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# Effect of Anomalies of the Kinetic Coefficients Near the Critical Points of Liquids on the Nature of High-Frequency Sound Propagation

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Owing to the growth of the thermal conductivity near the critical point of a liquid at frequencies $\sim 10^9$ sec$^{-1}$, the adiabatic condition in a sound wave should be violated and negative dispersion of the sound velocity should be observed. Because of similar growth of thermal conductivity for a constant chemical potential, and of the mobility, the dispersion of the sound velocity near the critical point of a binary mixture may be related to violation of the condition of constancy of entropy and concentration in the sound wave. Estimates of the characteristic frequencies, absorption and dispersion are in satisfactory agreement with the experimental data.

SOUND propagation in liquids with large kinetic coefficients (viscosity, thermal conductivity) possesses a number of features.[1,2] Near the critical point, the anomalous growth of the kinetic coefficients is a well-known fact (the results of theoretical calculations[3-5] are confirmed by experiment[6-8]). For example, near the critical point of a single-component liquid, the thermal conductivity increases in proportion to the increase in the correlation radius ($r_c$), while the bulk viscosity ($\xi$) changes according to the law $\xi \sim r_c^3$.

The effect of the increase in the bulk viscosity on the sound propagation near the critical points of liquids has been considered in[9,10]. It has been shown that growth in $\xi$ leads to a positive dispersion in the sound velocity and to strong absorption in the range of frequencies $\omega_0 = \text{const}/\xi$. Thus, for $\tau = 10^{-2}$ ($\tau = (T - T_c)/T_c$ is the dimensionless deviation of the temperature from the critical value) for single-component liquids $\omega_0 \approx 10^8$–$10^9$ sec$^{-1}$, while for critical points of binary mixtures, $\omega_0 \approx 10^6$–$10^7$ sec$^{-1}$ and decreases rapidly upon further approach to the critical point.

It will be shown in this paper that the appearance of additional mechanisms of dispersion and absorption of sound are possible at frequencies $\omega \gg \omega_0$. These are associated with anomalies of other kinetic coefficients. Here the condition $\omega \gg \omega_0$ allows us to take into account the growth of the bulk viscosity only in the fact that all the characteristics of the material are taken at the frequency $\omega$. It then turns out that near the critical points of single-component liquids and binary mixtures a decrease can be observed in the sound velocity with increase in frequency, i.e., negative dispersion exists.

## 1. CRITICAL POINT OF A SINGLE-COMPONENT LIQUID

The solution of the dispersion equation for frequencies

$$\omega > \omega^* = \frac{(\partial P/\partial\rho)_T}{\varkappa/\rho C_P} \equiv \frac{(\partial P/\partial\rho)_S}{\varkappa/\rho C_V} \qquad (1)$$

(P is the pressure, $\rho$ the density, S the entropy, $C_p$ and $C_V$ the heat capacity at constant pressure and volume, respectively) leads to the following result for the sound velocity:[2]

$$u = (\partial P/\partial\rho)_T^{1/2} < (\partial P/\partial\rho)_S^{1/2}. \qquad (2)$$

In other words, for $\omega > \omega^*$, the adiabatic condition on the sound wave is violated—the sound becomes "isothermal." The absorption remains small in this case:

$$\delta = \frac{\omega}{2}\left\{\frac{\omega^*}{\omega}\left(1 - \frac{C_V}{C_P}\right)\right\}. \qquad (3)$$

However, it is not possible experimentally to observe the transition to "isothermal" sound in liquids far from the critical point, since $\omega^* \sim 10^{12}$–$10^{13}$ sec$^{-1}$.[11] At such currently unattainable frequencies, the sound wavelength is comparable with the inter-atomic distances ($\sim 10^{-8}$ cm), the medium ceases to be continuous and the sound cannot propagate at $\omega > \omega^*$. As a consequence of the growth in the thermal conductivity, the frequency should decrease near the critical point, which allows us to raise the question of the experimental observation of "isothermal" sound.

We make the following estimates of the value of $\omega^*$. Assuming

$$\varkappa / \rho C_P = kT / 6\pi\eta r_c, \qquad (4)$$

in correspondence with the results of theoretical calculations[3,9] and experiment[12], with $(\partial P/\partial\rho)_T \approx \tilde{u}^2 r_0^2/r_c^2$ ($\tilde{u}$ is the sound velocity far from the critical point, $\eta$ the high-frequency shear viscosity, $r_c = r_0\tau^{-\nu}$), we get

$$\omega^* \approx \frac{6\pi\tilde{u}^2\eta r_0}{kT}\tau^\nu. \qquad (5)$$

Near the critical points of xenon and carbon dioxide, for example, we have $\omega^* \approx 3.5 \times 10^{11}\,\tau^{2/3}$ sec$^{-1}$ and $\omega^* \approx 1.5 \times 10^{13}\,\tau^{2/3}$ sec$^{-1}$. We have taken $\nu \approx 2/3$ and $r_0 \approx 10^{-8}$ cm in agreement with the experimental results of[6,8,12]. The data on $\tilde{u}$ and $\eta$ were taken from[13-15]. For the materials studied, the sound velocity was measured at frequencies $\omega \approx (3$–$5) \times 10^9$ sec$^{-1}$ from the shift of the Mandel'shtam-Brillouin components in the spectrum of scattered light.[13,14] For $\tau \approx 10^{-3}$–$10^{-4}$, we have $\omega/\omega^* \approx 0.3$–$3$, i.e., the values of the frequencies studied lie as a whole in the range of transition to "isothermal" sound. This could explain the reduced value of the velocity dispersion of hypersound in comparison with ultrasonic data and the additional absorption for $Kr_c \sim 1$, observed in[13] close to the critical point of xenon.

To date, no one has considered the dependence of the thermodynamic quantities and kinetic coefficients on the frequency. However, near the critical point, this dependence is important. Thus, for $Kr_c \gg 1$ ($K = \omega/u$ is the wave number of the sound), all the quantities cease to depend on the nearness to the critical point ($r_c$ in the corresponding dependences changes by $K^{-1}$[16]). It is not difficult to see that the condition $\omega = \omega^*$ near the critical point is equivalent to the condition $Kr_c = \text{const}$, and this constant is near unity in order of magnitude (just as we would have $Kr_0 \sim 1$ far from the critical point), i.e., the violation of adiabaticity in the sound wave usually occurs in the region of strong spatial dispersion. For Xe and $CO_2$, for example, the condition $\omega = \omega^*$ corresponds to $Kr_c = 1/2$. Therefore, for further increase in the frequency, the ratio $\omega/\omega^*$ remains a constant quantity near unity, and the transition to "isothermal" sound does not take place at all.

The effect considered is analogous to a known degree to the violation of adiabaticity in a sound wave propagating in gases[17] at $Kl \sim 1$ ($l$ is the free path length of the molecules). However, in contrast with gases near the critical point for $Kr_c \sim 1$, the medium remains continuous (the absorption over a wavelength remains small small).

## 2. CRITICAL POINTS OF BINARY MIXTURES

We shall show that not only the condition of constant entropy in a sound wave can be violated in binary mixtures at high frequencies (the transition to "isothermal" sound), but also the condition of constancy of concentration (x) the transition to sound at constant chemical potential ($\mu$). These effects lead, as in the case of a pure substance, to a negative dispersion of the sound velocity.

The dispersion equation for the binary liquid mixtures has the form

$$-K^6 P_\rho^{T\mu}\alpha\varkappa + i\Gamma_2\omega K^4(1 - i\omega/\omega_2) - \omega^4 T\rho^2 x_\mu^{T\rho} S_T^{\rho x} + T\rho^2 x_\mu^{T\rho} S_T^{\rho x} P_\rho^{Sx} K^2\omega^2 (1 - i\omega/\omega_1) = 0. \tag{6}$$

Here we have introduced the notation $P_\rho^{T\mu} = (\partial P/\partial\rho)_{T,\mu}$ and so on:

$$\omega_1 = T\rho^2 x_\mu^{T\rho} S_T^{\rho x} P_\rho^{Sx}/\Gamma_1, \quad \omega_2 = \Gamma_2/\alpha\varkappa,$$

$$\Gamma_1 = \rho(\alpha T S_T^{\rho\mu} + \gamma x_\mu^{T\rho} - 2T\beta S_\mu^{T\rho}),$$

$$\Gamma_2 = P_\rho^{T\mu}\Gamma_1 + \rho^{-1}\{T(P_T^{\rho\mu})^2\alpha + \rho^4(x_\rho^{T\mu})^2\gamma + 2T\rho^2 x_\rho^{T\mu} P_T^{\rho\mu}\beta\};$$

$\alpha, \beta, \gamma$ are kinetic coefficients ($\gamma - T\beta^2/\alpha = \kappa$), which determine the entropy flow ($q = -\gamma\nabla T - T\beta\nabla\mu$) and the mass of one of the components ($j = -\alpha\nabla\mu - \beta\nabla T$) in binary mixtures.[2] It can be shown that $\omega \ll \omega_1$ always. Then the sound velocity u and the absorption coefficient $\delta$ at $\omega \ll \omega_1$ (lower frequencies) have the form

$$u_0 = (P_\rho^{Sx})^{1/2}, \qquad \delta_0 = \frac{\omega}{2}\left\{\frac{\omega}{\omega_1}\left(1 - \frac{\Gamma_2}{\Gamma_1 P_\rho^{Sx}}\right)\right\}. \tag{7}$$

In the intermediate region of frequencies $\omega_1 \ll \omega \ll \omega_2$, we have

$$u_\omega = (\Gamma_2/\Gamma_1)^{1/2},$$

$$\delta_\omega = \frac{\omega}{2}\left\{\frac{\omega_1}{\omega}\left(1 - \frac{\Gamma_2}{\Gamma_1 P_\rho^{Sx}}\right) + \frac{\omega}{\omega_2}\left(1 - \frac{\Gamma_1 P_\rho^{T\mu}}{\Gamma_2}\right)\right\}. \tag{8}$$

Thus the sound velocity in this region is determined by the rather complicated combination of kinetic coefficients and various thermodynamic derivatives. In the high frequency region $\omega \gg \omega_2$ we have

$$u_\infty = (P_\rho^{T\mu})^{1/2} \qquad \delta_\infty = \frac{\omega}{2}\left\{\frac{\omega_2}{\omega}\left(1 - \frac{\Gamma_1 P_\rho^{T\mu}}{\Gamma_2}\right)\right\}, \tag{9}$$

i.e., the sound velocity is determined by the compressibility at constant chemical potential and temperature ("$T - \mu$ sound"), and $u_\infty < u_\omega < u_0$.

In the case in which terms appear in $\Gamma_1$ and $\Gamma_2$ which contain $\gamma$ (a medium with high thermal conductivity), we find

$$\omega_1 = \frac{P_\rho^{Tx}}{\gamma/\rho T S_T^{Px}}, \quad \omega_2 = \frac{P_\rho^{T\mu}}{\alpha/x_\mu^{T\rho}} \tag{10}$$

and $u_\omega = (P_\rho^{Tx})^{1/2}$ ("$T - x$ sound"). If terms appear in $\Gamma_1$ and $\Gamma_2$ which contain $\alpha$ (medium with anomalously large mobility), then

$$\omega_1 = \frac{P_\rho^{S\mu}}{\alpha/x_\mu^{\rho T}}, \quad \omega_2 = \frac{P_\rho^{T\mu}}{\varkappa/\rho T S_T^{P\mu}} \tag{11}$$

and $u_\omega = (P_\rho^{S\mu})^{1/2}$ ("$S - \mu$ sound").

Near the critical points of the mixtures, the kinetic coefficients $\alpha$, $\beta$ and $\gamma$ increase like the thermal conductivity coefficient in a pure substance (for example, the thermal conductivity in the case of a constant chemical potential $\gamma = \gamma_0 + \Delta\gamma$, where $\Delta\gamma \sim r_c$ and $\gamma_0$ is the regular part),[4,5,7] while $\kappa$ (the thermal conductivity at constant concentration) remains a finite quantity. Taking it into account that the singular parts of $\alpha$, $\beta$ and $\gamma$ are connected by the relations

$$\Delta\alpha = \{\rho^4 T^{-1}(x_\rho^{T\mu})^2/(P_T^{\rho\mu})^2\}\Delta\gamma, \qquad \Delta\beta = \{-\rho^2 x_\rho^{T\mu}/P_T^{\rho\mu}\}\Delta\gamma, \tag{12}$$

we obtain

$$\omega_1 \approx P_\rho^{Tx}[\varepsilon\gamma/\rho T S_T^{Px}]^{-1}, \quad \omega_2 \approx P_\rho^{S\mu}[\alpha\varkappa/\gamma_0 x_\mu^{T\rho}]^{-1}$$

$$u_\omega = \left(\frac{\gamma_0}{\varepsilon\gamma} P_\rho^{Tx}\right)^{1/2}, \tag{13}$$

for the intermediate region of frequencies close to the critical point of the mixture, where $\epsilon = P_\rho^{Tx}/P_\rho^{S\mu} + 2P_T^{\rho x}/P_T^{\rho\mu} - 1$, $\omega_2 \sim \gamma_0\epsilon\omega_1/\kappa$ ($\gamma_0\epsilon/\kappa \gtrsim 1$). Upon substitution of (12) in the expression for $\Gamma_2$, the singular parts of $\alpha$, $\beta$ and $\gamma$ are reduced and we have left of the regular parts only the term containing $\gamma_0$ ($\gamma_0 \gtrsim \kappa$). Thus, near the critical point of the mixture, as a consequence of the growth of the kinetic coefficients, the characteristic frequencies for which the condition of constancy of S and x in the sound wave are reduced.

For an estimate of the quantity $\omega_1$ (and, consequently, the value of $\omega_2$, which is of the order of $\omega_1$ but larger than it) we use the expression for the anomalous parts of the kinetic coefficients in binary mixtures:[5,18]

$$\gamma/\rho T S_T^{P\mu} = kT/6\pi\eta r_c,$$

$$P_\rho^{Tx} S_T^{Px} \equiv P_\rho^{Sx} S_T^{\rho x} \approx P_\rho^{Sx} S_T^{P\mu} r_0^2/r_c^2. \tag{14}$$

The numerical estimate of the quantity $\epsilon$ is difficult, which is due to the presence in the expression for $\epsilon$ of quantities that are hard to measure. Assuming the contribution of each of the kinetic mechanisms to be the same, we use $\epsilon = 3$ for the estimates. Then we get

$$\omega_1 \approx 2\pi\frac{u_0^2\eta r_0}{kT}\tau^\nu. \tag{15}$$

The experimental study of the velocity of hypersound at frequencies (2—4) × $10^{10}$ $sec^{-1}$ has been carried out near the critical points of the binary mixtures nitrobenzene-hexane[19] and nitroethane-iso-octane.[20] In both cases, a decrease was observed in the sound velocity by 1—2% upon approach to the critical point. This could be interpreted as a violation of the constancy of S and $\mu$ in the sound wave. Actually, under these conditions, and for $\tau \approx 10^{-3}-10^{-4}$, we get $\omega/\omega_1 \approx 0.03-0.2$ (the necessary data for the estimate were taken from[15,19,21]). In the beginning of the transitional region, the relative decrease in the sound velocity $\Delta u/u \sim (\omega/\omega_1)^2 \approx 0.1-4\%$. For $\tau \approx 10^{-4}$, we have $Kr_c \approx 1$; therefore the decrease in the sound velocity ought to cease upon closer approach to the critical point. The growth of the absorption by an amount $\delta/\omega \approx 0.07$ for $\tau \approx 10^{-3}-10^{-4}$ in the high frequency region, observed in[19], can also be connected with the anomalous growth of the kinetic coefficients ($\alpha \sim \gamma \sim r_c$). From (7), we get the value $\delta/\omega \approx 0.015-0.1$ for $\tau \approx 10^{-3}-10^{-4}$.

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