

Bulk Viscosity near the Critical Point

Akira ONUKI

Department of Physics, Kyoto University, Kyoto 606-01

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An intuitive derivation of the critical bulk viscosity is presented for one- and two-component fluids in a general form. In addition to critical acoustics, we examine slowly relaxing pressure, temperature, and density relaxations after stepwise volume or pressure changes. Their measurement will yield information of the time correlation function on the diagonal part of the stress.

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The critical behavior of the bulk viscosity near the critical point of classical fluids is known to be very singular.^{1,2)} However, theories regarding such behavior are not clear-cut, involving complicated combinations of thermodynamic derivatives,³⁾ introducing phenomenological parameters,⁴⁾ or lacking derivations from first principles.⁵⁾ One reason for such inadequacy is that no exact expression for the relevant part of the stress tensor induced by the critical fluctuations has been derived. Another reason is that important renormalization contributions to the critical bulk viscosity arise from the order-parameter fluctuations with wave numbers much larger than the inverse correlation length, and hence a dynamic renormalization group theory is needed to properly account for the effect. Recently we developed a renormal-

ization group theory of one-component fluids near the gas-liquid critical point with emphasis on adiabatic processes to derive the frequency-dependent bulk viscosity.⁶⁾ Because this theory is complex, we present in this letter first an intuitive derivation of the bulk viscosity for one-component fluids. Then we generalize our arguments for the case of binary mixtures and make some new predictions.

Bulk viscosity has been measured indirectly through measurement of sound 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

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

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 (1), the expression for the frequency-dependent shear viscosity $\eta^*(\omega)$ is obtained. Because $\zeta^*(\omega)$ grows strongly near the critical point, we may neglect $\eta^*(\omega)$, whose critical singularity is very weak, and the background bulk viscosity. 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.⁷⁾ In one-component fluids near the gas-liquid critical point it is expressed in terms of a universal complex function $\mathcal{F}(z)$ by⁶⁾

$$i\omega\zeta^*(\omega) = \rho c^2 \mathcal{F}(i\omega/\Gamma_\xi). \quad (2)$$

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

$$\zeta^*(0) \cong R_B \rho c^2 / \Gamma_\xi \propto \xi^{z-\alpha/\nu}, \quad (3)$$

where $R_B = \epsilon/24 + \dots$ in the $\epsilon = 4 - d$ expansion.⁶⁾ From data by Roe and Meyer⁸⁾ at 1 MHz on ³He we have also

obtained $R_B \cong 0.03$. 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,⁹⁾ so more experiments are needed to reliably determine R_B . In the high frequency regime $\omega \gg \Gamma_\xi$ we obtain the Ferrell-Bhattacharjee result⁵⁾

$$\mathcal{F}(z) \cong (z/2)^{\alpha/\nu\hat{z}} - 1, \quad (4)$$

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

To treat complicated critical behavior in fluids we start with the assumption of isomorphism between fluids and Ising spin systems.¹⁰⁻¹²⁾ That is, in one-component fluids, the deviations of field variables such as the pressure p and the temperature T are assumed to be functions of the two relevant fields, h and τ , in Ising systems. Here h is the magnetic field and $\tau (\propto T - T_c)$ is the reduced temperature. For example,

$$\delta p \cong \left(\frac{\partial p}{\partial h} \right) h + \left(\frac{\partial p}{\partial \tau} \right) \tau, \quad (5)$$

$$\delta T \cong \left(\frac{\partial T}{\partial h} \right) h + \left(\frac{\partial T}{\partial \tau} \right) \tau. \quad (6)$$

In Ising systems the conjugate fluctuating variables of h

$$\mathcal{H} = \int d\mathbf{r} \left[\frac{1}{2} \bar{r}_0 \psi^2 + \frac{1}{4} u_0 \psi^4 + \frac{1}{2} K_0 |\nabla \psi|^2 - h \psi + \frac{1}{2C_0} m^2 + \gamma_0 m \psi^2 - \tau m \right], \quad (7)$$

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.¹³⁾

Note that (5) and (6) represent the average fields in equilibrium. However, the pressure and temperature are dynamical variables fluctuating around the averages (5) and (6). The fluctuations superposed on the averages have the following expressions in the Ginzburg-Landau scheme:

$$\delta \hat{p} = \frac{\partial p}{\partial h} \frac{\delta \mathcal{H}}{\delta \psi} + \frac{\partial p}{\partial \tau} \frac{\delta \mathcal{H}}{\delta m}, \quad (8)$$

$$\delta \hat{T} = \frac{\partial T}{\partial h} \frac{\delta \mathcal{H}}{\delta \psi} + \frac{\partial T}{\partial \tau} \frac{\delta \mathcal{H}}{\delta m}. \quad (9)$$

The caret on p and T is introduced to differentiate these fluctuating variables from the averages (5) and (6). In the long wavelength limit or after the renormalization procedure, we may set $\delta \mathcal{H}/\delta \psi \cong \psi/\chi$ and $\delta \mathcal{H}/\delta m \cong m/C$, where $\chi (\sim \xi^{1/\nu})$ 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 ψ are neglected because of the large size of χ . Using the famous fluctuation relations for the pressure and the temperature¹⁴⁾ we find

$$k_B T \rho c^2 = \lim_{k \rightarrow 0} \langle |\delta \hat{p}_k|^2 \rangle \cong \left(\frac{\partial p}{\partial \tau} \right)^2 \frac{1}{C}, \quad (10)$$

$$k_B T^2 / \rho C_V = \lim_{k \rightarrow 0} \langle |\delta \hat{T}_k|^2 \rangle \cong \left(\frac{\partial T}{\partial \tau} \right)^2 \frac{1}{C}, \quad (11)$$

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 theory⁶⁾ and may be used to determine the coefficients $\partial p/\partial \tau$ and $\partial T/\partial \tau$ for each fluid. To the bulk viscosity expression (1), the dominant nonlinear pressure fluctuation is given by $(\partial p/\partial \tau) \gamma_0 \psi^2$ arising from $\delta \mathcal{H}/\delta m$ in (8). Then it is straightforward to derive an expression for the universal function \mathcal{F} using the $\epsilon = 4 - d$ expansion

$$\mathcal{F}(i\omega/\Gamma_\xi) = (\alpha/2\nu) i\omega C \int_0^\infty d\Lambda \Lambda^{3-\epsilon} \left/ \left\{ C_A (\Gamma_A + \frac{i}{2}\omega) (\xi^{-2} + \Lambda^2)^{2-\epsilon/2} \right\} \right. \quad (12)$$

Here C_A is the spin specific heat with the renormalization contribution from fluctuations with wave numbers larger than the cut-off Λ , so $C = \lim_{\Lambda \rightarrow 0} C_A$, while Γ_A is the decay rate at the wave number Λ .

Next we consider a binary mixture near the critical line. In this case the thermodynamic state is characterized by three field variables.¹⁰⁾ Let w be the coordinate along the critical line. Then, p and T are functions of h , τ , and w . Derivatives along the critical line are written as $(\partial a/\partial b)_c = (\partial a/\partial w)_{h\tau} / (\partial b/\partial w)_{h\tau}$ for any thermodynamic variables a and b . The pressure and temperature fluctuations, the counterparts of (8) and (9), read

$$\delta \hat{p} = \frac{\partial p}{\partial h} \frac{\delta \mathcal{H}}{\delta \psi} + \frac{\partial p}{\partial \tau} \frac{\delta \mathcal{H}}{\delta m} + \frac{\partial p}{\partial w} Q, \quad (13)$$

$$\delta \hat{T} = \frac{\partial T}{\partial h} \frac{\delta \mathcal{H}}{\delta \psi} + \frac{\partial T}{\partial \tau} \frac{\delta \mathcal{H}}{\delta m} + \frac{\partial T}{\partial w} Q, \quad (14)$$

where Q is a nonsingular fluctuating variable conjugate to w in the spin system. Its variance $R_0 = \lim_{k \rightarrow 0} \langle |Q_k|^2 \rangle$ is related to the sound velocity c_c at the critical point by

$$k_B T_c \rho c_c^2 = (\partial p/\partial w)^2 R_0, \quad (15)$$

so $c^2 - c_c^2 \propto \xi^{-\alpha/\nu}$. The frequency-dependent bulk viscosity in binary fluid mixtures is then given by a remarkably simple form,

$$i\omega \zeta^*(\omega) = \rho (c^2 - c_c^2) \mathcal{F}(i\omega/\Gamma_\xi), \quad (16)$$

where $\mathcal{F}(z)$ is common to that in the one-component case. Ferrell and Bhattacharjee⁵⁾ obtained a similar result at high frequencies, where $c^2 - c_c^2$ in (16) is replaced by $(gc_c^2)^2 / T C_{pX}$, where C_{pX} is the specific heat at constant p and X . However, their expression $g = \rho T (\partial s/\partial p)_c$ for the coefficient g is not consistent with (16) in general. Our result (16) can be used even in the dilute case (where $X \ll 1$ and $c_c^2 \propto X$) and in the nearly azeotropic case¹⁰⁾ (where C_{pX} grows strongly).

Let us then examine adiabatic processes where the averages of the entropy and the concentration variables are unchanged. The nonequilibrium averages of the deviations of the density, pressure, and temperature are written as $\delta \bar{\rho}$, $\delta \bar{p}$, and $\delta \bar{T}$. We may assume that they depend on time as $\exp(i\omega t)$ without loss of generality. The adiabatic pressure-density relation reads

$$\delta \bar{p} = \left[c^2 + (c^2 - c_c^2) \mathcal{F}(i\omega/\Gamma_\xi) \right] \delta \bar{\rho}. \quad (17)$$

The adiabatic temperature deviation is given by

$$\delta \bar{T} = A \delta \bar{p} + (B - A) c_c^2 \delta \bar{\rho}, \quad (18)$$

where

$$A = (\partial T/\partial \tau) / (\partial p/\partial \tau) = (\partial T/\partial p)_{hw}, \quad (19)$$

$$B = (\partial T/\partial p)_{h\tau} = (\partial T/\partial p)_c. \quad (20)$$

Use has been made of (13) and (14). Experimentally the difference $A - B$ may also be estimated from the following

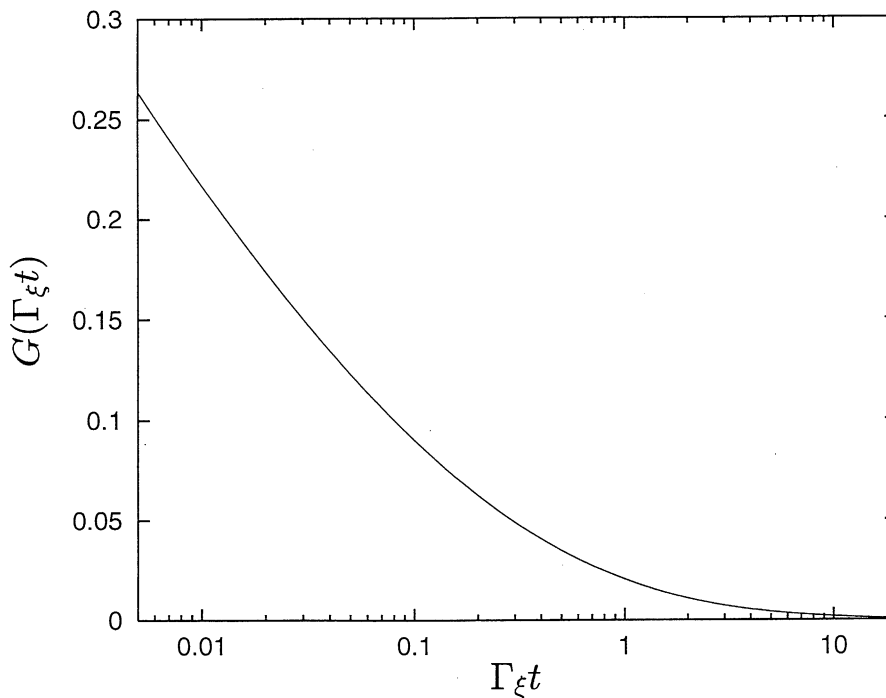


Fig. 1. The dimensionless stress correlation function $G(\Gamma_\xi t) = G_{xx}(t)/\rho(c^2 - c_c^2)$, which is a universal function of $\Gamma_\xi t$.

relation, for example,

$$(c^2 - c_c^2)C_{pX} \cong (T/\rho^2)/(A - B)^2, \quad (21)$$

which holds near the critical line.

Finally we propose two experiments on near-critical binary mixtures aside from acoustic measurements. See ref. 6 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

$$\begin{aligned} \delta\bar{p}(t)/\rho_1 &= c^2 + \rho^{-1}G_{xx}(t) \\ &= c_c^2 + (c^2 - c_c^2) \left[1 + G(\Gamma_\xi t) \right], \end{aligned} \quad (22)$$

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 (1). See the sentences below (1). Then $G(\Gamma_\xi t) = G_{xx}(t)/\rho(c^2 - c_c^2)$ is a universal function of $\Gamma_\xi t$ common to one- and two-component fluids. As shown in Fig. 1, $G(x) \cong x^{-\alpha/\nu z} - 1$ for $x \ll 1$ and $G(x) \sim (\alpha/2\nu)x^{-3/2}$ for $x \gg 1$ as in one-component fluids.⁶⁾ However, for one-component fluids, another adiabatic effect, called the piston effect,¹⁵⁾ due to the presence of isothermal boundaries is crucial and the above expression (22) cannot be used. Secondly, 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

$$\delta\bar{p}(t) = \hat{K}(t)p_1/c^2, \quad (23)$$

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

$$\int_0^\infty dt e^{-i\omega t} \hat{K}(t) = 1 / \left\{ i\omega \left[1 + (1 - c_c^2/c^2) \mathcal{F}(i\omega/\Gamma_\xi) \right] \right\}. \quad (24)$$

The temperature also relaxes in the same manner due to the second term of (18). For $x = \Gamma_\xi t \ll 1$, $\hat{K}(t)$ quickly grows close to 1 as $c^2/[c_c^2 + (c^2 - c_c^2)x^{-\alpha/\nu z}]$. For $x \gg 1$ we have $\hat{K}(t) \cong 1 - \zeta(t)/\rho c^2$, so $\hat{K}(t)$ has also a long tail decaying as $t^{-3/2}$.

We have presented a first systematic theory of the critical bulk viscosity with very simple and general expressions. As a closely related effect we also remark that slow adiabatic temperature changes have been observed in binary mixtures undergoing spinodal decomposition after a pressure jump.^{16,17)} We will study such adiabatic effects in spinodal decomposition in a forthcoming paper.

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