

### Dynamic scaling theory for the critical ultrasonic attenuation in a binary liquid

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A theory of critical ultrasonic attenuation in binary liquids based on the frequency-dependent specific heat is presented. Excellent agreement with experiment, without any adjustable parameters, is found for the frequency dependence of the consolute point attenuation and for the temperature dependence away from the consolute point. The latter is exhibited for two different mixtures at several different frequencies.

Because of the absence of strains, fluids have sharp second-order phase transitions and consequently provide excellent tests for theories of critical phenomena. A special feature of the binary liquids is that they can be chosen so as to match the index of refraction of the components. In this way the problem of multiple scattering is eliminated, making possible a thorough and complete study of both the statics and dynamics by means of light scattering. Such a binary system, 3-methylpentane–nitroethane, has been examined in great detail in this laboratory. The equal-time correlation function and anomalous dimension critical index have been measured. The experimental value<sup>1</sup> of  $0.03 \pm 0.02$  is in satisfactory agreement with our sum rule value<sup>2</sup> of 0.04. The slight deviation<sup>3</sup> of the concentration fluctuations from exponential decay is exactly accounted for by our theoretical calculations.<sup>4</sup> Furthermore, the role of the critical viscosity<sup>5,6</sup> in the dynamic scaling of the Rayleigh linewidth has been verified precisely.<sup>7,8</sup> The purpose of this Communication is to point out that with this basic information at hand, it is possible to *predict* an important remaining dynamic critical property, namely, the ultrasonic attenuation. In fact, we will demonstrate that the theory that we present here is in excellent agreement with the recent measurements by Harada *et al.*<sup>9</sup> of the attenuation in 3-methylpentane–nitroethane.

Our theory of the ultrasonic attenuation differs from that of Kawasaki<sup>10</sup> and of Kroll and Ruhland<sup>11</sup> in that it contains no adjustable parameters. A more fundamental difference is that we do not attempt to calculate a bulk viscosity from pressure fluctuations. In such an approach it is difficult to take into account the constraint of constant entropy. Our theory is instead based on the temperature fluctuations resulting from the alternate adiabatic compression and expansion of the fluid. This effect was noted by Laplace<sup>12</sup> and was later made the cornerstone of the relaxation theory of ultrasonic attenuation by Herzfeld and Rice.<sup>13</sup> A complex frequency-dependent specific heat, representing the lagging response of the internal degrees of freedom, gives hysteresis and energy dissipation.

We use the same idea here with, however, the “internal” degrees of freedom being the Fourier components of the order parameter (concentration) rather than vibrational modes within the molecules. In spirit, our approach is similar to that of Fixman.<sup>14</sup> In practice, we have had more success in implementing the idea because of a more realistic choice of the frequency-dependent specific heat.

We begin by reviewing briefly the theory of the critical sound velocity in the thermodynamic limit. Assume for the moment that a change in the pressure  $P$  produces a shift in the critical temperature  $T_c$  but not in the critical concentration. This means that the concentration is not directly coupled to the pressure changes, and that we can limit ourselves to the two independent thermodynamic variables  $P$  and  $T$ . The critical point traces out a  $\lambda$  line described by the function  $T_\lambda(P)$ . It is advantageous to change from the variables  $P$  and  $T$  to  $P$  and  $\Delta T \equiv T - T_\lambda(P)$ . Integrating away from the  $\lambda$  line at constant pressure gives the Gibbs function

$$G(P, \Delta T) = G_\lambda(P) - \int_0^{\Delta T} S d\Delta T \quad (1)$$

All extensive quantities correspond to unit mass. The volume is

$$\begin{aligned} V &= \left( \frac{\partial G}{\partial P} \right)_T = \left( \frac{\partial G}{\partial T} \right)_{\Delta T} + \left( \frac{\partial \Delta T}{\partial P} \right)_T \left( \frac{\partial G}{\partial \Delta T} \right)_P \\ &= \left( \frac{\partial G}{\partial P} \right)_{\Delta T} - T'_\lambda \left( \frac{\partial G}{\partial \Delta T} \right)_P \\ &= G'_\lambda + ST'_\lambda - S'_\lambda \Delta T \quad (2) \end{aligned}$$

Further differentiation at constant  $S$  gives

$$-\frac{\delta V}{V} = \beta_\lambda \delta P + g \frac{\delta \Delta T}{T_\lambda} \quad (3)$$

where, close to the  $\lambda$  line,  $V\beta_\lambda \approx G''_\lambda + S_\lambda T''_\lambda$ . The dimensionless coupling constant is  $g = T_\lambda S'_\lambda / V_\lambda$ . Critical behavior enters Eq. (3) only through the fluctuation in  $\Delta T$ . This is related to the impressed pres-

sure fluctuation by the isentropic condition

$$0 = T \delta S' = T \left( \frac{\partial S}{\partial P} \right)_{\Delta T} \delta P + T \left( \frac{\partial S}{\partial T} \right)_P \delta \Delta T$$

$$\approx T_\lambda S'_\lambda \delta P + C_p \delta \Delta T \quad (4)$$

It follows that

$$\delta \Delta T = -g \frac{V_\lambda}{C_p} \delta P \quad (5)$$

which substituted into Eq. (3), gives for the sound velocity  $v$

$$\frac{1}{v^2} = -\frac{1}{V^2} \left( \frac{\partial V}{\partial P} \right)_S = -\frac{1}{V^2} \frac{\delta V}{\delta P} = \frac{1}{u_c^2} - \frac{g^2}{T_\lambda} \frac{1}{C_p} \quad (6)$$

where  $u_c$  is the velocity at the critical point. Let  $u$  be the small critical part. The critical fraction from Eq. (6) is approximately

$$\frac{u}{u_c} \approx -\frac{g^2}{2} \frac{u_c^2}{T_c B^2} \Delta C \quad (7)$$

Here we have substituted  $C_p^{-1} = (B + \Delta C)^{-1} \approx B^{-1} - B^{-2} \Delta C$  and have dropped the first term. The approximation is justified by  $\Delta C \ll B$ , where  $B$  is the large-constant-background specific heat and  $\Delta C$  is the small critical portion.

Elsewhere<sup>15</sup> we have studied the more general problem posed by a pressure dependence of the critical concentration. The  $\lambda$  line then becomes a curve in the three-dimensional variable space of  $T$ ,  $\mu$ , and  $P$ . It is specified parametrically by the functions  $T_\lambda(P)$  and  $\mu_\lambda(P)$ , where the latter is the chemical potential along the  $\lambda$  line. We find in this more general case that Eq. (7) is still valid, where, however, the coupling constant is now  $g = (T_\lambda/V_\lambda) [S'_\lambda + c'_\lambda (\partial \mu / \partial T)_c]$ .  $c_\lambda(P)$  is the critical concentration along the  $\lambda$  line and the thermodynamic derivative accompanying it is taken along the critical isochore at constant pressure.

We make contact with the critical dynamics of the fluid by recalling that the relaxation rate of a concentration fluctuation of wave number  $k$  is  $k^2 D$ , where the critical diffusion coefficient is  $D(\xi) = k_B T_c / (6\pi\eta\xi)$ .  $k_B$ ,  $\eta$ ,  $\xi = \xi_0 t^{-2/3}$ , and  $t = (T - T_c)/T_c$  are Boltzmann's constant, the shear viscosity, the correlation length, and the reduced temperature, respectively. The energy decay rate of a fluctuation at  $k = \xi^{-1}$  gives consequently the characteristic temperature-dependent relaxation rate

$$\gamma = 2\xi^{-2} D(\xi) = \frac{k_B T_c}{3\pi\eta\xi_0^3} t^2 = \gamma_0 t^2 \quad (8)$$

Equation (8) enables us to eliminate  $t$  in terms of  $\gamma$ , as the variable that indicates how close the system is to the critical point. The temperature- and frequency-dependent specific heat becomes, thereby,

the function  $\Delta C(\gamma, \omega)$ . The thermodynamic ( $\omega = 0$ ) limit is

$$\Delta C(\gamma, 0) = A t^{-\alpha_0} = A \left( \frac{\gamma_0}{\gamma} \right)^{\alpha_0/2} \quad (9)$$

We can immediately go to the opposite limit of  $\gamma \rightarrow 0$  by means of the dynamic-scaling requirement<sup>16</sup> that the dependence of Eq. (9) on  $\gamma$  disappears when  $\gamma$  becomes less than  $\omega$ .  $\gamma$  is then replaced by  $-i\omega$  so that the frequency-dependent specific heat at the critical point is

$$\Delta C(0, \omega) = \Delta C(-i\omega, 0) = A \left( \frac{\gamma_0}{-i\omega} \right)^{\alpha_0/2}$$

$$= A e^{i\pi\alpha_0/2} \left( \frac{\gamma_0}{\omega} \right)^{\alpha_0/2} \quad (10)$$

[As seen below, a numerical factor of order unity enters upon replacing  $\gamma$  by  $-i\omega$ . But this has only a negligible 10% effect on Eq. (10).]

Substitution of Eq. (10) into Eq. (7) gives the complex critical velocity components  $u_1 + iu_2$ . The negative imaginary part corresponds to the attenuation per wavelength

$$\alpha_c \lambda_c = -2\pi \frac{u_2}{u_c} = \frac{\pi g^2 u_c^2 A}{T_c B^2} \sin \frac{\pi\alpha_0}{2} \left( \frac{\gamma_0}{\omega} \right)^{\alpha_0/2}$$

$$\approx \frac{\pi^2 \alpha_0 g^2 u_c^2 A}{2T_c B^2} \left( \frac{\gamma_0}{2\pi} \right)^{\alpha_0/2} f^{-\alpha_0/2} \quad (11)$$

where  $f = \omega/2\pi$  is the frequency. Multiplying Eq. (11) by  $(u_c f)^{-1}$  predicts a linear proportionality between  $\alpha_c/f^2$  and  $f^{-1-\alpha_0/2}$ . Figure 1 shows such a plot for the data of Harada *et al.*,<sup>9</sup> with  $\alpha_0 = 0.12$ . The good straight-line fit is excellent confirmation of the frequency dependence predicted by Eq. (11). The monotonic decrease contrasts with the increase

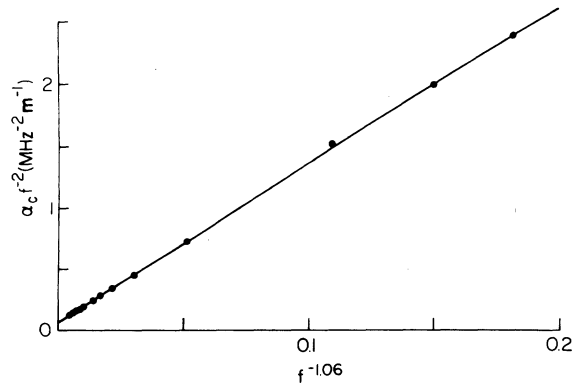


FIG. 1.  $\alpha_c/f^2$  vs  $f^{-1-\alpha_0/2}$  where  $\alpha_c$  is the critical-point attenuation,  $f$  the frequency, and  $\alpha_0 = 0.12$  the specific-heat exponent. The linear fit confirms the theory and the intercept determines the background attenuation.

in  $\alpha_c \lambda_c$  for the monatomic gasses<sup>17</sup> (except for <sup>3</sup>He). This is because of the relatively small critical specific heat in the binary liquids, which permits bringing  $\Delta C$  up into the numerator. The  $f \rightarrow \infty$  intercept in Fig. 1 determines the background attenuation [not included in Eq. (11)] as  $\alpha_c^B = 0.070 f^2 \text{ m}^{-1}$  when  $f$  is measured in MHz. The slope of the straight-line fit in Fig. 1 can be compared to that predicted from Eq. (11). Rayleigh linewidth measurements<sup>7</sup> give  $\gamma_0/2\pi = 15$  GHz, while Brillouin scattering<sup>18</sup> provides  $u_c = 10^3$  m/sec. Unfortunately, specific-heat measurements are lacking. This forces us to interpolate  $B = 1.7$  J/gK between the pure components and to estimate  $A = 0.22$  J/gK from  $\xi_0 = 2.2 \text{ \AA}$  and two-scale factor universality. Even more uncertainty is associated with the value of  $g$ . A recent preliminary thermodynamic determination in this laboratory<sup>19</sup> gave  $g = 0.5 \pm 0.2$ . The slope in Fig. 1 is at the lower end of the range predicted by these numbers. Alternatively, we can use the experimental slope to infer  $g = 0.3$ , in satisfactory accord with the thermodynamic value. Once actual measurements are made of  $A$  and  $B$ , the ultrasonic attenuation may prove to be the most convenient and accurate method of determining  $g$ .

In the approach to the critical point the attenuation relative to its critical point value,  $\alpha/\alpha_c$ , rises monotonically as a function of the reduced frequency  $\Omega = \omega/\gamma$ . The calculation of the scaling function for this onset is a straightforward technical task which we have solved for the  $\lambda$  transition<sup>19</sup> in liquid <sup>4</sup>He by means of the  $\epsilon$  expansion. Because of the conserved order in the present case the distribution of relaxation rates extends down to zero rather than having a finite threshold value as for the  $\lambda$  transition. The lowest-order  $\epsilon$  expansion gives a weighting of the modes that leads to a scaling function of the form

$$\frac{\alpha}{\alpha_c} = \frac{2}{\pi} (1+p) \Omega \int_0^\infty \frac{u du}{(u+1)^2} \frac{u(1+u)^p}{\Omega^2 + u^2(1+u)^{2p}} \quad (12)$$

( $\sqrt{u}$  corresponds to the wave number of a relaxing order-parameter fluctuation). The parameter  $p$  in the relaxational factor of the integrand is equal to one in the  $\epsilon \rightarrow 0$  limit. The resulting integral has been exhibited in terms of elementary functions [ $L_2$  of Eq.

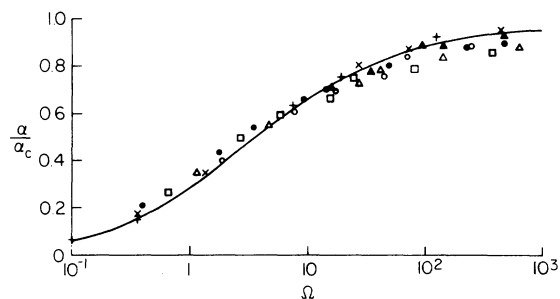


FIG. 2. Attenuation relative to the critical point vs reduced frequency  $\Omega = \omega/\gamma$ . The theoretical curve corresponds to Eq. (12). 3-methylpentane-nitroethane (Ref. 9) data: ●—16.5; □—27; △—48; ○—80; ▲—165. 2,2,4-trimethylpentane-nitrobenzene (Ref. 20) data: +—3; X—11. (All frequencies in MHz.)

(11) of Ref. 17]. Here, however, we use  $p = \frac{1}{2}$ , which is more appropriate for the three-dimensional fluid and which yields the curve shown in Fig. 2. The agreement with the scaled data of Harada *et al.* at various frequencies ranging from 16.5 to 165 MHz is seen to be excellent. We emphasize that this results *without any adjustable parameter*. The frequency scale is already set by  $\gamma_0/2\pi = 15$  GHz, as determined *a priori* from the Rayleigh linewidth. Also shown in Fig. 2 are recent data of Fenner<sup>20</sup> at 3 and 11 MHz in 2,2,4-trimethylpentane-nitrobenzene, for which we take  $\gamma_0/2\pi = 2.67$  GHz.

To summarize, we have demonstrated that the thermal-lag effect, supplemented by dynamic-scaling considerations, gives an excellent account of the experimentally observed critical ultrasonic attenuation in a binary liquid. This agreement results without the use of any fitting parameters, because all of the constants of the system are known *a priori*.

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