

Dynamic equations and bulk viscosity near the gas-liquid critical point

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We derive dynamic equations of the mass, energy, and momentum densities to describe dynamics of highly compressible fluids near the gas-liquid critical point. In particular, the complete expression for the stress tensor is presented, which is nonlinear with respect to the fluctuations of the mass and energy densities. The most dominant nonlinearity in the stress tensor can then be identified and a very simple and systematic theory can be constructed on the enhanced bulk viscosity near the critical point with no adjustable parameter. We introduce the frequency-dependent adiabatic compressibility and constant-volume specific heat. Our theory is essentially equivalent to Kawasaki's theory [Phys. Rev. A **1**, 1750 (1970)] at low frequencies and reproduces Ferrell and Bhattacharjee's phenomenology [Phys. Lett. A **36**, 109 (1981); **88**, 77 (1982); Phys. Rev. A **31**, 1788 (1985)] at high frequencies. We explicitly calculate strikingly slow decay of the time correlation function of the diagonal part of the stress tensor. As proposed experiments we examine how the density changes adiabatically in two situations with a fixed volume or pressure. As a by-product we also derive some relations among the critical amplitudes of the constant-volume specific heat above and below T_c . It is shown to correspond to the specific heat at constant magnetization in Ising spin systems. [S1063-651X(97)04201-3]

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I. INTRODUCTION

Hydrodynamics and thermodynamics are inseparably coupled near the critical point of fluids. This dynamical coupling gives rise to the well-known critical divergence of the transport coefficients such as the thermal conductivity and the shear viscosity [1–4]. Moreover, it produces a variety of complex effects observable on macroscopic spatial scales. Such effects are particularly unique near the gas-liquid critical point, where fluids are highly compressible even against very small pressure and temperature variations. As a classic example severe density stratification under gravity has long been studied near the gas-liquid critical point mainly from statics [5], whereas it was recognized in an early period that thermal relaxation under gravity can be highly nonlinear with respect to both gravity and heat current [6]. In addition a crucial role of adiabatic heating effects has recently been established both theoretically [7] and experimentally [8]. That is, if a sample with a fixed volume is warmed from the boundary, sounds created by a thermal expansion near the boundary cause instantaneous, adiabatic temperature changes throughout the container. This effect, sometimes called the Piston effect, results in critical speeding up of thermal equilibration. This mechanism has turned out to explain an early experiment in space by Nitsche and Straub [9].

At the present stage the research in this direction has not yet attracted enough attention and still remains premature. Above all, there is no systematic analysis on the interplay between adiabatic processes and thermal relaxation on various space and time scales on the basis of a reliable dynamical model of compressible near-critical fluids. To this end, we need to know the complete expression for the relevant part of the stress tensor induced by the critical fluctuations. Because in near-critical fluids the sound mode has a fast time scale and does not affect the diffusive mode of the entropy relaxation, the mode coupling theory [1–3] and the dynamic renormalization group theory [4] start with dynamic models

in which only the entropy density and the transverse part of the velocity field are involved. Although this treatment is allowable in calculating the diffusive relaxation, there can be a number of problems in which the high compressibility of fluids is crucial. We mention adiabatic effects in the fixed volume condition against time-dependent external perturbations such as an oscillating boundary temperature. There are also only a few theories as to how the temperature and the pressure vary in time in the course of spinodal decomposition [10] or nucleation [11] in the adiabatic condition or in the fixed volume condition. The latter aspect is very important near the gas-liquid critical point. Molecular dynamic simulations face this problem seriously also.

It is established that, while the sound mode does not affect the diffusive mode, its attenuation is drastically enhanced by slow relaxation of a pressure deviation bilinear with respect to the entropy fluctuations. However, theories of critical sound attenuation have not yet been fully satisfactory just because of the lack of the exact expression for the stress tensor in the Ginzburg-Landau scheme. A brief summary of previous theories is as follows. Developing an idea of Botch and Fixman [12], Kawasaki predicted strong critical divergence of the sound attenuation or the bulk viscosity in his mode coupling theory [13]. However, it involves complicated combinations of thermodynamic quantities and is in disagreement with experiments at high frequencies. Mistura presented a formal theory of complex frequency-dependent adiabatic compressibility and specific heat [12,14]. Ferrell and Bhattacharjee developed a scaling theory on the frequency dependence of the complex specific heat [15]. They predicted that, at high frequencies $\omega \gg \Gamma_\xi$, the frequency-dependent specific heat behaves as $(i\omega)^{-\alpha/\nu z}$ and this excellently explains the observed high-frequency anomaly. Here $\Gamma_\xi \propto \xi^{-z}$ with $z \cong 3$ is the order parameter relaxation rate, and $\alpha/\nu z \cong 0.057$ is a universal number, α and ν being the critical exponents. This argument was originally devised for ^4He near the superfluid transition [16]. Kroll and Ruhland

applied the renormalization group method at small $\epsilon = 4 - d$ to calculate the generalized frequency-dependent bulk viscosity or adiabatic compressibility [17]. They obtained a scaling form for the adiabatic compressibility as a function of $i\omega/\Gamma_\xi$. It exhibits the singular frequency dependence $(i\omega)^{-\alpha/\nu z}$ in the high frequency regime in agreement with the Ferrell-Bhattacharjee prediction. In the Kroll and Ruhland theory coupled Langevin equations containing some phenomenological coefficients were assumed for the entropy $s(\mathbf{r}, t)$ and the pressure $p(\mathbf{r}, t)$ at the starting point of the renormalization group procedure. Afterwards Dengler and Schwable [18] presented a theory by generalizing the model of Kroll and Ruhland and calculated a universal amplitude ratio for the sound attenuation above and below T_c . Very recently Folk and Moser [19] have briefly reported a calculation of the sound attenuation to be in good agreement with experiments. In summary, however, we note that the relationships among these theories have not yet been adequately clarified. In particular, we need to link Kawasaki's theory and Ferrell and Bhattacharjee's theory from first principles.

The main aim of this paper is to present a theory in which the mass density and the energy density are dynamic variables. They are more fundamental than the entropy and the pressure used in the previous theories and their dynamic equations can be obtained unambiguously from the conservation laws. The organization of this paper is as follows. In Sec. II we will discuss the mapping relationship between pure fluids and Ising spin systems because the Ginzburg-Landau-Wilson Hamiltonian for Ising spin systems will be used in our dynamic equations. In other words, to correctly calculate the bulk viscosity, we need to know what variables in fluid systems correspond to the spin (or order parameter) variable ψ and the energy variable m in Ising spin systems. The latter two variables have strong and weak critical singularities characterized by the critical exponents γ and α , respectively. In fluid binary mixtures the identification of the correct order parameter is indispensable even apart from the sound mode to calculate three kinetic coefficients for the two diffusive modes of heat and composition. Thus this approach has already been taken in theories for diffusive transport in binary fluid mixtures [20–22]. In Sec. III we will derive proper Langevin equations describing dynamics near the gas-liquid critical point and obtain an expression for the stress tensor in terms of ψ and m . In Sec. IV we will calculate the frequency-dependent bulk viscosity using the ϵ expansion method in dynamic renormalization group theory and introduce a frequency-dependent specific heat. In Sec. V we will examine macroscopic adiabatic processes as applications of our theory.

II. THERMODYNAMICS NEAR THE GAS-LIQUID CRITICAL POINT

A. Mapping onto Ising spin systems

We describe the critical behavior of pure fluids near the gas-liquid critical point in terms of the mass density $\hat{\rho}(\mathbf{r}, t)$ and the energy density $\hat{e}(\mathbf{r}, t)$. These two variables have well-defined microscopic expressions in terms of the particle coordinates and momenta. Therefore we choose them as the fundamental variables in our theory. In this section the variables with the caret, such as $\hat{\rho}$ and \hat{e} , denote dynamic vari-

ables with molecular expressions, while those without the caret are thermodynamic quantities in equilibrium or simply constants. The equilibrium averages of \hat{e} and $\hat{\rho}$ are written as

$$u = \langle \hat{e}(\mathbf{r}, t) \rangle, \quad \rho = \langle \hat{\rho}(\mathbf{r}, t) \rangle, \quad (2.1)$$

where $\langle \rangle$ is the average over the grand canonical distribution. We note that the energy supported by each particle may be arbitrarily shifted by a constant value, say ϵ_0 . This means that the physical properties of the system are invariant with respect to the following redefinition of the energy variable,

$$\hat{e}' = \hat{e} + \epsilon_0 \hat{\rho}, \quad (2.2)$$

ϵ_0 being arbitrary.

In our case it is convenient to choose $\omega = p/k_B T$ as the thermodynamic potential dependent on the following two field variables [22–27],

$$B = \frac{1}{k_B} \left(\frac{1}{T_c} - \frac{1}{T} \right), \quad (2.3)$$

$$\nu = \frac{1}{k_B} \left(\frac{\mu}{T} - \frac{\mu_c}{T_c} \right), \quad (2.4)$$

where μ is the chemical potential per unit mass, T_c is the critical temperature, μ_c is the critical value of μ , and k_B is the Boltzmann constant. Our definitions of B and ν are slightly different from those of Leung and Griffiths [27] because we have made them vanish at the critical point. The entropy per unit mass is expressed as

$$s = (\rho\mu - u - p)/\rho T, \quad (2.5)$$

so the Gibbs-Duhem relation $d\mu = -sdT + \rho^{-1}dp$ may be rewritten as

$$d\omega = u dB + \rho d\nu. \quad (2.6)$$

The choice of ω as the thermodynamic potential is most natural theoretically due to the above relation or equivalently due to the fact that the logarithm of the grand canonical partition function is the space integral of ω . We may thus postulate that ω corresponds to $-f/k_B T$ of Ising systems where f is the free energy density in Ising systems. This correspondence is obviously exact for lattice gas models. See Appendix A for more discussions. There, we shall find the following exact relations among the thermodynamic derivatives and the fluctuation variances [20,21,28,29]:

$$\langle \hat{\rho} : \hat{\rho} \rangle = \frac{\partial^2 \omega}{\partial \nu^2} = \frac{\partial \rho}{\partial \nu} = k_B T \rho^2 K_T, \quad (2.7)$$

$$\langle \hat{e} : \hat{e} \rangle = \frac{\partial^2 \omega}{\partial B^2} = \frac{\partial u}{\partial B}, \quad (2.8)$$

$$\langle \hat{\rho} : \hat{e} \rangle = \frac{\partial^2 \omega}{\partial \nu \partial B} = \frac{\partial \rho}{\partial B} = \frac{\partial u}{\partial \nu}, \quad (2.9)$$

where ω , ρ , and u are regarded as functions of B and ν and $K_T = \rho^{-1}(\partial \rho / \partial p)_T$ is the isothermal compressibility. We introduce the notation

$$\langle \hat{A} : \hat{B} \rangle = \int d\mathbf{r} \langle \delta \hat{A}(\mathbf{r}, t) \delta \hat{B}(\mathbf{r}_0, t) \rangle, \quad (2.10)$$

where $\hat{A}(\mathbf{r}, t)$ and $\hat{B}(\mathbf{r}, t)$ are arbitrary local density variables, $\delta \hat{A} = \hat{A} - \langle \hat{A} \rangle$ and $\delta \hat{B} = \hat{B} - \langle \hat{B} \rangle$ being the deviations from the equilibrium averages.

It has been assumed in the literature that $\omega = p/k_B T$ consists of a singular part and a regular part dependent on two relevant field variables, h and τ , as

$$\omega = \omega_{\text{sing}}(h, \tau) + \omega_{\text{reg}}(h, \tau). \quad (2.11)$$

To leading order in the critical singularity, $\omega_{\text{sing}}(h, \tau)/|\tau|^{2-\alpha}$ is a universal function of $\tau/|h|^{1/(\beta+\gamma)}$, where α , β , and γ are the usual critical exponents. The two relevant parameters h and τ correspond to the magnetic field and the reduced temperature $(T - T_c)/T_c$ in Ising spin systems. In pure fluids h and τ are related to B and ν in Eqs. (2.3) and (2.4) by the following linear relations:

$$h = \alpha_1 \nu + \alpha_2 B, \quad (2.12)$$

$$\tau = \beta_1 \nu + \beta_2 B. \quad (2.13)$$

The coefficients α_1 , α_2 , β_1 , and β_2 will be assumed to be simply constants and not singular on approaching to the critical point. In particular, because $h=0$ on the coexistence curve, the ratio α_2/α_1 is written as

$$\frac{\alpha_2}{\alpha_1} = - \left(\frac{\partial \nu}{\partial B} \right)_h \cong - \left(\frac{\partial \nu}{\partial B} \right)_{\text{cx}} = -T_c \left(\frac{\partial \mu}{\partial T} \right)_{\text{cx}} + \mu_c. \quad (2.14)$$

Hereafter $(\partial \dots / \partial \dots)_{\text{cx}}$ is the derivative on the coexistence curve in the limit $T \rightarrow T_c$. With this postulate we can map the critical behavior of pure fluids onto that of Ising spin systems. It follows that pure fluids belong to the Ising universality class in static critical behavior.

In Ising spin systems the order parameter denoted by $\hat{\psi}(\mathbf{r}, t)$ is the spin variable, whose conjugate field is h . The free energy is an even function of h due to the inherent symmetry of the system. The equilibrium average and variance of $\hat{\psi}$ are thus given by

$$M = \langle \hat{\psi} \rangle = \partial \omega / \partial h, \quad (2.15)$$

$$\chi = \langle \hat{\psi} : \hat{\psi} \rangle = \partial^2 \omega / \partial h^2 = \partial M / \partial h. \quad (2.16)$$

In Ising spin systems the energy density variable denoted by $\hat{m}(\mathbf{r}, t)$ exhibits weak critical fluctuations characterized by the critical exponent $\alpha (\cong 0.1)$. Its conjugate field is τ , so that

$$\langle \hat{m} \rangle = \partial \omega / \partial \tau, \quad (2.17)$$

$$C_H = \langle \hat{m} : \hat{m} \rangle = \partial^2 \omega / \partial \tau^2. \quad (2.18)$$

We measure \hat{m} from the critical value and $\langle \hat{m} \rangle = 0$ at the critical point. The C_H is proportional to the specific heat at constant h . In particular, $\chi \propto |\tau|^{-\gamma}$ with $\gamma \cong 1.25$ and $C_H \propto |\tau|^{-\alpha}$ as $h \rightarrow 0$. As regards the cross correlation we have

$$\langle \hat{\psi} : \hat{m} \rangle = \partial^2 \omega / \partial h \partial \tau = \partial M / \partial \tau, \quad (2.19)$$

which vanishes as $h \rightarrow 0$ in the disordered phase. But it is equal to $\pm \beta B'_0 |\tau|^{\beta-1}$ from $\langle \hat{\psi} \rangle = \pm B'_0 |\tau|^\beta$ on the coexistence curve. Here we also introduce the specific heat at constant magnetization $M = \langle \hat{\psi} \rangle$,

$$C_M = \partial^2 \omega / \partial \tau^2 - [\partial^2 \omega / \partial h \partial \tau]^2 / [\partial^2 \omega / \partial h^2] \\ = \langle \hat{m} : \hat{m} \rangle - \langle \hat{\psi} : \hat{m} \rangle^2 / \langle \hat{\psi} : \hat{\psi} \rangle. \quad (2.20)$$

We will show that the constant-volume specific heat C_v for a single phase of fluids asymptotically corresponds to C_M (not to C_H) in Ising spin systems.

In fluid systems it is not obvious how to define the corresponding density variables, $\hat{\psi}$ and \hat{m} , in contrast to Ising spin systems or equivalent lattice gas models. Here we stress that the postulate of Eqs. (2.12) and (2.13) simply implies the following linear mapping relations [16],

$$\hat{\rho} - \rho_c = \alpha_1 \hat{\psi} + \beta_1 \hat{m}, \quad (2.21)$$

$$\hat{e} - e_c = \alpha_2 \hat{\psi} + \beta_2 \hat{m}, \quad (2.22)$$

where ρ_c and e_c are the critical values and the coefficients α_1 , β_1 , α_2 , and β_2 are introduced in Eqs. (2.12) and (2.13). The inverse relations of Eqs. (2.21) and (2.22) read

$$\hat{\psi} = (\alpha_1 \beta_2 - \alpha_2 \beta_1)^{-1} [\beta_2 (\hat{\rho} - \rho_c) - \beta_1 (\hat{e} - e_c)], \quad (2.23)$$

$$\hat{m} = (\alpha_1 \beta_2 - \alpha_2 \beta_1)^{-1} [-\alpha_2 (\hat{\rho} - \rho_c) + \alpha_1 (\hat{e} - e_c)]. \quad (2.24)$$

We derive these relations by requiring

$$h \hat{\psi} + \tau \hat{m} = \nu (\hat{\rho} - \rho_c) + B (\hat{e} - e_c). \quad (2.25)$$

We may confirm that Eqs. (2.21) and (2.22) are consistent with the thermodynamic relations involving the fluctuation variances, Eqs. (2.7)–(2.9), (2.16), (2.18), and (2.19), under the mapping relations of the field variables, Eqs. (2.12) and (2.13). It then follows that the shifted energy variable

$$(\hat{e} - e_c) - (\alpha_2 / \alpha_1) (\hat{\rho} - \rho_c) = (\beta_2 - \alpha_2 \beta_1 / \alpha_1) \hat{m} \quad (2.26)$$

is proportional to \hat{m} and is weakly singular as in Ising spin systems. Recall that the energy may be shifted as Eq. (2.2). Thus the coefficient α_2 is arbitrary and may be set equal to zero from the beginning [22,27]. Furthermore, the relation (2.21) indicates that the average density on the coexistence curve behaves as

$$\rho - \rho_c = \pm \alpha_1 B'_0 |\tau|^\beta + \beta_1 B'_1 |\tau|^{1-\alpha}, \quad (2.27)$$

where the plus sign is for the liquid density ρ_l and the minus sign for the gas density ρ_g , and we have set $h=0$, so

$$\tau = b(T/T_c - 1) \quad (2.28)$$

with

$$b = (\beta_2 - \beta_1 \alpha_2 / \alpha_1) / k_B T_c. \quad (2.29)$$

The coefficients B'_0 and B'_1 in Eq. (2.27) arise from $\partial\omega_{\text{sing}}/\partial h$ and $\partial\omega_{\text{sing}}/\partial\tau$, respectively. The cross coefficient β_1 gives rise to the second term in Eq. (2.27) causing singular asymptotic behavior of the coexistence-curve diameter

$$(\rho_{\neq} + \rho_g)/2 - \rho_c \cong \beta_1 B'_1 b^{1-\alpha} (1 - T/T_c)^{1-\alpha}. \quad (2.30)$$

While α_2 may be set equal to zero as stated above, nonvanishing of β_1 can be detected from Eq. (2.30). β_1 is often referred to as the mixing parameter [22–26].

B. Entropy variable and specific heats

In the literature an entropy variable, which will be denoted by $\hat{s}(\mathbf{r}, t)$, has often been used instead of the energy variable $\hat{e}(\mathbf{r}, t)$ [1–4, 17–22]. In dynamics this choice is convenient because \hat{s} is decoupled from the sound mode at long wavelengths. In terms of $\hat{\rho}$ and \hat{e} it may be expressed as [20]

$$\hat{s} = \frac{1}{\rho T} [\hat{e} - H\hat{\rho}] + \frac{p}{\rho T} + s, \quad (2.31)$$

where $H = (u + p)/\rho = \mu + Ts$ is the enthalpy per unit mass. The coefficients in front of \hat{e} and $\hat{\rho}$ and the last two terms are thermodynamic quantities. They depend on ν and B (or h and τ) and are not regular with respect to them near the critical point [30]. However, the variable \hat{s} has the following merits even in statics. (i) \hat{s} is invariant with respect to the shift of the energy Eq. (2.2) because H is also shifted as $H + \epsilon_0$. (ii) The variances of \hat{s} are related to the specific heat C_p at constant pressure and the specific heat C_v at constant volume as [20]

$$C_p = T \left(\frac{\partial s}{\partial T} \right)_p = k_B^{-1} \rho \langle \hat{s} : \hat{s} \rangle, \quad (2.32)$$

$$C_v = T \left(\frac{\partial s}{\partial T} \right)_v = k_B^{-1} \rho [\langle \hat{s} : \hat{s} \rangle - \langle \hat{s} : \hat{\rho} \rangle^2 / \langle \hat{\rho} : \hat{\rho} \rangle]. \quad (2.33)$$

From the definition Eq. (2.31) C_v may also be rewritten in terms of $\hat{\rho}$ and \hat{e} in a form due to Schofield [28],

$$C_v = (\rho k_B T^2)^{-1} [\langle \hat{e} : \hat{e} \rangle - \langle \hat{e} : \hat{\rho} \rangle^2 / \langle \hat{\rho} : \hat{\rho} \rangle], \quad (2.34)$$

which is obviously invariant with respect to the transformation (2.2). See the first line of Eq. (2.38) below also. The first relation (2.32) follows from the thermodynamic relation $\rho ds = (du - Hd\rho)/T$ and Eq. (A8). In the second relation (2.33) we have used

$$\langle \hat{s} : \hat{\rho} \rangle = \rho^{-1} k_B T \left(\frac{\partial \rho}{\partial T} \right)_p = \rho k_B T \left(\frac{\partial s}{\partial p} \right)_T. \quad (2.35)$$

If we are interested only in the most singular part, we may set $\delta\hat{s} \cong \alpha_s \hat{\psi}$ with

$$\alpha_s = \frac{1}{\rho T} (\alpha_2 - H\alpha_1) = -\frac{1}{\rho^2} \left(\frac{\partial p}{\partial T} \right)_h \alpha_1 \cong -\frac{1}{\rho_c^2} \left(\frac{\partial p}{\partial T} \right)_{\text{cx}} \alpha_1, \quad (2.36)$$

where use has been made of Eq. (2.14). Therefore we obtain strongly divergent variances,

$$\rho C_p \cong T \left(\frac{\partial p}{\partial T} \right)_{\text{cx}}^2 K_T \cong k_B^{-1} \rho_c^2 \alpha_s^2 \langle \hat{\psi} : \hat{\psi} \rangle, \quad (2.37)$$

where K_T is the isothermal compressibility appearing in Eq. (2.7). To examine the right hand side of (2.33) we note the following relation,

$$\begin{aligned} \langle \hat{s} : \hat{s} \rangle \langle \hat{\rho} : \hat{\rho} \rangle - \langle \hat{s} : \hat{\rho} \rangle^2 &= (\rho T)^{-2} [\langle \hat{e} : \hat{e} \rangle \langle \hat{\rho} : \hat{\rho} \rangle - \langle \hat{e} : \hat{\rho} \rangle^2] \\ &= [(\alpha_1 \beta_2 - \alpha_2 \beta_1) / \rho T]^2 [\langle \hat{\psi} : \hat{\psi} \rangle \langle \hat{m} : \hat{m} \rangle \\ &\quad - \langle \hat{\psi} : \hat{m} \rangle^2], \end{aligned} \quad (2.38)$$

which follows from Eqs. (2.31), (2.21), and (2.22). Then, to leading order in the critical singularity, we obtain

$$C_v \cong (\rho^{-1} k_B b^2) C_M = (\rho^{-1} k_B b^2) (1 - R_v) C_H, \quad (2.39)$$

where b is defined by Eq. (2.29). Thus $C_v \propto C_M$, where C_M is the specific heat at constant magnetization defined by Eq. (2.20) in the corresponding Ising spin system. R_v is defined by

$$\begin{aligned} R_v &= \langle \hat{\psi} : \hat{m} \rangle^2 / [\langle \hat{\psi} : \hat{\psi} \rangle \langle \hat{m} : \hat{m} \rangle] \\ &= [\partial^2 \omega / \partial h \partial \tau]^2 / [\partial^2 \omega / \partial^2 h] [\partial^2 \omega / \partial \tau^2] \end{aligned} \quad (2.40)$$

and is a universal function of $\tau/|h|^{1/(\beta+\gamma)}$. Obviously, it is non-negative-definite, smaller than 1, and vanishes on the critical isochore above T_c . On the coexistence curve we can easily check $R_v \rightarrow 3/4$ as $\epsilon \rightarrow 0$, but we estimate $R_v \cong 0.50$ using Eq. (2.43) below and relations among the critical amplitudes in Ising spin systems [31].

C. Universal numbers

If the mapping Eqs. (2.12) and (2.13) onto the Ising spin systems is correct, some combinations of the critical amplitudes become universal numbers independent of fluids [23,24]. For example, let us express C_v and K_T as $C_v/k_B \cong A(T/T_c - 1)^{-\alpha}/\alpha$ and $\rho k_B T K_T \cong \Gamma(T/T_c - 1)^{-\gamma}$ on the critical isochore above T_c and $C_v/k_B \cong A'(1 - T/T_c)^{-\alpha}/\alpha$ and $\rho k_B T K_T \cong \Gamma'(1 - T/T_c)^{-\gamma}$ on the coexistence curve. The coefficients A' and Γ' are common in the liquid and gas phases. The density on the coexistence curve is expressed as $(\rho - \rho_c)/\rho_c \cong \pm B'(1 - T/T_c)^\beta$. Then we readily find using Eq. (2.28) that $A\Gamma/\alpha B'^2$ and Γ'/Γ are independent of the parameter b in Eq. (2.29) and are equal to the corresponding universal numbers, $A_0\Gamma_0/\alpha B_0'^2 \cong 0.581$ and $\Gamma'_0/\Gamma_0 \cong 0.202$, in Ising spin systems [31], where we write $C_H \cong A_0 \tau^{-\alpha}/\alpha$ and $\chi \cong \Gamma_0 \tau^{-\gamma}$ for $h=0$ above T_c and $C_H \cong A'_0 |\tau|^{-\alpha}/\alpha$, $\chi \cong \Gamma'_0 |\tau|^{-\gamma}$, and $\langle \hat{\psi} \rangle \cong \pm B'_0 |\tau|^\beta$ for $h=0$ below T_c in Ising spin systems. However, from Eq. (2.39) the specific heat amplitudes satisfy

$$A'/A = (1 - R_v) A'_0/A_0, \quad (2.41)$$

where $A'_0/A_0 \cong 1.91$. Some calculation shows that R_v on the coexistence curve may be expressed from Eqs. (2.16), (2.18), and (2.19) as

$$R_v = \alpha \beta^2 B_0'^2 / A_0 \Gamma_0'. \quad (2.42)$$

See the sentences below Eq. (2.19) for the behavior of $\langle \hat{\psi} : \hat{m} \rangle$ on the coexistence curve. We also introduce another universal number a_c defined on the coexistence curve by [32]

$$a_c^2 = \alpha \beta^2 B'^2 / A' \Gamma' = R_v / (1 - R_v). \quad (2.43)$$

This number is close to 1 and characterizes acoustic properties of phase-separating fluids near the gas-liquid critical point. This is because the adiabatic temperature increase due to a pressure variation in a sound can be different in the gas phase (the plus sign) and the liquid phase (the minus sign) as [32]

$$\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial T}{\partial p} \right)_{\text{cx}} [1 \pm a_c (C_v / C_p)^{1/2} + \dots]. \quad (2.44)$$

The temperature inhomogeneities thus induced give rise to a very large acoustic attenuation at very low frequencies when the fluid is undergoing phase separation [32]. The above relation is also important in explaining slow thermal equilibration in two-phase coexistence [7,8,33].

In real experiments on the coexistence curve, however, the constant-volume specific heat has been measured mostly in two phase coexistence [33–36]. In this case the volume fraction of each phase adjusts to change such that the pressure and temperature stay on the coexistence curve. Near the critical point the resultant specific heat denoted by $(C_v)_{\text{cx}}$ behaves as

$$(C_v)_{\text{cx}} \cong (1 + a_c^2) C_v, \quad (2.45)$$

which will be derived in Appendix B. We thus have the critical behavior $(C_v)_{\text{cx}} / k_B \cong A_{\text{cx}} (1 - T/T_c)^{-\alpha} / \alpha$ with

$$A_{\text{cx}} = (1 + a_c^2) A' = (1 - R_v)^{-1} A'. \quad (2.46)$$

That is, the critical behavior of the so-called isochoric heat capacity, which is C_v above T_c and $(C_v)_{\text{cx}}$ below T_c , is the same as that of C_H at $h=0$ in Ising spin systems. We now obtain

$$A_{\text{cx}} / A = A'_0 / A_0 \cong 1.91, \quad A' / A \cong 0.95. \quad (2.47)$$

In our notation C_v is the constant-volume specific heat of a single phase, whereas in previous experimental reports C_v is used to denote $(C_v)_{\text{cx}}$ below T_c . We note that C_v in our notation can be measured in the presence of a liquid (or gas) region only, where phase separation has not yet occurred and the other phase should not wet the boundary wall. As far as the present author has noticed, Dahl and Moldover [37] first measured C_v in single phases of liquid states near the coexistence curve indeed in accord with $A' / A \sim 1$. Brown and Meyer [33] also reported similar data in single phases, which are listed in their unpublished tabulation of C_v . We also note that the relation $A' / A \sim 1$ follows even from the so-called linear model of parametric equation of state for fluids [38].

Furthermore, the two-scale factor universality [39] implies that $\xi^d \omega_{\text{sing}}$ and hence

$$\begin{aligned} R_\xi &= (T/T_c - 1)^{2/d} \xi (\alpha \rho C_v / k_B)^{1/d} \\ &= \tau^{2/d} \xi (\alpha C_H)^{1/d} \end{aligned} \quad (2.48)$$

are universal numbers on the critical isochore above T_c , where ξ is the correlation length. The first line of Eq. (2.48) consisting of the quantities of fluids becomes independent of the parameter b in Eq. (2.29) and equal to the second line consisting of those of Ising spin systems. It is known that $R_\xi \cong 0.25$ at $d=3$ theoretically and experimentally [40,23,24]. The above relation will be used in Appendix D.

III. MODEL EQUATIONS

A. Statics

From this section the caret on $\hat{\rho}$, \hat{e} , $\hat{\psi}$, and \hat{m} will not be written to avoid the heavy notation. We recall that the mass density deviation $\rho - \rho_c$ and the energy density deviation $e - e_c$ are related to ψ and m by the linear relations (2.21) and (2.22). We can set up the Ginzburg-Landau-Wilson free energy functional for ψ and m as [41]

$$\mathcal{H} = k_B T_c \int d\mathbf{r} [f(\psi, m) + \frac{1}{2} K_0 |\nabla \psi|^2], \quad (3.1)$$

where

$$f = \frac{1}{2} \bar{r}_0 \psi^2 + \frac{1}{4} \bar{u}_0 \psi^4 - h \psi + \frac{1}{2C_0} m^2 + \gamma_0 m \psi^2 - \tau m. \quad (3.2)$$

Here \bar{r}_0 , \bar{u}_0 , K_0 , γ_0 , and C_0 are the parameters dependent on the initial upper cutoff wave number Λ_0 . As in Sec. II h and τ are the two relevant field variables given in Eqs. (2.12) and (2.13), so they are independent of Λ_0 . Obviously in the equilibrium distribution, the variable

$$\mathcal{M} = \frac{\delta}{\delta m} \mathcal{H} = \frac{1}{C_0} m + \gamma_0 \psi^2 - \tau \quad (3.3)$$

obeys a Gaussian distribution independent of ψ . In fact we may rewrite f as

$$f = \frac{1}{2} r_0 \psi^2 + \frac{1}{4} u_0 \psi^4 - h \psi + \frac{1}{2} C_0 \mathcal{M}^2, \quad (3.4)$$

where

$$r_0 = \bar{r}_0 + 2C_0 \gamma_0 \tau, \quad (3.5)$$

$$u_0 = \bar{u}_0 - 2C_0 \gamma_0^2. \quad (3.6)$$

We notice that \bar{r}_0 is determined automatically if we impose the condition that τ vanishes at the critical point. This model was studied in the $\epsilon = 4 - d$ expansion method of renormalization group theory [41], where d is the spatial dimensionality. Without loss of generality we may set $K_0 = 1$ by the simple rescaling $K_0^{1/2} \psi \rightarrow \psi$.

In the usual renormalization group scheme, the fluctuations are coarse-grained in a stepwise manner and the rescalings of the space coordinates and the order parameter are performed simultaneously to obtain the fixed point Hamiltonian. In this paper, to obtain the physical quantities directly without rescaling factors, we perform the coarse graining only. This approach was taken by Kawasaki and Gunton for dynamics [42]. Then the upper cutoff wave number Λ is

decreased from the initial value Λ_0 . When Λ becomes of the order of the inverse correlation length ξ^{-1} , the fluctuation contributions can eventually be treated within the usual normal perturbation scheme. The parameters in the model (3.1) become functions of Λ and will be written as $\bar{r}(\Lambda)$, $r(\Lambda)$, $u(\Lambda)$, $K(\Lambda)$, $\gamma(\Lambda)$, and $C(\Lambda)$, whose initial values are \bar{r}_0 , r_0 , u_0 , K_0 , γ_0 , and C_0 , respectively. In the region $\xi^{-1} \ll \Lambda \ll \Lambda_0$ we have the following asymptotic power law:

$$r(\Lambda) - \bar{r}(\Lambda) = 2C(\Lambda)\gamma(\Lambda)\tau \sim \Lambda^{2-\eta-1/\nu}\tau. \quad (3.7)$$

The other coefficients behave as

$$\begin{aligned} u(\Lambda) &\sim \Lambda^{\epsilon-2\eta}, \quad K(\Lambda) \sim \Lambda^{-\eta}, \\ \gamma(\Lambda) &\sim \Lambda^{(\epsilon+\alpha/\nu)/2-\eta}, \quad C(\Lambda) \sim \Lambda^{-\alpha/\nu}, \end{aligned} \quad (3.8)$$

where α , ν , and η are the usual critical exponents. The relation (3.7) is consistent with the power laws for $C(\Lambda)$ and $\gamma(\Lambda)$ from the exponent relation $\nu d = 2 - \alpha$. The exponent η is of order ϵ^2 and is very small, so we may be set $\eta = 0$ and $K(\Lambda) = 1$ in rough estimates. In addition, η should not be confused with the shear viscosity. It goes without saying that, when Λ becomes smaller than ξ^{-1} , the fluctuation contributions are no longer significant and the parameters in Eqs. (3.7) and (3.8) stay on the order of the values at $\Lambda \sim \xi^{-1}$.

We have introduced $K(\Lambda)$ to check exact scaling relations valid to all orders in ϵ . For example, we obtain $r(\Lambda) \cong 1/\chi \cong K(\Lambda)\xi^{-2}$ for $\Lambda \lesssim \xi^{-1}$. We note that $\bar{r}(\Lambda)$ is small for small ϵ and $r(\Lambda) \cong 2C(\Lambda)\gamma(\Lambda)\tau$ from Eq. (3.7) for $\Lambda \lesssim \xi^{-1}$. Thus we may calculate $\gamma(\Lambda)$ for $\Lambda \ll \xi^{-1}$, which will be written as γ_R . Particularly on the critical isochore above T_c (or $h=0$ and $\tau > 0$), we set $\xi = \xi_0(T/T_c - 1)^{-\nu}$ and $\tau = b(T/T_c - 1)$ to obtain

$$\gamma_R \cong (T/T_c - 1)^{\gamma-1} / (2b\xi_0^2 C_H). \quad (3.9)$$

Here ξ_0 is a microscopic length, b is defined by Eq. (2.29), $\gamma \cong 1.24$ is the usual critical exponent, $C_H = C(0)$ is the specific heat at constant magnetic field defined by Eq. (2.18), and $K(\Lambda)$ has been replaced by $(\xi/\xi_0)^\eta$.

It is convenient to introduce the following dimensionless numbers [41],

$$g(\Lambda) = [K_d u(\Lambda)] / [K(\Lambda)^2 \Lambda^\epsilon], \quad (3.10)$$

$$v(\Lambda) = [K_d \gamma(\Lambda)^2 C(\Lambda)] / [K(\Lambda)^2 \Lambda^\epsilon], \quad (3.11)$$

where $K_d = (2\pi)^{-d} 2\pi^{d/2} / \Gamma(d/2)$. Sufficiently close to the critical point (or for small r_0) g and v are known to tend to fixed point values as Λ is decreased. In fact their renormalization group equations to leading order in ϵ are

$$-\Lambda \frac{\partial}{\partial \Lambda} g = \epsilon g - 9g^2, \quad (3.12)$$

$$-\Lambda \frac{\partial}{\partial \Lambda} v = \epsilon v - 6gv - 2v^2. \quad (3.13)$$

The stationary solutions of Eqs. (3.12) and (3.13) give fixed point values as $\Lambda \rightarrow 0$,

$$g^* = \frac{1}{9} \epsilon + \dots, \quad (3.14)$$

$$v^* = \frac{1}{6} \epsilon + \dots. \quad (3.15)$$

Therefore $u(\Lambda) \sim \gamma(\Lambda)^2 C(\Lambda) \sim \Lambda^\epsilon$ to first order in ϵ for $\xi^{-1} \leq \Lambda \ll \Lambda_0$.

The $C(\Lambda)$ tends to the specific heat C_H of Ising spin systems as $\Lambda \rightarrow 0$. Its differential recursion relation is

$$-\Lambda \frac{\partial}{\partial \Lambda} C(\Lambda) = 2v(\Lambda)C(\Lambda). \quad (3.16)$$

Setting $v(\Lambda) = v^*$ yields the asymptotic behavior,

$$C(\Lambda) \sim \Lambda^{-2v^*}. \quad (3.17)$$

As Λ is decreased down to the inverse correlation length ξ^{-1} , the well-known critical behavior $C(\xi^{-1}) \sim C_H \sim \xi^{\alpha/\nu}$ is obtained with [41]

$$v^* = \alpha/2\nu, \quad (3.18)$$

which holds to first order in ϵ . The fixed point value v^* will appear in the bulk viscosity as an important coefficient in the next section. From Eqs. (3.9) and (3.11) we also notice the relation $v^* \cong K_d / (4\tau^2 \xi^d C_H)$, which is consistent with the following ϵ expansion of R_ξ in Eq. (2.48) of the two scale factor universality [31,39–41],

$$R_\xi^d = K_d \left(\frac{\alpha}{4v^*} \right) \left(1 + \frac{1}{3} \epsilon \right) + O(\epsilon^2). \quad (3.19)$$

Furthermore, we should note that the approach of $v(\Lambda)$ to v^* is slow or the correction to the power law behavior Eq. (3.16) is not small as demonstrated by Siggia and Nelson [41]. That is, in the region $\xi^{-1} < \Lambda \ll \Lambda_0$, Eqs. (3.12) and (3.13) are solved to give

$$\begin{aligned} v^*/v(\Lambda) &\cong 1 + (g^*/g_0)^{1/3} (3g_0/2v_0 - 1) (\Lambda/\Lambda_0)^{\epsilon/3} \\ &\sim C(\Lambda) \Lambda^{\epsilon/3}, \end{aligned} \quad (3.20)$$

where g_0 and v_0 are the initial values at $\Lambda = \Lambda_0$. The correction of order $(\Lambda/\Lambda_0)^{\epsilon/3}$ in Eq. (3.20) gives rise to the background heat capacity C_0 , where C_H is expressed as $C_H \cong A_0 \tau^{-\alpha} / \alpha + C_0$. However, it cancels to vanish in the product $C(\Lambda)\gamma(\Lambda)$ in Eq. (3.7) as ought to be the case. As a result this product deviates from its asymptotic behavior Eq. (3.7) only by $(\Lambda/\Lambda_0)^\epsilon$ as well as $g - g^*$. In this paper we are interested in the leading singularity and neglect transient behavior such as in Eq. (3.20) for simplicity.

B. Dynamic equations

In constructing dynamic equations we choose ρ , e , and the momentum density \mathbf{J} as the fundamental gross variables. We believe that the choice of the entropy and the pressure as the gross variables from the starting point is misleading. The velocity field is defined by

$$\mathbf{v} = \frac{1}{\rho} \mathbf{J}. \quad (3.21)$$

The kinetic energy in the system is then

$$\mathcal{H}_K = \int d\mathbf{r} \frac{1}{2} \rho \mathbf{v}^2 = \int d\mathbf{r} \frac{1}{2} \mathbf{J}^2. \quad (3.22)$$

These three variables are conserved quantities and are governed by nonlinear Langevin equations with Gaussian noises,

$$\frac{\partial}{\partial t} \rho = -\nabla \cdot \mathbf{J}, \quad (3.23)$$

$$\frac{\partial}{\partial t} e = -\nabla \cdot [(e+p)\mathbf{v}] + \lambda_0 T_c \nabla^2 \frac{\delta \mathcal{H}}{\delta e} + \theta, \quad (3.24)$$

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{J} = & -\nabla \cdot (\rho \mathbf{v} \mathbf{v}) - \nabla \cdot \overleftrightarrow{\Pi} + \eta_0 \nabla^2 \mathbf{v} \\ & + \left[\zeta_0 + \left(1 - \frac{2}{d}\right) \eta_0 \right] \nabla (\nabla \cdot \mathbf{v}) + \boldsymbol{\zeta}. \end{aligned} \quad (3.25)$$

In Eq. (3.24) the pressure p may be replaced by its equilibrium average ($\cong p_c$, p_c being the critical pressure) near the critical point since its fluctuation is small as compared to that of e . The λ_0 is the background thermal conductivity because $\delta \mathcal{H} / \delta e$ is the fluctuation part of the temperature divided by T_c [see Eq. (3.36) below]. The $\theta(\mathbf{r}, t)$ is the random source term characterized by

$$\langle \theta(\mathbf{r}, t) \theta(\mathbf{r}', t') \rangle = -2k_B T_c^2 \lambda_0 \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (3.26)$$

In Eq. (3.25) $\overleftrightarrow{\Pi}$ is the reversible stress tensor arising from the deviations of ρ and e , while η_0 and ζ_0 are the background shear and bulk viscosities, respectively. The random source field $\boldsymbol{\zeta}(\mathbf{r}, t)$ is a vector and satisfies

$$\begin{aligned} \langle \zeta_i(\mathbf{r}, t) \zeta_j(\mathbf{r}', t') \rangle = & -2 \left\{ \eta_0 \delta_{ij} \nabla^2 + \left[\zeta_0 + \left(1 - \frac{2}{d}\right) \eta_0 \right] \right. \\ & \left. \times \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} \right\} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \end{aligned} \quad (3.27)$$

The noise relations (3.26) and (3.27) are examples of the so-called fluctuation-dissipation theorem. Obviously, we obtain the usual hydrodynamic equations of one component compressible fluids far from the critical point if $\overleftrightarrow{\Pi}$ in Eq. (3.25) is replaced by p , p is regarded as the usual pressure dependent on space and time, and the noise terms are omitted.

In Appendix C the reversible stress tensor will be shown to be of the form

$$\Pi_{ij} = (p + \delta p_f) \delta_{ij} + \tilde{\Pi}_{ij}. \quad (3.28)$$

The fluctuation contribution in the first term is diagonal and

$$\delta p_f = \langle \rho \rangle \frac{\delta}{\delta \rho} \mathcal{H} + (u + p) \frac{\delta}{\delta e} \mathcal{H}$$

$$= c_1 \frac{\delta}{\delta \psi} \mathcal{H} + c_2 \frac{\delta}{\delta m} \mathcal{H}, \quad (3.29)$$

where $\langle \rho \rangle$ and u are the equilibrium averages of the mass and energy densities. (Note that the average mass density has been written as ρ in Sec. II). They may well be replaced by the critical values ρ_c, e_c as well as p in Eq. (3.29). Here \mathcal{H} is regarded as a functional of $\delta \rho$ and δe on the first line of Eq. (3.29) and a functional of ψ and m on the second line. Using Eqs. (2.24) and (2.25) the coefficients c_1 and c_2 are expressed as

$$c_1 = \langle \rho \rangle (\beta_2 - H \beta_1) / (\alpha_1 \beta_2 - \alpha_2 \beta_1), \quad (3.30)$$

$$c_2 = \langle \rho \rangle (-\alpha_2 + H \alpha_1) / (\alpha_1 \beta_2 - \alpha_2 \beta_1), \quad (3.31)$$

where H is the enthalpy per unit mass. We note that the deviations $\delta \nu$, δB , and δp are related by $\delta p = k_B T \langle \rho \rangle (\delta \nu + H \delta B)$. Furthermore, using Eqs. (2.12) and (2.13), c_1 and c_2 may be rewritten into more convenient forms,

$$c_1 = (k_B T_c)^{-1} \left(\frac{\partial p}{\partial h} \right)_\tau, \quad (3.32)$$

$$c_2 = (k_B T_c)^{-1} \left(\frac{\partial p}{\partial \tau} \right)_h = (k_B b)^{-1} \left(\frac{\partial p}{\partial T} \right)_h, \quad (3.33)$$

where b is defined by Eq. (2.29). In Eq. (3.33) the derivative at constant h may well be approximated as that on the coexistence curve. On the other hand, the second fluctuation contribution $\tilde{\Pi}_{ij}$ is given by

$$\begin{aligned} \tilde{\Pi}_{ij} = & \left[\delta \psi \frac{\delta}{\delta \psi} \mathcal{H} + \delta m \frac{\delta}{\delta m} \mathcal{H} - k_B T_c (f + \frac{1}{2} |\nabla \psi|^2) \right] \delta_{ij} \\ & + k_B T_c \frac{\partial \psi}{\partial x_i} \frac{\partial \psi}{\partial x_j}, \end{aligned} \quad (3.34)$$

where $\delta \psi = \psi - \langle \psi \rangle$ and $\delta m = m - \langle m \rangle$ are the deviations and we have set $K_0 = 1$. This form (but without $\delta m \delta \mathcal{H} / \delta m$) has already been known [43]. The first term of Eq. (3.34) is diagonal and is generally much smaller than δp_f near the critical point, while the second term of Eq. (3.34) can be the sole off-diagonal contribution giving rise to the weak shear viscosity anomaly near the critical point. Recently, however, considerable attention has been paid to rheology in two phase states of near-critical fluids, in which the second term of Eq. (3.34) behaves like a δ function at the interfaces and gives rise to significant contributions to the shear viscosity and the normal stress effect [44].

In Eq. (3.25) the divergence of $-\Pi_{ij}$ appears as the force density acting on the fluid. It has a rather simple form,

$$\begin{aligned} -\nabla \cdot \overleftrightarrow{\Pi} = & -\rho \nabla \frac{\partial \mathcal{H}}{\partial \rho} - (e+p) \nabla \frac{\partial \mathcal{H}}{\partial e} \\ = & -\nabla \delta p_f - \delta \psi \nabla \frac{\delta \mathcal{H}}{\delta \psi} - \delta m \nabla \frac{\delta \mathcal{H}}{\delta m}. \end{aligned} \quad (3.35)$$

Folk and Moser have obtained essentially the same expression as Eq. (3.35) for binary fluid mixtures [21], where the entropy per unit volume is used instead of the energy density.

Similarly to the pressure fluctuation δp_f , we may introduce the fluctuating part of the temperature by

$$\delta T_f = T_c \delta \mathcal{H} / \delta e = (k_B b)^{-1} \left[-\frac{\beta_1}{\alpha_1} \frac{\delta}{\delta \psi} \mathcal{H} + \frac{\delta}{\delta m} \mathcal{H} \right]. \quad (3.36)$$

The equilibrium fluctuation of the above quantity will be examined at the end of Appendix A. This expression allows us to calculate the effect of the bulk viscosity on the temperature deviation in nonequilibrium situations as will be shown in Sec. V.

We note that Eqs. (3.23)–(3.25) are stochastic equations and that the equilibrium distribution functional $\exp[-(\mathcal{H} + \mathcal{H}_K)/k_B T_c]$ is the stationary solution of the corresponding Fokker-Planck equation. This is surely ensured by the reversible terms in (3.23)–(3.25). Equivalently, we can confirm $d(\mathcal{H} + \mathcal{H}_K)/dt \leq 0$ in the absence of noises and externally applied flow field, where the equality holds only in homogeneous equilibrium. This property is equivalent to the usual statement that the entropy production rate is non-negative definite in nonequilibrium states.

C. Thermal conductivity and shear viscosity

The critical fluctuations of the entropy are known to be convected by the transverse velocity \mathbf{v}_\perp (which satisfies $\nabla \cdot \mathbf{v}_\perp = 0$). Consequently the dynamics of δs is governed by the hydrodynamic interaction and the thermal diffusivity at long wavelengths ($q\xi \ll 1$) is given by the well-known Einstein-Kawasaki formula [1]

$$D = \frac{k_B T_c}{6\pi\eta_R \xi}, \quad (3.37)$$

η_R being the renormalized shear viscosity. This formula is one of the main results of the original mode coupling theory. On the other hand, the transverse velocity is only weakly affected by δs through the last term of Eq. (3.34) as will be shown below.

From Eq. (3.24) the reversible energy current turns out to be $H\mathbf{J}$ where $H = (u + p)/\rho \cong (u + p_c)/\rho$ is the fluctuating enthalpy. Its nonlinear part with respect to the gross variables is then

$$\mathbf{J}_e \cong T_c (\delta s) \mathbf{J}, \quad (3.38)$$

because

$$\delta H = T \delta s + \frac{1}{\rho} \delta p \cong T \delta s. \quad (3.39)$$

The renormalized thermal conductivity is thus expressed formally as [45,1]

$$\lambda_R = \lambda_0 + (k_B T_c^2)^{-1} \int_0^\infty dt \int d\mathbf{r} \langle \mathbf{J}_{\text{ex}}(\mathbf{r}, t) \mathbf{J}_{\text{ex}}(\mathbf{0}, 0) \rangle, \quad (3.40)$$

where J_{ex} is the x component of \mathbf{J}_e . Indeed the above formula with Eq. (3.38) was the starting point of the mode coupling theory. On the other hand, the xy component of the stress tensor Π_{ij} is written as

$$\Pi_{xy}(\mathbf{r}, t) = k_B T_c \left[\frac{\partial}{\partial x} \psi(\mathbf{r}, t) \right] \left[\frac{\partial}{\partial y} \psi(\mathbf{r}, t) \right]. \quad (3.41)$$

The renormalized shear viscosity is written in the correlation function expression as

$$\eta_R = \eta_0 + (k_B T_c)^{-1} \int_0^\infty dt \int d\mathbf{r} \langle \Pi_{xy}(\mathbf{r}, t) \Pi_{xy}(\mathbf{0}, 0) \rangle. \quad (3.42)$$

The original mode coupling theory predicted a logarithmic divergence $\eta_R/\eta_0 \sim \ln(\xi\Lambda_0)$, while the dynamic renormalization group theory yielded a power law form with a small exponent as will be shown in Eq. (3.51) below.

Kawasaki and Gunton [42] showed that the mode coupling theory may be formulated in general spatial dimensions for various systems. It yields the same results as those from the dynamic renormalization group theory [4] to first order in ϵ . The predictions of the mode coupling theory at $d=3$ and those of the dynamic renormalization group theory to leading order in ϵ are surprisingly close for classical fluids. The reason for this agreement can be traced to the fact that the shear viscosity anomaly is very weak in near-critical fluids. Hereafter we will briefly summarize Kawasaki and Gunton's results, because the same approach will be taken in Sec. IV for the bulk viscosity. As in Sec. III A on statics, let us decrease the upper cutoff wave number Λ of the fluctuations and examine how the kinetic coefficient $\lambda(\Lambda)$ and the shear viscosity $\eta(\Lambda)$ are renormalized in the ϵ expansion scheme. To recover the results in the literature we introduce

$$L(\Lambda) = k_B \lambda(\Lambda) / (\rho_c \alpha_s)^2, \quad (3.43)$$

where α_s is defined by Eq. (2.36). The thermal diffusivity in the long wavelength limit is then

$$D = \lambda_R / \rho C_p = L_R / \chi, \quad (3.44)$$

where λ_R and L_R are the values of $\lambda(\Lambda)$ and $L(\Lambda)$ in the renormalized limit $\Lambda \rightarrow 0$ and χ is the variance of ψ given in Eq. (2.16). It is known that the dimensionless number

$$f(\Lambda) = k_B T_c K_d / [K(\Lambda) \eta(\Lambda) L(\Lambda) \Lambda^\epsilon] \quad (3.45)$$

tends to a fixed point value as Λ is decreased at the critical point [4]. To first order in $\epsilon = 4 - d$, Kawasaki and Gunton's results read

$$-\Lambda \frac{\partial}{\partial \Lambda} L(\Lambda) = \frac{3}{4} k_B T_c K_d / [\eta(\Lambda) \Lambda^\epsilon], \quad (3.46)$$

$$-\Lambda \frac{\partial}{\partial \Lambda} \eta(\Lambda) = \frac{1}{24} k_B T_c K_d / [L(\Lambda) \Lambda^\epsilon]. \quad (3.47)$$

In deriving these equations the fluctuations in the thin shell region $\Lambda - \delta\Lambda < q < \Lambda$ are assumed to obey the Gaussian distribution and to relax exponentially with the rate $L(\Lambda)\Lambda^4$. Then $f(\Lambda)$ obeys

$$-\Lambda \frac{\partial}{\partial \Lambda} f(\Lambda) = \epsilon f(\Lambda) - \frac{19}{24} f(\Lambda)^2. \quad (3.48)$$

As $\Lambda \rightarrow 0$ we obtain $f(\Lambda) \rightarrow f^*$ with

$$f^* = \frac{24}{19} \epsilon + \dots \quad (3.49)$$

Therefore, we find the asymptotic behavior $L(\Lambda) \sim \Lambda^{-x_\lambda}$ and $\eta(\Lambda) \sim \Lambda^{-x_\eta}$ with

$$x_\lambda = \frac{18\epsilon}{19} + \dots, \quad (3.50)$$

$$x_\eta = \epsilon - \eta - x_\lambda = \frac{\epsilon}{19} + \dots \quad (3.51)$$

The renormalized kinetic coefficients behave as $L_R \sim \lambda_R \sim \xi^{18\epsilon/19}$ and $\eta_R \sim \xi^{\epsilon/19}$ to first order in ϵ . It was shown generally [4] that the relation $L_R \eta_R \sim \xi^{\epsilon-\eta}$ holds to all orders in ϵ . The entropy fluctuations with wave numbers of order ξ^{-1} have a very slow decay rate,

$$\Gamma_\xi = D \xi^{-2} = L_R \xi^{-2} / \chi \sim \xi^{-z}, \quad (3.52)$$

where z is the so-called dynamic critical exponent. We have found $z=3$ in the mode coupling theory at $d=3$ as shown in Eq. (3.37) and $z=4-18\epsilon/19+\dots$ in the ϵ expansion scheme from Eq. (3.50).

We have discussed the asymptotic behavior of the kinetic coefficients. We note that it is important to extend the theory into the nonasymptotic critical region in pure fluids [19,46]. Also in binary fluid mixtures considerable efforts have been made on the crossover from the pure fluid behavior to the mixture behavior near the gas-liquid critical point [20–22].

IV. BULK VISCOSITY AND FREQUENCY-DEPENDENT SPECIFIC HEAT

A. General relations

We can show that a nonlinear part of δp_f in Eq. (3.29) gives rise to a strongly divergent bulk viscosity. The dominant nonlinear term is given by

$$p_{\text{nl}}(\mathbf{r}, t) = k_B T_c c_2 \gamma_0 \psi(\mathbf{r}, t)^2. \quad (4.1)$$

The first term $c_1 \delta \mathcal{H} / \delta \psi$ in Eq. (3.29) is very small near the critical point. It is a general aspect valid in many near-critical systems that the field variable $\delta \mathcal{H} / \delta m$ relaxes slowly in a sound and gives rise to enhancement of acoustic attenuation. The resultant frequency-dependent bulk viscosity is written in the time correlation function expression,

$$\xi_R^*(\omega) = \zeta_0 + \frac{1}{k_B T_c} \int_0^\infty dt \int d\mathbf{r} e^{-i\omega t} \langle \delta p_{\text{nl}}(\mathbf{r}, t) \delta p_{\text{nl}}(\mathbf{0}, 0) \rangle, \quad (4.2)$$

where δp_{nl} is the deviation. We assume that the acoustic wave number $|k|$ is much smaller than the inverse correlation length ξ^{-1} , but the acoustic frequency ω can be either smaller or larger than Γ_ξ . Hereafter ω will be assumed to be positive.

For a small amplitude sound varying as $\exp(-ikx+i\omega t)$, the dispersion relation is of the form

$$k^2 = \rho K_s^*(\omega) \omega^2, \quad (4.3)$$

where $K_s^*(\omega)$ is the frequency-dependent, complex adiabatic compressibility defined by

$$K_s^*(\omega) = 1 / [\rho c^2 + i\omega \zeta_R^*(\omega)]. \quad (4.4)$$

Obviously $K_s^*(\omega)$ has the following physical meaning. Let long wavelength pressure and density variations be expressed as $\delta p = \text{Re}[p_1 \exp(-ikx+i\omega t)]$ and $\delta \rho = \text{Re}[\rho_1 \exp(-ikx+i\omega t)]$ in a sound. Then the complex amplitudes p_1 and ρ_1 are related by

$$\rho_1 / \rho = K_s^*(\omega) p_1. \quad (4.5)$$

In the low frequency limit we obtain the usual adiabatic compressibility $K_s = \rho^{-1} (\partial \rho / \partial p)_s$.

Next let us express the sound speed $c = (1/\rho K_s)^{1/2}$ in the low frequency limit in terms of the constant-volume specific heat C_v by the thermodynamic identity

$$\rho^2 c^2 C_v = T \left(\frac{\partial p}{\partial T} \right)_s \left(\frac{\partial p}{\partial T} \right)_\rho. \quad (4.6)$$

Here $(\partial p / \partial T)_\rho$ and $(\partial p / \partial T)_s = (\partial p / \partial T)_\rho / (1 - C_v / C_p)$ both tend to $(\partial p / \partial T)_{\text{cx}}$ near the critical point, so that we find the critical behavior

$$\rho c^2 \cong T \left(\frac{\partial p}{\partial T} \right)_{\text{cx}}^2 / \rho C_v \sim \xi^{-\alpha/\nu}. \quad (4.7)$$

In calculating $\zeta_R^*(\omega)$ we must carefully take into account of the strong Λ dependence of $\gamma(\Lambda)$ as shown in Eq. (3.8). In particular, for $\Lambda \leq \xi^{-1}$ and on the critical isochore above T_c , we have found Eq. (3.9) for γ_R , which is the renormalized value of $\gamma(\Lambda)$. Then in the hydrodynamic regime ($\Lambda \leq \xi^{-1}$) on the critical isochore above T_c , the dominant nonlinear pressure fluctuation is expressed as

$$p_{\text{nl}R} \cong \rho c^2 \left(\frac{k_B T_c}{T - T_c} \right) \left(\frac{\partial T}{\partial p} \right)_{\text{cx}} \left(\frac{\psi^2}{\chi} \right), \quad (4.8)$$

where χ is the variance of ψ defined by Eq. (2.16). As far as the most singular term is concerned, ψ^2 / χ in Eq. (4.8) may be replaced by $\rho (\delta s)^2 / C_p$ or $(\delta \rho)^2 / (k_B T \rho^2 K_T)$ from Eq. (2.7) or Eq. (2.32). We note that essentially the same expression can be derived from general thermodynamic relations (A11) and (A12), which was indeed used in Kawasaki's theory [13] as will be discussed in Appendix D.

It is easy to check that $\zeta_R^*(0) \sim \xi^{-d} \gamma_R^2 \chi^2 / \Gamma_\xi \sim \xi^{z-\alpha/\nu}$ at $\omega=0$ from the fluctuations with wave number q in the hydrodynamic region $q < \xi^{-1}$. Here the first factor ξ^{-d} is the volume of the wave number region ($q < \xi^{-1}$) and Γ_ξ is the entropy decay rate $D \xi^{-2}$ given in Eq. (3.52). We shall see the following simple scaling relation in the low frequency limit,

$$\zeta_R^*(0) \cong R_B \rho c^2 / \Gamma_\xi, \quad (4.9)$$

where the coefficient R_B is a universal dimensionless number to be calculated later. The attenuation per wavelength is

$$\alpha_\lambda = \pi \omega \zeta_R^*(0) / \rho c^2 = \pi R_B \omega / \Gamma_\xi. \quad (4.10)$$

B. Calculation at small ϵ

As in Kawasaki and Gunton's theory [42] we gradually decrease the upper cutoff wave number Λ of ψ and m . When the fluctuations with wave number q in the thin shell region $\Lambda - \delta\Lambda < q < \Lambda$ are coarse grained, their contribution to $p_{\text{nl}}(\mathbf{r}, t)$ should be regarded as a *random* pressure. Its zero wave number component is of the form

$$p_{\text{nl}}^> = k_B T_c c_2 \gamma(\Lambda) (2\pi)^{-d} \int^> d\mathbf{q} \psi_q \psi_{-q}, \quad (4.11)$$

where the integral is in the region $\Lambda - \delta\Lambda < q < \Lambda$. From Eq. (4.2) the incremental contribution $\delta\zeta^*(\omega, \Lambda)$ can be calculated if $\psi_q(t)$ is assumed to relax exponentially in time. In the limit $\delta\Lambda \rightarrow 0$ we obtain

$$-\Lambda \frac{\partial}{\partial \Lambda} \zeta^*(\omega, \Lambda) = k_B T_c c_2^2 K_d \gamma(\Lambda)^2 \Lambda^d S_\Lambda^2 \left/ \left[\Gamma_\Lambda + \frac{i}{2} \omega \right], \right. \quad (4.12)$$

where S_Λ is the structure factor at $q = \Lambda$ and Γ_Λ is the decay rate at $q = \Lambda$. We next simplify the right hand side of Eq. (4.12) using the following steps. First, we set

$$K(\Lambda) S_\Lambda = 1 / [\xi^{-2} + \Lambda^2]. \quad (4.13)$$

Second, we assume that the dimensionless parameter $v(\Lambda)$ defined by Eq. (3.12) is equal to the fixed point value v^* for $\Lambda_0 \gg \Lambda > \xi^{-1}$. Third, $C(\Lambda)$ is scaled as

$$\bar{C}(\Lambda) = \rho_c^{-1} k_B b^2 C(\Lambda), \quad (4.14)$$

From $C(0) = C_H$ and Eq. (2.39) we have in the long wavelength limit

$$\bar{C}(0) = (1 - R_v)^{-1} C_v, \quad (4.15)$$

where C_v is the constant-volume specific heat and R_v is defined by Eq. (2.40). Note that $\bar{C}(0) = C_v$ only on the critical isochore above T_c . Now Eq. (4.12) may be rewritten as

$$-\Lambda \frac{\partial}{\partial \Lambda} \zeta^*(\omega, \Lambda) = \frac{T_c}{\rho_c} \left(\frac{\partial p}{\partial T} \right)_{\text{cx}}^2 v(\Lambda) \Lambda^4 \left/ \left[\bar{C}(\Lambda) (\xi^{-2} + \Lambda^2)^2 \left(\Gamma_\Lambda + \frac{i}{2} \omega \right) \right], \right. \quad (4.16)$$

Integration of this equation yields

$$\zeta_R^*(\omega) = \frac{T_c}{\rho_c} \left(\frac{\partial p}{\partial T} \right)_{\text{cx}}^2 \int_0^\infty d\Lambda v(\Lambda) \Lambda^3 \left/ \left[\bar{C}(\Lambda) (\xi^{-2} + \Lambda^2)^2 \right. \right. \\ \left. \left. \times \left(\Gamma_\Lambda + \frac{i}{2} \omega \right) \right], \right. \quad (4.17)$$

where the background part is omitted.

With Eq. (4.17) we notice that we can introduce a frequency-dependent specific heat $C_v^*(\omega)$ by

$$1/C_v^*(\omega) = [1 + i\omega \zeta_R^*(\omega) / \rho c^2] / C_v \\ = \frac{1}{C_v} + i\omega \int_0^\infty d\Lambda \\ \times \frac{v(\Lambda) \Lambda^3}{\bar{C}(\Lambda) (\xi^{-2} + \Lambda^2)^2 \left(\Gamma_\Lambda + \frac{i}{2} \omega \right)}. \quad (4.18)$$

The first term is the zero-frequency limit and the second term arises from nonvanishing ω . The frequency-dependent adiabatic compressibility defined by Eq. (4.4) is simply proportional to $C_v^*(\omega)$ in the scaling limit as

$$K_s^*(\omega) = T^{-1} \left(\frac{\partial T}{\partial p} \right)_{\text{cx}}^2 \rho C_v^*(\omega). \quad (4.19)$$

From Eq. (4.3) the dispersion relation is expressed as

$$\omega^2 / k^2 = T \left(\frac{\partial p}{\partial T} \right)_{\text{cx}}^2 \left/ \rho^2 C_v^*(\omega). \right. \quad (4.20)$$

We may equally use $K_s^*(\omega)$ and $C_v^*(\omega)$ because they are related by the simple relation (4.19). In the following we will use $C_v^*(\omega)$ to directly check Ferrell and Bhattacharjee's prediction.

1. Low frequency limit

In the low frequency limit $\omega \ll \Gamma_\xi$ Eq. (4.18) surely yields the scaling form (4.9). The coefficient R_B in Eq. (4.9) is expanded in powers of ϵ as

$$R_B \cong \frac{1}{4} v^* (1 - R_v) \cong \left(\frac{1}{24} \epsilon + \dots \right) (1 - R_v). \quad (4.21)$$

The frequency-dependent specific heat behaves as

$$C_v^*(\omega) = C_v [1 - R_B i \omega / \Gamma_\xi + \dots]. \quad (4.22)$$

Unfortunately the second order term in ϵ is not small in R_B . In Appendix D we will show that the mode coupling theory [13] [or use of Eq. (4.8) in three dimensions] leads to $R_B \cong 0.27/\pi$ on the critical isochore above T_c , which is about two times larger than our value to first order in ϵ . See Appendix D for more details. In future experiments it is very informative to directly check the simple scaling behavior (4.9) or (4.10) rather than using Kawasaki's original expressions [47,48].

Using a dynamic model similar to that of Ref. [17], Denzler and Schwable [18] calculated the critical amplitude ratio α_+ / α_- for the sound attenuation above and below T_c in the low frequency limit to be $(A'/A)^{1/2} \alpha^{+\nu_z}$ to first order in ϵ . They have then estimated it to be about 5 in three dimensions using the incorrect value $A'/A \cong 2$ [see Eq. (2.47)]. Our theory yields $(A'/A)^{1/2} \alpha^{+\nu_z} (1 + a_c^2)$ to first order in ϵ , a_c being defined by Eq. (2.43). The ratio is estimated to be about $5\sqrt{2} \sim 7$ in our theory.

2. High frequency limit

In the high frequency limit $\omega \gg \Gamma_\xi$, we calculate Eq. (4.17) replacing $v(\Lambda)$ by v^* and the lower limit of the integration by ξ^{-1} . Further we set $\xi^{-2} + \Lambda^2 \cong \Lambda^2$ and $\Gamma_\Lambda \cong \Gamma^* \Lambda^z$ and transform the second term of Eq. (4.18) into

$$i\omega \int_{\xi^{-1}}^{\infty} \frac{d\Lambda}{\Lambda} \frac{v^*}{\bar{C}(\Lambda)[\Gamma^* \Lambda^z + (i/2)\omega]} \cong 2v^* \frac{\nu}{\alpha} \left[\frac{1}{\bar{C}(\Lambda^*)} - \frac{1}{\bar{C}(\xi^{-1})} \right]. \quad (4.23)$$

Use has been made of the behavior $\bar{C}(\Lambda) = C^* \Lambda^{-\alpha/\nu}$, C^* being a constant. The contribution from the region $\Lambda < \xi^{-1}$ is of order v^*/C_v and is very small. We introduce a complex wave number Λ^* defined by

$$\Lambda^* = (i\omega/2\Gamma^*)^{1/z}. \quad (4.24)$$

Therefore,

$$\bar{C}(\Lambda^*) = C^* (i\omega/2\Gamma^*)^{-\alpha/\nu z} \alpha \exp(-i\pi\alpha/\nu z). \quad (4.25)$$

In Eq. (4.23), $1/\bar{C}(\Lambda^*)$ may be readily obtained if we change Λ to $x = \Lambda/\Lambda^*$ and take the integration path of real x , while $1/\bar{C}(\xi^{-1})$ arises from the integration of the region $\Lambda \sim \xi^{-1} \ll |\Lambda^*|$. Further we find $2v^* \nu/\alpha \cong 1$ from Eq. (3.18) and transform Eq. (4.18) into

$$\frac{1}{C_v^*(\omega)} \cong \frac{1}{C^*} \left(\frac{i\omega}{2\Gamma^*} \right)^{\alpha/\nu z} + \frac{R_v}{C_v}. \quad (4.26)$$

The Bhattacharjee and Ferrell result [15] follows on the critical isochore above T_c or for $R_v = 0$, where

$$C_v^*(\omega) \cong C^* (i\omega/2\Gamma^*)^{-\alpha/\nu z}. \quad (4.27)$$

Thus on the critical isochore above T_c the sound velocity weakly depends on ω as

$$c(\omega) \cong c(\omega/2\Gamma_\xi)^{\alpha/2\nu z} \omega^{\alpha/2\nu z}, \quad (4.28)$$

and the attenuation per wavelength tends to be a universal number,

$$\alpha_\lambda \cong \pi^2 \alpha/2\nu z. \quad (4.29)$$

Bhattacharjee and Ferrell [15] claimed that data of ^4He by Roe and Meyer [48] exactly supports Eq. (4.29), which will also be shown in Fig. 2 below, and that data of other fluids may be fitted to a more general formula that takes into account the background heat capacity. See the sentences below Eq. (3.20) for the background heat capacity in the renormalization group scheme. However, near the coexistence curve R_v is close to 0.5 and the second term of Eq. (4.26) can be important. For $R_v \neq 0$ we have

$$\alpha_\lambda \cong (\pi^2 \alpha/2\nu z) \left/ \left[1 + \frac{R_v}{1-R_v} \left(\frac{\omega}{2\Gamma_\xi} \right)^{-\alpha/\nu z} \right] \right. \quad (4.30)$$

3. General behavior on the critical isochore

To examine the behavior of general ω let us limit ourselves to the critical isochore above T_c for simplicity. There, the ratio $C_v/C_v^*(\omega)$ is a universal function of

$$\zeta = i\omega/2\Gamma_\xi, \quad (4.31)$$

and is analytic in the upper complex region $\text{Im}\zeta > 0$. Its normal ϵ expansion may be expressed as $C_v/C_v^*(\omega) = 1 + v^* F(\zeta) + \dots$ with

$$F(\zeta) = -1 + \frac{1}{2} \left(1 - \frac{1}{\zeta} \right) \ln \zeta + \frac{1}{\Delta} \left(\frac{3}{2} - \frac{1}{2\zeta} \right) \ln \left(\frac{1+\Delta}{1-\Delta} \right), \quad (4.32)$$

where $\Delta = (1-4\zeta)^{1/2}$. In accord with Eqs. (4.21) and (4.25) we find $F(\zeta) \cong \frac{1}{2}\zeta$ for $|\zeta| \ll 1$ and $F(\zeta) \cong \frac{1}{2}\ln \zeta - 1 + 3i\pi/2\Delta + \dots$ for $|\zeta| \gg 1$. To recover Eq. (4.25) we should exponentiate the logarithmic factor, so we obtain an exponentiated form,

$$C_v/C_v^*(\omega) \cong (1+\zeta)^{\alpha/\nu z} \{ 1 + v^* [F(\zeta) - \frac{1}{2}\ln(1+\zeta)] \}. \quad (4.33)$$

This expression holds only in the scaling limit in which $\xi\Lambda_0 \rightarrow 0$ with ω/Γ_ξ held fixed. Kroll and Ruhland [17] derived an expression of the frequency-dependent adiabatic compressibility essentially equivalent to Eq. (4.33) [Eq. (5) of their first paper] and confirmed that the above scaling function agrees well with the data of Roe and Meyer [48]. Some further calculations show that $F(\zeta) - \frac{1}{2}\ln(1+\zeta)$ is negligibly small for $\omega \ll \Gamma_\xi$ and behaves as $-1 + (3\pi/8)(1-i)(2\Gamma_\xi/\omega)^{1/2} + \dots$ for $\omega \gg \Gamma_\xi$. Thus we obtain

$$\alpha_\lambda = (\pi^2 \alpha/2\nu z) [1 - 3(\Gamma_\xi/2\omega)^{1/2} + \dots] \quad (4.34)$$

in the high frequency regime and hence α_λ slowly approaches the universal value (4.29) even in the scaling limit. Moreover, we should not forget the fact that the slow transient behavior of $v(\Lambda)$ and $C(\Lambda)$, which is neglected in Eq. (4.33), will give rise to significant corrections to the asymptotic behavior.

Now we display the scaling behavior derived from Eq. (4.33). We set $\alpha/\nu z = 0.057$ and $v^* = 0.114$ in Eq. (4.33) and plot $c(\omega)/c - 1$ and α_λ in Figs. 1 and 2, respectively, as functions of $\omega/2\Gamma_\xi$, where

$$c/c(\omega) = \text{Re}[\sqrt{C_v/C_v^*(\omega)}], \quad (4.35)$$

$$\alpha_\lambda = 2\pi \text{Im}[\sqrt{C_v/C_v^*(\omega)}]/\text{Re}[\sqrt{C_v/C_v^*(\omega)}]. \quad (4.36)$$

In the figures we also show data of Roe and Meyer [48] for ^3He on the critical isochore at 1 MHz, where we have set $D = k_B T_c / 6\pi \eta_R \xi = 5.6 \times 10^{-5} \times (T/T_c - 1)^\nu$ cm²/sec and $\xi = 2.6 \times 10^{-8} \times (T/T_c - 1)^{-\nu}$ cm from Table I of Ref. [49]. The agreement is satisfactory in view of the fact that the scaling function $F(\zeta)$ in Eq. (4.32) is obtained only to first order in ϵ . Note that α_λ from (4.36) behaves as $\pi(\alpha/2\nu z)\omega/\Gamma_\xi$ at low frequencies. The data of Ref. [48] at low frequencies thus indicates $R_B \cong \alpha/2\nu z \cong 0.029$ on the

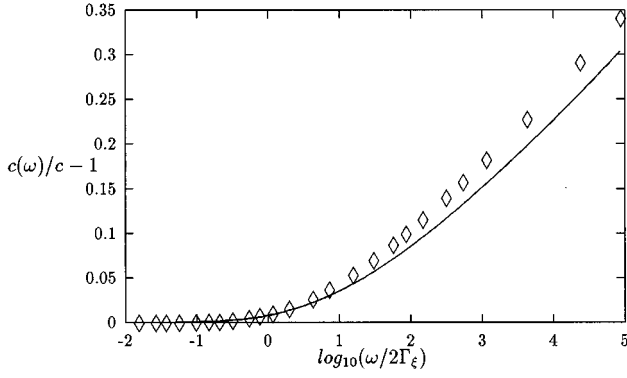


FIG. 1. $c(\omega)/c - 1$ vs $\omega/2\Gamma_\xi$ on the critical isochore above T_c obtained from Eqs. (4.33) and (4.35) on a semilogarithmic scale. It is compared with the data of Ref. [48].

critical isochore above T_c for the universal number R_B in Eqs. (4.9) and (4.10). This value is about 70% of the value to first order in ϵ in Eq. (4.21).

C. Slow relaxation of stress correlation function

Finally we examine the slow relaxation of the stress time correlation function, whose Laplace transformation gives the frequency-dependent bulk viscosity. In Eq. (4.2) the second term is the dominant contribution in the slowly decaying part. Let us examine the explicit time dependence of

$$\begin{aligned} G_{xx}(t) &= (k_B T_c)^{-1} \int d\mathbf{r} \langle \delta \Pi_{xx}(\mathbf{r}, t) \delta \Pi_{xx}(\mathbf{0}, 0) \rangle \\ &\cong (k_B T_c)^{-1} \int d\mathbf{r} \langle \delta p_{nl}(\mathbf{r}, t) \delta p_{nl}(\mathbf{0}, 0) \rangle, \end{aligned} \quad (4.37)$$

which is the inverse Laplace transformation of Eq. (4.17). In the time region $\Gamma_\xi t \lesssim 1$ we obtain a strikingly slow relaxation,

$$G_{xx}(t) \cong \left(\frac{\partial p}{\partial T} \right)_{cx}^2 \left(\frac{T_c}{\rho_c C^*} \right) (2\Gamma^* t)^{-\alpha/\nu z} \cong \rho c^2 (2\Gamma_\xi t)^{-\alpha/\nu z}, \quad (4.38)$$

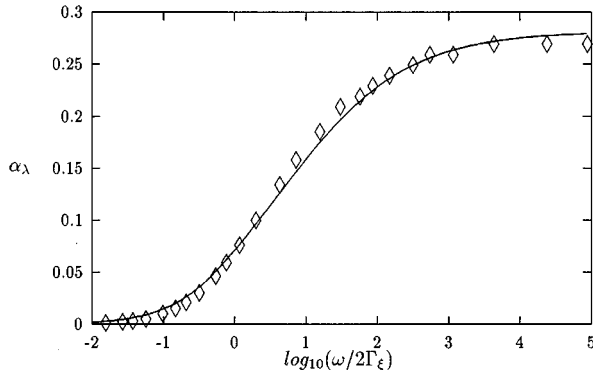


FIG. 2. α_x vs $\omega/2\Gamma_\xi$ on the critical isochore above T_c obtained from Eqs. (4.33) and (4.36) on a semilogarithmic scale. It is compared with the data of Ref. [48].

where $C^* = C(\Lambda)\Lambda^{\alpha/\nu}$ and $\Gamma^* = \Gamma(\Lambda)\Lambda^{-z}$ are the critical amplitudes. Notice that Eq. (4.38) holds for time scales much longer than microscopic times. On the other hand, in the time region $\Gamma_\xi t \gg 1$, the hydrodynamic wave number region $\Lambda < \xi^{-1}$ gives rise to an algebraic decay,

$$G_{xx}(t) \cong \rho c^2 \nu^* \Gamma(d/2) (2\Gamma_\xi t)^{-d/2}, \quad (4.39)$$

where $\Gamma(x)$ is the Γ function. This tail is of the same origin as that of the so-called long time tail first found in computer simulations [50]. We note that this tail can be derived readily from Eq. (4.8). Corresponding to the presence of the hydrodynamic long tail Eq. (4.39) the frequency-dependent bulk viscosity behaves singularly in the low frequency limit $\omega \ll \Gamma_\xi$ as

$$\begin{aligned} \zeta_R^*(\omega) &= (\rho c^2 / \Gamma_\xi) \{ R_B - [\pi \nu^* / 2 \sin(\epsilon \pi / 2)] (\omega / 2\Gamma_\xi)^{1-\epsilon/2} \\ &\quad + \dots \}. \end{aligned} \quad (4.40)$$

V. EFFECT OF THE BULK VISCOSITY ON MACROSCOPIC HYDRODYNAMICS

Let us consider a nonequilibrium situation with hydrodynamic disturbances varying very slowly in space compared with the correlation length. However, their time scale can be shorter than the average lifetime of the critical fluctuations $1/\Gamma_\xi$. Hereafter the averages over the thermal fluctuations will be written as $\delta \bar{\rho}$, $\delta \bar{s}$, $\delta \bar{p}$, and $\delta \bar{T}$, for the deviations of density ρ , entropy s , pressure δp_f , and temperature δT_f , where δp_f and δT_f are defined by Eqs. (3.29) and (3.36). For the pressure deviation $\delta \bar{p}$ the usual thermodynamic relation is modified by the frequency-dependent bulk viscosity. For sinusoidal disturbances we obtain

$$\delta \bar{p}(\mathbf{r}, t) = \left(\frac{\partial p}{\partial s} \right)_\rho \delta \bar{s}(\mathbf{r}, t) + [c^2 + i\omega \zeta_R^*(\omega) / \rho] \delta \bar{p}(\mathbf{r}, t). \quad (5.1)$$

For general time dependence we have

$$\begin{aligned} \delta \bar{p}(\mathbf{r}, t) &= \left(\frac{\partial p}{\partial s} \right)_\rho \delta \bar{s}(\mathbf{r}, t) + c^2 \delta \bar{p}(\mathbf{r}, t) \\ &\quad + \rho^{-1} \int_{-\infty}^t dt_1 G_{xx}(t-t_1) \frac{\partial}{\partial t_1} \delta \bar{p}(\mathbf{r}, t_1), \end{aligned} \quad (5.2)$$

where use has been made of the stress correlation function $G_{xx}(t)$ in Eq. (4.37). The relation (4.5) holds in the adiabatic case ($\delta \bar{s} = 0$).

Then we are interested in how $\delta \bar{T}$ is influenced by the frequency-dependent bulk viscosity. Since the non-Markovian part of $\delta \bar{T}$ arises from $\delta \mathcal{H} / \delta m$, the definitions (3.33) and (3.36) indicate that it is equal to that of $\delta \bar{p}$ multiplied by $(\partial T / \partial p)_h \equiv (\partial T / \partial p)_{cx}$, h being defined by Eq. (2.12). We propose the following simple relation:

$$\delta \bar{T}(\mathbf{r}, t) = \frac{T}{C_p} \delta \bar{s}(\mathbf{r}, t) + \left(\frac{\partial T}{\partial p} \right)_s \delta \bar{p}(\mathbf{r}, t). \quad (5.3)$$

Here we have replaced $(\partial T/\partial p)_h$ by $(\partial T/\partial p)_s$, whose difference is at most of order C_v/C_p on the critical isochore above T_c . This is because $(\partial p/\partial T)_s - (\partial p/\partial T)_h = \rho^2(\partial s/\partial T)_h/(\partial \rho/\partial T)_p \sim C_v/C_p$ on the critical isochore above T_c . However, on the coexistence curve below T_c , the difference is of order $(C_v/C_p)^{1/2}$ as shown in Eq. (2.44) and cannot be neglected generally.

A. Density change in the fixed volume condition

Let us suppose a near-critical fluid on the critical isochore above T_c in a container with a fixed volume [7,8] and oscillate the boundary temperature as

$$\delta T_b = T_1 \cos(\omega t) \quad (5.4)$$

in the following frequency range,

$$D/L^2 \ll \omega \ll c/L, \quad (5.5)$$

where D is the thermal diffusivity and L is the length of the container. The pressure deviation $\delta \bar{p}$ may be assumed to be homogeneous throughout the container when ω is much smaller than the inverse acoustic time c/L , so that

$$\delta \bar{p} \cong (\partial p/\partial T)_\rho \langle \delta \bar{T} \rangle, \quad (5.6)$$

where $\langle \delta \bar{T} \rangle$ is the average over space. Furthermore, from Eq. (5.5) the entropy deviation is nonvanishing only near the boundary wall,

$$\delta \bar{s}(\mathbf{r}, t) = A_s \exp(-x \sqrt{i\omega/D}), \quad (5.7)$$

where x is the distance from the wall. The thickness of the thermal diffusion layer is $(D/\omega)^{1/2}$ and is much shorter than L from Eq. (5.5). The coefficient A_s can be calculated using Eqs. (5.4), (5.6), and (5.7). In the one-dimensional geometry in Ref. [7] some calculations show that the density deviation is expressed as $\text{Re}[(\delta \rho)_{\text{in}} \exp(i\omega t)] = [\text{Re}(\delta \rho)_{\text{in}}] \cos(\omega t) - [\text{Im}(\delta \rho)_{\text{in}}] \sin(\omega t)$ far from the boundary, where

$$(\delta \rho)_{\text{in}} \cong \rho \left(\frac{\partial p}{\partial T} \right)_\rho T_1 \left/ \left\{ \left[1 + \frac{L}{2\gamma_s} \sqrt{i\omega/D} \right] [\rho c^2 + i\omega \zeta_R^*(\omega)] \right\}, \quad (5.8)$$

$\gamma_s = C_p/C_v$ being the specific heat ratio growing as $(T/T_c - 1)^{-\gamma + \alpha}$ on the critical isochore above T_c . The density deviation thus becomes out of phase with respect to the boundary temperature oscillation due to the piston effect and the frequency-dependent bulk viscosity. On the other hand, if Eq. (5.3) is assumed, the temperature deviation in the interior region is not affected by the bulk viscosity as

$$(\delta T)_{\text{in}} \cong T_1 \left/ \left[1 + \frac{L}{2\gamma_s} \sqrt{i\omega/D} \right], \quad (5.9)$$

which is of the same form as in Ref. [7]. We are interested in the frequency dependence and imaginary part of the above quantities. In other geometries such as a rectangular or

spherical cell, the relations (5.8) and (5.9) still hold if L is interpreted as V/A , where V and A are the volume and the surface area of the cell.

B. Density change in a fixed pressure

As the second example we change the pressure at $t=0$ infinitesimally from p to $p+p_1$ in a stepwise manner and keep it constant at later times. We follow the time development of the density change $(\delta \rho)_{\text{in}}(t)$ far from the boundary where the entropy is unchanged. From Eq. (5.1) we obtain

$$(\delta \rho)_{\text{in}}(t) = \hat{K}(t) p_1 / c^2, \quad (5.10)$$

where the relaxation function $\hat{K}(t)$ is related to the complex adiabatic compressibility in Eq. (4.4) by

$$\int_0^\infty dt e^{-i\omega t} \hat{K}(t) = \rho c^2 K_s^*(\omega) / i\omega = \rho c^2 / \{i\omega [\rho c^2 + i\omega \zeta_R^*(\omega)]\}. \quad (5.11)$$

By taking the inverse Laplace transformation of $K_s^*(\omega)/i\omega$ we obtain a very singular short-time behavior,

$$\hat{K}(t) \cong (2\Gamma_\xi t)^{\alpha/vz}, \quad (5.12)$$

which holds for $\Gamma_\xi t \ll 1$. For $\Gamma_\xi t \gg 1$ the long tail Eq. (4.39) appears as

$$\hat{K}(t) = 1 - v^* \Gamma(d/2) (2\Gamma_\xi t)^{-d/2} + \dots \quad (5.13)$$

Thus $(\delta \rho)_{\text{in}}(t)$ increases from 0 very steeply as Eq. (5.12) for $\Gamma_\xi t \ll 1$ and approaches to p_1/c^2 slowly as Eq. (5.13).

VI. SUMMARY

We summarize our main results. In Sec. II we discussed the logical consequences of the mapping relations (2.12) and (2.13) of the field variables. In our Ginzburg-Landau approach the mapping relations (2.21) and (2.22) of the density variables are most crucial. We have introduced the entropy variable as in Eq. (2.31) and have found the exact specific heat relations (2.32)–(2.34). The C_v for fluids is asymptotically proportional to the specific heat C_M for Ising spin systems defined by Eq. (2.20) and is related to C_H by Eq. (2.39). Then we have found the presence of the factor $1 - R_v$ in the critical amplitude relation (2.41), whereas it does not appear in the relation (2.47) for the specific heat $(C_v)_{\text{cx}}$ in two phase coexistence. In previous experiments $(C_v)_{\text{cx}}$ has been measured, leading to the conclusion that the specific heat ratio coincides with that of C_H at $h=0$ in Ising spin systems. However, if C_v is measured close to the coexistence curve in the presence of one phase only, the relation $A'/A \cong 1$ should be obtained [37]. An alternative method will be to measure the sound speed c in the low frequency limit on the coexistence curve, which will give information of C_v on the basis of Eq. (4.6). On the other hand, the two-scale factor universality relation (2.48) readily follows in terms of C_v from the mapping relations (2.12) and (2.13).

In Sec. III we introduced the Ginzburg-Landau-Wilson Hamiltonian (3.1), which can describe the strong singularity of the order parameter ψ and the weak singularity of the

energy variable m . Then we have presented the dynamic equations (3.24)–(3.26). They have been derived generally from the conservations of mass, energy, and momentum and are natural extensions of the usual hydrodynamic equations of compressible fluids. As derived in Appendix C we have presented the complete expression for the stress tensor (3.28)–(3.34) arising from the fluctuations of the mass and energy densities. The expression for the temperature fluctuation δT_f is also given in Eq. (3.36). We have briefly reviewed the critical dynamics of the entropy and the transverse velocity in the mode coupling theory and the dynamic renormalization group theory.

In Sec. IV we have identified the nonlinear pressure fluctuation (4.1), whose slow temporal relaxation [explicitly calculated in Eqs. (4.38) and (4.39)] gives rise to the anomalous frequency-dependent bulk viscosity $\zeta_R^*(\omega)$ defined by Eq. (4.2). It may be transformed into the integral form (4.17). The frequency-dependent adiabatic compressibility $K_s^*(\omega)$ and specific heat $C_v^*(\omega)$ can be naturally introduced by Eqs. (4.4), (4.18), and (4.19). The $C_v^*(\omega)$ behaves as Eq. (4.22) in the low frequency regime and as Eqs. (4.26) and (4.27) in the high frequency regime. The Ferrell-Bhattacharjee form (4.27) is valid on the critical isochore above T_c , but $C_v^*(\omega)$ is more complex on the coexistence curve as shown in Eq. (4.26). We have also given the explicit expression for the leading nonlinear pressure fluctuation in Eq. (4.8) at long wavelength.

In Sec. V we have presented the fundamental constitutive equations (5.1)–(5.3). Note that Eq. (5.3) holds only to leading order in the critical singularity. As applications we have examined two examples. First we have calculated the density variation against an oscillatory boundary temperature in the fixed volume condition and secondly that after a small pressure jump in the isobaric condition.

In Appendix A we have summarized the relationship between the thermodynamic derivatives and the equilibrium correlation functions. In Appendix B the specific heat $(C_v)_{\text{ex}}$ in two phase coexistence below T_c has been calculated. In Appendix C the reversible stress tensor of pure fluids has been derived. In Appendix D the relation between Kawasaki's theory and our theory will be discussed. They give essentially the same results at low frequencies.

We finally make some remarks. (i) Though we have limited ourselves to pure fluids, we have shown the general mechanism of critical acoustic anomaly applicable to many near-critical systems. That is, we should first identify an energy variable m as well as the order parameter ψ in the model Hamiltonian \mathcal{H} , where m is nonlinearly coupled to ψ in \mathcal{H} as in Eq. (3.2) and has the weak critical singularity with the critical exponent α . There should be a linear term of the field variable $\delta\mathcal{H}/\delta m$ generally in the fluctuating pressure as in Eq. (3.29). It contains a bilinear term of ψ and relaxes slowly in a sound giving rise to enhanced dissipation. We should verify this scenario in other systems such as binary fluid mixtures near the consolute critical point and ^4He near the superfluid transition. (ii) As noted below Eq. (2.44), acoustic properties become much more anomalous than in one-phase states when a fluid is phase separating in the course of nucleation or spinodal decomposition. An enhanced frequency-dependent adiabatic compressibility in

such two-phase states was already calculated in Ref. [32].

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APPENDIX A

We first give some exact thermodynamic relations, which are valid even away from the critical point. To derive them we consider the grand canonical distribution of pure fluids with slowly varying temperature $T(\mathbf{r}) = T + \delta T(\mathbf{r})$ and chemical potential $\mu(\mathbf{r}) = \mu + \delta\mu(\mathbf{r})$,

$$\rho_{\text{local}} = \frac{1}{\Xi_{\text{local}}} \exp \left\{ - \int d\mathbf{r} \frac{1}{k_B T(\mathbf{r})} [\hat{e}(\mathbf{r}) - \mu(\mathbf{r}) \hat{\rho}(\mathbf{r})] \right\}. \quad (\text{A1})$$

where Ξ_{local} is the partition function in local equilibrium [51,20,21]. As in Sec. II quantities with the caret will denote dynamical variables with molecular expressions. We neglect the time dependence of all the quantities, so the time variable t will not be written explicitly. When the deviations are infinitesimal, ρ_{local} deviates from the equilibrium distribution ρ_{eq} as

$$\rho_{\text{local}} = \rho_{\text{eq}} \left\{ 1 + \int d\mathbf{r} [\delta\hat{\Omega}(\mathbf{r}) - \langle \delta\hat{\Omega}(\mathbf{r}) \rangle] \right\} \quad (\text{A2})$$

with

$$\delta\hat{\Omega}(\mathbf{r}) = \hat{e}(\mathbf{r}) \delta B(\mathbf{r}) + \hat{\rho}(\mathbf{r}) \delta\nu(\mathbf{r}), \quad (\text{A3})$$

where $\delta B = \delta T/k_B T^2$ and $\delta\nu = \delta\mu/k_B T - (\mu/k_B T^2) \delta T$ from the definitions (2.3) and (2.4). The logarithm of the local equilibrium partition function Ξ_{local} is expanded as

$$k_B \ln(\Xi_{\text{local}}) = pV/T + \int d\mathbf{r} [u \delta B + \rho \delta\nu] + \dots, \quad (\text{A4})$$

where p is the pressure and V is the volume of the system. From Eq. (2.6) the second term of Eq. (A4) is the space integral of the deviation $\delta\omega = u \delta B + \rho \delta\nu$ as ought to be the case.

The average of any local variable, say $\hat{A}(\mathbf{r})$, over ρ_{local} is expressed as

$$\langle \hat{A}(\mathbf{r}) \rangle_{\text{local}} = \langle \hat{A} \rangle + \langle \hat{A}; \hat{e} \rangle \delta B + \langle \hat{A}; \hat{\rho} \rangle \delta\nu, \quad (\text{A5})$$

where use has been made of the definition (2.10). This leads to relations between thermodynamic derivatives and variances,

$$(\partial \mathcal{A} / \partial B)_v = \langle \hat{A}; \hat{e} \rangle, \quad (\text{A6})$$

$$(\partial \mathcal{A} / \partial \nu)_B = \langle \hat{A}; \hat{\rho} \rangle. \quad (\text{A7})$$

Here $\mathcal{A} = \langle \hat{A} \rangle$ is a thermodynamic quantity. The relations (2.7)–(2.9) readily follow as special examples.

Next we rewrite Eqs. (A6) and (A7) in terms of the more usual field variables, p and T . From $\delta\nu = [\delta p - (\rho H)\delta T/T]/\rho k_B T$, H being the enthalpy per unit mass, we find

$$(\partial\mathcal{A}/\partial T)_p = \frac{\rho}{k_B T} \langle \hat{\mathcal{A}} : \hat{s} \rangle, \quad (\text{A8})$$

$$(\partial\mathcal{A}/\partial p)_T = \frac{1}{\rho k_B T} \langle \hat{\mathcal{A}} : \hat{\rho} \rangle, \quad (\text{A9})$$

where the variable \hat{s} in Eq. (A8) is defined by Eq. (2.31). We can use these relations to derive (2.32)–(2.35). As another example we set $\hat{\mathcal{A}}(\mathbf{r}) = \hat{\Pi}_{ij}(\mathbf{r})$, where $\hat{\Pi}_{ij}$ is the ij component of the stress tensor. Because $\langle \hat{\Pi}_{ij} \rangle = p \delta_{ij}$ we find

$$\langle \hat{\Pi}_{ij} : \hat{s} \rangle = 0, \quad \langle \hat{\Pi}_{ij} : \hat{\rho} \rangle = \rho k_B T \delta_{ij}, \quad (\text{A10})$$

We may then introduce the projection operator \mathcal{P}_{hyd} onto the linear part of the gross variables in the long wavelength limit. Its operation on the diagonal component $\hat{\Pi}_{ii}$ yields the hydrodynamic pressure variable

$$\delta\hat{p} = \mathcal{P}_{\text{hyd}} \delta\hat{\Pi}_{ii} = c^2 \left[\delta\hat{\rho} - \left(\frac{\partial\rho}{\partial s} \right)_p \delta\hat{s} \right]. \quad (\text{A11})$$

This variable has been discussed in the literature [28,52] and the relation $\langle \hat{p} : \hat{p} \rangle = k_B T \rho c^2$ is well known. It is known that the variance of $\hat{\Pi}_{ii}$ is larger than the variance of \hat{p} and remains nonvanishing even at the critical point [13]. More generally, for arbitrary $\hat{\mathcal{A}}(\mathbf{r})$ we obtain

$$\langle \hat{\mathcal{A}} : \hat{p} \rangle = k_B T \rho c^2 (\partial\mathcal{A}/\partial p)_s. \quad (\text{A12})$$

In Sec. II we have considered the variances involving $\hat{\rho}$, \hat{e} , and \hat{s} in the long wavelength limit. The distribution of the fluctuations of $\hat{\rho}$ and \hat{e} with wave numbers much smaller than ξ^{-1} is Gaussian of the form $\exp(-\int d\mathbf{r} \mathcal{H}_{\text{hyd}}/k_B T)$ with

$$\mathcal{H}_{\text{hyd}}/T = -\frac{1}{2} \left(\frac{\partial^2 S}{\partial \rho^2} \right) (\delta\hat{\rho})^2 - \left(\frac{\partial^2 S}{\partial \rho \partial u} \right) \delta\hat{\rho} \delta\hat{e} - \frac{1}{2} \left(\frac{\partial^2 S}{\partial u^2} \right) (\delta\hat{e})^2, \quad (\text{A13})$$

where $S = \rho s$ is the entropy per unit volume. From $dS = (du - \mu d\rho)/T$ we obtain

$$\frac{\partial^2 S}{\partial \rho^2} = -k_B \frac{\partial \nu}{\partial \rho}, \quad \frac{\partial^2 S}{\partial \rho \partial u} = -k_B \frac{\partial B}{\partial \rho}, \quad \frac{\partial^2 S}{\partial u^2} = -k_B \frac{\partial B}{\partial u}. \quad (\text{A14})$$

These thermodynamic relations again lead to Eqs. (2.7)–(2.9). Furthermore we obtain

$$T \frac{\partial}{\partial \hat{e}} \mathcal{H}_{\text{hyd}} = \left(\frac{\partial T}{\partial \rho} \right)_u \delta\hat{\rho} + \left(\frac{\partial T}{\partial u} \right)_\rho \delta\hat{e} = \frac{T}{C_v} \left[\delta\hat{s} - \left(\frac{\partial s}{\partial \rho} \right)_T \delta\hat{\rho} \right]. \quad (\text{A15})$$

This is the hydrodynamic temperature fluctuation induced by the fluctuations of the gross variables similarly to the hydrodynamic pressure fluctuation (A11). The fluctuation variance of the above quantity is $k_B T^2 / \rho C_v$ as is well known in the

literature [52]. We note that the free energy functional \mathcal{H} in Eq. (3.1) should tend to \mathcal{H}_{hyd} in the long wavelength limit or after the renormalization ($\Lambda \ll \xi^{-1}$) in equilibrium. Thus the temperature deviation δT_f defined by Eq. (3.36) should tend to Eq. (A15) in the long wavelength limit around equilibrium.

APPENDIX B

Let us consider macroscopic coexistence of a liquid region and a gas region confined in a cell with a fixed total volume V . In terms of the mass densities, ρ_ℓ and ρ_g , and the masses, M_ℓ and M_g , V may be expressed as

$$V = \frac{1}{\rho_\ell} M_\ell + \frac{1}{\rho_g} M_g. \quad (\text{B1})$$

Here quantities with the subscript ℓ (or g) are those of the liquid (or gas) phase. We then change the temperature T infinitesimally to $T + \delta T$. When V is fixed, M_ℓ and M_g change as $M_\ell \rightarrow M_\ell + \delta M_\ell$ and $M_g \rightarrow M_g + \delta M_g$. Here $\delta M_\ell + \delta M_g = 0$ and

$$\delta V = \left(\frac{1}{\rho_\ell} - \frac{1}{\rho_g} \right) \delta M_\ell + M_\ell \delta \left(\frac{1}{\rho_\ell} \right) + M_g \delta \left(\frac{1}{\rho_g} \right) = 0. \quad (\text{B2})$$

This mass transformation takes place as a mass current through the interface. Hence the thermal equilibration time in C_v measurements in two phase states is much longer than that in one phase states for the same $|T - T_c|$. Papers in Ref. [33] report or discuss abnormally long thermal relaxations in the presence of an interface separating gas and liquid regions.

In the final stage the pressure change is given by

$$\delta p = \left(\frac{\partial p}{\partial T} \right)_{\text{cx}} \delta T, \quad (\text{B3})$$

because the final state is again on the coexistence curve. Here $(\partial \dots / \partial \dots)_{\text{cx}}$ is the derivative along the coexistence curve. We are interested in the total entropy change,

$$\begin{aligned} \delta S_{\text{total}} &= (s_\ell - s_g) \delta M_\ell + M_\ell \delta s_\ell + M_g \delta s_g \\ &= M_\ell \left[\delta s_\ell - \left(\frac{\partial p}{\partial T} \right)_{\text{cx}} \delta \left(\frac{1}{\rho_\ell} \right) \right] \\ &\quad + M_g \left[\delta s_g - \left(\frac{\partial p}{\partial T} \right)_{\text{cx}} \delta \left(\frac{1}{\rho_g} \right) \right], \end{aligned} \quad (\text{B4})$$

where s_ℓ and s_g are the entropies in the two phases and use has been made of Eq. (B2). By eliminating δp using Eq. (B3) we obtain the relations

$$\delta s = \frac{1}{T} C_p \left[1 - \left(\frac{\partial p}{\partial T} \right)_{\text{cx}} \left(\frac{\partial T}{\partial p} \right)_s \right] \delta T, \quad (\text{B5})$$

$$\delta \left(\frac{1}{\rho} \right) = \frac{1}{T} C_p \left(\frac{\partial T}{\partial p} \right)_s \left[1 - \left(\frac{\partial p}{\partial T} \right)_{\text{cx}} \left(\frac{\partial T}{\partial p} \right)_\rho \right] \delta T, \quad (\text{B6})$$

where δs and $\delta(1/\rho)$ are the entropy and volume changes in the liquid (or gas) phase if the thermodynamic derivatives are those of the liquid (or gas) phase. The specific heat in two-phase coexistence per unit mass is defined by

$$(M_l + M_g)(C_v)_{\text{cx}} = T \left(\frac{\delta S_{\text{total}}}{\delta T} \right). \quad (\text{B7})$$

After some calculations we obtain

$$(M_l + M_g)(C_v)_{\text{cx}} = M_l C_{v,l} [1 + Z'_l] + M_g C_{v,g} [1 + Z'_g], \quad (\text{B8})$$

where $C_{v,l}$ and $C_{v,g}$ are the specific heat C_v in the two phases and

$$Z' = \left(\frac{C_p}{C_v} - 1 \right) \left[\left(\frac{\partial T}{\partial p} \right)_\rho \left(\frac{\partial p}{\partial T} \right)_{\text{cx}} - 1 \right]^2 = \frac{T}{\rho^3 C_v K_T} \left(\frac{\partial \rho}{\partial T} \right)_{\text{cx}}^2. \quad (\text{B9})$$

The Z'_l and Z'_g in Eq. (B8) are the values of Z' in the two phases. From Eq. (2.44) and $(\partial T/\partial p)_s = (\partial T/\partial p)_\rho (1 - C_v/C_p)$ we find $Z' \rightarrow a_c^2 \cong 1$ as $T \rightarrow T_c$ on the coexistence curve. Thus we obtain Eq. (2.45) near the critical point. The relation (B9) is equivalent to that due to Fisher [36].

APPENDIX C

We derive the reversible part of the stress tensor $\overleftrightarrow{\Pi} = \{\Pi_{ij}\}$ arising from the fluctuations of ρ and e neglecting dissipation. We consider a small fluid element at position \mathbf{r} and at time t . Due to the velocity field $\mathbf{v}(\mathbf{r}, t)$ the element is displaced to a new position, $\mathbf{r}' = \mathbf{r} + \mathbf{u}$ with $\mathbf{u} = \mathbf{v} \delta t$, after a small time interval δt . Then the density ρ is changed to ρ' as

$$\rho' \cong \rho(1 - \nabla \cdot \mathbf{u}). \quad (\text{C1})$$

On the other hand, the change of the internal energy density e is written as

$$e' \cong e(1 - \nabla \cdot \mathbf{u}) - \sum_{i,j} \Pi_{ij} \frac{\partial}{\partial x_j} u_i. \quad (\text{C2})$$

We derive the second term of Eq. (C2) by calculating the change of the total energy density $e + \frac{1}{2}\rho v^2$ in the fluid element. We can confirm that the deviation of Π_{ij} from the average $p \delta_{ij}$ ($\cong p_c \delta_{ij}$, p_c being the critical pressure) is very small and that Eq. (C2) may be further approximated by

$$e' \cong e - (e + p) \nabla \cdot \mathbf{u}. \quad (\text{C3})$$

Against these changes the Ginzburg-Landau free energy (3.1) is changed as

$$\delta \mathcal{H} = \mathcal{H}' - \mathcal{H} = - \int d\mathbf{r} \sum_{i,j} (\delta \Pi_{ij}) \frac{\partial}{\partial x_j} u_i, \quad (\text{C4})$$

which is nothing but the definition of $\delta \Pi_{ij} = \Pi_{ij} - p \delta_{ij}$. The displaced free energy is written as

$$\mathcal{H}' = k_B T_c \int d\mathbf{r}' \left[f(\rho', e') + \frac{1}{2} |\nabla' \psi'|^2 \right]. \quad (\text{C5})$$

From $\mathbf{r}' = \mathbf{r} + \mathbf{u}$ we obtain $d\mathbf{r}' = d\mathbf{r}(1 + \nabla \cdot \mathbf{u})$. The space derivatives are changed as

$$\partial / \partial x'_i \cong \partial / \partial x_i - \sum_j (\partial u_j / \partial x_i) \partial / \partial x_j. \quad (\text{C6})$$

Using these relations together with (C1) and (C2) we obtain

$$\begin{aligned} \Pi_{ij} = & \left[p + \rho \frac{\delta \mathcal{H}}{\delta \rho} + (e + p) \frac{\delta \mathcal{H}}{\delta e} - k_B T_c \left(f + \frac{1}{2} |\nabla \psi|^2 \right) \right] \delta_{ij} \\ & + k_B T_c \frac{\partial \psi}{\partial x_i} \frac{\partial \psi}{\partial x_j}, \end{aligned} \quad (\text{C7})$$

where \mathcal{H} is regarded as a functional of ρ and e in the derivatives. From this expression we can confirm that the deviation $\Pi_{ij} - p \delta_{ij}$ is very small and Eq. (C3) is surely a good approximation. Furthermore, under the linear relations (2.21) and (2.22) we notice the identity

$$\delta \rho \frac{\delta}{\delta \rho} + \delta e \frac{\delta}{\delta m} = \delta \psi \frac{\delta}{\delta \psi} + \delta m \frac{\delta}{\delta m}. \quad (\text{C8})$$

Then using $\rho = \langle \rho \rangle + \delta \rho$ and $e = u + \delta e$, we may rewrite Eq. (C7) as in Eq. (3.28) with Eqs. (3.29) and (3.34).

APPENDIX D

In the original mode coupling theory [13] the sound attenuation and dispersion are expressed in terms of complicated combinations of thermodynamic derivatives and subsequent analyses used these expressions [47,48]. Hence let us first simplify the sound attenuation per wavelength α_λ in Kawasaki's theory using the two-scale factor universality (2.48) and (3.19). It reads

$$\alpha_\lambda = 2 \pi c^2 \mathcal{A} I(\omega^*), \quad (\text{D1})$$

where

$$\mathcal{A} = \frac{k_B T^3}{2 \pi^2 \rho^3} \frac{1}{c^4 C_v^2} \left(\frac{\partial p}{\partial T} \right)_\rho^2 \kappa \left(\frac{\partial \kappa}{\partial T} \right)_s, \quad (\text{D2})$$

$\kappa = \xi^{-1}$ being the inverse correlation length. The $I(\omega^*)$ is a function of the dimensionless frequency $\omega^* = \omega/2\Gamma_\xi$ defined by

$$I(\omega^*) = \int_0^\infty dx \frac{x^2}{(1+x^2)^2} \frac{\omega^* K(x)}{K(x)^2 + (\omega^*)^2}, \quad (\text{D3})$$

where $K(x) = \frac{3}{4} [1 + x^2 + (x^3 - x^{-1}) \arctan(x)]$ is the so-called Kawasaki function. We first use Eq. (4.7) to eliminate c^2 to obtain

$$2 \pi c^2 \mathcal{A} = \left(\frac{k_B T}{\pi \rho C_v} \right) \kappa \left(\frac{\partial \kappa}{\partial T} \right)_s. \quad (\text{D4})$$

Next we set [48] $(\partial\kappa/\partial T)_s \equiv (\partial\kappa/\partial T)_\rho \equiv \nu\kappa/(T-T_c)$ on the critical isochore above T_c . Further using the relation (2.48) of the two-scale factor universality, we arrive at

$$\alpha_\lambda \equiv (\alpha\nu^2/\pi R_\xi^3)I(\omega^*), \quad (\text{D5})$$

where $R_\xi \equiv 0.25$ is defined by Eq. (2.48). For $\omega^* \ll 1$ we integrate (D3) by setting $K(x) \equiv x^2(1+x^2)^{1/2}$ following Perl and Ferrell [3] to obtain $I(\omega^*) \equiv 2\omega^*/3$. Thus,

$$\alpha_\lambda \equiv (\alpha\nu^2/3\pi R_\xi^3)\omega/\Gamma_\xi \equiv 0.27\omega/\Gamma_\xi. \quad (\text{D6})$$

The coefficient 0.27 is of the same order as our ϵ expansion value $\pi R_b = (\pi/24)\epsilon + \dots$ obtained from Eqs. (4.10) and (4.21).

Next we clarify the relationship between the mode coupling theory and our theory. The mode coupling theory [2,13] treated the time correlation function of the zero wave number component of $(1-\mathcal{P}_{\text{hyd}})\delta\Pi_{xx}$, where \mathcal{P}_{hyd} is the projection operator onto the gross variables in (A11). This

nonlinear pressure fluctuation was then approximated as a linear combination of $\psi_q\psi_{-q}$, in which the coefficient is called the vertex function V_q . Kawasaki and Tanaka [53] found microscopically that the projection of $\delta\Pi_{xx}$ onto the bilinear part of the order parameter is very small at long wavelengths, which is also the case in our Ginzburg-Landau scheme because $\delta\mathcal{H}/\delta m$ is orthogonal to any powers of ψ as is evident from Eq. (3.4). From Eqs. (A11) and (A12) it follows Kawasaki's result

$$V_q \equiv -k_B T \rho c^2 \left(\frac{\partial}{\partial p} S_q \right)_s S_q^{-2} \equiv k_B T p c^2 \left(\frac{\partial}{\partial p} k^2 \right). \quad (\text{D7})$$

Because the structure factor S_q is of the Ornstein-Zernike form at small q , V_q turns out to be independent of q . After some calculations we find that $V_q (=V_0)$ is equal to the coefficient of our nonlinear pressure Eq. (4.8) multiplied by $\gamma \equiv 2\nu$. Thus the difference is only in the coefficient and vanishes as $\epsilon \rightarrow 0$.

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