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Frequency-Dependent Bulk Viscosity in One- and Two-Component Near-Critical Fluids[1]

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We assume isomorphism between near-critical fluids and Ising spin systems to calculate the critical anomaly of transport coefficients. As an example we present a very simple and general expression for the frequency-dependent bulk viscosity $\zeta^*(\omega)$ in one- and two-component fluids near the critical point. It reads $\zeta^*(\omega) = \rho(c^2 - c_c^2)\,\mathscr{F}(i\omega/\Gamma_\xi)/i\omega$, where $\mathscr{F}(z)$ is a universal complex function, c is the zero-frequency sound velocity, c_c is its critical value, and Γ_ξ is the order parameter relaxation rate. We also examine macroscopic adiabatic relaxations of pressure, temperature, and density after stepwise changes of pressure or density. Such measurements give information on the time correlation function of the diagonal part of the stress, which relaxes anomalously slowly near the critical point.

KEY WORDS: adiabatic processes; binary fluids; bulk viscosity; critical dynamics.

1. INTRODUCTION

Isomorphism between critical behavior of fluids and that of Ising spin systems is a widely used proposition [1–3], though resultant critical singularities of various thermodynamic quantities are complicated particularly for multicomponent fluids. In Ising systems we can use a coarse-grained Ginzburg–Landau–Wilson free energy functional at the starting point of renormalization group calculations. Therefore, on the basis of the isomorphism assumption, we may develop renormalization group theories also for fluids. In this paper we point out some general relationships newly derived from this correspondence. We then apply our scheme to examine

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adiabatic processes, which have not been adequately examined in early work in critical dynamics [4]. In particular, a strong acoustic anomaly has long been observed near the critical point of classical fluids [5–9]. However, theories regarding such behavior have not been clear-cut so far, involving complicated combinations of thermodynamic derivatives [10], introducing phenomenological parameters [11], or lacking derivations from first principles [12]. Recently we have presented a renormalization group theory of critical dynamics putting emphasis on adiabatic processes for one-component fluids [13] and two-component fluids [14]. This paper briefly summarizes our results in these papers.

2. ISOMORPHISM BETWEEN FLUIDS AND ISING SYSTEMS

2.1. One-Component Fluids

For one component fluids we take $\omega = p/k_B T$ as the thermodynamic potential and

$$B = \frac{1}{k_B}\left(\frac{1}{T_c} - \frac{1}{T}\right), \qquad v = \frac{1}{k_B}\left(\frac{\mu}{T} - \frac{\mu_c}{T_c}\right) \tag{1}$$

as the independent field variables, where μ is the chemical potential per unit mass. We define them such that they vanish at the critical point by subtracting the critical values. The Gibbs–Duhem relation may be rewritten as

$$d\omega = e\, dB + \rho\, dv \tag{2}$$

so that B and v are conjugate to the internal energy density e and the mass density ρ, respectively.

We assume that B and v may be expressed as linear combinations of h and τ in Ising systems with regular coefficients, where h represents a magnetic field conjugate to the order parameter ψ and τ is the reduced temperature conjugate to the energy density m. The ψ fluctuates strongly and m weakly, being characterized by the critical exponents γ and α, respectively. The free energy functional is of the standard form,

$$\mathscr{H}\{\psi, m\} = \int d\mathbf{r}\left[\frac{1}{2}\bar{r}_0\psi^2 + \frac{1}{4}u_0\psi^4 + \frac{1}{2}K_0\,|\nabla\psi|^2 - h\psi + \frac{1}{2C_0}m^2 + \gamma_0 m\psi^2 - \tau m\right] \tag{3}$$

where $\bar{r}_0$, u_0, K_0, C_0, and γ_0 are parameters of the model and obey the well-established renormalization group equations [4, 15].

Generally, deviations of any field variables in fluids are functions of h and τ in the corresponding Ising system. For example, the average pressure and temperature deviations from the critical values are expressed as

$$\delta p \cong \left(\frac{\partial p}{\partial h}\right) h + \left(\frac{\partial p}{\partial \tau}\right) \tau \tag{4}$$

$$\delta T \cong \left(\frac{\partial T}{\partial h}\right) h + \left(\frac{\partial T}{\partial \tau}\right) \tau \tag{5}$$

Note that Eqs. (4) and (5) represent the average fields in equilibrium. However, the pressure and temperature may be extended to be dynamical variables fluctuating around the averages given in Eqs. (4) and (5). The fluctuations superposed on the averages have the following expressions in the Ginzburg–Landau scheme,

$$\delta \hat{p} = \frac{\partial p}{\partial h} \frac{\delta \mathscr{H}}{\delta \psi} + \frac{\partial p}{\partial \tau} \frac{\delta \mathscr{H}}{\delta m} \tag{6}$$

$$\delta \hat{T} = \frac{\partial T}{\partial h} \frac{\delta \mathscr{H}}{\delta \psi} + \frac{\partial T}{\partial \tau} \frac{\delta \mathscr{H}}{\delta m} \tag{7}$$

The caret above p and T is introduced to differentiate these fluctuating variables from the averages in Eqs. (4) and (5). In the long-wavelength limit or after the renormalization procedure, we may set $\delta \mathscr{H}/\delta \psi \cong \psi/\chi$ and $\delta \mathscr{H}/\delta m \cong m/C$, where $\chi(\sim \xi^{\gamma/\nu})$ is the susceptibility and $C(\sim \xi^{\alpha/\nu})$ is the specific heat of the corresponding spin system. Therefore, we obtain $\delta \hat{p} \cong (\partial p/\partial \tau)\, m/C$ and $\delta \hat{T} \cong (\partial T/\partial \tau)\, m/C$ in the long-wavelength limit, where the terms proportional to + are neglected because of the large size of χ. Using the famous fluctuation relations for the pressure and the temperature [16], we find

$$k_B T \rho c^2 = \lim_{k \to 0} \langle |\delta \hat{p}_{\mathbf{k}}|^2 \rangle \cong \left(\frac{\partial p}{\partial \tau}\right)^2 \frac{1}{C} \tag{8}$$

$$\frac{k_B T^2}{\rho C_V} = \lim_{k \to 0} \langle |\delta \hat{T}_{\mathbf{k}}|^2 \rangle \cong \left(\frac{\partial T}{\partial \tau}\right)^2 \frac{1}{C} \tag{9}$$

where $\mathbf{k}$ is the wave vector and C_V is the constant-volume specific heat. These relations have been confirmed also in the formal theory [13] and may be used to determine the coefficients $\partial p/\partial \tau$ and $\partial T/\partial \tau$ for each fluid.

2.2. Binary Mixtures

Next we consider a binary mixture near the critical line. In this case the thermodynamic state is characterized by three field variables. Let ζ be the coordinate along the critical line. Then any field variables are functions of h, τ, and ζ. Derivatives along the critical line are written as $(\partial a/\partial b)_c = (\partial a/\partial\zeta)_{h\tau}/(\partial b/\partial\zeta)_{h\tau}$ for any thermodynamic variables a and b. We assume that B and $\nu_K = \mu_K/k_B T - \mu_{Kc}/k_B T_c$ $(K = 1, 2)$ may be expressed as linear combinations of h, τ, and ζ with regular coefficients. The free energy functional is

$$\mathscr{H}\{\psi, m, q\} = \mathscr{H}\{\psi, m\} + \int d\mathbf{r}\left[\frac{1}{2Q_0}q^2 - \zeta q\right] \tag{10}$$

where $\mathscr{H}\{\psi, m\}$ is given by Eq. (3) and q is a nonsingular fluctuating variable conjugate to ζ with $\langle |q_{\mathbf{k}}|^2\rangle = Q_0$. The average pressure and temperature deviations are expressed as

$$\delta p \cong \left(\frac{\partial p}{\partial h}\right) h + \left(\frac{\partial p}{\partial \tau}\right)\tau + \left(\frac{\partial p}{\partial \zeta}\right)\zeta \tag{11}$$

$$\delta T \cong \left(\frac{\partial T}{\partial h}\right) h + \left(\frac{\partial T}{\partial \tau}\right)\tau + \left(\frac{\partial T}{\partial \zeta}\right)\zeta \tag{12}$$

The pressure and temperature fluctuations, the counterparts of Eqs. (6) and (7), read

$$\delta\hat{p} = \frac{\partial p}{\partial h}\frac{\delta\mathscr{H}}{\delta\psi} + \frac{\partial p}{\partial\tau}\frac{\delta\mathscr{H}}{\delta m} + \frac{\partial p}{\partial\zeta}\frac{\delta\mathscr{H}}{\delta q} \tag{13}$$

$$\delta\hat{T} = \frac{\partial T}{\partial h}\frac{\delta\mathscr{H}}{\delta\psi} + \frac{\partial T}{\partial\tau}\frac{\delta\mathscr{H}}{\delta m} + \frac{\partial T}{\partial\zeta}\frac{\delta\mathscr{H}}{\delta q} \tag{14}$$

The sound velocity $c = \sqrt{(\partial p/\partial\rho)_{sX}}$ is related to the pressure fluctuations as Eq. (8), so in binary mixtures we obtain

$$k_B T\rho c^2 \cong \left(\frac{\partial p}{\partial\zeta}\right)^2\frac{1}{Q_0} + \left(\frac{\partial p}{\partial\tau}\right)^2\frac{1}{C} \tag{15}$$

The sound velocity c_c at the critical point is thus related to Q_0 by $k_B T_c\rho_c c_c^2 = (\partial p/\partial\zeta)^2/Q_0$. The second term of Eq. (15) behaves as $\xi^{-\alpha/\nu}$ as in c^2 in one-componenet fluids. Similarly, the critical behavior of the specific heat C_{VX} at constant volume and composition is expressed as

$$\frac{k_B T^2}{\rho C_{VX}} \cong \left(\frac{\partial T}{\partial \zeta}\right)^2 \frac{1}{Q_0} + \left(\frac{\partial T}{\partial \tau}\right)^2 \frac{1}{C} \tag{16}$$

We may examine various crossover effects in binary fluid mixtures using Eqs. (15) and (16). For example, the derivative $(\partial T/\partial p)_c$ is nearly zero in many fluid binary mixtures near the consolute critical point (incompressible limit) [3]. In such cases, C_{VX} exhibits the weak critical singularity with the critical exponent α as Eq. (16) shows. We also note that C in Eqs. (8), (9), (15), and (16) is the specific heat at constant magnetization, to be precise. It coincides with the specific heat at constant h only for $h = 0$ (which may be assumed on the critical isochore above T_c in one-component fluids). Systematic derivations of the results in this section and more detailed discussions will appear in a forthcoming paper.

3. BULK VISCOSITY

The frequency-dependent bulk viscosity may be obtained through measurement of the sound dispersion and attenuation. For example, the sound attenuation α_λ per wavelength is given by $\alpha_\lambda \cong \pi\omega\zeta^*(0)/\rho c^2$ in the low-frequency limit, $\omega \ll \Gamma_\xi$, where ω is the acoustic frequency and c is the sound velocity. Generally, $\zeta^*(\omega)$ is the frequency-dependent bulk viscosity defined by the fluctuation-dissipation relation,

$$\zeta^*(\omega) + \frac{4}{3}\eta^*(\omega) = (k_B T)^{-1} \int_0^\infty dt\, e^{-i\omega t} \int d\mathbf{r} \langle \delta\Pi_{xx}(\mathbf{r}, t)\, \delta\Pi_{xx}(\mathbf{0}, 0)\rangle \tag{17}$$

Here, $\delta\Pi_{ij}(\mathbf{r}, t)$ is the deviation of the stress tensor variable. If $\delta\Pi_{xx}(\mathbf{r}, t)$ is replaced by $\delta\Pi_{xy}(\mathbf{r}, t)$ in Eq. (17), the expression for the frequency-dependent shear viscosity $\eta^*(\omega)$ is obtained. The $\zeta^*(\omega)$ grows strongly near the critical point and $\eta^*(\omega)$ has only weak critical singularity, so $\frac{4}{3}\eta^*(\omega)$ may be omitted on the left-hand side of Eq. (17). The relaxation of the order parameter fluctuation is characterized by the average decay rate $\Gamma_\xi \cong (k_B T/6\pi\eta)\,\xi^{-3} \propto \xi^{-\hat{z}}$ with $\hat{z} \cong 3$, where η is the shear viscosity and ξ is the correlation length growing near the critical point [4].

In one-component fluids near the gas–liquid critical point it is expressed in terms of a universal complex function $\mathscr{F}(z)$ from Ref. 13 as

$$\zeta^*(\omega) = (\rho c^2/i\omega)\, \mathscr{F}(i\omega/\Gamma_\xi) \tag{18}$$

On the critical isochore we have $\mathscr{F}(z) \cong R_{\mathrm{B}} z$ for $|z| \ll 1$, R_{B} being a universal number, so we obtain the strong anomaly,

$$\zeta^*(0) \cong R_{\mathrm{B}} \rho c^2 / \Gamma_\xi \propto \xi^{z-\alpha/\nu} \tag{19}$$

where $R_{\mathrm{B}} = \varepsilon/24 + \cdots$ in the $\varepsilon = 4 - d$ expansion on the critical isochore above T_{c} [13]. From data by Roe and Meyer [7] at 1 MHz on ^{3}He we have also obtained $R_{\mathrm{B}} \cong 0.03$. However, their data in the low-frequency regime ($\omega \ll \Gamma_\xi$) were taken in a temperature region where the background correction to the thermal diffusivity is not negligible [17], so more experiments are needed at smaller ω to determine R_{B}. In the high-frequency regime $\omega \gg \Gamma_\xi$ we obtain the Ferrell–Bhattacharjee result [12],

$$\mathscr{F}(z) \cong (z/2)^{\alpha/\nu\hat{z}} - 1 \tag{20}$$

where α and ν are the usual critical exponents and $\alpha/\nu\hat{z} \cong 0.057$.

For the bulk viscosity the dominant nonlinear pressure fluctuation is given by $(\partial p/\partial \tau)\gamma_0 \psi^2$ arising from $\delta\mathscr{H}/\delta m$ in Eq. (6) or (13). Then it is straightforward to derive an expression for the universal function $\mathscr{F}$ using the $\varepsilon = 4 - d$ expansion

$$\mathscr{F}(i\omega/\Gamma_\xi) = (\alpha/2\nu)\, i\omega C \int_0^\infty d\Lambda\, \Lambda^{3-\varepsilon} \Big/ \left\{ C_\Lambda \left(\Gamma_\Lambda + \frac{i}{2}\omega \right) (\xi^{-2} + \Lambda^2)^{2-\varepsilon/2} \right\} \tag{21}$$

Here C_Λ is the spin specific heat with the renormalization contribution from fluctuations with wave numbers larger than the cutoff Λ, so $C = \lim_{\Lambda \to 0} C_\Lambda$, while Γ_Λ is the decay rate at the wave number Λ.

In binary fluid mixtures the frequency-dependent bulk viscosity is given by a remarkably simple form,

$$\zeta^*(\omega) = [\rho c^2 - \rho_{\mathrm{c}} c_{\mathrm{c}}^2)/i\omega]\, \mathscr{F}(i\omega/\Gamma_\xi) \tag{22}$$

where $\mathscr{F}(z)$ is common to that in the one-component case. Ferrell and Bhattacharjee [12] obtained a similar result at high frequencies, where $\rho c^2 - \rho_{\mathrm{c}} c_{\mathrm{c}}^2$ in Eq. (22) is replaced by $\rho_{\mathrm{c}}\, (g c_{\mathrm{c}}^2)^2 / T C_{pX}$, where C_{pX} is the specific heat at constant p and X. It remains unclear, however, whether or not their expression $g = \rho T (\partial s/\partial p)_{\mathrm{c}}$ for the coefficient g is consistent with Eq. (22). Our result in Eq. (22) can be used even in the dilute case (where $X \ll 1$ and $c_{\mathrm{c}}^2 \propto X$) and in the nearly azeotropic case [1] (where C_{pX} grows strongly), while their result is not valid in these cases. Very recently Folk and Moser [18] have derived an expression equivalent to Eq. (22) in the scheme of renormalization group theory.

4. MACROSCOPIC ADIABATIC PROCESSES

Let us then examine adiabatic processes in binary fluid mixtures where the averages of the entropy and the concentration variables are unchanged. The nonequilibrium averages of the fluctuations of the density, pressure, and temperature are written as $\delta\bar{\rho} = \langle \delta\rho \rangle$, $\delta\bar{p} = \langle \delta\hat{p} \rangle$, and $\delta\bar{T} = \langle \delta\hat{Y} \rangle$. We may assume that they depend on time as $\exp(i\omega t)$ without loss of generality. At $\rho \cong \rho_c$ the adiabatic pressure–density relation reads

$$\delta\bar{p} = [c^2 + (c^2 - c_c^2)\,\mathscr{F}(i\omega/\Gamma_\xi)]\,\delta\bar{\rho} \tag{23}$$

The adiabatic temperature deviation is given by

$$\delta\bar{T} = A_c\,\delta\bar{p} + (B_c - A_c)\,c_c^2\,\delta\bar{\rho} \tag{24}$$

where

$$A_c = (\partial T/\partial\tau)/(\partial p/\partial\tau) = (\partial T/\partial p)_{h\zeta} \tag{25}$$

$$B_c = (\partial T/\partial\zeta)/(\partial p/\partial\zeta) = (\partial T/\partial p)_c \tag{26}$$

Use has been made of Eqs. (13) and (14). Experimentally the difference $A_c - B_c$ may be estimated from the relation, $(c^2 - c_c^2)\,C_{pX} \cong (T/\rho^2)/(A_c - B_c)^2$, valid near the critical line, for example.

We propose two experiments on near-critical binary mixtures other than acoustic measurements. See Ref. 13 for such experiments in one-component fluids. First, let us change the average density at $t = 0$ by a small amount ρ_1 in a stepwise manner. Then the pressure change is

$$\delta\bar{p}(t)/\rho_1 = c^2 + \rho^{-1}G_{xx}(t) = c_c^2 + (c^2 - c_c^2)[1 + G(\Gamma_\xi t)] \tag{27}$$

where $G_{xx}(t)$ is the time correlation function of the zero-wave number component of Π_{xx} divided by $k_B T$ or its Laplace transform is $\zeta^*(\omega)$ from Eq. (17). Then

$$G(\Gamma_\xi t) = G_{xx}(t)/\rho(c^2 - c_c^2) \tag{28}$$

is a universal function of $\Gamma_\xi t$ common to one- and two-component fluids. As shown in Fig. 1,

$$G(x) \cong x^{-\alpha/\nu z} - 1 \tag{29}$$

for $x \ll 1$ and

$$G(x) \sim (\alpha/2\nu)\,x^{-3/2} \tag{30}$$

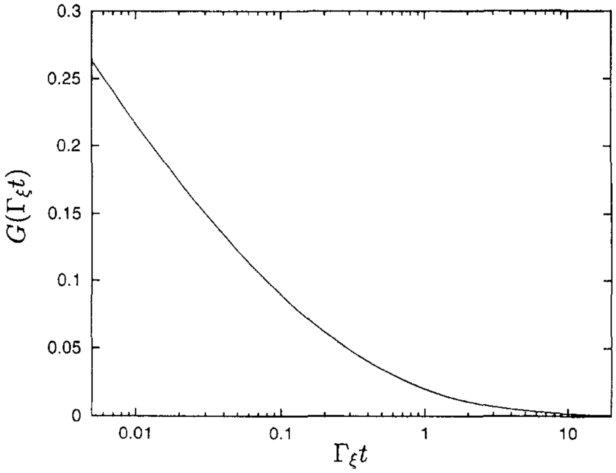

Fig. 1. The dimensionless stress correlation function $G(\Gamma_\xi t) = G_{xx}(t)/\rho(c^2 - c_c^2)$, which is a universal function of $\Gamma_\xi t$.

for $x \gg 1$. However, for one-component fluids [19], another adiabatic effect, called the piston effect, due to the presence of isothermal boundaries gives rise to a larger pressure change and the above expression, Eq. (27), cannot be used. Thus, we propose this experiment for a near-critical binary mixture.

Second, we change the average pressure at $t = 0$ by a small amount p_1 in a stepwise manner. Then, we expect slow relaxation of the density as

$$\delta\bar{\rho}(t) = \hat{K}(t)\, p_1/c^2 \tag{31}$$

where the Laplace transform of the relaxation function $\hat{K}(t)$ is written as

$$\int_0^\infty dt\, e^{-i\omega t}\hat{K}(t) = 1/\{i\omega[1 + (1 - c_c^2/c^2)\,\mathscr{F}(i\omega/\Gamma_\xi)]\} \tag{32}$$

The temperature also relaxes in the same manner due to the second term in Eq. (24). For $\Gamma_\xi t \ll 1$, $\hat{K}(t)$ quickly grows close to 1 as

$$\hat{K}(t) \cong c^2/[c_c^2 + (c^2 - c_c^2)(\Gamma_\xi t)^{-\alpha/\nu z}] \tag{33}$$

For $\Gamma_\xi t \gg 1$ we have

$$\hat{K}(t) \cong 1 - \zeta(t)/\rho c^2 \tag{34}$$

so $\hat{K}(t)$ has also a long tail decaying as $t^{-3/2}$.

5. SUMMARY

We have presented a first systematic theory of the critical bulk viscosity with very simple and general expressions on the basis of the isomorphism between fluids and Ising systems. We also point out that adiabatic temperature and pressure changes in the course of phase separation are closely related effects, which have begun to be investigated very recently [20, 21].

NOTE ADDED IN PROOF

We can also calculate the transient behavior of the light scattering amplitude from a near-critical binary mixture after an adiabatic pressure change. Such an experiment was already performed in Ref. 22.

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