $K_{ij}$  ( $=K_{ji}$ ) are the Onsager kinetic coefficients and the current densities  $\mathbf{J}_i$  are written as

$$\mathbf{J}_i = -\sum_{j=1}^2 K_{ij} \nabla h_j. \quad (4.5)$$

A mode-coupling calculation yields<sup>42,43</sup>

$$K_{ij} = K_{ij}^0 + \alpha_i \alpha_j S, \quad (4.6)$$

where  $K_{ij}^0$  are the background parts and

$$S = D k_B T_c \left[ \frac{\partial n}{\partial p} \right]_{T\Delta}. \quad (4.7)$$

The  $D$  is the diffusion constant of the critical fluctuations given by (2.15),  $(\partial n / \partial p)_{T\Delta} \propto \epsilon^{-\gamma}$ , and hence we have roughly  $S \propto \xi$ . The  $\alpha_1$  and  $\alpha_2$  are dimensionless parameters defined by<sup>43</sup>

$$\alpha_1 = -k_B^{-1} v_c \left[ \frac{\partial p}{\partial T} \right]_{\Delta, \text{coex}}, \quad (4.8)$$

$$\alpha_2 = -v_c \left[ \frac{\partial p}{\partial \Delta} \right]_{T, \text{coex}}, \quad (4.9)$$

where  $v_c$  is the critical point value and  $(\partial \cdots / \partial T)_{\Delta, \text{coex}}$  and  $(\partial \cdots / \partial \Delta)_{T, \text{coex}}$  are the derivatives on the coexistence surface. We assume that  $\alpha_1$  and  $\alpha_2$  are neither zero nor infinity. The critical azeotropy occurs when  $\alpha_2 = 0$  at a critical point on the critical line. Let us define a dimensionless pressure deviation  $h_3$  by

$$h_3 = (v_c / k_B T_c) \delta p. \quad (4.10)$$

Then  $\alpha_i = -(\partial h_3 / \partial h_i)_{\text{coex}}$  and hence the vector  $(\alpha_1, \alpha_2, 1)$  is orthogonal to the coexistence surface in the  $h_1$ - $h_2$ - $h_3$  space.

To linear orders in the deviations we have

$$m_i = \sum_{j=1}^3 \left[ \frac{\partial m_i}{\partial h_j} \right] h_j . \quad (4.11)$$

After some manipulations we may rewrite (4.4) in the form

$$\frac{\partial}{\partial t} h_i = W_i \frac{\partial}{\partial t} h_3 + \sum_{\gamma=1}^2 L_{ij} \nabla^2 h_j , \quad (4.12)$$

where  $W_i$  are the adiabatic coefficients given by

$$W_1 = \left[ \frac{\partial h_1}{\partial h_3} \right]_{sX} = k_B n_c \left[ \frac{\partial T}{\partial p} \right]_{sX} , \quad (4.13)$$

$$W_2 = \left[ \frac{\partial h_2}{\partial h_3} \right]_{sX} = n_c \left[ \frac{\partial \Delta}{\partial p} \right]_{sX} , \quad (4.14)$$

$n_c = 1/v_c$  being the critical density. The differences of  $W_1$  and  $W_2$  between the two phases are at most of order  $\epsilon^{\alpha+\beta}$  (see Appendix D). The matrix  $\{L_{ij}\}$  is a product of two matrices,

$$L_{ij} = \sum_{k=1}^2 A_{ij} K_{kj} , \quad (4.15)$$

with

$$A_{ij} = A_{ji} = \left[ \frac{\partial h_i}{\partial m_j} \right]_p , \quad (4.16)$$

where the derivatives are performed with  $p$  and the other density ( $m_1$  or  $m_2$ ) held fixed. In the usual notation  $A_{ij}$  are given by

$$\begin{aligned} A_{11} &= \left[ \frac{k_B}{T_c} \right] \left[ \frac{\partial T}{\partial s} \right]_{pX} , \\ A_{12} &= \frac{1}{T_c} \left[ \frac{\partial \Delta}{\partial s} \right]_{pX} = \frac{1}{T_c} \left[ \frac{\partial T}{\partial X} \right]_{ps} , \\ A_{22} &= \frac{1}{k_B T_c} \left[ \frac{\partial \Delta}{\partial X} \right]_{ps} . \end{aligned} \quad (4.17)$$

It is known that  $\vec{L}$  has two eigenvectors,  $\vec{e}_1$  and  $\vec{e}_2$ ,

$$\vec{L} \cdot \vec{e}_j = D_j \vec{e}_j . \quad (4.18)$$

The first mode has a small diffusion constant  $D_1$ , which may be equated to  $D$  given by (2.15). The second mode is insensitive to  $\epsilon$  and has a nearly constant diffusion constant  $D_2$ . Therefore  $D_1 \ll D_2$  near criticality. The conjugate eigenvectors  $\vec{e}_j$  are defined by

$$\vec{e}_j = \vec{A} \cdot \vec{e}_j . \quad (4.19)$$

It readily follows that  $\vec{e}_i \cdot \vec{e}_j \propto \delta_{ij}$ . Reference 43 shows that  $\mathbf{e}_1 \cong (\alpha_1, \alpha_2)$  and  $\vec{e}_1 \cdot \mathbf{e}_1 \cong (\partial p / \partial n)_{T\Delta} / k_B T \sim \epsilon^{-\gamma} \gg 1$ , whereas  $\mathbf{e}_2$  and  $\vec{e}_2$  are nearly independent of  $\epsilon$  and  $\vec{e}_2 \cdot \mathbf{e}_2 = O(1)$ . We decompose  $\mathbf{h} = (h_1, h_2)$  into the two modes,

$$\mathbf{h} = f_1 (\vec{e}_1 \cdot \mathbf{e}_1)^{-1} \vec{e}_1 + f_2 (\vec{e}_2 \cdot \mathbf{e}_2)^{-1} \vec{e}_2 , \quad (4.20)$$

where

$$f_j = \mathbf{e}_j \cdot \mathbf{h} . \quad (4.21)$$

The diffusion equations for  $f_1$  and  $f_2$  are decoupled from (4.12) as

$$\frac{\partial}{\partial t} f_j = (\mathbf{e}_j \cdot \mathbf{W}) \frac{\partial}{\partial t} h_3 + D_j \nabla^2 f_j , \quad (4.22)$$

where  $\mathbf{W} = (W_1, W_2)$ .

## B. Boundary conditions

Far from the interface  $\delta T$  and  $\delta \Delta$  are perturbed by  $\delta p$  adiabatically (or with fixed  $s$  and  $X$ ) and  $h_i = W_i h_3$  [which is the counterpart of (2.3)]. At the interface we require the continuity of  $h_1, h_2, h_3$ , and  $\delta \mu_2$ . Then (3.1) yields a generalization of (2.12),

$$-(\Delta s) \delta T - (\Delta X) \delta \Delta + (\Delta v) \delta p = 0 , \quad (4.23)$$

where  $\Delta s, \Delta v$ , and  $\Delta X$  are the differences between the two phases all of order  $\epsilon^\beta$ . Because (4.23) holds for any  $(\delta T, \delta \Delta, \delta p)$  on the coexistence surface in the  $T$ - $\Delta$ - $p$  space, so from (4.8) and (4.9) we find

$$\Delta s = -k_B \alpha_1 \frac{\Delta v}{v_c} , \quad (4.24)$$

$$\Delta X = -\alpha_2 \frac{\Delta v}{v_c} . \quad (4.25)$$

We may rewrite (4.23) in terms of the dimensionless field variables as

$$\alpha_1 h_1 + \alpha_2 h_2 + h_3 = 0 . \quad (4.26)$$

In Ref. 41 we find  $\mathbf{e}_1 \cong (\alpha_1, \alpha_2)$  as  $\epsilon \rightarrow 0$  and (4.26) becomes the boundary condition for the slow mode,  $f_1 + h_3 \cong 0$  at the interface. We introduce  $\Psi$  by

$$\Psi = f_1 + h_3 \cong \alpha_1 h_1 + \alpha_2 h_2 + h_3 . \quad (4.27)$$

The field  $\Psi$  vanishes at the interface and obeys

$$i\omega \Psi = i\omega W h_3 + D \nabla^2 \Psi , \quad (4.28)$$

where  $D$  is defined by (2.15) and

$$\begin{aligned} W &= \alpha_1 W_1 + \alpha_2 W_2 + 1 \\ &= 1 - \left[ \frac{\partial p}{\partial T} \right]_{\Delta, \text{coex}} \left[ \frac{\partial T}{\partial p} \right]_{sX} - \left[ \frac{\partial p}{\partial \Delta} \right]_{T, \text{coex}} \left[ \frac{\partial \Delta}{\partial p} \right]_{sX} . \end{aligned} \quad (4.29)$$

The  $W$  goes to zero at criticality and in Appendix D we shall see

$$W \sim \epsilon^{(\gamma+\alpha)/2} \theta . \quad (4.30)$$

Therefore the inhomogeneities of  $f_1$  (or  $\Psi$ ) due to domains are of the following order:

$$(f_1)_{\text{inh}} \sim \epsilon^{(\gamma+\alpha)/2} h_3 . \quad (4.31)$$

Furthermore, we define

$$F = \Psi / W h_3 . \quad (4.32)$$

Then  $F$  obeys (2.17) and (2.18) and is the counterpart for  $F$  for pure fluids.

We should then analyze the equation for  $f_2$ . Because the difference of  $\mathbf{e}_2 \cdot \mathbf{W}$  in the two phases is of order  $\epsilon^{\alpha+\beta}$  (see Appendix D), the inhomogeneities of  $f_2$  are of the following order:

$$(f_2)_{\text{inh}} \sim \epsilon^{\alpha+\beta} h_3. \quad (4.33)$$

The boundary condition can be found as follows. The discontinuities of the currents  $\mathbf{J}_1$  and  $\mathbf{J}_2$ , (4.5), along the normal vector  $\mathbf{n}$  should be proportional to  $(\Delta m_1)w$  and  $(\Delta m_2)w$ , where  $\Delta m_1 = \Delta s/k_B$ ,  $\Delta m_2 = \Delta X$ , and  $w$  is the mass current through the interface (see Appendix C). From (4.24) and (4.25) we thus obtain at the interface,

$$\frac{1}{\alpha_1} \mathbf{n} \cdot [\mathbf{J}_1] = \frac{1}{\alpha_2} \mathbf{n} \cdot [\mathbf{J}_2], \quad (4.34)$$

where  $[\ ]$  denotes taking the discontinuity at the interface. Using  $\vec{\mathbf{K}} \cdot \vec{\mathbf{e}}_j = D_j \mathbf{e}_j$  we may rewrite (4.34) as

$$\sum_{j=1}^2 D_j (\mathbf{n} \cdot \nabla f_j) C_j = 0, \quad (4.35)$$

where  $C_j \equiv (\alpha_1 \cdot \mathbf{e}_j) / (\vec{\mathbf{e}}_j \cdot \mathbf{e}_j)$  with  $\alpha_1 = (-\alpha_2, \alpha_1)$  being orthogonal to  $\alpha = (\alpha_1, \alpha_2)$ . We note that  $C_1$  and  $C_2$  are of order 1 from results of Ref. 43, the spatial scale of  $f_1$  is shorter than that of  $f_2$  by the factor  $(D_1/D_2)^{1/2}$ , and  $(f_1)_{\text{inh}}$  and  $(f_2)_{\text{inh}}$  are given by (4.31) and (4.33). These relations indicate that (4.35) reduces to the condition for  $f_2$  as  $\epsilon \rightarrow 0$ ,

$$\mathbf{n} \cdot [\nabla f_2] \cong 0. \quad (4.36)$$

This boundary condition is the same as that for temperature variations in emulsions and implies no latent-heat effect from the fast mode in binary mixtures.

### C. Heat production

We next calculate the heat production rate, which is related to  $\alpha_D$  as in (2.19),<sup>8</sup>

$$\begin{aligned} 2(\alpha_D/\rho c) |\delta p|^2 &= nk_B T \int d\mathbf{r} \sum_{i,j} K_{ij} (\nabla h_i) \cdot (\nabla h_j) \\ &= nk_B T \int d\mathbf{r} \sum_j D_j (\vec{\mathbf{e}}_j \cdot \mathbf{e}_j)^{-1} |\nabla f_j|^2, \end{aligned} \quad (4.37)$$

where the integral is within a unit volume. We will show that the slow mode  $j=1$  gives the dominant contribution on the second line. This means that, on the first line, the critical part of  $K_{ij}$ , the second term in (4.6), gives rise to the dominant contribution in (4.37). The contributions from  $j=1,2$  will be written as  $\dot{Q}_1$  and  $\dot{Q}_2$ . When the diffusion length  $l_{D_1} = (D_1/\omega)^{1/2}$  for the slow mode is shorter than  $R$ ,  $\dot{Q}_1$  is estimated as in (1.4),

$$\dot{Q}_1 \sim D_1 \epsilon^{-\gamma} (f_1)_{\text{inh}}^2 A l_{D_1}^{-1} \sim \epsilon^{\nu/2+\alpha} A \omega^{1/2}, \quad (4.38)$$

where  $A$  is the surface area per unit volume. If  $l_{D_2} = (D_2/\omega)^{1/2}$  for the fast mode is shorter than  $R$ , we obtain

$$\dot{Q}_2 \sim D_2 (f_2)_{\text{inh}}^2 A l_{D_2}^{-1} \sim \epsilon^{2\alpha+2\beta} A \omega^{1/2}. \quad (4.39)$$

For  $l_{D_2} > R$  the relaxation of  $f_2$  can follow the sound due to (4.36) and  $\dot{Q}_2$  behaves as for emulsions,

$$\dot{Q}_2 \sim \epsilon^{2\alpha+2\beta} A R^{-1} (\omega R^2/D_2)^2. \quad (4.40)$$

The coefficient in (4.40) is determined such that (4.39) and (4.40) are connected smoothly at  $\omega \simeq D_2 R^{-2}$ . Comparing (4.38), (4.39), and (4.40) we conclude that  $\dot{Q}_1$  asymptotically dominates over  $\dot{Q}_2$ , although the difference between (4.38) and (4.39) is not large.

Retaining only the slow mode (4.38) becomes

$$2(\alpha_D/\rho c) |\delta p|^2 = nk_B T \int d\mathbf{r} S |\nabla f_1|^2, \quad (4.41)$$

where  $S$  is defined by (4.7). Therefore the attenuation  $\alpha_D$  or  $\alpha_{D\lambda}$  assumes the same form as (2.21) or (2.25) except that  $a_c^2$  is replaced by another coefficient  $A_b$  given by

$$A_b = \left[ \frac{\partial p}{\partial n} \right]_{sX} \left[ \frac{\partial n}{\partial p} \right]_{T\Delta} |W|^2. \quad (4.42)$$

In Appendix D we shall see that the asymptotic behavior of  $A_b$  is of the form

$$A_b = a_c^2 b_c^2 / \gamma_s, \quad (4.43)$$

where

$$b_c = \frac{1 + \left[ \frac{\partial \Delta}{\partial T} \right]_{p,\text{coex}} \left[ \frac{dX}{ds} \right]_c}{1 + \left[ \frac{d\Delta}{dT} \right]_c \left[ \frac{dX}{ds} \right]_c - \left[ \frac{dv}{dT} \right]_c \left[ \frac{dp}{ds} \right]_c}, \quad (4.44)$$

$$\gamma_s = C_{pX} / C_{vX} = K_{TX} / K_{sX}. \quad (4.45)$$

Here  $(d \cdots / d \cdots)_c$  denotes taking the derivative along the critical line. The specific-heat ratio  $\gamma_s$  behaves as  $\epsilon^{-\alpha}$ ,  $K_{TX}$  and  $K_{sX}$  being the compressibilities, so that  $A_b \propto \epsilon^\alpha$ . Note the above result cannot be used at critical azeotropy, where  $\alpha_2 = 0$  or  $(\partial \Delta / \partial T)_{p,\text{coex}} = \infty$ .

## V. SUMMARY AND CONCLUDING REMARKS

We summarize our main results. Section II treats near-critical pure fluids. We have first calculated a small difference of the adiabatic coefficient  $(\partial T / \partial p)_s$  between the two phases, which leads to inhomogeneous temperature variations (2.11) due to domains. The boundary condition at the interface is given by (2.13) from the continuity of the chemical potential. It is different from the boundary condition for emulsions, in which the mass flow through the interfaces is prohibited. With the above two results the heat conduction equation (2.14) with the adiabatic effect has been solved for planar and spherical interfaces. In terms of a dimensionless temperature variation  $F(\mathbf{r})$  defined by (2.16), the attenuation  $\alpha_{D\lambda}$  has been expressed in a simple form as (2.25). In the adiabatic frequency region  $\omega > DR^{-2}$  the behavior of  $\alpha_{D\lambda} (\propto 1/\sqrt{\omega})$  has been commonly found in other systems such as polycrystals or emulsions. However, as a new result, latent-heat generation can be crucial for  $\omega < DR^{-2}$  when drop-

lets are sparsely distributed. Section III gives an elegant expression for the effective adiabatic compressibility  $K_D(\omega)$  of two-phase pure fluids, where we have taken into account heat conduction and latent-heat generation through the interfaces. Section IV treats binary mixtures, whose thermodynamics and hydrodynamics are, in principle, well understood but are cumbersome in actual calculations. We have shown that the slow diffusive mode gives rise to acoustic anomalies in two-phase states, which are nearly the same as for pure fluids at least close to criticality.

We make further remarks in the following.

(1) For near-critical pure fluids the analysis is very simple and the results are universally independent of fluids. Particularly simple is (3.22), which states that the zero-frequency sound velocity is decreased by 18% in the presence of domains. It is similar to the relation for the specific heat in two-phase coexistence found by Bailey and Cannell.<sup>39</sup>

(2) We should stress that essentially the same effects exist in general two-phase fluids, although they are expressed in more complicated forms than near criticality. Our expression for the adiabatic compressibility  $K_D(\omega)$ , (3.19), incorporates two apparently contradicting theories for sounds in bubbly fluids, the effective-medium theory, and the Landau-Lifshitz theory, as its high- and low-frequency limits. Furthermore, it gives expressions for attenuation, which was neglected in the above two theories.

(3) It is of great interest to detect the anomalous attenuation,  $\alpha_{D\lambda} \propto 1/\omega$ , due to latent-heat generation. The theoretical formula is given by (2.39) near criticality and by (3.30) far from criticality. This attenuation mechanism seem to have not been noticed in the literature and should also be present in other two-phase systems.

(4) Experiments should be much easier in binary mixtures than in pure fluids, although our analysis in Sec. IV is limited only to the case near criticality and the acoustic relations involve the nonuniversal coefficient  $A_b$  of the order of  $\epsilon^\alpha$ .

(5) I hope that this paper will be the first one to revive the idea of Zener and Isakovich and to investigate acoustic anomalies in various phase-separating materials including solids. Such phenomena seem to have not drawn enough attention so far. I would expect that the effect may be used to measure the surface-area density in two-phase states and to detect a small fraction of nucleating droplets.

(6) As a similar effect we could mention enhancement of the effective shear viscosity due to domains in phase-separating near-critical fluids.<sup>46,47</sup>

#### APPENDIX A

We here prove that  $a_c$  defined by (2.8) or (2.9) is a universal number. We choose  $\omega = p/T$  as a thermodynamic potential and  $B = 1/T$  and  $\nu = \mu/T$  as independent field variables.<sup>48,12,28,45</sup> Then,

$$d\omega = -u dB + p d\nu, \quad (\text{A1})$$

where  $u$  is the internal energy density. The entropy per

unit mass  $s$  satisfies

$$\rho T ds = du - Hd\rho = -d\omega_B - Hd\omega_\nu, \quad (\text{A2})$$

where  $H = \mu + sT = (u + p)/\rho$  is the enthalpy per unit mass,  $\omega_B = \partial\omega/\partial B$ , and  $\omega_\nu = \partial\omega/\partial\nu$ . We then regard  $\omega$  as a function of two scaling fields,  $h$  and  $\tau$ , where  $h$  corresponds to the magnetic field and  $\tau$  to the reduced temperature in Ising spin systems. The  $B$  and  $\nu$  are assumed to be regular functions of  $h$  and  $\tau$ . On the coexistence curve the critical power laws are

$$\begin{aligned} \omega_{hh} &= \frac{\partial^2 \omega}{\partial h^2} \sim \epsilon^{-\gamma}, \\ \omega_{h\tau} &= \frac{\partial^2 \omega}{\partial h \partial \tau} \sim \epsilon^{\beta-1} \theta, \\ \omega_{\tau\tau} &= \frac{\partial^2 \omega}{\partial \tau^2} \sim \epsilon^{-\alpha}. \end{aligned} \quad (\text{A3})$$

Note that  $\omega_{h\tau}$  has different signs in the two phases and  $\theta$  ( $= \pm 1$  in the two phases) has been multiplied.

Picking up only divergent parts (A2) may be rewritten as

$$\begin{aligned} \rho T ds = & - \left[ \left( \frac{\partial h}{\partial B} \right)_\nu + H \left( \frac{\partial h}{\partial \nu} \right)_B \right] d\omega_h \\ & - \left[ \left( \frac{\partial \tau}{\partial B} \right)_\nu + H \left( \frac{\partial \tau}{\partial \nu} \right)_B \right] d\omega_\tau + \dots, \end{aligned} \quad (\text{A4})$$

where  $d\omega_h = \omega_{hh} dh + \omega_{h\tau} d\tau$ ,  $d\omega_\tau = \omega_{h\tau} dh + \omega_{\tau\tau} d\tau$ , and the derivatives of  $(\partial h/\partial B)_\nu$ , etc. are finite as  $\epsilon \rightarrow 0$  and are not written explicitly. We may also choose  $p$  and  $T$  as independent field variables. Then,

$$\begin{aligned} \left( \frac{\partial}{\partial T} \right)_p &= -B^2 \left[ \frac{\partial}{\partial B} + H \frac{\partial}{\partial \nu} \right], \\ \left( \frac{\partial}{\partial p} \right)_T &= (\rho T)^{-1} \frac{\partial}{\partial \nu}, \end{aligned} \quad (\text{A5})$$

so that

$$\rho T ds = T^2 \left[ \left( \frac{\partial h}{\partial T} \right)_p d\omega_h + \left( \frac{\partial \tau}{\partial T} \right)_p d\omega_\tau \right] + \dots \quad (\text{A6})$$

By fixing  $p$  we obtain

$$\rho C_p \cong \left[ T \left( \frac{\partial h}{\partial p} \right)_T \right]^2 \omega_{hh}. \quad (\text{A7})$$

In the same manner from  $\rho = \omega_\nu$  we obtain

$$d\rho = \rho T \left[ \left( \frac{\partial h}{\partial p} \right)_T d\omega_h + \left( \frac{\partial \tau}{\partial p} \right)_T d\omega_\tau \right] + \dots \quad (\text{A8})$$

Therefore, if  $\rho$  is fixed, we have

$$d\omega_h \cong - \left[ \frac{\partial \tau}{\partial h} \right]_T d\omega_\tau, \quad (\text{A9})$$

$$dh \cong -(\omega_{h\tau}/\omega_{hh}) d\tau. \quad (\text{A10})$$

Further, using  $d\tau \cong (\partial\tau/\partial T)_h dT$  from (A10) we find

$$\rho C_v = T^2 \left[ \frac{\partial\tau}{\partial T} \right]_h^2 (\omega_{\tau\tau} - \omega_{h\tau}^2/\omega_{hh}) . \quad (\text{A11})$$

The specific-heat ratio  $\gamma_s$  behaves as

$$\gamma_s = \left[ \left[ \frac{\partial T}{\partial\tau} \right]_h \left[ \frac{\partial h}{\partial T} \right]_p \right]^2 \omega_{hh}^2 / (\omega_{hh}\omega_{\tau\tau} - \omega_{h\tau}^2) . \quad (\text{A12})$$

It is worth noting that the form (A11) assures the two-scale-factor universality in pure fluids.<sup>12,24,28,29</sup>

If one density variable is fixed, any field variable  $\psi$  satisfies on the coexistence curve

$$\left[ \frac{\partial\psi}{\partial\tau} \right]_s \cong \left[ \frac{\partial\psi}{\partial\tau} \right]_\rho \cong \left[ \frac{\partial\psi}{\partial\tau} \right]_h - \left[ \frac{\partial\psi}{\partial h} \right]_\tau \frac{\omega_{h\tau}}{\omega_{hh}} . \quad (\text{A13})$$

Therefore,

$$\left[ \frac{\partial T}{\partial p} \right]_s \cong \left[ \frac{\partial T}{\partial p} \right]_h \left[ 1 + \left[ \frac{\partial\tau}{\partial h} \right]_T \frac{\omega_{h\tau}}{\omega_{hh}} \right] / \left[ 1 + \left[ \frac{\partial\tau}{\partial h} \right]_p \frac{\omega_{h\tau}}{\omega_{hh}} \right] \cong \left[ \frac{\partial T}{\partial p} \right]_h \left[ 1 - \left[ \frac{\partial\tau}{\partial T} \right]_h \left[ \frac{\partial T}{\partial h} \right]_p \frac{\omega_{h\tau}}{\omega_{hh}} \right] , \quad (\text{A14})$$

where use has been made of the relation,

$$\left[ \frac{\partial\tau}{\partial h} \right]_p - \left[ \frac{\partial\tau}{\partial h} \right]_T = \left[ \frac{\partial\tau}{\partial T} \right]_h \left[ \frac{\partial T}{\partial h} \right]_p . \quad (\text{A15})$$

Comparing (A12) and (A14) we thus have

$$a_c^2 = \omega_{h\tau}^2 / (\omega_{hh}\omega_{\tau\tau} - \omega_{h\tau}^2) . \quad (\text{A16})$$

The right-hand side of (A16) is asymptotically universal if the singular part of  $\omega$  is a universal singular function of  $h$  and  $\tau$ . This is a postulate supported by existing experiments.

## APPENDIX B

In the limit of small  $\phi$  droplets may be regarded as point sources with charges  $Q_i$ . Taking this into account we rewrite (2.17) as

$$(-\nabla^2 + \kappa^2)(F - 1) = \sum_i Q_i \delta(\mathbf{r} - \mathbf{r}_i) , \quad (\text{B1})$$

where  $\kappa$  is defined by (2.28) and  $\mathbf{r}_i$  is the center of the  $i$ th droplet. We average (B1) over a unit volume to obtain

$$\kappa^2(\langle F \rangle - 1) = n_D Q , \quad (\text{B2})$$

where  $n_D$  is the droplet density and  $Q$  is the average of  $\{Q_i\}$ . We then integrate (B1) as

$$F = 1 + \frac{1}{4\pi} \sum_i \frac{1}{|\mathbf{r} - \mathbf{r}_i|} Q_i \exp(-\kappa|\mathbf{r} - \mathbf{r}_i|) , \quad (\text{B3})$$

which holds outside the droplets. We should recall the boundary condition  $F = 0$ , (2.18), on the droplet surfaces, so that for each  $i$  we require

$$4\pi + \frac{1}{R} Q_i + \sum_{j \neq i} \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} Q_j \exp(-\kappa|\mathbf{r}_i - \mathbf{r}_j|) = 0 . \quad (\text{B4})$$

We have set  $e^{-\kappa R} \cong 1$  by assuming  $\hat{\omega} \ll 1$ . The average over  $i$  yields

$$Q = -4\pi R / (1 + 4\pi n_D R / \kappa^2) . \quad (\text{B5})$$

The average of the last term of (B4) has been performed as follows:

$$\begin{aligned} (n_D V)^{-1} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} Q_j \exp(-\kappa|\mathbf{r}_i - \mathbf{r}_j|) \\ \cong \frac{1}{V} \int d\mathbf{r} \sum_j \frac{1}{|\mathbf{r} - \mathbf{r}_j|} Q_j \exp(-\kappa|\mathbf{r} - \mathbf{r}_j|) \\ \cong 4\pi n_D Q / \kappa^2 . \end{aligned} \quad (\text{B6})$$

The summation over  $i$  has been replaced by the space integral.

Now (B2) and (B5) lead to

$$\langle F \rangle = 1 / (1 + 3\phi / i\hat{\omega}) . \quad (\text{B7})$$

## APPENDIX C

We follow the calculations of Turski and Langer<sup>33</sup> to derive (2.44) and (3.13). We consider a point on a gas-liquid interface. Let  $v_g, v_l, v_{\text{int}}$  be the fluid velocity along the normal  $\mathbf{n}$  on the gas-phase side, on the liquid-phase side, and the interface velocity along  $\mathbf{n}$ , respectively. Then the mass flux  $w$  through the interface along  $\mathbf{n}$  is expressed as<sup>37</sup>

$$w = \rho_g(v_g - v_{\text{int}}) = \rho_l(v_l - v_{\text{int}}) , \quad (\text{C1})$$

$\rho_g$  and  $\rho_l$  being the densities on the gas- and liquid-phase sides. On the other hand, the heat balance at the interface requires

$$T s_g w - \lambda_g T'_g = T s_l w - \lambda_l T'_l , \quad (\text{C2})$$

where  $s_g$  and  $s_l$  are the entropies per unit mass on the two-phase sides,  $\lambda_g$  and  $\lambda_l$  are the thermal conductivities,  $T'_g$  and  $T'_l$  are the values of  $\mathbf{n} \cdot \nabla T$  on the two-phase sides. We then obtain (3.13).

Generally  $w$  is nonvanishing in the course of domain growth. In addition, if a small-amplitude sound wave is sent into the fluid, we have an oscillating mass flux given by

$$\delta w = \frac{\lambda}{T(s_g - s_l)} \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \frac{a_c}{\sqrt{\gamma_s}} (F'_g + F'_l) \delta p . \quad (\text{C3})$$

We have used (2.16) and have set  $\lambda_l = \lambda_g = \lambda$ . The  $F'_g$  and  $F'_l$  are  $\mathbf{n} \cdot \nabla F$  on the two-phase sides. From (2.4) and (2.8) we notice

$$\Delta s = s_g - s_l \cong (2/\beta) a_c C_p (1 - T/T_c) / \gamma_s^{1/2}. \quad (\text{C4})$$

Further, using (2.1) we find

$$\delta w = \frac{\beta}{2} \rho D (F'_g + F'_l) \delta p / (p_c - p). \quad (\text{C5})$$

In the case of planar interfaces (2.27) indicates  $F'_g + F'_l = 0$  at the interface and hence there is almost no mass flux,  $\delta w = 0$ . (However,  $\delta w \neq 0$  even for planar interfaces far from criticality.) In the case of isolated spheres we have  $F' \cong 1/R$  immediately outside the sphere and  $F' \cong 0$  inside the sphere for  $\hat{\omega} \ll 1$  from (2.35). The velocity field inside the sphere is also nearly zero, so that (C1) leads to  $\delta w \cong -\rho_l \partial(\delta R) / \partial t$  for a liquid droplet and we obtain (2.44) near criticality. It is worth noting that (2.44) can also be derived from the Lifshitz-Slyozov equation<sup>49</sup> for the droplet growth,

$$\frac{\partial}{\partial t} R = \frac{D}{R} \left[ \Delta - \frac{2d_0}{R} \right], \quad (\text{C6})$$

where  $\Delta$  is the supersaturation and  $d_0$  ( $\propto \xi$ ) is the capillary length. In near-critical pure fluids  $d_0$  is given by<sup>33</sup>

$$d_0 = \sigma C_p / \rho T (\Delta s)^2 \propto \epsilon^{-\nu}, \quad (\text{C7})$$

$\sigma$  being the surface tension. When  $|\Delta| \ll 1$ , we may express  $\Delta$  in terms of  $T$  or  $p$  as

$$\begin{aligned} \Delta &\cong \frac{1}{2} \beta (T_{\text{coex}} - T) / (T_c - T_{\text{coex}}) \\ &\cong \frac{1}{2} \beta (p_{\text{coex}} - p) / (p_c - p_{\text{coex}}), \end{aligned} \quad (\text{C8})$$

where  $T_{\text{coex}}$  and  $p_{\text{coex}}$  are the temperature and pressure on the coexistence curve. In the presence of sounds  $p$  is composed of the average (without sounds) and the acoustically induced deviation  $\delta p$ . Then (C6) yields

$$\frac{\partial}{\partial t} \delta R \cong \frac{D}{R} \delta \Delta \cong -\frac{1}{2} \beta \left[ \frac{D}{R} \right] \delta p / (p_c - p_{\text{coex}}), \quad (\text{C9})$$

which coincides with (2.44) because  $p_c - p_{\text{coex}} \cong p_c - p$ .

We should note that the discontinuity of the pressure is  $2\sigma / (R + \delta R) = 2\sigma / R - 2\sigma \delta R / R^2 + \dots$  at the interface in the presence of a sound. Therefore, to be precise, the acoustic pressure variation  $\delta p = \delta p_g$  outside a liquid droplet is larger than that  $\delta p_l$  inside it by

$$\delta p_g - \delta p_l = 2\sigma \delta R / R^2. \quad (\text{C10})$$

Assuming the continuity of  $\delta T$  and  $\delta \mu = -s \delta T + v \delta p$  at the interface, the temperature variation at the interface then becomes

$$\delta T = \left[ \frac{\partial T}{\partial p} \right]_{\text{coex}} \delta p + \left[ \frac{2\sigma v_l}{\Delta s} \right] \frac{\delta R}{R^2}. \quad (\text{C11})$$

The second term of (C11) is a correction to (2.13), so we should compare it with  $(\delta T)_{\text{inh}} = [(\partial T / \partial p)_{\text{coex}} - (\partial T / \partial p)_s] \delta p$  given by (2.11). Using (C4) and (C7) it may be transformed into  $(4/\beta) a_c (T_c - T) \gamma_s^{-1/2} d_0 (\delta R) / R^2$ . If we further use (2.44), it becomes

$$(2\sigma v_l / \Delta s) \delta R / R^2 \sim \frac{1}{i \hat{\omega}} \frac{d_0}{R} (\delta T)_{\text{inh}}. \quad (\text{C12})$$

Here we may assume that  $R \gg R_c = d_0 / \Delta$  (the critical radius) and  $\Delta \cong \phi$  (the volume fraction) in late stages of nucleation. We thus find that the magnitude of the ratio of the second term in (C11) to  $(\delta T)_{\text{inh}}$  is smaller than 1 for  $\hat{\omega} > d_0 / R$ . The same conclusion may be drawn even in the case far from criticality.

## APPENDIX D

We examine the behavior of the adiabatic coefficients  $W_1$  and  $W_2$  in (4.13) and (4.14) on the coexistence surface. Leung and Griffiths<sup>45</sup> showed that the critical behavior near the critical line in binary mixtures can be conveniently represented by three field variables,  $h$ ,  $\tau$ , and  $\xi$ . Here  $h$  and  $\tau$  are the relevant two scaling fields as in Appendix A and  $\xi$  is the coordinate along the critical line. Therefore, if  $\xi$  is fixed at a particular value, the critical behavior in the  $h$ - $\tau$  space is the same as that in pure fluids. Leung and Griffiths chose  $\omega \equiv p / T$  as a thermodynamic potential,<sup>48</sup> which consists of a regular part and a singular part, the latter being a universal function of  $h$  and  $\tau$  if scaled appropriately.

In binary mixtures the critical behavior of thermodynamic derivatives can be very different from that in pure fluids when the path of taking derivatives is nearly parallel to the critical line. This is particularly the case when two density variables,  $s$  and  $X$  in our case, are fixed. Let us express infinitesimal increments of  $s$  and  $X$  in terms of those  $\omega_h = \partial \omega / \partial h$  and  $\omega_\tau = \partial \omega / \partial \tau$  as

$$ds = \bar{\alpha}_1 d' \omega_h + \bar{\beta}_1 d' \omega_\tau + \left[ \frac{ds}{d\xi} \right]_c d\xi, \quad (\text{D1})$$

$$dX = \bar{\alpha}_2 d' \omega_h + \bar{\beta}_2 d' \omega_\tau + \left[ \frac{dX}{d\xi} \right]_c d\xi, \quad (\text{D2})$$

where

$$d' \omega_h \equiv \omega_{hh} dh + \omega_{h\tau} d\tau, \quad (\text{D3})$$

$$d' \omega_\tau \equiv \omega_{h\tau} dh + \omega_{\tau\tau} d\tau. \quad (\text{D4})$$

Here  $\omega_{hh} = \partial^2 \omega / \partial h^2$ ,  $\omega_{h\tau} = \partial^2 \omega / \partial h \partial \tau$ ,  $\omega_{\tau\tau} = \partial^2 \omega / \partial \tau^2$ , and  $(d \dots / d \dots)_c$  denotes taking derivatives along the critical line. Notice that (D1) is a generalization of (A6) and (D1) and (D2) are general if the coefficients,  $\bar{\alpha}_1, \bar{\alpha}_2, \bar{\beta}_1, \bar{\beta}_2$ , are allowed to depend on  $h, \tau, \xi$ . The essential point in the following calculation is that they tend to well-defined finite values as  $\epsilon \rightarrow 0$ . We adopt the definitions of Leung and Griffiths of  $h$ ,  $\tau$ , and  $\xi$ , except that quantities per mole in their paper are replaced by the corresponding quantities per particle. Then the critical values of the coefficients are as follows:<sup>43</sup>

$$\bar{\alpha}_1 \cong \frac{1}{n_c} \alpha_1 \cong -k_B n_c^{-2} \left[ \frac{\partial p}{\partial T} \right]_{\Delta, \text{coex}}, \quad (\text{D5})$$

$$\bar{\alpha}_2 \cong \frac{1}{n_c} \alpha_2 \cong -n_c^{-2} \left[ \frac{\partial p}{\partial \Delta} \right]_{T, \text{coex}}, \quad (\text{D6})$$

$$\bar{\beta}_1 \cong (n_c T_c)^{-1} \left/ \left[ 1 - \frac{\Delta_c}{T_c} \left( \frac{dT}{d\Delta} \right)_c \right] \right., \quad (\text{D7})$$

$$\bar{\beta}_2 \cong - \left( \frac{dT}{d\Delta} \right)_c \bar{\beta}_1. \quad (\text{D8})$$

Here  $\alpha_1$  and  $\alpha_2$  are defined by (4.8) and (4.9), while  $\bar{\beta}_1$  and  $\bar{\beta}_2$  coincide with  $\beta_1$  and  $\beta_2$  in Ref. 43 if multiplied by  $n_c T_c$ . The first two relations (D5) and (D6) readily follow from the theory of Griffiths and Wheeler.<sup>44</sup> We can also directly show (D5)~(D8) using (2.25) and (2.35) in Leung and Griffiths's paper. Another way to derive (D7) and (D8) is to calculate the specific heat  $C_{vX}$  or the compressibility  $K_{sX}$  using (D1) and (D2) and use formulas for their critical-point-values given by Griffiths and Wheeler<sup>44</sup> [see (D18) below]. The following relation holds among the above coefficients:<sup>43</sup>

$$1 - (\bar{\alpha}_2/\bar{\alpha}_1)(\bar{\beta}_1/\bar{\beta}_2) = \left( \frac{dp}{dT} \right)_c \left/ \left( \frac{\partial p}{\partial T} \right)_{\Delta, \text{coex}} \right. \quad (\text{D9})$$

We then set  $ds = dX = 0$  to obtain

$$\left( \frac{\partial h}{\partial \xi} \right)_{sX} = (\omega_{h\tau} a_2 - \omega_{\tau\tau} a_1) / (\omega_{hh} \omega_{\tau\tau} - \omega_{h\tau}^2), \quad (\text{D10})$$

$$\left( \frac{\partial \tau}{\partial \xi} \right)_{sX} = (\omega_{h\tau} a_1 - \omega_{hh} a_2) / (\omega_{hh} \omega_{\tau\tau} - \omega_{h\tau}^2), \quad (\text{D11})$$

where

$$a_1 = \left[ \bar{\beta}_2 \left( \frac{ds}{d\xi} \right)_c - \bar{\beta}_1 \left( \frac{dX}{d\xi} \right)_c \right] / (\bar{\alpha}_1 \bar{\beta}_2 - \bar{\alpha}_2 \bar{\beta}_1), \quad (\text{D12})$$

$$a_2 = \left[ \bar{\alpha}_1 \left( \frac{dX}{d\xi} \right)_c - \bar{\alpha}_2 \left( \frac{ds}{d\xi} \right)_c \right] / (\bar{\alpha}_1 \bar{\beta}_2 - \bar{\alpha}_2 \bar{\beta}_1). \quad (\text{D13})$$

Here,  $a_1$  and  $a_2$  are nearly constants and  $\omega_{hh}$ ,  $\omega_{h\tau}$ , and  $\omega_{\tau\tau}$  behave as (A3). Therefore, on the coexistence surface, we find that  $(\partial h / \partial \xi)_{sX} \propto \epsilon^{1-\beta\theta}$  and  $(\partial \tau / \partial \xi)_{sX} \propto \epsilon^\alpha$ , and hence the derivative with fixed  $s$  and  $X$  is nearly parallel to the  $\xi$  axis.

For an arbitrary field variable  $\psi$  we obtain

$$\begin{aligned} \left( \frac{d\psi}{d\xi} \right)_{sX} &= \psi_\xi + \psi_h \left( \frac{\partial h}{\partial \xi} \right)_{sX} + \psi_\tau \left( \frac{\partial \tau}{\partial \xi} \right)_{sX} \\ &\cong \left( \frac{d\psi}{d\xi} \right)_c - \frac{(a_2 \psi_h + a_1 \psi_\tau) \omega_{h\tau}}{\omega_{hh} \omega_{\tau\tau} - \omega_{h\tau}^2} \\ &\quad + a_2 \psi_\tau / (\omega_{\tau\tau} - \omega_{h\tau}^2 / \omega_{hh}), \end{aligned} \quad (\text{D14})$$

where  $\psi$  is regarded as a function of  $h$ ,  $\tau$ , and  $\xi$  and  $\psi_h$ ,  $\psi_\tau$ , and  $\psi_\xi$  are its derivatives. Thus,  $(\partial \psi / \partial \xi)_{sX} \rightarrow (d\psi / d\xi)_c$  as  $\epsilon \rightarrow 0$  and the last two terms in (D14) give corrections going to zero as  $\epsilon \rightarrow 0$ . For  $(\partial \psi_1 / \partial \psi_2)_{sX}$  with

two arbitrary field variables  $\psi_1$  and  $\psi_2$  we may use

$$\left( \frac{\partial \psi_1}{\partial \psi_2} \right)_{sX} = \left( \frac{\partial \psi_1}{\partial \xi} \right)_{sX} \left/ \left( \frac{\partial \psi_2}{\partial \xi} \right)_{sX} \right. \quad (\text{D15})$$

However, to calculate the difference of  $(\partial \psi_1 / \partial \psi_2)_{sX}$  between the two phases, we must further examine a weak temperature dependence of the coefficient  $a_2$ . A careful analysis on the basis of Leung-Griffiths's theory shows that

$$a_2 = \lim_{\epsilon \rightarrow 0} a_2 + A_2(n - n_c) + \cdots, \quad (\text{D16})$$

where  $n - n_c \propto \epsilon^{\beta\theta}$  and  $A_2$  is a constant. Thus the difference of  $(\partial \psi_1 / \partial \psi_2)_{sX}$  is at most of order  $\epsilon^{\alpha+\beta}$ , leading to (4.33).

We proceed to calculate  $W$  and  $A_b$ , (4.29) and (4.42), in more detailed forms. Let the coexistence surface be represented by  $p = p_{\text{coex}}(T, \Delta)$ . Then, if we define  $\hat{h} = p - p_{\text{coex}}$  we obtain

$$W = \left( \frac{\partial \hat{h}}{\partial p} \right)_{sX}. \quad (\text{D17})$$

Obviously  $\hat{h}$  is a function of  $h$  only near criticality and  $\hat{h}/h \cong nT$  for Leung and Griffiths's choice of  $h$ . Therefore,

$$\begin{aligned} W &\cong nT \left( \frac{\partial h}{\partial p} \right)_{sX} \\ &\cong nT \left( \frac{d\xi}{dp} \right)_c a_2 \omega_{h\tau} / (\omega_{hh} \omega_{\tau\tau} - \omega_{h\tau}^2), \end{aligned} \quad (\text{D18})$$

where use has been made of (D10). This relation leads to (4.30). We then calculate  $A_b$ . Griffiths and Wheeler showed that  $K_{sX} = n^{-1}(\partial n / \partial p)_{sX}$  tends to the following value on the critical line:

$$\begin{aligned} K_{sX} &\cong n_c \left[ \left( \frac{ds}{dp} \right)_c \left( \frac{dT}{dp} \right)_c - \left( \frac{dv}{dp} \right)_c \right. \\ &\quad \left. + \left( \frac{d\Delta}{dp} \right)_c \left( \frac{dX}{dp} \right)_c \right]. \end{aligned} \quad (\text{D19})$$

On the other hand, the isothermal compressibility  $K_{TX} = n^{-1}(\partial n / \partial p)_{TX}$  behaves as

$$K_{TX} \cong (n^2 k_B T)^{-1} (\bar{\beta}_2 / \bar{\alpha}_2)^2 (\omega_{\tau\tau} - \omega_{h\tau}^2 / \omega_{hh}), \quad (\text{D20})$$

which follows from (4.27) of Ref. 43. Then we find

$$\omega_{hh} \left( \frac{\partial h}{\partial p} \right)_{sX}^2 \cong a_c^2 b_c^2 K_{sX}^2 / TK_{TX}, \quad (\text{D21})$$

where use has been made of (D9) and  $b_c$  is defined by (4.44). Noting that  $\omega_{hh} = nk_B T (\partial n / \partial p)_{T\Delta}$  in the theory of Leung and Griffiths and using (A16), we arrive at (4.43).

- <sup>1</sup>C. Zener, *Phys. Rev.* **53**, 90 (1938); R. H. Randall, F. C. Rose and C. Zener, *ibid.* **56**, 343 (1939); C. Zener, *Proc. R. Soc. London* **52**, 152 (1940).
- <sup>2</sup>L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1986). In Chap. 5 Zener's work is explained.
- <sup>3</sup>M. A. Isakovich, *Zh. Ek. Teor. Fiz.* **18**, 907 (1948). He examined the acoustic modes for one-dimensional layer systems and dilute spherical emulsions.
- <sup>4</sup>P. S. Epstein and R. R. Carhart, *J. Acoust. Soc. Am.* **25**, 553 (1953).
- <sup>5</sup>J. R. Allegra and S. A. Hawley, *J. Acoust. Soc. Am.* **51**, 1545 (1972).
- <sup>6</sup>S. Komura, T. Miyazawa, T. Izuyama, and Y. Fukumoto, *J. Phys. Soc. Jpn.* **59**, 101 (1990). Here an excellent review of Isakovich's work is reported.
- <sup>7</sup>As experimental papers see, for example, P. A. Allinson and E. G. Richardson, *Proc. Phys. Soc. (London) Ser. A* **72**, 833 (1958); A. Schroder, *J. Phys. Paris. Colloq.* **51**, C2-9 (1990).
- <sup>8</sup>L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1987), Chap. 8.
- <sup>9</sup>R. Wanner, H. Meyer and R. L. Mills, *J. Low Temp. Phys.* **13**, 337 (1973); R. Banke, X. Li, and H. Meyer, *Phys. Rev. B* **37**, 7337 (1988).
- <sup>10</sup>D. B. Fenner, *J. Chem. Phys.* **88**, 2021 (1988).
- <sup>11</sup>J. Bodensohn and P. Leiderer, *Phys. Rev. Lett.* **65**, 1368 (1990); A. Onuki, *J. Phys. Soc. Jpn.* **60**, 1176 (1991). The latter reference presents a theory to explain data in the former. The mechanism proposed is similar to the one in this paper.
- <sup>12</sup>J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley, Chichester, England, 1978); J. V. Sengers and J. M. H. Levelt Sengers, *Annu. Rev. Phys. Chem.* **37**, 189 (1986).
- <sup>13</sup>K. Kawasaki and J. D. Gunton, in *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley, Chichester, England, 1978).
- <sup>14</sup>W. I. Goldberg, in *Light Scattering Near the Phase Transition*, edited by H. Z. Cummins and A. P. Levanyuk (North-Holland, Amsterdam, 1983).
- <sup>15</sup>A. Onuki, *Int. J. Thermophys.* **10**, 293 (1989); *Prog. Theor. Phys. Suppl.* **99**, 382 (1990).
- <sup>16</sup>D. Y. Hsieh and M. S. Plessert, *Phys. Fluids* **4**, 970 (1961); A. Crespo, *ibid.* **12**, 2274 (1969). In the former paper they rederived the expression for the sound velocity of Ref. 20. Despite their claim the heat-conduction mechanism is not properly taken into account.
- <sup>17</sup>R. I. Nigmatulin, N. S. Khabeev, and Zuong Ngok Hai, *J. Fluid. Mech.* **186**, 85 (1988).
- <sup>18</sup>C. Coste, C. Laroche, and S. Fauve, *Europhys. Lett.* **11**, 343 (1990).
- <sup>19</sup>L. van Wijngaarden, in *Theoretical and Applied Mechanics*, edited by P. Germain, M. Piau, and D. Callerie (North-Holland, Amsterdam, 1989).
- <sup>20</sup>A. B. Wood, *A Textbook of Sound* (Bell, London, 1941); R. J. Urlick, *J. Appl. Phys.* **18**, 983 (1947); P. L. Chambré, *J. Acoust. Soc. Am.* **263**, 29 (1954).
- <sup>21</sup>J. W. Strutt Lord Rayleigh, *Theory of Sound* (Dover, New York, 1945).
- <sup>22</sup>I. M. Lifshitz and G. D. Parkhomovskii, *Zh. Eksp. Teor. Fiz.* **20**, 175 (1950); L. G. Merkulov, *Zh. Tekh. Fiz.* **1**, 64 (1956) [*Sov. Phys.—Tech. Phys.* **1**, 59 (1956)]; A. B. Bhatia and R. A. Moore, *J. Acoust. Soc. Am.* **31**, 1140 (1959).
- <sup>23</sup>K. Kawasaki, in *Phase Transition and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5A.
- <sup>24</sup>D. M. Kroll and J. M. Ruhland, *Phys. Lett.* **80A**, 45 (1989).
- <sup>25</sup>R. A. Ferrell and J. K. Bhattacharjee, *Phys. Rev. A* **31**, 1788 (1981).
- <sup>26</sup>E. D. Siggia, B. I. Halperin, and P. C. Hohenberg, *Phys. Rev. B* **13**, 2110 (1976).
- <sup>27</sup>P. C. Hohenberg, in *Microscopic Structure and Dynamics of Liquids*, edited by J. Dupuy and A. J. Dianoux (Plenum, New York, 1978).
- <sup>28</sup>M. R. Moldover, in *Phase Transitions*, Vol. 72 of *NATO Advanced Study Institute Series B: Physics*, edited by M. Levy, J.-C. Le Guillou, and J. Zinn-Justin (Plenum, New York, 1980).
- <sup>29</sup>A. Aharony and P. C. Hohenberg, *Phys. Rev. B* **13**, 3081 (1976); A. J. Liu and M. E. Fisher, *Physica A* **156**, 35 (1989).
- <sup>30</sup>A. Onuki and R. A. Ferrell, *Physica A* **164**, 245 (1990).
- <sup>31</sup>G. R. Brown and H. Meyer, *Phys. Rev. A* **6**, 364 (1972).
- <sup>32</sup>D. Dahl and M. R. Moldover, *Phys. Rev. A* **6**, 1915 (1972).
- <sup>33</sup>L. A. Turski and J. S. Langer, *Phys. Rev. A* **22**, 2189 (1980).
- <sup>34</sup>The amplitude of the pressure deviation is supposed to decay as  $\exp(-\alpha_D x)$  as the sound propagates with a given frequency.
- <sup>35</sup>J. A. Marqusee and J. Ross, *J. Chem. Phys.* **80**, 536 (1984); M. Tokuyama and K. Kawasaki, *Physica A* **123**, 386 (1984).
- <sup>36</sup>Strong dispersion and attenuation occur in the vicinity of the bubble resonance frequency  $\omega_{\text{res}}$ . See for example, R. P. Kokernak and C. L. Feldman, *ASHARAE J.* **14**, 35 (1972). For  $\omega \ll \omega_{\text{res}}$  the attenuation per wavelength due to scattering is proportional to  $\phi\omega^3 \propto \phi(kR)^3$  (see Chap. 8 of Ref. 8).
- <sup>37</sup>H. K. Forster and N. Zuber, *J. Appl. Phys.* **25**, 474 (1954); M. S. Plessert and S. A. Zwick, *ibid.* **25**, 493 (1954); L. E. Scriven, *Chem. Eng. Sci.* **10**, 1 (1959).
- <sup>38</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1964), Chap. 8.
- <sup>39</sup>A. Bailey and D. Cannell (private communication). Let us define  $Z' \equiv (C_v)_{\text{coex}}/C_v - 1$ . It is expressed as
- $$Z' = (\gamma_s - 1)[(\partial T/\partial p)_{\text{coex}}(\partial p/\partial T)_v - 1]^2$$
- at any temperatures. Since
- $$(\partial p/\partial T)_v = (1 - 1/\gamma_s)(\partial p/\partial T)_s$$
- we obtain  $Z' \cong Z \cong a_c^2$  near criticality. The  $(C_v)_{\text{coex}}$  was also discussed in the context of deriving a relation among critical exponents: M. E. Fisher, *J. Math. Phys.* **5**, 944 (1964).
- <sup>40</sup>L. D. Landau and E. M. Lifshitz, Ref. 8, p. 254, problem 1. Note that their formulas are written in terms of the mass fraction  $x = \phi_g n_g / (\phi_g n_g + \phi_l n_l)$  instead of the volume fractions. Using the first line of (2.4), (2.22), etc. we can show the equivalence of their formula for  $dv/dp$  and our expression (3.24).
- <sup>41</sup>In the case of solid-fluid systems like granular composites multiple-scattering theories give somewhat different expressions for the sound velocity. See for example, P. N. Sen and D. L. Johnson, *Phys. Rev. B* **27**, 3133 (1983); L. Schwartz and J. J. Plona, *J. Appl. Phys.* **55**, 3971 (1984).
- <sup>42</sup>L. Mistura, *Nuovo Cimento B* **12**, 35 (1972).
- <sup>43</sup>A. Onuki, *J. Low Temp. Phys.* **61**, 101 (1985).
- <sup>44</sup>R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A* **2**, 1047 (1970).
- <sup>45</sup>S. S. Leung and R. B. Griffiths, *Phys. Rev. A* **8**, 953 (1973).
- <sup>46</sup>A. Onuki, *Phys. Rev. A* **35**, 5149 (1987).
- <sup>47</sup>A. H. Krall, J. V. Sengers, and K. Hamano, *Int. J. Thermophys.* **10**, 293 (1989).
- <sup>48</sup>M. Ley-Koo and M. S. Green, *Phys. Rev. A* **16**, 2483 (1977).
- <sup>49</sup>I. M. Lifshitz and V. V. Slyozov, *J. Phys. Chem. Solid* **19**, 35 (1961).