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Sound propagation in ^{3}He-^{4}He mixtures near the liquid-vapor critical point

T. Doiron,* D. Gestrich, and H. Meyer
Department of Physics, Duke University, Durham, North Carolina 27706

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Measurements of the acoustic attenuation and the dispersion are reported for two ^{3}He-^{4}He mixtures, along the critical isochore near the liquid-vapor critical point. At the frequencies of 1, 3, and 5 MHz used in the experiments, these properties showed no difference from those of pure ^{3}He or ^{4}He. The results are discussed in terms of the two energy dissipation mechanisms, thermal diffusion and mass diffusion, and the approach suggested by the postulate of Griffiths and Wheeler for mixtures.

I. INTRODUCTION

This paper is concerned with experiments on the critical acoustic propagation for two ^{3}He-^{4}He mixtures near their liquid-vapor critical point. Besides the sound energy dissipation from thermal diffusion (as in a pure fluid), such mixtures are expected to show additional energy losses from concentration diffusion. Therefore we expected an increase in the critical attenuation and dispersion amplitudes over those in the pure ^{3}He and ^{4}He fluids. However, our experiments showed no pronounced difference between the pure fluids and the mixtures.

In Sec. II, the dissipation mechanisms in mixtures are discussed. Section III presents the experimental method and the procedures in calculating the zero frequency sound velocity. In Sec. IV, the results are presented, followed by a short discussion.

II. SHORT REVIEW

Experiments[1–5] on sound attenuation and dispersion near the liquid-vapor critical point have been reported for several pure fluids along the critical isochore, $\rho = \rho_c$, and have been interpreted in terms of the theory by Kawasaki,[6] as extended by Mistura.[1] Likewise, the critical acoustic properties have been measured for liquid mixtures near their consolute critical point, and Kawasaki's theory has been applied to analyze these data.[7–9]

For pure fluids, the large acoustic attenuation near the liquid-vapor critical point is caused by a hysteresis loss from heat diffusion induced by density fluctuations. The effective bulk viscosity of the fluid increases as the characteristic decay rate of the fluctuations, τ^{-1}, slows down. The attenuation then reaches a sharp, finite peak at the critical point. The density fluctuations are coupled to spontaneous entropy fluctuations, and these determine the characteristic rate τ^{-1}. Let us restrict the following discussion to the *hydrodynamic regime,* $\omega < \tau_\chi^{-1}$, where ω is the sound frequency and[6]

$$\tau_\chi^{-1} = \chi\kappa^2 \tag{1a}$$

with

$$\chi = \Lambda/\rho C_p \tag{1b}$$

and

$$\Lambda = \Lambda_{\rm reg} + \Lambda_{\rm sing} \ . \tag{1c}$$

Here κ is the inverse correlation length, Λ is the thermal conductivity, ρ is the mass density, and C_p is the specific heat per gram at constant pressure. The subscripts "reg" and "sing" denote the regular and singular contributions. In terms of the reduced temperature, t, the quantities of interest have the following asymptotic behavior along the critical isochore:

$$\begin{aligned} &\Lambda_{\rm sing} \propto t^{-x_\lambda}, \quad x_\lambda \approx \nu \ , \\ &C_p \propto t^{-\gamma}, \quad \kappa \propto t^{\nu} \ , \end{aligned} \tag{2}$$

where $t = (T - T_c)/T_c$, T_c being the critical temperature, and where $\gamma \approx 1.24$ and $\nu \approx 0.63$ are the well-known critical exponents. Hence the characteristic fluctuation rate has a reduced temperature dependence of $\tau_\chi^{-1} = At^{\gamma+2\nu} + Bt^{3\nu}$ where A and B are constants. Close enough to T_c, the second term is the leading one, and the first one the correction. In the following discussion, we set for simplicity's sake $\gamma = 2\nu$.

By contrast, in *liquid* mixtures near the *consolute critical point,* the density fluctuations caused by mass concentration gradients couple more weakly with sound waves. Therefore, at a given ω and t, the critical attenuation and dispersion are considerably smaller than near the pure fluid liquid-vapor critical point. Here the analysis of the data[8] is again based on Kawasaki's theory, where now the entropy fluctuations are replaced by concentration fluctuations with a rate $\tau_D^{-1} = D\kappa^2$, where $D = D_{\text{reg}} + D_{\text{sing}}$ is the mass diffusion. Since in a binary liquid mixture[10] $D_{\text{sing}} \propto \kappa$, τ_D^{-1} has the same singularity as τ_χ^{-1} in the pure fluids.

The *liquid-vapor binary* system combines critical fluctuations in both entropy (of the same order of magnitude as in pure fluids) and concentration (as in binary liquid-liquid mixtures). The critical static properties of this system have been studied in detail for ^{3}He-^{4}He mixtures, both experimentally[11–13] and theoretically[14] and also for other mixtures.[15] As can be deduced from the postulates of Griffiths and Wheeler,[16] several of the static properties at constant composition X in mixtures have a different critical behavior from that in a pure fluid. For instance, the specific heat, $C_{p,X}$, is predicted in the limit $t \rightarrow 0$ to diverge only weakly.[14] However, experiments[11,13] and theory[14] indicate that for $t > t^*(X)$ [where $T^*(X)$ is a crossover temperature] the compressibility, and hence $C_{p,X}$, should diverge strongly just as for a pure fluid.

Mistura[17] predicted the asymptotic behavior of the transport properties for a fluid multicomponent system and obtained

$$\chi_{\text{sing}} = \frac{\Lambda_{\text{sing},X}}{\rho C_{p,X}} = \frac{k_B T}{6\pi\eta}\kappa \ , \tag{3}$$

where η is the bulk viscosity, and where $\kappa \propto t^\nu$ along the critical isochore. Furthermore the mass diffusion D was found to be[17]

$$D = A\left(\frac{\partial\mu}{\partial c}\right)_{T,P} + \frac{k_B T}{6\pi\eta}\kappa \ , \tag{4}$$

where A is a nonsingular factor, $(\partial c/\partial\mu)_{T,P}$ is the concentration susceptibility which is proportional to κ^{-2}, μ is the chemical potential difference, and c is the ^{3}He mass concentration, related to the ^{3}He mole fraction X by

$$c = XM_3[XM_3 + (1-X)M_4]^{-1} \ . \tag{5}$$

Both χ and D then have the same form, namely,

$$\chi = B_\chi\kappa^2 + (k_B T/6\pi\eta)\kappa \ , \tag{6a}$$

$$D = B_D\kappa^2 + (k_B T/6\pi\eta)\kappa \ . \tag{6b}$$

Since η has only a weak singularity (see Ref. 18) it follows that along the critical isochore, the asymptotic singularities for $t \rightarrow 0$ are

$$D = \chi_{\text{sing}} \propto t^\nu \quad (t \rightarrow 0) \ . \tag{7}$$

It is well known that in a binary fluid the dynamic time-dependent behavior is governed by two coupled differential diffusion equations[19] that give the dispersion relation[20]

$$\Gamma/q^2 = \tfrac{1}{2}\{D_T + D \pm [(D_T+D)^2 - 4D\chi]^{1/2}\} \ . \tag{8a}$$

Here q is the wave vector,

$$D_T = \frac{\Lambda_s}{\rho C_{p,c}} \ , \tag{8b}$$

and

$$\Lambda_s = \Lambda + \left(\frac{\partial\mu}{\partial c}\right)_{P,T}\frac{k_T^2 D\rho}{T} \ . \tag{8c}$$

Mistura[17] predicts that the singular part of the thermal diffusion ratio, $k_{T,\text{sing}}$, is identically zero and that $k_T = k_{T,\text{reg}} \propto \kappa^{-1}$. Remembering that $(\partial\mu/\partial c)_{T,P} \propto \kappa^2$, it follows that the second term on the right-hand side of Eq. (8c) has the same singular behavior as D. This second term will become negligible with respect to $\Lambda_{\text{reg}} \approx \Lambda$ as T_c is approached. Thus $\Lambda = \Lambda_s$ sufficiently close to T_c. Then the two solutions of Eq. (8a) are given by Eqs. (6a) and (6b) and they become identical close enough to T_c.

In the hydrodynamic regime, let us assume the critical acoustic attenuation α to be the sum from the two dissipation contributions, the thermal and concentration fluctuations, respectively. They will be expressed in terms of the two characteristic frequencies, $\omega_D = 2D\kappa^2$ and $\omega_\chi = 2\chi\kappa^2$, namely,

$$\alpha_{\text{tot}}(\omega) = \alpha_\chi(\omega,\omega_\chi) + \alpha_D(\omega,\omega_D) \tag{9}$$

and a similar equation for the dispersion. (For a pure liquid and a liquid-liquid binary system, the complete expressions for the critical attenuation and dispersion are given in Ref. 9, Sec. VIII.) Along the critical isochore, and in the hydrodynamic regime, we then expect both contributions, α_χ and α_D, to have the form

$$\alpha_{\chi,D} \propto \omega^2/\omega_{\chi,D} \propto \omega^2(C_{\chi,D}t^{4\nu} + Et^{3\nu})^{-1} \ , \tag{10}$$

which is the same as for pure fluids, and where C and E are nonsingular factors of T. At present, there are no predictions on the magnitudes of the two contributions α_χ and α_D in such mixtures.

We mention here the related light scattering experiments for a 10% mixture of propylene in CO$_2$ near the liquid-vapor critical point.[21] While theory[20] predicts that the central Rayleigh line is made up of two Lorentzians, one due to the concentration diffusion D and one due to thermal diffusion, only one line was observed, and it was very similar in width and intensity to that of pure CO$_2$. The authors[21] concluded that there was only one observable diffusivity and it was similar to the pure field diffusivity χ in magnitude and temperature dependence.

III. EXPERIMENTAL

Two mixtures with respective composition of $X_3 = 0.82$ and 0.45 were investigated. In addition, control experiments were carried out under the same conditions with pure ^{3}He and ^{4}He. The experiments

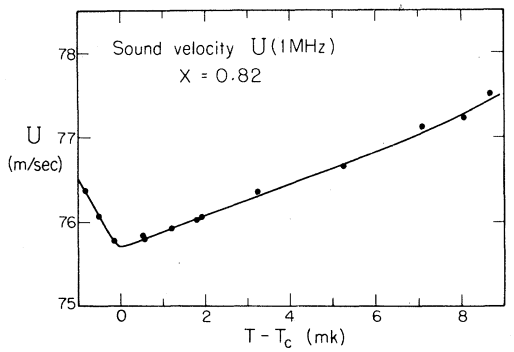

FIG. 1. Location of the critical temperature from sound velocity measurements at 1 MHz for the mixture $X = 0.82$.

were carried out along the critical isochore over the temperature range $0 \leq t \leq 2 \times 10^{-1}$.

The measurements were done on the same apparatus as described in Ref. 4, using an acoustic etalon with x-cut quartz transducers, which were 2.54 cm in diameter and separated by 1.33 mm by a convoluted spacer. At the fundamental frequency of 1.0 MHz, the sound velocity and attenuation could be measured right to the critical point. However, at the harmonic frequencies of 3 and 5 MHz, the attenuation became so large that the detected signal vanished close to the critical point. As before,[4] the critical isochore was determined from the location of the sound velocity minimum along an isotherm slightly above T_c. The critical temperature, in turn, was located from the sharp minimum in the sound velocity measured along the critical isochore, as shown in Fig. 1 for the mixture $X = 0.82$.

The velocity was measured by using a phase comparison technique to determine the time of flight of a sound pulse through the sample, as described previously.[4,5] A resolution of approximately 10^{-3} m/sec out of 80 m/sec was obtained. However, the reproducibility from one temperature cycling to another was about 10^{-2} m/sec. Close to T_c, or where the received amplitude was very small, the reproducibility became approximately 3×10^{-2} m/sec. The effective acoustic spacing and the electronic delay in the time of flight were determined both by calibration with ^{3}He (under identical conditions as in Ref. 5) and by extending the velocity measurements for each mixture to a temperature well above T_c at a pressure of a few centimeters of Hg. For the latter case, ideal gas conditions were expected to hold, so that the velocity, U, obeys the well-known relation $U^2 = \sigma RT/M$, where $\sigma = C_{p,X}/C_{v,X}$, R is the gas constant, and M is the molar mass of the mixture. In this way, the absolute velocity could be determined within a few percent. It was not possible to find out whether far way from T_c there was a constant background dispersion between 1 and 5 MHz, and we have assumed it to be zero, as in the situation for the pure fluids.

The attenuation measurements were conducted, analyzed, and corrected (for acoustical mismatch between the fluid and the transducer) as described in Ref. 5. It must be emphasized that our experimental arrangement (using an etalon with a constant path length) could determine the temperature-dependent contribution of the attenuation, α, but *not* a temperature-independent background term.

In order to obtain the dispersion $\Delta U = U(\omega) - U(0)$ in the absence of any low-frequency sound velocity measurements for mixtures, the limiting (or thermodynamic) velocity $U_{\text{therm}}(0)$ has been calculated from the relation

$$U^2_{\text{therm}}(0) = \frac{1}{\rho K_{s,X}} = \frac{1}{\rho K_{T,X}} + \frac{T}{\rho^2 C_{v,X}} \left(\frac{\partial P}{\partial T} \right)^2_{v,X} . \quad (11)$$

Here $K_{s,X}$ and $K_{T,X}$ are the adiabatic and isothermal compressibilities at constant composition and $C_{v,X}$ is the specific heat at constant volume per unit mass. For the 82 at.% ^{3}He, 18 at.% ^{4}He mixture (or $X = 0.82$), the available data on ρ, $K_{T,X}$, $(\partial P/\partial T)_{X,v}$, and $C_{v,X}$ from Refs. 10–12 were used. For the $X = 0.45$ mixture, the thermodynamic data were scarce, but fortunately an interpolation from some available $K_{T,X}$ results[11] for $X = 0.40$ and 0.60 was possible. Also, an examination of $(\partial P/\partial T)_{X,v}$ and $C_{v,X}$ for pure ^{3}He,[22] the $X = 0.80$ mixture,[13] and pure ^{4}He,[23,24] along their respective critical isochores, indicates that an almost linear interpolation to the $X = 0.45$ mixture can be made for these quantities. Within the experimental uncertainties of the thermodynamic quantities, the calculated $U_{\text{therm}}(0)$ was in very good agreement with U(1 MHz) far away from

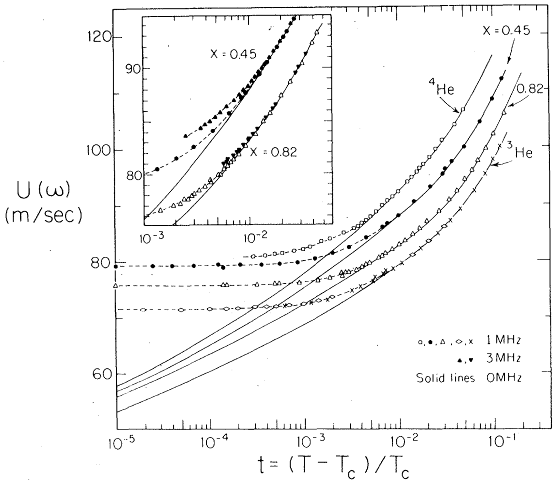

FIG. 2. The sound velocity $U(\omega)$ at 1 and 3 MHz for pure ^{3}He, ^{4}He, and the two mixtures as a function of reduced temperature. The calculated thermodynamic sound velocities $U(0)$ are shown by solid lines. For ^{4}He, these calculations are consistent with the data at 20 kHz by Barmatz (Ref. 25) (not shown).

T_c, where dispersion effects are negligible. The calculated thermodynamic velocities for the two mixtures, as well as for pure ^{3}He and ^{4}He are presented in Fig. 2. For ^{4}He, the calculated velocity differs by only ~0.5 m/sec from the direct measurements by Barmatz, made at $\omega/2\pi = 20$ kHz. For the sake of internal consistency with the mixtures and ^{3}He, we have used in our analysis the calculated $U(0)$ for ^{4}He rather than the data of Barmatz.[25] We note that the increasing uncertainty in the thermodynamic quantities as T_c is approached introduces an uncertainty of approximately ± 3 m/sec at $t = 10^{-5}$.

IV. RESULTS AND DISCUSSION

Tabulations of the measured sound velocities and acoustic attenuation have been compiled in a separate report.[26] Here we show in Fig. 2 the sound velocities for the pure fluids and the two mixtures at 1 and 3 MHz. Measurements for 5 MHz could not be carried out for $t < 10^{-2}$ because of the large attenuation (see Fig. 4). Because the dispersion is small above $t = 10^{-2}$, these data are hardly distinguishable from the 1- and 3-MHz results and are not shown in Fig. 2. The dispersion results at 1 MHz are shown in Fig. 3. Within the uncertainty in the calculation of $U(0)$ as $t \rightarrow 0$, there are no systematic differences between the mixtures and the pure fluids. This observation is also confirmed by the measurements at higher frequencies, where however the reduced temperature range is smaller than for 1 MHz.

Figure 4 shows the attenuation results at 1, 3, and 5 MHz for the $X = 0.82$ mixture, expressed as $\alpha_\lambda = \alpha\lambda$, the attenuation per wavelength. This representation was used in previous publications.[2–5] Finally, Fig. 5 compares the critical attenuation at 1 MHz for the two mixtures and the pure fluids. Again, no differences are noticeable within the experimental uncertainty, and the higher-frequency results confirm this observation.

The analysis for the attenuation and dispersion for the pure fluids has been carried out[5] according to the theory of Kawasaki as extended by Mistura. The consistency with theory in the hydrodynamic regime and the systematic discrepancies in the high-frequency regime ($\omega > 2\tau_\chi^{-1}$) were discussed in detail and will not be repeated here. The differences between the results for the two fluids can be easily attributed to the transport and static properties that appear in the general expressions for the critical attenuation and dispersion (see Sec. VIII in Ref. 9) and also to the experimental uncertainties in the determination of α_λ and of $U(\omega) - U(0)$. From our present results, it appears that the mixtures are also accounted for by the Kawasaki-Mistura theory, at least in the hydrodynamic regime and where the parameters used (both static and transport properties) are intermediate between those of the pure fluids.

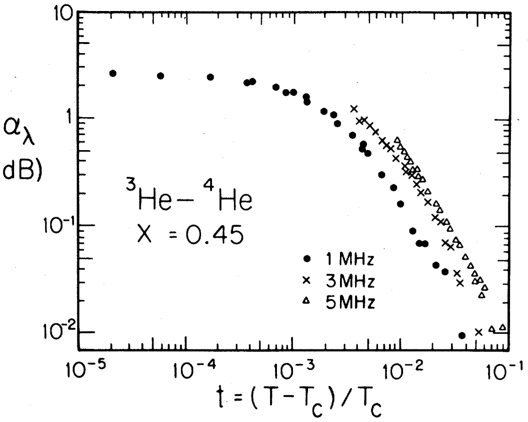

FIG. 4. The acoustic attenuation results for $X = 0.45$ at 1, 3, and 5 MHz.

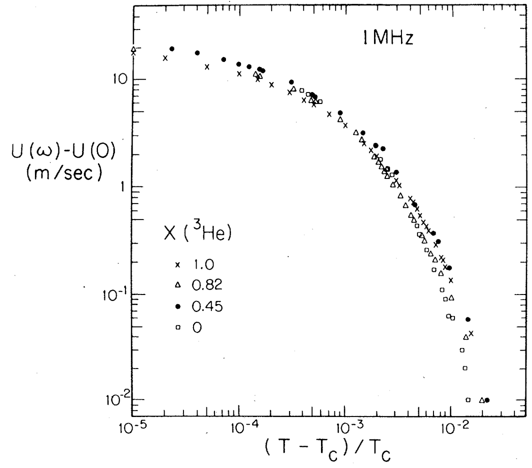

FIG. 3. The dispersion at 1 MHz for pure ^{3}He, ^{4}He, and the mixtures as a function of the reduced temperature.

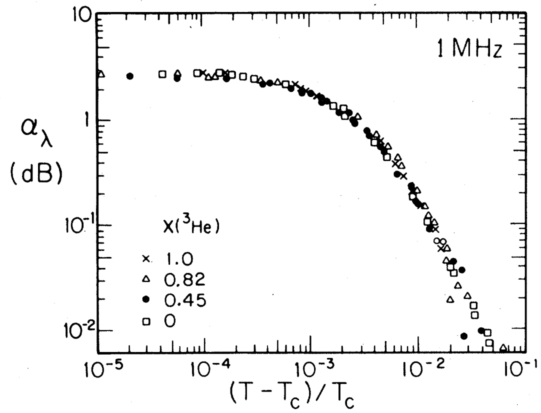

FIG. 5. The acoustic attenuation data at 1 MHz for pure ^{3}He, ^{4}He, and the two mixtures.

There are two possible explanations for these observations, neither of which can be proven without a comprehensive acoustic theory for these mixtures. Assume the validity of Eq. (9), then the *first* possibility is that $\alpha_X >> \alpha_D$, namely, the coupling of concentration fluctuations to the sound modes may be much weaker than that of the thermal fluctuations. The *second* possibility is that the respective effects of these two types of fluctuations cannot be separated into components such as in Eq. (9) because of their strong correlation. A different approach would then be to look at the mixture in the perspective of Griffiths and Wheeler.[16] If we consider the phase diagram using the *field* variables P-T-μ instead of the mixed variables P-T-X (see, for instance, Fig. 4 and 1 of Ref. 13) then we see that the difference between mixtures and pure fluids vanishes for properties at constant field variables, such as $(\partial V/\partial P)_{T,\mu}$ or $C_{P,\mu}$ [instead of $(\partial V/\partial P)_{T,X}$ or $C_{P,X}$]. The properties then will be intermediate between those of pure fluids. One might therefore speculate that acoustic attenuation, critical light scattering intensity, and linewidth in mixtures, when expressed in terms of properties at fixed field variables, will turn out to be intermediate between those of the pure fluids. In this approach, there is no formal differentiation between D_{sing} and χ_{sing}, which are the same according to Mistura's prediction. This means that diffusive motions resulting from fluctuations are strongly coupled. We are inclined to believe that this second possibility makes more sense than the first one.

V. SUMMARY

We have observed no noteworthy difference in the critical acoustic attenuation and dispersion (at frequencies of 1, 3, and 5 MHz) between pure ^{3}He and ^{4}He, on one hand, and two mixtures ($X_3 = 0.82$ and 0.45) on the other hand, near their respective liquid-vapor critical point. Theory shows that in pure fluids and in liquid binary mixtures near their consolute point, the order-parameter fluctuation rate is determined by the thermal diffusivity and the mass diffusivity, respectively. The theories for critical acoustic attenuation and dispersion have been formulated some time ago for these two systems.[9] However, there is no such theory for binary mixtures near their liquid-vapor critical line. Here *both* types of diffusivity (thermal and mass) will become relevant, and theory predicts that the singular fluctuation decay rates of these two processes should be very similar. We have suggested two possible interpretations for our observations. It is clear that further progress—both experimental and theoretical—on transport properties in such binary systems near the liquid-vapor critical point would be very desirable.

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