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Sound Absorption in Critical Mixtures

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Previous ultrasonic measurements in the binary mixtures aniline cyclohexane and nitrobenzene *n*-hexane have been analyzed according to a method recently proposed for Xe. The experimental results are compared with numerical calculations based on a theoretical formulation by Fixman and Kawasaki. At high frequency ($f^* > 1$), the behavior of the sound absorption is quite different from that observed in Xe. We find that the low-frequency form of the theory can be used to fit the data in the entire frequency range. In particular, the Kawasaki prediction $\alpha_\lambda \sim f^0 \epsilon^0$ when $f^* \gg 1$, which seems to be confirmed by the experimental results in Xe, is not verified for the two mixtures examined here. We suggest that this different behavior is a consequence of the different behavior of the specific heats at constant volume.

In two previous papers[1,2] we reported extensive measurements of the sound-absorption coefficient in the binary mixtures nitrobenzene and n-hexane[1] $(n+n-h)$, and aniline and cyclohexane[2] $(a+c)$. In the first case $(n+n-h)$ attention has been concentrated on the composition dependence of the attenuation, while the frequency dependence was the major concern of the second paper $(a+c)$. In both cases the experimental results were compared with the prediction of the Fixman theory[3] finding that the relaxation model proposed by Fixman provides an excellent qualitative explanation of sound propagation in binary mixtures. At the same time, however, we pointed out[2] that many of the additional assumptions introduced by Fixman in order to evaluate his model quantitatively can lead to a breakdown of the theory close to T_c or alternatively at high frequency.

The problem of sound propagation near a critical point has recently been reconsidered by Kawasaki[4] in a more general context. Although the physical model proposed by Fixman has been retained by Kawasaki, the calculation has been performed in a different way, and many of the difficulties mentioned in Ref. 2 are not present in the Kawasaki formulation. The predictions of this Fixman-Kawasaki theory have been compared successfully with sound-absorption data in xenon above its critical temperature along a near-critical isochore.[5] In this connection it has been proposed to analyze the experimental results in terms of a reduced frequency $\omega^* = \omega/\omega_D$, where the characteristic frequency ω_D is equal to $(2\Lambda/\rho C_p)\xi^{-2}$, Λ being the coefficient of thermal conductivity, C_p the specific heat at constant pressure, and ξ the correlation length for density fluctuations. The critical attenuation per wavelength α_λ in xenon depends on temperature and frequency through the single reduced variable ω^*.

In this paper we wish to report the results of a similar analysis of the sound-absorption data for the binary mixtures $(n+n-h)$ and $(a+c)$ mentioned above.

The data analyzed here refer to the critical concentration (43% mole fraction of nitrobenzene and 44% mole fraction of aniline, respectively) above the critical temperature (21 and 29.8 °C, respectively) in the frequency range 1–95 MHz.

The most interesting result is that the absorption per wavelength at high frequency behaves quite differently in xenon than in the two mixtures examined here.

Although Kawasaki has explicitly formulated his calculations for the liquid-gas critical point, one can apparently use the correspondence suggested by Swift[6] to translate the result for the liquid-liquid critical point.

For our purposes it is convenient to write the result of the Fixman-Kawasaki theory in the form

$$\frac{\alpha}{f^2} = \frac{2\pi A(T)}{u_0(T) f_D(T)} I(f^*) + b(\infty, T), \tag{1}$$

where α is the absorption coefficient per unit length, $f = \omega/2\pi$ is the frequency, $u_0(T)$ is the thermodynamic sound velocity, $f_D(T) = (D/\pi)\xi^{-2}$ (D being the diffusion coefficient) is the characteristic frequency corresponding to $\omega_D/2\pi$ previously defined for a fluid, and

$$A(T) = \frac{K_B T^3}{2\pi^2 \rho^3} \frac{1}{u_0^2 C_V^2} \left(\frac{\partial P}{\partial T}\right)_V^2 \xi^{-1} \left(\frac{\partial \xi^{-1}}{\partial T}\right)^2, \tag{2}$$

where K_B is the Boltzmann's constant, C_V is the specific heat at constant volume, p is the pressure, and

$$I(f^*) = \int_0^\infty dx \frac{x^2}{(1+x^2)^2} \frac{K(x)}{[K(x)]^2 + f^{*2}}, \tag{3}$$

where $f^* = f/f_D$, $x = k\xi$, and

$$K(x) = \tfrac{3}{4}\left[1 + x^2 + (x^3 - 1/x)\tan^{-1} x\right] \tag{4}$$

TABLE I. Parameters of the Fixman-Kawasaki theory [Eq. (1)] in nitrobenzene *n*-hexane.

	T (°C)	$A(T)$	$b(\infty, T)$ ($\mathrm{cm}^{-1}\,\mathrm{sec}^2$)	$f_D(T)$ (MHz)	$u_0(T)$ (m/sec)	χ^2/df[a]
FIX	56.9	0.0005	118	2.30	291	19.3
KAW		0.0005	118	2.30	291	19.3
FIX	41.0	0.0033	128	7.48	764	28.6
KAW		0.0033	128	7.48	764	28.6
FIX	30.4	0.0113	65	8.77	917	1.6
KAW		0.0112	67	8.12	919	1.5
FIX	24.3	0.0198	76	1.52	1186	0.3
KAW		0.0198	76	1.52	1186	0.3
FIX	21.0	0.0284	87	0.29	1120	1.5
KAW		0.0285	87	0.29	1120	1.5

[a] χ^2/df = chi square over degrees of freedom.

according to Kawasaki,[4,7] or

$$K(x) = x^2(1 + x^2) \tag{5}$$

according to Fixman.

The $b(\infty, T)$ describes the sound absorption due to other effects than that described by the first term.

At each temperature, the experimental values of α/f^2 for the various frequencies have been fitted to Eq. (1) assuming $A(T)$, $u_0(T)$, $f_D(T)$, and $b(\infty, T)$ as parameters. The fits have been done using both the Kawasaki form [Eq. (4)] and the Fixman form [Eq. (5)] for the function $K(x)$. The results for the best fits are reported in Table I for $(n+n-h)$ and in Table II for $(a+c)$. Then the experimental values of $(\alpha_\lambda)^*$ plotted in Figs. 1 and 2 have been evaluated according to the definition

$$(\alpha_\lambda)^* = \frac{f^{-2} - b(\infty, T)}{A(T)}\, u_0 f\ . \tag{6}$$

The solid line represents the same quantity according to the theory using the Kawasaki form for $K(x)$.

We wish now to add a few remarks:

(i) Within the accuracy of our experimental data both the Fixman and the Kawasaki forms of the theory provide a good representation of the experimental results. In other words, sound-absorption measurements in binary mixtures cannot be used to discriminate between the two proposed forms for $K(x)$. The same conclusion has been reached for xenon. Fortunately, light-scattering measurements can be used to decide on this point and the experimental indication are strongly in favor of the Kawasaki form both in Xe [8] and aniline cyclohexane.[9]

(ii) For the mixture $(n+n-h)$, large deviations are observed for the two sets of data taken at temperatures farthest from the critical point.

(iii) The $b(\infty, T)$ represents the sound absorption at high frequency when the relaxation process due to diffusion is no longer effective. In a binary mixture, like those considered here, where the two components have internal degrees of freedom, it is not possible to evaluate the critical absorption simply by subtracting the classical attenuation from the observed one, as it has been done for Xe.[5] The

TABLE II. Parameters of the Fixman-Kawasaki theory [Eq. (1)] in aniline cyclohexane.

	T (°C)	$A(T)$	$b(\infty, T)$ ($\mathrm{cm}^{-1}\,\mathrm{sec}^2$)	$f_D(T)$ (MHz)	$u_0(T)$ (m/sec)	χ^2/df[a]
FIX	36.20	0.005 98	112	1.35	1363	4.5
KAW		0.004 90	115	1.62	1324	4.7
FIX	34.40	0.006 89	93	1.43	1306	4.5
KAW		0.005 92	98	1.62	1341	4.5
FIX	33.30	0.006 86	94	0.71	1166	1.8
KAW		0.006 79	100	0.88	1365	1.9
FIX	32.70	0.007 71	111	0.29	1318	3.3
KAW		0.006 98	116	0.47	1401	3.6
FIX	32.40	0.008 24	124	0.14	1321	0.8
KAW		0.008 02	129	0.28	1532	0.6
FIX	31.20	0.008 92	103	0.29	1334	0.6
KAW		0.008 24	108	0.48	1451	0.7
FIX	30.5	0.009 94	95	0.34	1323	5.1
KAW		0.008 92	107	0.32	1334	6.1

[a] χ^2/df = chi square over degrees of freedom.

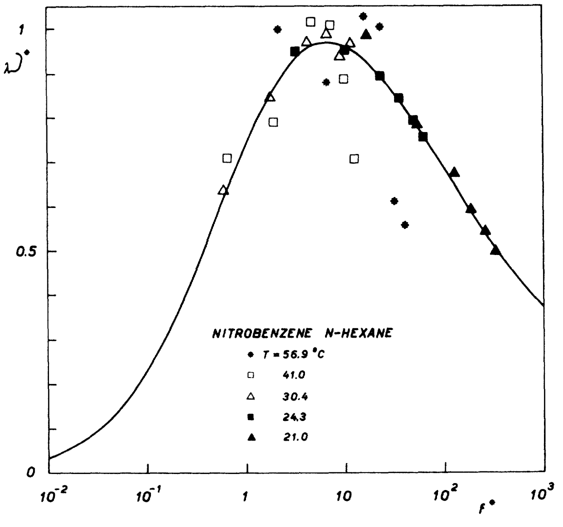

FIG. 1. Reduced critical-sound attenuation per wavelength $(\alpha_\lambda)^*$ in nitrobenzene n-hexane as a function of the reduced frequency $f^* = f/f_D$. The $(\alpha_\lambda)^*$ is defined by Eq. (6). The solid curve represents the result of the Kawasaki theory.

classical contribution arising from the shear viscosity can be readily evaluated with the help of the data on kinematic viscosity.[10,11] It turns out that $(\alpha/f^2)_{\eta\mathrm{class}} \simeq 20\times10^{-17}$ cm^{-1} sec^2 for $(a+c)$ and $(\alpha/f^2)_{\eta\mathrm{class}} \simeq 14\times10^{-17}$ cm^{-1} sec^2 for $(n+n-h)$, and its increase due to the anomalous increase in viscosity[10] can be entirely neglected. Even a smaller contribution can be calculated arising from the thermal conductivity. However, one must take into account that in the pure components the observed absorption ($\alpha/f^2 = 50\times10^{-17}$ cm^{-1} sec^2 for aniline, 200×10^{-17} cm^{-1} sec^2 for cyclohexane, 70×10^{-17} cm^{-1} sec^2 for nitrobenzene, and 50×10^{-17} cm^{-1} sec^2 for n-hexane) far exceeds the classical one.

The values reported in Tables I and II and their temperature independence are in agreement with the assumption that $b(\infty, T)$ is due to some relaxation process occurring in the pure components.

(iv) $f_D(T) = (D/\pi)\xi^{-2}$. According to Swift,[6] $D \propto \xi^{-1}$ and therefore $f_D(T) \propto \xi^{-3}$. Assuming $\xi \propto \epsilon^{-\nu}$, we can write $f_D(T) = a\epsilon^{3\nu}$ with $\nu \simeq \frac{2}{3}$.

For the system $(a+c)$ it is possible to compare our results for $f_D(T)$ as a function of temperature with recent light-scattering data obtained by Berge *et al.*[9] The data reported in Table II have been fitted in Eq. (7) using b, ν, and T_c as parameters. Since we have not evaluated the errors in the various $f_D(T)$, this fit gives only qualitative indications. The values obtained are

$$a_s = 0.40\times10^{10}\ \mathrm{sec}^{-1}, \quad \nu_s = 0.65, \quad T_c = 30.0\ ^\circ\mathrm{C}.$$

The values obtained for a and ν from the quite independent linewidth measurements are

$$a_L = (0.43\pm0.06)\times10^{10}, \quad \nu_L = 0.588\pm0.06.$$

This noticeable coincidence must be considered a further verification of the correctness of the proposed model.

(v) $A(T)$ is a purely thermodynamic quantity given by Eq. (2). The situation is different here for one-component and two-component systems. In the one-componenet case, use can be made of the scaling relation $\alpha = 2 - 3\nu$ to predict, at most, a very weak temperature dependence for $A(T)$. The experiments in xenon[5] seem to confirm this prediction. For a binary mixture there are suggestions[12] that u_0, C_V, and $(\partial P/\partial T)_V$ are not singular at a consolute point. As far as u_0 is concerned there are experimental verifications of this suggestion.[1,2] Accordingly, we expect $A(T)$ to diverge, approaching the critical point with an exponent $\alpha = 2 - 3\nu$. Again a best fit of our data with a power-law behavior $A(T) = A_0\epsilon^{3\nu-2}$ has given $A_0 = 0.0024\pm0.0002$, $\alpha = 0.22\pm0.05$.

(vi) Finally, we wish to point out that the different behavior, mentioned above, for certain thermodynamic quantities near a critical and a consolute point may be at the origin of the different behavior of the sound absorption at high frequency. According to Kawasaki[4] for $f^* \gg 1$ (but still with $\lambda \gg \xi$), α_λ must be independent of frequency and practically independent of temperature. This prediction, which is confirmed by the experimental results in xenon,[5] is clearly not verified for the two mixtures examined here. The reason for this different behavior might be the following. At high frequency, a large contribution to the absorption coefficient comes from

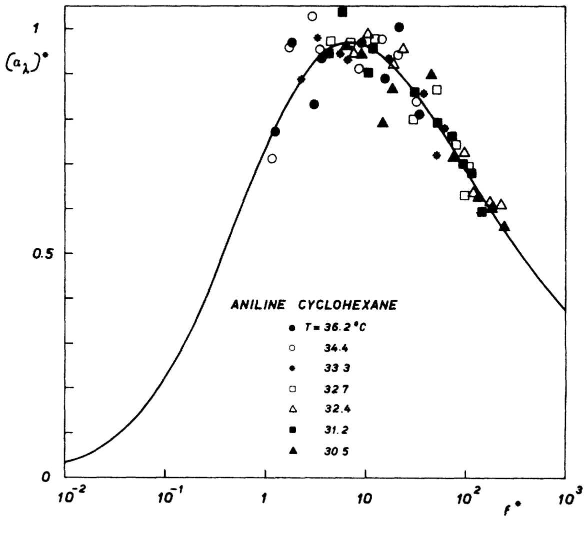

FIG. 2. Reduced critical-sound attenuation per wavelength $(\alpha_\lambda)^*$ in aniline cyclohexane as a function of the reduced frequency f^*.

density or concentration fluctuations with high wave number ($k\xi > 1$). In a one-component system, the correlation function for density fluctuations at high values of k has a strong temperature dependence since it must contain the specific-heat singularity.[13] In a binary mixture, even if deviations from the Ornstein-Zernike form are expected for high values of k, there is apparently no argument—in particular there is no singularity in the specific heat at constant volume—to support a strong temperature dependence of the short-range part of the correlation function for concentration fluctuations. On the other hand, it is just the temperature dependence of the correlation function which determines the necessary coupling mechanism between the sound waves and the density or concentration fluctuations.

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Scattering of a Laser Beam by High-Temperature Plasmas

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The time-average intensity of electromagnetic radiation scattered by a 50-kV electron beam from a Q-switched laser beam, incident at 90° and polarized with $\vec{E}$ perpendicular to the electron beam, is measured as a function of angle with respect to the electron beam. The measured values agree with those calculated using a model that corrects for the fact that the scattering electrons pass through the scattering region during the period of observation. This correction is important in the measurement of plasma distribution functions by laser scattering for plasmas with electron temperatures greater than 10 keV.

The intensity of electromagnetic radiation scattered from a small-amplitude ($eE\lambda/2\pi m_0 c^2 \ll 1$) electromagnetic wave by a free electron is given by the Thomson cross section ($\sigma = \frac{8}{3}\pi r_0^2$). If the scattering electron is moving with a low velocity ($v \ll c$), the scattered radiation is Doppler shifted to a higher or lower frequency depending on the angle of observation. This Doppler shift of the scattered radiation has been used to measure the temperature or velocity distribution of dense, low-temperature ($T_e < 1.0$ keV) plasmas[1-3] (by measuring the Doppler broadening of the laser linewidth for radiation scattered from a laser beam by a plasma). A Maxwellian plasma distribution function produces a Gaussian-shaped spectral distribution of scattered radiation with a width proportional to the plasma temperature.

For plasmas with electron temperatures greater than 10 keV, the spectrum of scattered radiation is not Gaussian in shape, but rather is skewed and shifted to shorter wavelengths.[4] The wavelength of radiation scattered by a given high-velocity electron in a particular direction depends only on that electron's velocity. However, in a laboratory-size hot-electron plasma ($T_e > 10$ keV), electrons will pass completely through the scattering region during the observation time, and as a result there is a correction to the intensity of scattered radiation