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Abstract

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INTERPRETATION OF THE SPECTRAL COMPOSITION OF LIGHT SCATTERED BY FLUCTUATIONS OF ANISOTROPY IN A LIQUID

(Presented by Academician M. A. Leontovich, 5 VII 1963)

The nature of the "wing" of the Rayleigh line cannot as yet be regarded as fully clarified (1). Making a substantial contribution to the elucidation of the problem, the relaxation theory of M. A. Leontovich (2), subsequently generalized by S. M. Rytov (3), concerns that part of the anisotropy fluctuations which is associated with fluctuations of the strain tensor (4).

In the present note, anisotropy fluctuations not associated with fluctuations of the strain tensor are considered, and, in a somewhat different way than in (2,3), anisotropy fluctuations associated with elastic effects are taken into account.

1. Let us consider a linear molecule in a viscous medium in the space of angles and velocities. Solving the problem of its Brownian rotational motion by means of the Fokker–Planck equation (5,6), we obtain an expression for the intensity of light scattered by a medium consisting of such molecules*:

$$J_z = \frac{4}{3} J_x = \frac{4}{45\pi} \frac{\zeta/6kT}{\left(1 - \frac{I}{4kT}\omega^2\right)^2 + \omega^2(\zeta/6kT)^2} \tag{1}$$

under the condition that

$$kT \ll \frac{1}{4}\frac{\zeta^2}{I}, \qquad \omega \ll 2\frac{\zeta}{I}. \tag{2}$$

Here ζ, I, and ω are, respectively, the internal friction, the moment of inertia of the molecule, and the frequency counted from the frequency of the exciting light. In (1) the relaxation time is $\tau = \frac{1}{3}\tau_D$, where τ_D is the Debye relaxation time (7).

2. In a liquid, in addition to the diffusional motion considered above, molecules can undergo elastic oscillations. A crude model of such oscillations with friction can be described by the equation

$$I\frac{d^2\Delta\vartheta}{dt^2}+\zeta\frac{d\Delta\vartheta}{dt}+\mu\Delta\vartheta=M(t), \tag{3}$$

where $\Delta\vartheta$ is the angle of deviation of the molecular axis from its equilibrium direction; μ is the elastic constant; $M(t)$ is a random force. Such elastic oscillations will lead to the appearance of local anisotropy in the liquid. Using the stochastic equation (3), one can find ([8]) the spectral density of the correlation function $(\Delta\vartheta)^2_\omega$, and then also the expression for the spectral distribution of the intensity of the scattered light:

$$J_z=\frac{4}{3}J_x=\frac{4}{45\pi}\frac{6kT}{\mu}\frac{\zeta/\mu}{\left(1-\frac{I}{\mu}\omega^2\right)^2+\omega^2(\zeta/\mu)^2}. \tag{4}$$

A similar expression is given by the theory of M. A. Leontovich with allowance for the inertial term in the relaxation equation (Yu. N. Zhivlyuk). In (3) and (4) the quantities ζ and μ are assumed not to depend on frequency. Meanwhile it had already been pointed out ([1,9]) that such dependence should be taken into account. Therefore one can in (3) introduce the Maxwellian mechanism of viscosity relaxation, and then, as the solution, we obtain the same expression (4), but with parameters depending on the frequency:

$$\xi=\frac{\xi_0}{1+\omega^2\tau_\xi^2},\qquad \mu=\mu_0+\xi_0\tau_\xi\frac{\omega^2}{1+\omega^2\tau_\xi^2}, \tag{5}$$

where ξ_0 and μ_0 are the friction and elastic constant at low frequencies; τ_ξ is the relaxation time of the viscosity for elastic librations.

Table 1

Measured and calculated relaxation times ν_c of anisotropy*

* The incident light is linearly polarized. The observation is made at an angle of 90° to the direction of the in

$$\sim\frac{\omega_0^4}{R^2c^4}(\alpha_1-\alpha_2)^2,$$

where α_1 and $\alpha_2=\alpha_3$ are the principal polarizabilities of the molecule.

Substance	Viscosity (20°), poise	$\tau \cdot 10^{12}$, sec. according to (1)	$\tau \cdot 10^{12}$, sec. according to the author	$\tau \cdot 10^{12}$, sec. calculated
Carbon disulfide	0.0037	2.4	2.3	2.8
Benzene	0.0065	3.3	3.8	7.5
Chloroform	0.0057	–	5.9	5.8
Toluene	0.0059	5.3	4.1	8.6
Acetic acid	0.012	17.5	14	13

* In calculating τ, critical data (11) were used.

In a liquid, apparently, elastic librations, like elastic shear deformations at high frequencies (anisotropy waves, transverse shear waves), must at low frequencies pass over into another kind of motion (10). If it is assumed that at low frequencies the motion has the character of self-diffusion and, consequently, for the intensity of depolarized scattered light (1) is satisfied, then formally the transition from (4) to (1) may be represented as a dispersion of the parameters entering into (4). However, it is hardly possible to make such a transition by assuming in a liquid $\mu_0 = 6kT$, although, to within inertial terms, this gives a continuous transition from (4) to (1). Apparently, the transition from (4) and (5) to (1) must also be regarded as a relaxation process with a relaxation time equal to the lifetime of a molecule in a potential well. Then expression (4) with parameters (5) describes the intensity distribution at high frequencies, while (1) describes the intensity distribution at low frequencies, when the motion of molecules from one potential well to another can be regarded as rotational diffusion; moreover, as the viscosity increases, the region of transition from one distribution to the other must tend toward the unshifted line. Let us note that (4), together with (5), indicates the possibility of an intensity maximum at frequencies of the order of the frequency of elastic librations of molecules for large values of the relaxation time τ_ξ.

Table 2

Comparison of the libration frequencies of molecules in a liquid ν_c and the low-frequency spectrum of the corresponding crystals

Substance	$\nu_c = \frac{1}{2\pi c}\omega_c$, cm^{-1}	Low-frequency spectrum of crystals (12–16)
Carbon disulfide	71	69; 80
Benzene	80	35; 55; 65; 100
Toluene	84	48; 70; 88; 100; 128
Chloroform	60	75; 94
Acetic acid	49	49; 119

Figure 1

Figure 1: Figure 1

Substance	$\nu_c = \frac{1}{2\pi c}\omega_c$, cm^{-1}	Low-frequency spectrum of crystals (^{12}-^{16})

3. On the basis of the views expressed here concerning the nature of the different portions of the spectrum of depolarized scattering, we compared the experimental data of I. L. Fabelinskii (^{1}) and of the author of the present work on the time

relaxation times determined from the near part of the wing with those calculated from the expression

$$\tau = \frac{1}{3}\tau_D = \frac{\zeta}{6kT} = \frac{4}{3}\frac{\pi a^3}{kT}.$$

The results presented in Table 1 show that, for the liquids studied, the agreement between theory and experiment is quite satisfactory.

In the part of the wing far from the exciting line, corresponding to high frequencies, as a result of relaxation processes the viscosity becomes sufficiently small, the elastic constant reaches its limiting value, and the liquid behaves at these frequencies like a solid. Comparing (4) with the high-frequency part of the experimental curve, one can find $\omega_c = \sqrt{\mu/I}$—the frequency of elastic oscillations of the molecules. Table 2 gives the frequencies ν_c thus determined for a number of liquids and, for comparison, the spectra of the low frequencies of the corresponding crystals*.

Fig. 1. Change in the reciprocal value of the internal friction as a function of the square of the frequency: 1—carbon disulfide; 2—benzene; 3—chloroform

From the experimental data for the intensity distribution in the wing, beginning at 15-40 cm^{-1} toward higher frequencies, one can, on the basis of (4), find ζ for different parts of the wing, assuming that the dispersion of ζ and μ in each comparatively small region may be neglected. The results of such a determination for three liquids, using ζ found from the experimental data of Table 1 for low frequencies, are presented in Fig. 1. The linear dependence of $1/\zeta$ on the square of the frequency testifies to the relaxation character of the intensity distribution in the wing and to the appropriateness of the choice of the dispersion law (5). The relaxation times of the viscosity, determined from Fig. 1, are: for carbon disulfide $\tau_\zeta = 7.4 \cdot 10^{-14}$, for benzene $\tau_\zeta = 8.5 \cdot 10^{-14}$, for chloroform $\tau_\zeta = 2.4 \cdot 10^{-13}$, for toluene $\tau_\zeta = 8.5 \cdot 10^{-14}$ sec.

In conclusion, the author expresses gratitude to I. L. Fabelinskii, under whose guidance this work was carried out, and to V. L. Ginzburg and I. I. Sobel' man for valuable discussions of the questions touched upon in the work.

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* The considerations presented do not require the assumption of quascrystalline remnants or of short-range orientational order in liquids. Comparison of ω_c with the low-frequency spectrum of crystals assumes only that the elastic constants

in the liquid at high frequencies are of the same order as in the corresponding crystal.

Note: Figure translations are in progress. See original paper for figures.

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