Effect of biaxial fluctuations of the order parameter on sound absorption in nematic liquid crystals

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The existence of biaxial fluctuations in nematic liquid crystals may lead to peculiar effects in sound absorption. Allowance for such fluctuations noticeably increases the absorption coefficient in the high-frequency region and, under certain conditions, may lead to an additional maximum in the neighborhood of the nematic–isotropic liquid transition. The temperature behavior of the absorption coefficient may give additional information about the character of the phase transition.

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An extensive literature has been devoted to the investigation of various ultrasonic processes in liquid crystals (see, for example, the bibliography in Ref. 1). This is due both to the presence of an interesting and quite complicated physical phenomenon and to important applications. At present, a number of processes have been studied that are responsible for absorption of ultrasound near the phase transition from nematic liquid crystal to isotropic liquid. These processes are connected with Landau-Khalatnikov relaxation of the modulus of the order parameter, with a critical increase of the coefficients of bulk viscosity, and with the so-called excess heat capacity. The last originates because of the fact that near the phase transition, the fluctuations of the order parameter Q have a strong spatial correlation. During passage of a sound wave, a periodic modulation of the temperature occurs, and the change of the order parameter is not able to follow this modulation. The relaxation of the order parameter makes an additional, frequency-dependent contribution to the heat capacity. Since the velocity of sound is connected with the ratio of the specific heats, as a result a complex value of the sound velocity is obtained; its imaginary part corresponds to absorption.

A convenient method of calculating the surplus heat capacity was proposed by Fixman[2] for the case of mixtures and was generalized to liquid crystals by Imura and Okano.[3] In liquid crystals the order parameter has a quite complicated structure, and therefore fluctuations of all its components contributed to the excess heat capacity.

A very important fact is that the various absorption mechanisms mentioned above can, in principle, be separated experimentally. Thus, for example, the Landau-Khalatnikov absorption occurs only below the transition temperature; increase of the viscosity coefficients leads to anisotropic absorption, while the effect connected with excess heat capacity leads to isotropic. There are still absorption processes due to change of the conformation of the molecules, but they are unimportant in systems consisting of sufficiently short and rigid molecules. A recent analysis[4] of experimental data on sound absorption in CBOOA showed that in the nematic phase, the most important processes are those connected with the excess heat capacity. Therefore we shall hereafter consider only these processes.

References 3–6 considered the excess heat capacity due to fluctuations of the modulus of the order parameter and of the director. Such flucutations lead to bell-shaped dependences of the amount of absorption on the frequency, with maxima approximately in a single frequency range (of the order of a fraction of a MHz). The resultant dependence should therefore have the same form and should be simply a somewhat broadened bell-shaped curve:

$$\alpha_\lambda(\omega) \sim \omega\tau/(1+\omega^2\tau^2),$$

where α_λ is the amount of absorption per wavelength, and where τ is a characteristic relaxation time.

In actual fact, the $\alpha_\lambda(\omega)$ dependence is more complicated. Along with the maximum in the frequency range mentioned above, there is a new rise, and often even a complete second maximum in a frequency range of order 10–100 MHz. A typical $\alpha_\lambda(\omega)$ curve for butyloxyazoxybenzene[1] has the form shown in Fig. 1. The experimental data of Refs. 4–6 also exceed the calculated theoretical curves in the higher-frequency range. In Refs. 5 and 6, this systematic deviation was attributed to increase of the viscosity coefficients in the critical range. But the proposed mechanism predicts only a monotonic increase of the absorption and cannot explain the existence of an additional maximum on the high-frequency tail of the absorption curve.

In the present paper, a new mechanism is proposed, which in our opinion may be responsible for the increase and for the presence of an additional maximum of $\alpha_\lambda(\omega)$ in the high-frequency range. This mechanism is connected with

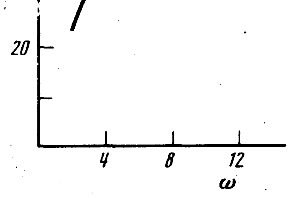

FIG. 1. Absorption curve for butyloxyazoxybenzene according to data of Ref. 1 (ω in MHz).

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biaxial fluctuations of the order parameter, which were not taken into account in Refs. 3–6 and which are important precisely in this frequency range. It was shown in Refs. 7 and 8 that the presence of biaxial fluctuations can lead to peculiarities in the scattering of electromagnetic waves. It is of interest to consider also their effect on sound absorption, which may provide additional possibilities for experimental detection of biaxial fluctuations.

For a description of the proposed mechanism, we shall use an expression for the free energy with allowance for biaxial fluctuations, which was obtained by Pokrovskiĭ and Kats.[7] In its general form, this free energy requires a quite cumbersome expression. We shall use the one-constant approximation (allowance for the difference in the Frank moduli greatly complicates the calculations but does not change the qualitative picture). In this case, the expression for the free energy has the simple form

$$F=\frac{1}{2}\sum_{\mathbf{q}}\left\{\sum_{i=1}^{4}Kq^2|\xi_i|^2+\Delta(\xi_3^2+\xi_4^2)\right\},\tag{1}$$

where the parameters ξ_1 and ξ_2 describe the fluctuation of the director, ξ_3 and ξ_4 describe the biaxial fluctuation, K is the Frank modulus, and Δ is the characteristic energy necessary for excitation of the biaxial fluctuation.

Following Fixman's method, we calculate the additional entropy resulting from the biaxial fluctuations:

$$\langle\Delta S\rangle=-\frac{1}{2}\sum_{\mathbf{q}}\sum_{i=3,4}\frac{\partial}{\partial T}(Kq^2+\Delta)G_i,\tag{2}$$

$$G_i=\langle|\xi_i|^2\rangle=k_\text{Б}T/(Kq^2+\Delta),$$

where G_i is the equilibrium correlation function. We represent the changes of the coefficients K and Δ and of the correlation function during passage of a sound wave in the following form:

$$K\to K+\frac{\partial K}{\partial T}(\Delta T)_\omega e^{-i\omega t},\quad \Delta\to\Delta+\frac{\partial\Delta}{\partial T}(\Delta T)_\omega e^{-i\omega t},$$
$$G(\mathbf{q},t)\to G(\mathbf{q})+G_1(\mathbf{q},\omega)e^{-i\omega t}.$$

On substituting these expressions in the equations of motion for the correlation functions,

$$\nu_i\frac{\partial G_i(\mathbf{q},t)}{\partial t}=-(Kq^2+\Delta)G_i(\mathbf{q},t),\tag{3}$$

we get

$$G_{1i}(\mathbf{q},\omega)=-\frac{(\partial K/\partial T)q^2+\partial\Delta/\partial T}{Kq^2+\Delta-i\omega\nu_i}(\Delta T)_\omega G(\mathbf{q});\tag{4}$$

here ν_i are effective-viscosity coefficients, and $(\Delta T)_\omega$ is the local change of temperature.

The dynamics of biaxial fluctuations in the general case is quite complicated because of interaction with the hydrodynamic degrees of freedom[8]; here, however, we have neglected for simplicity this interaction with other modes, as was done in Refs. 4–6.

The excess entropy due to passage of the sound wave is obtained by substitution of (4) in (2) and transition from a summation over $\mathbf{q}$ to an integration:

$$\langle\Delta S_1\rangle=-\frac{1}{(2\pi)^3}\int\left[q^2\left(\frac{\partial K}{\partial T}\right)+\frac{\partial\Delta}{\partial T}\right]G_1\,d^3q\tag{5}$$

(here we have set $\nu_3=\nu_4=\nu_0$ and have allowed for the contribution of both correlation functions).

On calculating the excess heat capacity $\Delta C^*(\omega)=T(\partial\Delta S_1/\partial T)$, we finally have the following expression for the absorption coefficient:

$$\alpha_\lambda=\frac{\pi(\gamma_0-1)}{C_p^0}\operatorname{Im}(\Delta C^*(\omega))=\frac{\gamma_0-1}{C_p^0}\frac{k_\text{Б}T^2}{2\pi}\frac{q_{max}^3(\partial K/\partial T)^2}{K^2}$$
$$\times\operatorname{Im}\int_0^1\frac{(\delta+t^2)^2t^2\,dt}{(\beta+t^2)(\beta+t^2-id)},\tag{6}$$

$$\beta=\frac{\Delta}{Kq_{max}^2},\quad d=\frac{\omega\nu_0}{Kq_{max}^2},\quad \delta=(\partial\Delta/\partial T)/(\partial K/\partial T)q_{max}^2,$$

$$\gamma_0=C_p^0/C_v^0,$$

where q_max is the upper limit of the integration with respect to momenta. The imaginary part of the integral in (6) can be represented as the sum of three terms:

$$\operatorname{Im}\int_0^1\frac{(\delta+t^2)^2t^2\,dt}{(\beta+t^2)(\beta+t^2-id)}=\delta^2I_1+2\delta I_2+I_3,$$

$$I_1=-\beta^{-1/2}[t^{-1}\operatorname{arctg}(\beta^{-1/2})-L+A],$$
$$I_2=\beta^{1/2}\{t^{-1}\operatorname{arctg}(\beta^{-1/2})-[2+(t^2+1)^{1/2}]L-[2-(t^2+1)^{1/2}]A\},$$
$$I_3=\beta^{3/2}\{t\beta^{-1/2}-t^{-1}\operatorname{arctg}(\beta^{-1/2})+[3-t^2+2(t^2+1)^{1/2}]L$$
$$+[3-t^2-2(t^2+1)^{1/2}]A\},\tag{7}$$
$$L=\frac{[(t^2+1)^{1/2}-1]^{1/2}}{2^{5/2}t}\ln\frac{1+(2\beta)^{1/2}[(1+t^2)^{1/2}-1]^{1/2}+\beta(t^2+1)^{1/2}}{1-(2\beta)^{1/2}[(1+t^2)^{1/2}-1]^{1/2}+\beta(t^2+1)^{1/2}},$$
$$A=\frac{[(t^2+1)^{1/2}+1]^{1/2}}{2^{5/2}t}\left(\pi-2\operatorname{arctg}\frac{\beta(t^2+1)^{1/2}-1}{(2\beta)^{1/2}[(t^2+1)^{1/2}+1]^{1/2}}\right),$$
$$t=\frac{\omega\nu_0}{\Delta}.$$

We have specially chosen this form of expression because it is convenient for comparison with the results of Refs. 3, 4, and 6, and furthermore it permits easy description of cases of phase transitions of various types.

As has already been mentioned above, absorption on fluctuations of the modulus of the order parameter and fluctuations of the director is described by approximately the same frequency and temperature dependencies; therefore it is sufficient for us to make a comparison of the results obtained with the results of Nagai[6] for absorption on fluctuations of the director. In this case the absorption coefficient has the following form[6]:

$$\alpha_\lambda(\omega)=BF(x),\tag{8}$$

where B coincides exactly with the coefficient of the integral in (6), and where $F(x)$ is a standard function[1)]:

$$F(x)=x\left\{1-\frac{x^{1/2}}{2^{5/2}}\left[\ln\frac{1+(2x)^{1/2}+x}{1-(2x)^{1/2}+x}+2\operatorname{arctg}\frac{(2x)^{1/2}}{x-1}\right]\right\},\tag{9}$$

$x=\omega\nu_1/Kq_\text{max}^2$, and ν_1 is the effective viscosity for a mode corresponding to fluctuations of the director. It is obvious that for comparison of the results it is necessary to compare only (7) and (9).

We first consider the case $\Delta = \text{const}$, which corresponds to the Landau approximation. Then the absorption due to biaxial fluctuations is described by the one term I_3 only of formula (7), which naturally coincides with (9) in the case $\Delta = 0$. Far from the transition point, the value of $Kq^2_{\max}$ exceeds the value of Δ, which has order of magnitude 10^6–10^7 erg/cm^3; this corresponds to $\beta < 1$. But with approach to the transition point, the coefficient K decreases ($K \sim Q^2$), and as a result the parameter β increases and may take values $\beta \gg 1$.

Another important parameter of the problem is the ratio of the effective viscosities for uniaxial and biaxial fluctuations, ν_1/ν_0, which determines the position of the maxima of the absorption curves in both cases. Unfortunately there are at present no experimental data enabling one to obtain the value of this parameter and its temperature dependence. But the very nature of the physics of the phenomena allows us to suppose that the effective viscosity for uniaxial fluctuations, due to a real deviation of the director from the axis of preferred orientation, must appreciably exceed the viscosity for biaxial fluctuations, due to the appearance in the order-parameter tensor of additional components, even far from the transition. On approach to the transition point, as is well known,[1] an increase is observed in the viscosity coefficients connected with soft modes-uniaxial fluctuations. As regards the behavior of the effective viscosity for biaxial fluctuations, when we allow for the hardness of this mode, such an increase, even if it occurs, should be considerably weaker; that is, the ratio ν_1/ν_0 can increase only in the neighborhood of the nematic-isotropic liquid transition.

Figure 2 shows the form of the function I_3 for several values of the parameter β. Here is also plotted the function F for the case $\eta = \beta\nu_1/\nu_0 = 10$. With approach to the transition point, i.e., increase of η, the curve $F(\omega\nu_0/\Delta)$ shifts to the left, while the curves corresponding to I_3 remain practically unchanged. Obviously this will promote formation of a second maximum for the absorption coefficient $\alpha_\lambda = (F + I_3)B$ on the high-frequency tail. Figure 3 shows the form of α_λ/B for $\eta = 20$ and for $\beta = 0.5$ and 1. In this case quite distinct maxima are observed.

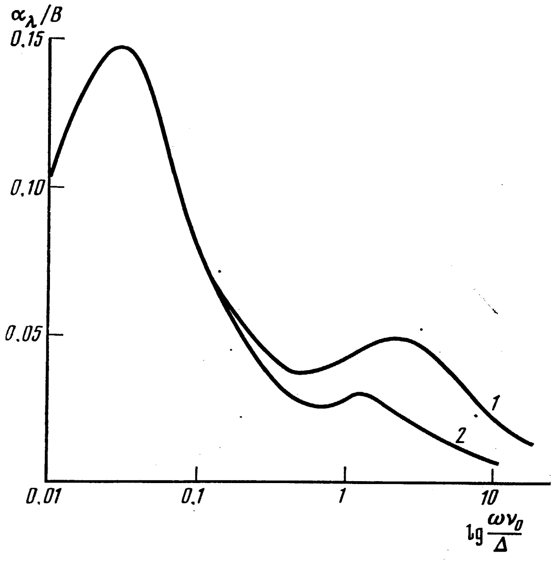

FIG. 3. Dependence of α_λ/B on frequency in the cases $\beta = 0.5$ (1) and $\beta = 1$ (2) for $\eta = 20$.

We note that to the values of β considered there must then correspond large ratios of the effective viscosities, 40 and 20. Thus the appearance of an additional maximum depends substantially on the value of the ratio of viscosities, as we have illustrated in Fig. 4 for the case $\beta = 1$. But we may hope, taking into account what was said above about the temperature dependence of this ratio, that in a number of materials the necessary conditions may be satisfied in the transition range.

We pass to consideration of a situation in which the

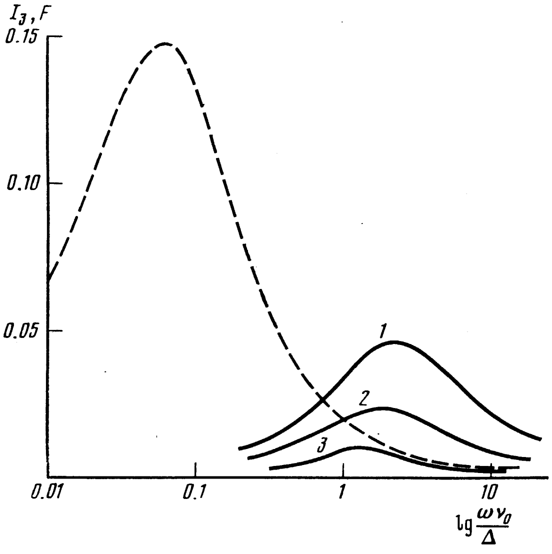

FIG. 2. Form of the function I_3 for $\beta = 0.5$ (1), $\beta = 1$ (2), and $\beta = 2$ (3). Dashed curve: the function F for $\eta = 10$.

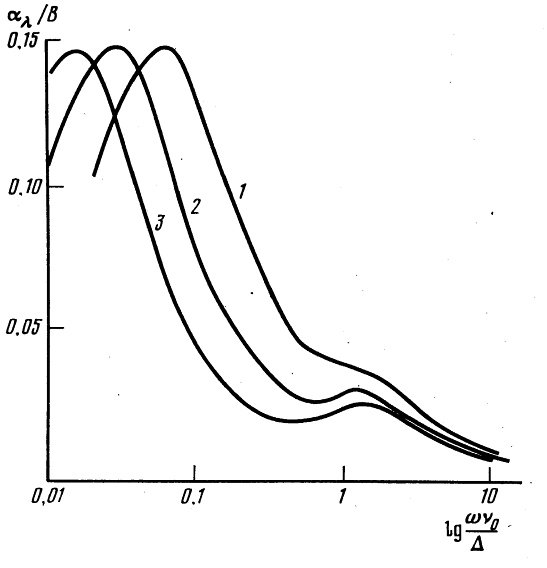

FIG. 4. Variation of α_λ/B in the case $\beta = 1$, for various values of ν_1/ν_0. 1—$\nu_1/\nu_0 = 10$; 2—$\nu_1/\nu_0 = 20$; 3—$\nu_1/\nu_0 = 40$.

value of Δ depends on temperature. In this case, the absorption may receive contributions from all three terms of formula (7), depending on their relative values and on the order of magnitude of δ.

As calculations show, the maxima of the curves corresponding to the functions I_1 and I_2 occur at frequencies near the frequencies of the maxima of I_3, with corresponding values of β; this coincidence improves with increase of β. The values of the maxima are in the following proportion:

$$I_1/I_2 \approx I_2/I_3 \approx 2 \text{ to } 3.$$

If we assume that the temperature dependence of Δ has the form $\Delta \sim [(T_c - T)/T_c]^\gamma$, then the parameter $\delta \approx \beta\gamma$; and obviously, for $\beta \gg 1$ and not too small γ, the functions I_1 and I_2 may make a noticeable contribution to the absorption coefficient and promote formation of an additional high-frequency maximum.

In the case of a transition close to an isolated critical point, $\gamma = 1/26$, and Δ, though dependent on temperature, is quite weakly so; therefore the positions of the maxima of I_3, I_2, and I_1 on approach to the transition point shift toward low frequencies much more slowly than does F, and on the whole the picture described above is retained.

In principle, there is also possible a more complicated situation, in which the phase transition is close to a fixed point of the renormalization-group equations, of the stable-focus type.[9] In this case $\gamma \approx 1$, and in the critical range the maximum of the biaxial absorption will, for $T \rightarrow T_c$, shift toward lower frequencies just as the maximum of F does. Therefore the occurrence of an additional maximum may be determined by the difference in the effective viscosities and their temperature behavior.

[1)] In Ref. 6 a typographical error apparently was made, since in front of the square brackets in (9) there is an x instead of $x^{1/2}$. The graph of the function $F(x)$ given there, however, coincides with that obtained by us with the corrected formula.

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