Dispersion and absorption of waves due to noncritical concentration fluctuations in stratifying solutions and similar phenomena in other media

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The velocity dispersion and the absorption of waves due to noncritical concentration fluctuations of the solute or defects are calculated. Two types of media are considered, in which the mechanism may explain the dispersion and absorption observed in the high-frequency range, viz., stratifying solutions and strongly viscous liquids.

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1. INTRODUCTION

In the present work, the wide-ranging phenomenon of the dispersion and absorption of waves is considered that is due to the noncritical fluctuations of the concentration of solute or defects. In our opinion, this has frequently been observed in different solutions and single-component media, but up to now it has not been correctly identified. This phenomenon can occur both in solids and in liquids; however, in the present work, we limit ourselves to liquids. The characteristic marks of dispersion and absorption associated with noncritical fluctuations of the concentration manifest themselves in special form in the dependences of the dispersion and the absorption on $\Omega\tau_0$. Here Ω is the frequency of the wave and τ_0 is a characteristic time. After setting up the basis of the theory, we shall consider in detail two examples of media in which the mechanism that is associated with the noncritical concentration of fluctuations can explain the features of the dispersion and absorption observed in high-frequency region: stratifying solutions and strongly viscous liquids.

We shall illustrate this mechanism by the example of sound propagation in an ordinary binary solution (one which is unstratified and which possesses no singular points or lines). The change in the pressure in a sound wave changes the mean square concentration fluctuations. The new concentration fluctuation distribution, which changes the volume of the system, is established through diffusion and lags the change in the pressure, and it is this which leads to dispersion of the sound velocity and to excess absorption. The only characteristic length in such a solution is the length r_0, which is of the order of the intermolecular distance. It plays the role of the correlation radius of the concentration fluctuations: the characteristic time of resorption of these fluctuations is the quantity $\tau_0 = r_0^2/D_0$, where D_0 is the diffusion coefficient. At room temperature, $D_0 \sim 10^{-5}$ cm^2/s. Setting $r_0 \sim 10^{-7}$ cm, we find $\tau_0 \sim 10^{-9}$ s. The greatest absorption per wavelength, due to this mechanism, should be observed at frequencies of the order of $\tau_0^{-1} = 10^9$ Hz.

In single-component liquids in the region of melting, where the free volume exists principally in the form of Frenkel holes, a similar mechanism can be connected with the concentration fluctuations of these holes. Actually, since the compressibility due to an individual hole, depends on the hole concentration in its vicinity, the expression for the compressibility will contains terms proportional to the square of the fluctuations of the holes concentration, which then leads to absorption of the type considered.

In contrast to the ordinary solutions, the concentration fluctuations in stratifying binary solutions are divided into noncritical fluctuations, similar to those considered above (their correlation radius is equal to r_0), and critical, which possess different properties. We call noncritical those concentration fluctuations in volumes with linear dimensions much less than the correlation radius ρ of the critical fluctuations, and we call critical (hydrodynamic) those fluctuations in volumes with linear dimensions greater than or of the order of ρ. Using the representation of the field of the correlations in the form of a Fourier spectrum, we can give an equivalent definition: the noncritical fluctuations are those in which there are only Fourier components c_k with wave numbers $k > b/\rho$, while the critical fluctuations are those in which there are only Fourier components with $k \leqslant b/\rho$, where b is a constant of the order of several units. Since, in the approximation that is used later, the thermodynamic potential is broken up into a sum of terms, each of which corresponds to fixed $\mathbf{k}$, the fluctuations with different $\mathbf{k}$ are independent. This enables us to consider separately the critical and noncritical fluctuations, which justifies the division discussed above. Such a consideration roughens the approach, since it excludes the transition region from consideration.

In the calculation of dispersion and absorption of waves in stratifying solutions, one should take into consideration both the critical and noncritical fluctuations. The dispersion and absorption produced by the critical fluctuations have been calculated previously,[1–4] while the dispersion and absorption produced by the noncritical fluctuations are first considered in the present work. The results that are obtained can be transferred automatically to solutions with singular points or singular lines,[5] except that ρ will have a different dependence on temperature and concentration than in stratifying solutions.

The region of applicability of the results obtained in the present work is not limited to the media mentioned. In particular, all that has been accomplished applies with equal measure to a material near the liquid-vapor critical point, the only difference being that the dispersion and absorption near this point are connected not with the concentration fluctuations, but with entropy fluctuations.

2. DERIVATION OF FORMULAS

The derivation of the formulas will be given in the following order. The derivation will first be given for the dispersion of the velocity and the absorption of sound waves due to noncritical fluctuations of the concentration in stratifying solutions. The corresponding formulas will then be obtained from them for electromagnetic and shear waves. Next, by small changes in the expressions, the corresponding formulas will be obtained for nonstratifying solutions and strongly viscous liquids.

The calculation of the dispersion of the velocity and the absorption of waves due to noncritical concentration fluctuations is carried out below by analogy with the calculation for critical fluctuations. It is based on the fact that most formulas for critical fluctuations take into account only the fact of the existence of the correlation radius ρ and not its specific properties, and therefore they can be used for noncritical fluctuations.

The search for additional mechanisms of dispersion and absorption in stratifying solutions, as a result of which the present research arose, has been stimulated by the following circumstances. As is well known, the basic properties of the propagation of ultrasound near a critical point of stratification can be explained by the existence of critical fluctuations of the concentration. The distinguishing feature of these fluctations is that as the critical point of stratification is approached their mean square value increases, as does the correlation radius and the correlation time, which reflects the fact that the coefficient of $\overline{|c_k|^2}$ in the thermodynamic potential vanishes as the critical point is approached. The change in the pressure in the sound wave, bringing the state of the solution to critical and moving it away from critical, changes the character of these fluctuations; a new fluctuation distribution is established with a delay and determines the diffusion dispersal time $\tau = \rho^2/D$. It is this delay which leads to dispersion and absorption of the ultrasound. In contrast to the diffusion coefficient D_0 introduced earlier, which determines the mobility of the molecules and does not have singularities near the critical point, the diffusion coefficient D in the expression for τ given above is determined by the mobility of the regions with dimensions of the order of ρ and tends to zero upon approach to the critical point.

All the existing theories of sound propagation take into account only the critical concentration fluctuations. A comparison of these theories with experiment shows that they do not describe the propagation of ultrasound badly at not too large $\Omega\tau$. However, as shown in Refs. 6–9, the sound propagation at large $\Omega\tau$, as also the propagation of hypersound in the entire critical region, cannot be described by these theories. Thus, in contrast to these theories, the ultrasound absorption per wavelength as a function of $\Omega\tau$ does not fall off at large $\Omega\tau$ and turns out to be one-two orders of magnitude smaller than the absorption per wavelength for hypersound. In the searches for the additional mechanism coresponding to the absorption of the ultrasound at large $\Omega\tau$ and of hypersound in stratifying solutions, attention was turned to the terms of higher order of smallness in the fluctuations in the thermodynamic potential.1) Thus, terms that are cubic in the fluctuations of the concentration were considered in Ref. 11, and terms of fourth order in Ref. 12. These terms, as can be judged from estimates carried out in these references, give a significant correction, but they do not remove the disparity of theory and experiment at hypersonic frequencies. However, before developing further mechanisms connected with terms of higher order in the fluctuations, it is natural to make full use of the contributions from the thermodynamic-potential terms that are quadratic in the fluctuations of the concentration, namely, along with account of the critical fluctations, we should also take into account the mechanism of noncritical concentration fluctuations described above. This will be done below. As estimates given in Sec. 3 show, the ultrasonic absorption at large $\Omega\tau$ and hypersonic absorption in stratifying solutions can be explained by this contribution.

Thus, we derive an expression for the velocity dispersion and for the excess absorption of the sound waves due to the noncritical fluctuations of the concentration in stratifying solutions. This derivation reduces to the derivation given in Refs. 3 and 4 for critical fluctuations if we replace a number of functions in the thermodynamic potential and in the equation of motion. We shall first concern ourselves with these replacements. Next, omitting the calculations, which are similar to those carried out in Refs. 3 and 4, we obtain the final formulas.

The part of the thermodynamic potential associated with the noncritical concentration fluctuations, with allowance for only those terms that are quadratic in the fluctuations, can be represented near the critical point in the following form:

$$\Delta\Phi = \frac{VB_0}{(2\pi)^3} \int \overline{|c_k|^2} \frac{1}{\chi_0(kr_0)} d\mathbf{k}. \tag{1}$$

Here V is the volume of the system, B_0 is a quantity proportional to the chemical potential for noncritical fluctuations (and has no singularities near the critical point); $\chi_0(kr_0)$ is a function that takes into account the nonlocality: the bar indicates averaging over the ensemble, integration is carried out over all directions of $\mathbf{k}$ and over all k from b/ρ to b'/r_0. (As follows from a comparison with experiment, which was carried out in Ref. 4, best agreement is obtained at $b = 5$.) It is not difficult to see, by comparing (1) with the expression given for the thermodynamic potential in Ref. 3, that Eq. (1) reduces to that part of the thermodynamic potential which depends on the critical fluctuations if we replace B_0 in it by B (the coefficient B vanishes at the critical point), replace $\chi_0(kr_0)$ by $\chi(k\rho) = [1 + (k\rho)^2]^{-1}$, which corresponds to the Ornstein–Zernike correlation function, and replace the limits of integration over k by $(0, b/\rho)$.

The expression given above for $\chi(k\rho)$ means that upon increase in $k\rho$ from 0 to b, only those terms that are quadratic in the gradient of the concentration appear in the thermodynamic potential, while terms of higher order in $k\rho$ make only an insignificant contribution. Since the presence of such terms is connected only with the fact of the existence of the correlation radius, and not with its specific properties, similar terms should appear also in the case of noncritical fluctuations, so that $\chi_0(kr_0)$ should have the similar form

$$\chi_0(kr_0)=[1+(kr_0)^2]^{-1}.$$

The velocity dispersion and excess absorption of sound of interest to us are caused by the delay in the change of the portion of the volume associated with the noncritical fluctuations relative to the change in the pressure. This delay arises as the result of the diffusion process of dispersal of the fluctuations, which is described by the equation

$$\dot{c}_k+D_0k^2\varphi_0(kr_0)c_k=-f_k\chi_0(kr_0)/2B_0. \tag{2}$$

Here f_k is the fluctuating force and φ_0 is an analog of the Kawasaki function. This equation, upon replacement of $\varphi_0(kr_0)$ by $\varphi(k\rho)$, of $\chi_0(kr_0)$ by $\chi(k\rho)$, of B_0 by B, and of D_0 by D reduces to the equation for the critical fluctuations used in Refs. 3 and 4. The function $\varphi(k\rho)$ has the form

$$\varphi(k\rho)={}^3/_4\{(k\rho)^{-2}+1+[k\rho-1/(k\rho)^3]\,\mathrm{arctg}\,k\rho\}.$$

Since the form of this function is also determined only by the fact of the existence of the correlation radius, and not its specific properties, $\varphi_0(kr_0)$ should have the analogous form:

$$\varphi_0(kr_0)={}^3/_4\{(kr_0)^{-2}+1+[kr_0-1/(kr_0)^3]\,\mathrm{arctg}\,kr_0\}.$$

Using (1) and (2) and repeating the derivation carried out in Ref. 3, it is not difficult to obtain the following equation for the complex compressibility:

$$\beta=\beta_0+\beta_1+\frac{k_BT}{2\pi^2r_0^3}\int_{br_0/\rho}^{b}\left[\frac{\partial}{\partial p}\left(\frac{B_0}{\chi(x)}\right)\right]^2\left(\frac{\chi(x)}{B_0}\right)^2\frac{x^4\varphi(x)\,dx}{i\Omega\tau_0+2x^2\varphi(x)} \tag{3}$$

where β_0 is the part of the compressibility associated with all the other processes except the one considered here, k_B is Boltzmann's constant, T is the absolute temperature, $x = kr_0$, and

$$\beta_1=-\frac{2}{(2\pi)^2}\int_{br_0/\rho}^{b}\left[\frac{\partial^2}{\partial p^2}\left(\frac{B_0}{\chi(kr_0)}\right)\right]\overline{|c_k|^2}k^2dk. \tag{4}$$

All the derivatives are taken at constant entropy, in which terms connected with the concentration fluctuations are not taken into account. The term β_1 is evidently small, since the second derivatives with respect to p enter into it. We shall neglect it in what follows.

Further, we make the following assumption: we regard $B_0r_0^2$ as practically independent of pressure, so that

$$\frac{\partial}{\partial p}\left[\frac{B_0}{\chi(x)}\right]=\frac{\partial B_0}{\partial p}.$$

Some justification of this assumption is that a similar situation holds for critical fluctuations. Using this assumption and introducing the notation

$$F_1\left(\Omega\tau_0,\frac{r_0}{\rho}\right)=\int_{br_0/\rho}^{b}x^4\cdot\frac{3}{4}\left[\frac{1}{x^2}+1+\left(x-\frac{1}{x^3}\right)\mathrm{arctg}\,x\right]$$
$$\times\left\{(\Omega\tau_0)^2+4x^4\cdot\frac{9}{16}\left[\frac{1}{x^2}+1+\left(x-\frac{1}{x^3}\right)\mathrm{arctg}\,x\right]^2\right\}^{-1}$$
$$(1+x^2)^{-2}dx, \tag{5}$$

$$F_2\left(\Omega\tau_0,\frac{r_0}{\rho}\right)=\int_{br_0/\rho}^{b}2x^6\cdot\frac{9}{16}\left[\frac{1}{x^2}+1+\left(x-\frac{1}{x^3}\right)\mathrm{arctg}\,x\right]^2$$
$$\times\left\{(\Omega\tau_0)^2+4x^4\cdot\frac{9}{16}\left[\frac{1}{x^2}+1+\left(x-\frac{1}{x^3}\right)\mathrm{arctg}\,x\right]^2\right\}^{-1}$$
$$(1+x^2)^{-2}dx, \tag{6}$$

we can represent (3) in the following form:

$$\beta=\beta_0+\frac{k_BT}{2\pi^2r_0^3B_0^2}\left(\frac{\partial B_0}{\partial p}\right)^2\left[-i\Omega\tau_0F_1\left(\Omega\tau_0,\frac{r_0}{\rho}\right)\right.$$
$$\left.+F_2\left(\Omega\tau_0,\frac{r_0}{\rho}\right)\right]. \tag{7}$$

From (7) we obtain the following equations for the sound velocity and the absorption coefficient referred to the frequency δ/Ω and connected with the considered process:

$$v=v_0\left\{1-Mv_0F_2\left(\Omega\tau_0,\frac{r_0}{\rho}\right)\right\}, \tag{8}$$

$$\frac{\delta}{\Omega}=MF_1(\Omega\tau_0,r_0/\rho)\Omega\tau_0, \tag{9}$$

where

$$M=\frac{k_BTgv_0}{4\pi^2r_0^3B_0^2}\left(\frac{\partial B_0}{\partial p}\right)^2,\quad v_0=\frac{1}{(g\beta_0)^{1/2}},$$

g is the density.

If we limit ourselves to the consideration of $\Omega\tau_0$ within the limits of the inequalities

$$\frac{3}{2}\left(\frac{br_0}{\rho}\right)^2\left[\left(\frac{br_0}{\rho}\right)^{-2}+1+\left(\frac{br_0}{\rho}-\left(\frac{br_0}{\rho}\right)^{-3}\right)\mathrm{arctg}\left(\frac{br_0}{\rho}\right)\right]$$
$$\ll\Omega\tau_0\ll\frac{3}{2}b^2\left[\frac{1}{b}+1+\left(b-\frac{1}{b^3}\right)\mathrm{arctg}\,b\right], \tag{10}$$

then the limits of integration in (5) and (6) can be replaced by $(0,\infty)$, since the principal contribution to the integrals of (5) and (6) are made by the poles. With such a substitution, the expressions for $F_1(\Omega\tau_0,0)$ and $F_2(\Omega\tau_0,0)$ will be identical with the expressions $F_1(\Omega\tau)$ and $F_2(\Omega\tau)$ obtained in Ref. 4, if we replace $\Omega\tau_0$ in them by $\Omega\tau$. The functions $F_1(\Omega\tau,0)$, $F_2(\Omega\tau)$ are thus a generalization of $F_1(\Omega\tau)$, $F_2(\Omega\tau)$ to the case of arbitrary $\Omega\tau$. Plots of $F_2(\Omega\tau_0,r_0/\rho)$ and $F_1(\Omega\tau_0,r_0/\rho)\Omega\tau_0$ at $b = 5$ are shown in Fig. 1. The plots of the functions $F_2(\Omega\tau_0;0)$, $F_1(\Omega\tau_0,0)\Omega\tau_0$ are shown as continuous curves, the others as dashed lines.

We now discuss these plots. As is seen from Fig. 1, $F_1(\Omega\tau_0,0)\Omega\tau_0$, the function that determines the absorption per wavelength, has a very broad peak as $r_0/\rho\to 0$ (the width of this peak at half-height is about three decades). In this connection, in the broad range of values of $\Omega\tau_0$ near the maximum (it corresponds to $\Omega\tau_0\approx 16$), the function $F_1(\Omega\tau_0,0)\Omega\tau_0$ depends weakly on $\Omega\tau_0$. The region of dependence of the function $F_2(\Omega\tau_0,0)$ on $\Omega\tau_0$—the dispersion region—is also broad. It comprises more than five decades, which is incomparably greater than the width of the dispersion curves for all the known dispersion mechanisms. The maximum absorption is close to the center of the dispersion curve. The enumerated features are the characteristic features of the considered mechanism of dispersion and absorption. With increase in r_0/ρ, the maximum of the function

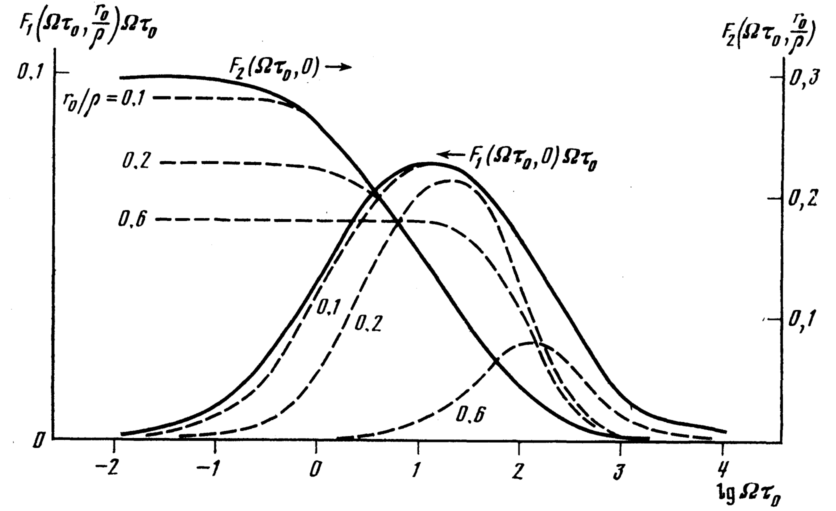

FIG. 1. $F_1(\Omega\tau_0, r_0/\rho)\Omega\tau_0$ and $F_2(\Omega\tau_0, r_0/\rho)$ as functions of $\Omega\tau_0$ at various r_0/ρ.

$F_1(\Omega\tau_0, r_0/\rho)\Omega\tau_0$ is lowered and the width of the peak, as also of the dispersion curve, is decreased.

The character of the noncritical fluctuations can change not only under the effect of pressure, but also under the effect of an electric field and of a shear stress. In the case of propagation of an electromagnetic wave, by replacing the pressure p in Eq. (3) by the electric field E and the compression by the polarization, we obtain the following equation for the complex dielectric susceptibility $\varkappa$:

$$\varkappa=\varkappa_0+\varkappa_1+\frac{k_BT}{2\pi^2r_0^3}\int_{br_0/\rho}^{b}\left[\frac{\partial}{\partial E}\left(\frac{B_0}{\chi(x)}\right)\right]^2\left(\frac{\chi(x)}{B_0}\right)^2\frac{x^4\varphi(x)\,dx}{i\Omega\tau_0+2x^4\varphi(x)},$$

where $\varkappa_0$ is the part not associated with the mechanism considered, and

$$\varkappa_1=-\frac{2}{(2\pi)^2}\int_{br_0/\rho}^{b}\left[\frac{\partial^2}{\partial E^2}\left(\frac{B_0}{\chi(kr_0)}\right)\right]\overline{|c_{\mathbf{k}}|^2}k^2\,dk.$$

We then obtain the following for the real ε' and imaginary ε'' parts of the permittivity:

$$\varepsilon'=\varepsilon_0+\frac{2k_BT}{\pi r_0^3}\left(\frac{\partial B_0}{\partial E}\right)^2F_2\left(\Omega\tau_0,\frac{r_0}{\rho}\right), \tag{11}$$

$$\varepsilon''=\frac{2k_BT}{\pi r_0^3}\left(\frac{\partial B_0}{\partial E}\right)^2F_1\left(\Omega\tau_0,\frac{r_0}{\rho}\right)\Omega\tau_0, \tag{12}$$

where $\varepsilon_0 = 1 + 4\pi(\varkappa_0 + \varkappa_1)$.

In the case of propagation of a shear wave, by replacing the pressure p in (3) with the shear stress σ, and the compression by the shear strain, it is not difficult to obtain similar formulas for the velocity W of the shear wave and its absorption coefficient divided by the frequency, α/Ω:

$$W=W_0\left\{1-\frac{k_BTgW_0^2}{4\pi^2r_0^3B_0^3}\left(\frac{\partial B_0}{\partial\sigma}\right)^2F_2(\Omega\tau_0,r_0/\rho)\right\}, \tag{13}$$

$$\frac{\alpha}{\Omega}=\frac{k_BTgW_0}{4\pi^2r_0^3B_0^2}\left(\frac{\partial B_0}{\partial\sigma}\right)^2F_1\left(\Omega\tau_0,\frac{r_0}{\rho}\right)\Omega\tau_0. \tag{14}$$

The indices of the components of the vectors and tensors do not appear in Eqs. (11)–(14). Since B_0 should depend on E^2 and on the contraction of the shear stress tensor, $(\partial B_0/\partial E)^2$ in (11) and (12) can be taken as the square of the vector $(\partial B_0/\partial \mathbf{E})$, directed along $\mathbf{E}$, while $(\partial B_0/\partial\sigma)^2$ in (13) and (14) can be understood as the contraction of the tensor $\partial B_0/\partial\sigma_{ik}$.

The high-frequency shear moduli and, hence the shear waves, are present in all liquids. However, in liquids of low viscosity, these shear moduli are significantly less than in strongly viscous liquids. In the latter, it should be taken into account that, in the propagation of a plane sound wave, not only hydrostatic compression of the medium occurs, but also shear. With account of the shear modulus, we get the following refined formula from (8), (9) and (13), (14) for the sound velocity $\tilde{v}$ and the absorption coefficient referred to the frequency δ/Ω:

$$\tilde{v}=\tilde{v}_0\{1-\tilde{M}\tilde{v}_0F_2(\Omega\tau_0,\ r_0/\rho)\}, \tag{15}$$

$$\delta/\Omega=\tilde{M}F_1(\Omega\tau_0,\ r_0/\rho)\Omega\tau_0, \tag{16}$$

where $\tilde{v}_0^2 = v_0^2 + \frac{4}{3} W_0^2$,

$$\tilde{M}=\frac{k_BTg}{4\pi^2r_0^3B_0^2\tilde{v}_0^3}\left[v_0^4\left(\frac{\partial B_0}{\partial p}\right)^2+{}^4/_3W_0^4\left(\frac{\partial B_0}{\partial\sigma}\right)^2\right].$$

For ordinary solutions, Eqs. (8) and (9) are preserved, but it is necessary to put $r_0/\rho = 0$ in them. Thus, the sound velocity and absorption, referred to the frequency, in an ordinary solution (non-stratifying and not possessing any singular points or lines), are described by the equations

$$v=v_0\left\{1-\frac{k_BTgv_0^2}{4\pi^2r_0^3B_0^2}\left(\frac{\partial B_0}{\partial p}\right)^2F_2(\Omega\tau_0,0)\right\},$$

$$\frac{\delta}{\Omega}=\frac{k_BTgv_0}{4\pi^2r_0^3B_0^2}\left(\frac{\partial B_0}{\partial p}\right)^2F_1(\Omega\tau_0,0)\Omega\tau_0.$$

Equations (11)–(16) are changed in similar fashion.

In the case of strongly viscous liquids, account of the fluctuations of the hole concentration in the ordered regions leads to Eqs. (8)–(16), where ρ should now be replaced by the radius a of the ordered region.

3. STRATIFYING SOLUTIONS

We now consider in greater detail the contribution of the critical fluctuations to the dispersion and absorption of

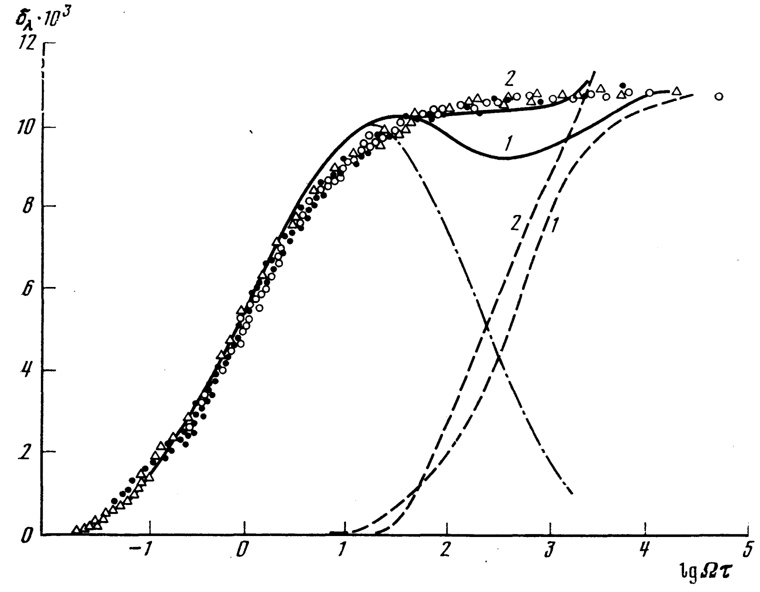

FIG. 2. Sound absorption per wavelength in a nitroethane-isooctane solution as a function of $\Omega\tau$; ● (4.2 MHz), △ (10.1 MHz), ○ (15.9 MHz)—experimental points taken from Ref. 6; the lines are theoretical curves: dash-dot—contribution from critical fluctuations of the concentration; dashed—contribution from noncritical fluctuations, solid—sum curves; curves 1 refer to the frequency 4.2 MHz, 2 to the frequency 15.9 MHz.

sound in stratifying solutions. Experimental data for sound absorption per wavelength δ_λ and for the sound-velocity dispersion $\Delta = [v(\Omega) - v(0)]/v(0)$ at fixed temperature for various frequencies as a functions of $\Omega\tau$ in a nitroethane-isooctane solution, taken from Ref. 6, are reproduced in Figs. 2 and 3. The dash-dot lines on these drawings show the contributions from the critical fluctuations. In the calculation of these contributions, we have used the plots of Fig. 1 and have assumed that quantity

$$(k_B T g v_0^2/2\pi\rho^3 B^2)\,(\partial B/\partial p)^2$$

which depends weakly on the nearness to the critical point, is equal to 0.135, and have also taken τ to be 3 times smaller than in Ref. 6. Such a change in τ can be admitted, in view of the inaccuracy of the determination of ρ and the use in Ref. 6 of a relation that is not always correct for the diffusion coefficient ($D = k_B\, T/6\pi\eta\rho$, where η is the coefficient of viscosity).

For the calculation of the contribution from the noncritical fluctuations, we have used Eqs. (8) and (9). Since there is no possibility of determining from independent measurements the quantity $2\pi M v_0$ that enters into these formulas, we must so choose it as to obtain the best agreement with experiment. For the nitroethane-isooctane solution, this quantity turns out to be equal to 1.3. At the beginning of the curves in Figs. 2 and 3, i.e., at values of log $\Omega\tau$ from -1 to 0, the correlation radius of the critical fluctuations ρ is of the order of 10^{-7} cm. Since ρ changes in proportional to $\tau^{1/3}$, at values of log $\Omega\tau$ from 2 to 3 the radius ρ will be of the order of 10^{-6} cm. The correlation radius of the critical fluctuations is of the same order as ρ at the beginning of the curves, so that at values of log $\Omega\tau$ from 2 to 3, r_0/ρ will be of the order of 0.1. At such r_0/ρ, the curves $F_2(\Omega\tau_0, r_0/\rho)$, $F_1(\Omega\tau_0, r_0/\rho)\Omega\tau_0$ with be close to $F_2(\Omega\tau_0, 0)$, $F_1(\Omega\tau_0, 0)\Omega\tau_0$. Thus, over a range of approximately three decades of change of $\Omega\tau$, the functions $F_2(\Omega\tau_0, r_0/\rho)$ and $F_1(\Omega\tau_0, r_0/\rho)\Omega\tau_0$ change from zero to their maximum values $F_2(\Omega\tau_0, 0)$, $F_1(\Omega\tau_0, 0)\Omega\tau_0$ corresponding to the given $\Omega\tau_0$. In correspondence with this, the on the plots of $\tilde{\delta}_\lambda$ and Δ vs $\Omega\tau$, the contributions $\tilde{\delta}_\lambda$ and $\tilde{\Delta}$ to these quantities from the noncritical fluctuations will take the following form beyond the range of $\tilde{\delta}_\lambda$ and $\tilde{\Delta}$ from zero to the limiting value, which comprises about three decades of $\Omega\tau$, there will follow a region in which $\tilde{\delta}_\lambda$ and $\tilde{\Delta}$ are practically independent of $\Omega\tau$. Assuming that $r_0/\rho = 1$ at $\log \Omega\tau = 0$ for a frequency of 4.2 MHz, and also that[2)] $\tau_0 = 3 \times 10^{-9}$ s, we obtain the curves for $\tilde{\delta}_\lambda$ and $\tilde{\Delta}$ that are shown as dashed lines in Figs. 2 and 3. The solid lines on these drawings indicate the total contribution of the critical and noncritical fluctuations. Curves 1 and 2 in Fig. 2 refer respectively to the frequencies of 4.2 and 15.9 MHz. The curves in Fig. 3 refer to the frequency of 27.7 MHz (at frequencies of 2 and 9 MHz

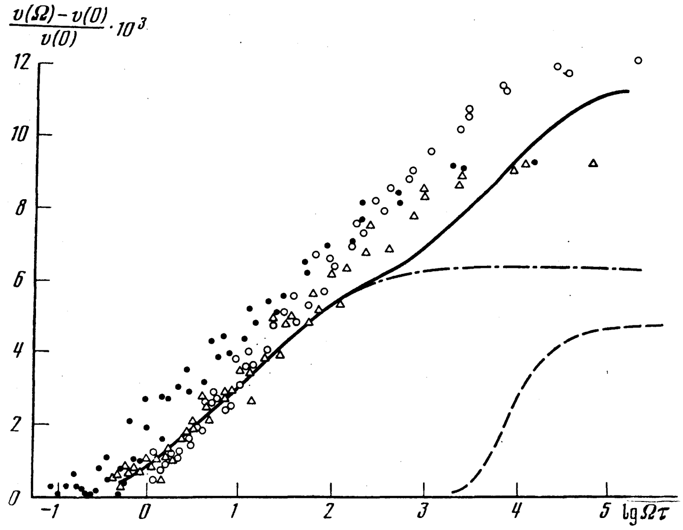

FIG. 3. Sound velocity dispersion in a nitroethane-isooctane solution as a function of $\Omega\tau$; ●, △, ○—(2 MHz, 9.3 MHz and 27.7 MHz, respectively)—experimental points taken from Ref. 6; the lines are theoretical curves, the dash-dot curves refer to the contribution from critical fluctuations of the concentration, the dashed curves to the contribution from noncritical fluctuations at 27.7 MHz, and the solid curve is their sum.

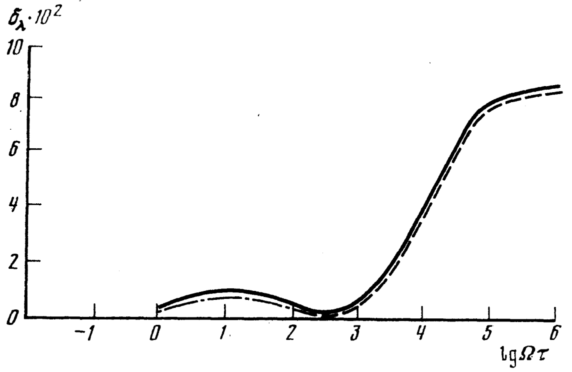

FIG. 4. Theoretical curve for the absorption per wavelength at a frequency of 4 GHz in nitroethane-isooctane solution; the dot-and-dash curve is the contribution from the critical fluctuations, the dashed curve, the contribution from noncritical fluctuations and the solid curve is the sum curve.

the contributions of the noncritical fluctuations to Δ are small). We turn our attention to the fact that consideration of the noncritical fluctuations leads to the result that Δ at large $\Omega\tau$ depends not only on $\Omega\tau$ but also (significantly) on the frequency, in accord with the results of Ref. 6. As is seen from Figs. 2 and 3, account of the noncritical fluctuations, along with the critical, can, with a certain choice of parameters, explain the dispersion of the velocity and the absorption of sound over the entire range of $\Omega\tau$ investigated in Ref. 6.

The calculated plot of δ_λ vs $\Omega\tau$ at a frequency of 4 GHz in the same solution is given in Fig. 4. The dash-dot curve is the contribution from the critical fluctuations, the dashed curve the contribution from the noncritical fluctuations, and the solid curve is the sum of the other two. As is seen from this drawing, the contributions from the critical and noncritical fluctuations diverge at this frequency; the absorption of hypersound increases upon approach to the critical point, up to a certain maximum value. At temperatures different from critical by less than 0.1 K, the value of $\Omega\tau$ at 4 GHz is more than 10^5, so that δ_λ is close to the maximum value, which is equal to 0.075. Since the wavelength at this frequency is equal to 2.5×10^{-5} cm, the absorption coefficient turns out to be equal to 3000 cm^{-1}. A value of 3000 cm^{-1} was also obtained in Ref. 13 at a frequency of 3.5 GHz for the absorption coefficient in this solution at a temperature close to the critical. Absorption coefficients of the same order of magnitude (from 8000 to 27,000 cm^{-1}) for hypersound of frequency 4 GHz, which increases upon approach to the critical point, have been observed in aniline-cyclohyxane and nitrobenzene-n-hexane solutions.[7] Such large values of the absorption coefficient of hypersound have not found explanation within the framework of existing theory; the possibility of their explanation is a persuasive argument in favor of the use of the representations developed here.

4. STRONGLY VISCOUS LIQUIDS

According to the local diffusion theory of wave propagation in strongly viscous liquids,[14] the dispersion and anomalous absorption in them are due to the an increase or decrease of degree of ordering because of the diffusion of holes through the boundaries of these regions. The characteristic time of this process (the time of rearrangement of the ordered region) is equal to $\tau_a = a^2/2D_h$, where a is the radius of the ordered region and D_h is the diffusion coefficient of the holes. Since D_h is inversely proportional to the viscosity η, $\tau_a \propto \eta$ and changes rapidly with temperature. In this connection, the dependence of the velocity dispersion and the absorption coefficient, referred to the frequency, on $\Omega\tau_a$ can be tracked not only by changing the frequency, but also by changing the temperature. The nonlocal diffusion theory is applicable[15] only if $\Omega\tau_a \ll (a/r_0)^2$. This theory gives a fair description of the propagation of shear, sound, and electromagnetic fields in a large number of highly viscous liquids at not too large $\Omega\tau_a$. At large $\Omega\tau_a$, i.e., at high frequencies and low temperatures, a systematic deviation from this theory is observed in a number of liquids.[16] These deviations are manifest by the fact that upon increase in $\Omega\tau_a$ the absorption coefficient, referred to the frequency, falls off more slowly than according to the law $(\Omega\tau_a)^{-1/2}$ given by the nonlocal diffusion theory. Similar deviations are observed also in the propagation of electromagnetic waves.[17] We can explain these deviations by inclusion of the mechanism of the wave absorption by of hole-concentration fluctuations (with wave numbers $k > b/a$) inside the ordered regions (the mutual influence of the holes in the disordered liquid should be significantly weaker than in the ordered regions). These fluctuations are analogous to the noncritical fluctuations considered above.

Account of the fluctuations of the hole concentration in ordered regions is a natural development of the nonlocal diffusion theory of wave propagation in such liquids. Actually, according to Ref. 14, the degree of order in the ordered regions can be characterized by the hole concentration ξ which takes on the equilibrium value ξ_0 at the specified pressure and temperature. This means that the thermodynamic potential of the ordered region can be represented in the form

$$\Phi=\Phi_0-\tilde{A}\xi+\tilde{B}\xi^2,$$

where $\tilde{A}$ and $\tilde{B}$ are certain functions of the pressure and temperature. From the condition that Φ be a minimum we find $\xi_0 = \tilde{A}/2\tilde{B}$. In order that the equilibrium value change appreciably upon change in the pressure p in the sound wave, as was assumed in Ref. 14, it is necessary that either $\tilde{A}$ or $\tilde{B}$ or both depend strongly on p. The parameter $\tilde{A}$ has the meaning of the energy of hole formation. It is known that this quantity does not change with p, so that it must be assumed that $(\partial\tilde{B}/\partial p)/\tilde{B}$ is sufficiently large in the ordered region. The term that depends on the fluctuations $\delta\xi$ in the thermodynamic potential of the ordered region has a form similar to Eq. (1):

$$\Delta\Phi=\frac{V\tilde{B}}{(2\pi)^3}\int\overline{|(\delta\xi)_{\mathbf{k}}|^2}\,\frac{1}{\chi(kr_0)}\,d\mathbf{k},$$

where the notation is the same as in (1), while integration over k extends from b/a to b/r_0. By changing the designation $\tilde{B}$ to B_0, we obtain for the velocity dispersion and the excess sound absorption Eqs. (15) and (16), in which ρ should be replaced by a. Since $(\partial\tilde{B}/\partial p)/\tilde{B}$ is large, we can expect the

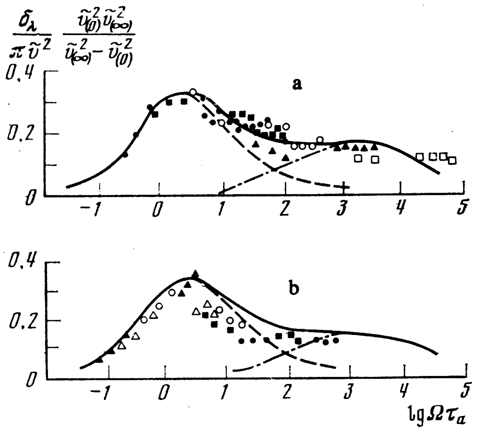

FIG. 5. Dependence of the sound absorption per wavelength δ_λ, multiplied by $(\pi\tilde{v}^2)^{-1}\tilde{v}^2_{(0)}\tilde{v}^2_{(\infty)}/(\tilde{v}^2_{(\infty)}-\tilde{v}^2_{(0)})$, on $\Omega\tau_a$ in 2–3 butanediole (a) and polytriethyleneglycolsuccinate (b); the experimental points are taken from Ref. 16; a) ●—0°, ■— – 10°, ○— – 20°, ▲— – 35°, ○— – 50 °C; b) ▲—40°, △—30°, ○—20°, ■— – 2°, ●— – 11 °C. The dashed curve is the dependence as given by the nonlocal diffusion theory, the dash-dot curve represents the contribution from fluctuations of the hole concentration, calculated from the equation of Ref. 16, the solid curve is their sum.

contribution of the fluctuations of ξ to the dispersion and sound absorption to be considerable. The same applies to the shear and electromagnetic waves.

A feature of the strongly viscous liquids is that the time of rearrangement of the ordered regions, $\tau_a = a^2/D_h$, which enters into the nonlocal diffusion theory, has the same dependence on the temperature as the time $\tau_0 = r_0^2/D_h$ in Eqs. (15) and (16), since a depends weakly on the temperature in comparison with D_h. Therefore, the total contribution of the two mechanisms (rearrangement of the ordered regions and fluctuations of the hole concentration inside these regions) to the velocity dispersion and the sound absorption per wavelength will be functions only of the products $\Omega\tau_a$ (or $\Omega\tau_0$), which are proportional to $\Omega\eta$.

The ratio τ_a/τ_0 is equal to $\frac{1}{2}(a/r_0)^2$. The maximum absorption per wavelength connected with τ_a is observed at $\Omega\tau_a \approx 2$, while the maximum associated with τ_0 occurs at $\Omega\tau_0 \approx 16$, so that the ratios of the quantities $\Omega\tau_a$ corresponding to these maxima are equal to

$$(\Omega\tau_a)_1/(\Omega\tau_a)_2 = {}^1/_4(r_0/a)^2.$$

Since the peak corresponding to τ_0 is very broad (about three decades of $\Omega\tau_a$) only at $(a/r_0)^2 > 100$ are the regions of dispersion associated with τ_a and τ_0 separated (they overlap weakly). In the opposite case, they are superimposed, giving a very complicated picture.

Figure 5 shows the experimental data for absorption at the wavelength δ_λ referred to

$$\pi\tilde{v}^2(\tilde{v}_{(\infty)}-\tilde{v}_{(0)})/\tilde{v}^2_{(0)}\tilde{v}_{(\infty)},$$

($\tilde{v}_{(\infty)}$ and $\tilde{v}_{(0)}$ are the limiting high-frequency and low-frequency values of the sound velocity $\tilde{v}$) as functions of $\Omega\tau_a$, taken from Ref. 16, for two strongly viscous liquids: 2–3 butanediol and polytriethyleneglycolsuccinate. The dashed curves are those computed from the nonlocal diffusion theory. The dash-dot curve shows the contribution from the fluctuations of ξ, constructed from Eq. (16) at

$$2\pi\tilde{v}_0 M\frac{\tilde{v}^2_{(0)}\tilde{v}^2_{(\infty)}}{\pi\tilde{v}^2(\tilde{v}^2_{(\infty)}-\tilde{v}^2_{(0)})} = 2, \quad \left(\frac{a}{r_0}\right)^2 = 200.$$

The values of these two quantities were chosen by us in order to obtain best agreement with the experiment. The solid line is their sum. As is seen from Fig. 5, the much weaker dependence of δ_λ on $\Omega\tau_a$ at large $\Omega\tau_a$, in comparison with what is provided by the nonlocal diffusion theory, can be explained by the contribution of the fluctuations of the hole concentration.

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[1)] Quadratic terms proportional to the concentration fluctuations and entropy fluctuations were considered in Ref. 10. Their maximum contribution to the absorption per wavelength is equal to 10^{-3} and constitutes at hypersonic frequencies a small fraction of the observed value.[7]

[2)] If the diffusion coefficient were known to us, then, using r_0 found from the first assumption, we could calculate τ_0.

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