Dynamic universality and the critical sound velocity in a binary liquid

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The absence of any critical temperature variation in the measured ultrasonic velocity in binary liquids is in apparent contradiction to the universally occurring critical behavior of all other types of fluids. We establish quantiatively that critical behavior must exist in binary liquids at sufficiently low but experimentally accessible frequencies.

The critical dynamics of the binary liquids have been under intensive study[1] lately, with special attention given to universality.[2,3] Because of the absence of strains, the binary liquids have sharp phase transitions at their consolute temperatures T_c. They consequently offer very precise tests of universality for the class $n=1$ (scalar order parameter). It is therefore a disturbing discrepancy that no critical temperature dependence has ever been observed in the sound velocity of binary liquids. This stands in sharp contrast to the widely observed critical variation of the velocity in the single-component fluids,[4,5] which are presumed to belong to the same universality class and for which a successful theory[6] has been advanced. The purpose of this note is to clarify this puzzlement and to offer guidance leading to experimental verification of the critical variation, which we claim *must exist.* Our quantitative prediction is presented on two levels: (a) general phenomenological arguments based on causality and dynamic scaling[7]; and (b) a totally new approach to the thermodynamics of binary liquids which supports and provides deeper understanding for (a).

We begin purely phenomenologically by noting a regularity in the measurements by Harada *et al.*[8] of the ultrasonic attenuation at $T=T_c$, the consolute point of 3-methylpentane-nitroethane. The attenuation in one wavelength, $\alpha\lambda$, is $-2\pi u_2/u_c$, where u_c is the zero-frequency sound velocity at the consolute point. $u=u_1+iu_2$ is the small complex critical component superposed on u_c. After subtraction of a background $7\times10^{-5}f$, where $f=\omega/2\pi$ is the frequency in MHz, we find the critical frequency variation $-2\pi u_2/u_c=0.014f^{-0.06}$ shown by the lower line in Fig. 1. Because u corresponds to a casual response function, its real and imaginary parts are related by the Kramers-Kronig relations.[9] It follows that $-u_1/u_c$ must have the same power-law dependence upon f, with the ratio of real-to-imaginary parts the same as that for $\exp(0.06\pi i/2)$—namely, $\cot(0.03\pi)\simeq(0.03\pi)^{-1}$. This enables us to draw the upper line in Fig. 1 for $-u_1/u_c$ with a slope greater than the lower one by the factor $(0.06\pi^2)^{-1}=1.6$.

The T_c frequency dependence is fixed. We now use dynamic scaling[7] to infer the critical dependence of the thermodynamic ($f=0$) velocity on the reduced temperature $t=(T-T_c)/T_c$. From Rayleigh linewidth measurements we know that the characteristic relaxation rate of the fluid is $\gamma=\gamma_0 t^2$ where $\gamma_0/2\pi=15$ GHz. Thus we replace f by $\gamma/2\pi$ to convert the upper line in Fig. 1 into the thermodynamic relation (up to an additive constant)

$$\frac{u_1}{u_c}=-0.022\left(\frac{\gamma_0}{2\pi}t^2\right)^{-0.06}=-0.012t^{-0.12}$$
$$\simeq \text{const}+0.0015\ln t\ . \qquad (1)$$

The sensitivity to the small exponent disappears in the final limiting form of Eq. (1). Figure 2 shows the critical variation of u_1 (relative to its value at $t=0.1$) that is predicted by Eq. (1). (Here we have used[10] $u_c=10^3$ m/sec.) The slight curvature in this semilog plot results from using the more precise power-law version of Eq. (1) rather than the logarithmic approximation. The horizontal lines indicate the critical-point frequency dependence of Fig. 1.

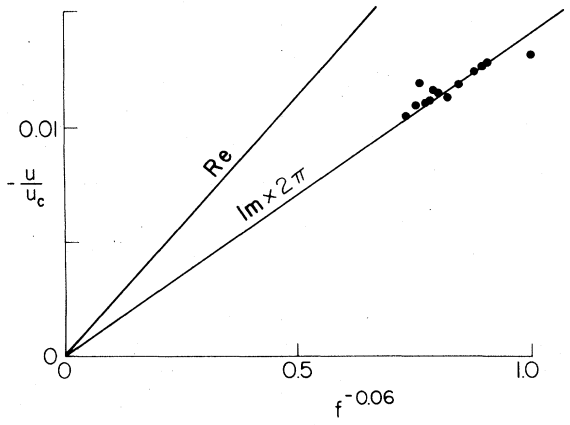

FIG. 1. Real and imaginary parts of the fractional critical sound velocity as a function of frequency at the consolute point. u_c is the large noncritical velocity and u_c+u is the full complex velocity. The attenuation data at different frequencies are taken from Harada *et al.* (Ref. 8).

They join the thermodynamic curve in the vicinity of $t=(2\pi f/\gamma_0)^{1/2}$ as required by dynamic scaling. It is evident from Fig. 2 that in order to observe the critical temperature variation the measurements should be carried out at the lowest possible frequency. For example, measurements at 10 kHz, such as would be possible with a resonant cavity,[5] should reveal a detectable drop in u_1. According to Fig. 2 this drop should amount to approximately 15 m/sec in passing from $t=0.1$ to 0.001, before leveling off at the critical-point value. By contrast, the velocity measurements in binary liquids have generally[11] been made in the MHz range, corresponding to the uppermost curve in Fig. 2. This is flat over most of the temperature range. Thus we see that *the frequencies have been too high, which explains the puzzle of the absence of critical temperature variation.*

We now turn to the thermodynamics for an alternative derivation of Eq. (1). Let w be a free energy defined by

$$dw=-SdT+VdP-cd\mu=-\bar{S}dT+VdP-cd\bar{\mu}\ , \quad (2)$$

where S and V are the entropy and volume, respectively. All of these extensive quantities are for a unit mass of the fluid. P, c, and μ are the pressure, mass fraction, and a suitably defined chemical potential,[12] respectively. The application of pressure shifts both T_c and μ_c, the consolute value of μ, along a λ line described by the functions $T_c=T_\lambda(P)$ and $\mu_c=\mu_\lambda(P)$. Similarly, $c=c_\lambda(P)$ along the λ line, while the extensive variables are described along the λ line by the functions $w_\lambda(P)$, $S_\lambda(P)$, and $V_\lambda(P)$. In the form line of Eq. (2) we have restored the symmetry along the critical isochore by introducing a shifted chemical potential $\bar{\mu}=\mu-(\partial\mu/\partial T)_c T$. $\bar{S}\equiv S+(\partial\mu/\partial T)_c c$ is an effective entropy for the fluid. Integrating away from the λ line at constant pressure gives

$$w=w_\lambda-\int_{T_\lambda}^{T}\bar{S}\,dT-\int_{\bar{\mu}_\lambda}^{\bar{\mu}}c\,d\bar{\mu}$$

$$=w_\lambda-\int_0^{\Delta T}\bar{S}\,d\Delta T-\int_0^{\Delta\bar{\mu}}c\,d\Delta\bar{\mu}\ , \quad (3)$$

where we have introduced the relative variables $\Delta T=T-T_\lambda$ and $\Delta\bar{\mu}=\bar{\mu}-\bar{\mu}_\lambda$. Because $(\partial\Delta T/\partial P)_{\bar{T}}=-T_\lambda'$ and $(\partial\Delta\bar{\mu}/\partial P)_{\bar{\mu}}=-\bar{\mu}_\lambda'$ we obtain

$$V=\left(\frac{\partial w}{\partial P}\right)_{T,\mu}=\left(\frac{\partial w}{\partial P}\right)_{\Delta T,\Delta\bar{\mu}}+T_\lambda'\bar{S}+\bar{\mu}_\lambda' c\ . \quad (4)$$

The first term requires differentiating $\bar{S}$ and c parallel to the λ line within the integrals. To first-order accuracy these derivatives can be replaced by their λ line values giving

$$V=w_\lambda'+T_\lambda'\bar{S}+\bar{\mu}_\lambda' c-\bar{S}_\lambda'\Delta T-c_\lambda'\Delta\bar{\mu}\ . \quad (5)$$

The coefficient of ΔT can be expressed in terms of the dimensionless coupling constant $g=T_\lambda\bar{S}_\lambda'/V$.

By differentiating Eq. (5) we can now obtain various thermodynamic quantities of interest, such as the isothermal compressibility and the expansion coefficient. These can then be combined according to the standard thermodynamic identity to give the isentropic compressibility. But we can reach the same goal more quickly by clamping $\bar{S}$ and c, so that the variations δP, $\delta\Delta T$, and $\delta\Delta\bar{\mu}$ produce the volume variation

$$\delta V=(w_\lambda''+T_\lambda''\bar{S}+\mu_\lambda'' c-\bar{S}_\lambda''\Delta T-c_\lambda''\Delta\bar{\mu})\delta P$$

$$-\frac{V_\lambda}{T_\lambda}g\delta\Delta T-c_\lambda'\delta\Delta\bar{\mu}\ . \quad (6)$$

The mass-fraction clamping condition is explicitly $\delta c=c_\lambda'\delta P+\chi\delta\Delta\bar{\mu}=0$, on the critical isochore, which yields $\delta\Delta\bar{\mu}=-(c_\lambda'/\chi)\delta P$, where χ is the isothermal susceptibility. Entropy clamping gives

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

$$=\bar{S}_\lambda'\delta P+\frac{C_{P,c}}{T}\delta\Delta T=0\ , \quad (7)$$

where we have introduced the specific heat along the critical isochore. The term containing $\delta\Delta\bar{\mu}$ vanishes because of the Maxwell relation $(\partial\bar{S}/\partial\bar{\mu})_{P,T}=(\partial c/\partial T)_{P,\Delta\bar{\mu}=0}=0$. Thus Eq. (7) yields

$$\delta\Delta T=-g\frac{V}{C_{P,c}}\delta P\ . \quad (8)$$

Substituting $\delta\Delta\bar{\mu}$ and $\delta\Delta T$ into Eq. (6) gives for v,

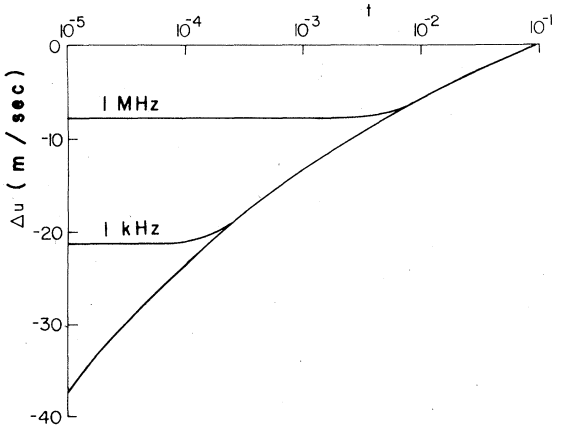

FIG. 2. Predicted critical sound velocity vs reduced temperature. The lowermost curve is the thermodynamic limit (zero frequency). The two upper curves show the effect of a finite frequency.

the velocity of sound,

$$\frac{1}{v^2} = -\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_{S,c} = -\frac{1}{V^2}\frac{\delta V}{\delta P}$$
$$= \frac{1}{u_c^2} - \frac{g^2}{T}\frac{1}{C_{P,c}} - \frac{c_\lambda'^2}{\chi V^2} \quad , \tag{9}$$

where the first term corresponds to the first term of Eq. (6). The second term is small by comparison and determines the critical component $u = v - u_c$ as

$$\frac{u}{u_c} \simeq \frac{g^2}{2}\frac{u_c^2}{T_c}\frac{1}{C_{P,c}} \quad . \tag{10}$$

[The third term of Eq. (9) is negligible in the critical region.]

Equation (9) is a generalization of Chase's formula,[13] applied so successfully by Barmatz and Rudnick[14] to the study of the critical sound velocity in the vicinity of the λ point of liquid ^{4}He. The advantage of the present derivation is that (a) account is taken of $c_\lambda' \neq 0$ (pressure dependence of the critical mass fraction) and (b) the coefficient of $\delta\Delta T$ in Eq. (6) is shown to be noncritical. The latter point, which is not evident in the treatment of Griffiths and Wheeler[15] is important for the application of Eq. (10) to the theory of the ultrasonic attenuation[16] in binary liquids because it ensures that the critical dynamics enters only via $C_{P,c}$. In this connection we should point out that the first term of Eq. (9) is not strictly constant but contains the temperature dependence of the first-order terms $T_\lambda''(\bar{S} - \bar{S}_\lambda) - \bar{S}_\lambda''\Delta T$ in Eq. (6). This type of nonfrequency-dependent background variation has been observed by Arrigo *et al.*[11] in their high-frequency measurements. It needs to be distinguished from the true critical variation coming from the second term in Eq. (9). Although, for the sake of simplicity, we have carried out the derivation of Eq. (9) only along the critical isochore, this equation is valid in the entire t, μ plane. Similarly, the assumption of pressure independence of $(\partial\mu/\partial T)_{P,c}$ can be relaxed.

The critical specific heat appearing in Eq. (10) can be written as $C_{P,c} = At^{-\alpha_0} + B$, where we set $\alpha_0 = 0.12$. We can expect $A << B$ because of the large number of internal degrees of freedom contributing to the background. Linearizing with respect to A gives

$$\frac{u_1}{u_c} \simeq \frac{g^2}{2}\frac{u_c^2}{T_c B}\left(1 - \frac{A}{B}t^{-\alpha_0}\right) \simeq \text{const} + \frac{g^2}{2}\frac{\alpha_0 A u_c^2}{T_c B^2}\ln t \quad , \tag{11}$$

thereby providing the alternative derivation of Eq. (1). The coefficient in Eq. (11) provides, in principle, an independent *a priori* prediction of the coefficient found phenomenologically in Eq. (1). Unfortunately, carrying this out in practice is hindered by the lack of specific-heat data for 3-methylpentane-nitroethane. We can, nevertheless, from the pure components interpolate the background at $B \simeq 1.7$ J/g K. From $\xi_0 = 2.2$ Å and two-scale factor universality we have $A = 0.22$ J/g K. A preliminary measurement of the coupling constant in this laboratory[17] gives $g = 0.5 \pm 0.2$. Substitution of these numbers yields $(4 \pm 2.5) \times 10^{-3}$ for the coefficient of $\ln t$ in Eq. (11), one standard deviation away from but consistent with Eq. (1). Clearly, more thermodynamic data would be highly desirable.

To summarize, we have made a quantitative prediction of the critical sound velocity which, as illustrated in Fig. 2, ought to be observable at sufficiently low frequencies. We emphasize that the logarithmic approximation has been used in Eqs. (1) and (11) only in the interest of simplicity and that it is generally better to use the finite α_0 versions. We also caution that the background specific heat may not always be large enough to justify the approximation $B >> A$. In this case, the critical specific heat should be kept in the denominator, as for the λ transition in liquid ^{4}He.

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