SOVIET PHYSICS JETP VOLUME 6(33) NUMBER 2 FEBRUARY, 1958

CORRELATION THEORY FOR RAYLEIGH SCATTERING OF LIGHT. I

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Submitted to JETP editor March 2, 1957

J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 514-524 (August, 1957)

A phenomenological theory for Rayleigh scattering of light in an isotropic visco-elastic medium is developed on the basis of the correlation theory proposed earlier by the author for such media. General (i.e., allowing arbitrary dispersion relations for the parameters of the medium) expressions (3.1) are obtained for the spectral intensities of the scattered light corresponding to various polarization conditions. As an application of the general formulas, an expression (4.3) is found for the integrated intensity of the light scattered by isotropic fluctuations (under certain assumptions as to the form of the dispersion relations). The case of a slightly viscous fluid is treated and the appropriate dispersion correction to the Einstein formula is considered.

INTRODUCTION

RECENTLY a large amount of experimental data has been accumulated concerning the Rayleigh scattering of light in liquids; in many cases these data do not agree with the thermodynamic theory of scattering.[1] Substantial discrepancies are found for different characteristics of the polarized component of the scattered light, i.e., the part due to density and temperature fluctuations (so-called isotropic scattering).* Thus, the integrated intensity of the isotropic component of the scattered light is, in many cases, less (sometimes by 20 — 25 percent) than that calculated by the Einstein formula. The ratio of the integrated intensities of the non-displaced line and the Mandel' shtam-Brillouin doublet is considerably greater than that given by the Landau-Placzek formula. Discrepancies between experiment and the thermodynamic theory are especially marked in liquids which exhibit strong dispersion effects in propagation of sound.[1] This is, of course, natural since the existence of frequency-dependent mechanical and thermal medium parameters (and a frequency dependence between these parameters and the index of refraction) makes the thermodynamic theory inapplicable, even in principle. The thermodynamic values of the parameters correspond only to rather low (strictly speaking, infinitely small) frequencies, whereas oscillations with frequencies up to 10^{11} are important in isotropic scattering.

Fabelinskii[1,2] derived a non-thermodynamic formula for the intensity of the doublet, which, because dispersion has been taken into account, is in much better agreement with experiment. This result, together with a detailed analysis of the relevant facts, led Fabelinskii to the conslusion that it is necessary to develop a non-thermodynamic theory of scattering, which will take into account the frequency dependence of the parameters of the scattering medium, The contemporary spectral theory of heat fluctuations can give a complete solution to this problem, which in turn affords one of the most interesting applications of the general theory. The appropriate results are the concern of the present paper.

As is well known, the spectral composition and intensity of light scattered under various polarization conditions is completely determined by the mean-square spectral components of the tensor $\epsilon_{\alpha\beta}$ which describes the fluctuations of the dielectric constant. The spectral amplitudes $\epsilon_{\alpha\beta}$, in turn, are linear functions (because the fluctuations are small) of the quantities which characterize the deviations from complete equilibrium in the medium, i.e., deformation and temperature. Thus the problem reduces to the search for spectral correlation functions for the thermal fluctuations in the deformation and temperature medium. However, the correlation theory for thermal fluctuations in distributed systems which is now available[5] makes it possible to solve this problem in a completely general way; this was done by the

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*As is well known, thermodynamic theory is, in general, not applicable to scattering by anisotropic fluctuations.

author in Ref. 5 for the case of an isotropic (but otherwise arbitrary) medium.* The spectral analysis approach is carried out in the same way in the case of a scattering medium which exhibits dispersion. Before proceeding to an exposition of this analysis it is convenient to characterize briefly some of its basic features.

First of all, it is clear that this is a phenomenological theory, i.e., it contains no assumptions as to the dispersion mechanism, and, correspondingly, in no way specifies the dispersion relations, except for the completely general requirement that these relations must not disturb the dissipation properties of the medium. Any further specification of the dispersion relations may be introduced externally.

As noted, the scattering medium is assumed to be isotropic, i.e., characterized by two (complex) elastic moduli, scalar thermal parameters (heat conductivity and of thermal expansion), and scalar mechanical and thermo-optical parameters. Thus, the visco-elastic medium under consideration could be either a liquid of arbitrary viscosity, or an amorphous solid. An analogous theory for crystals would be more complicated only from the computational point of view; in principle it would be formulated in the same way using precisely this same approach.

Since the spectral theory to be described includes arbitrary internal processes in the medium, it comprises in a single scheme both isotropic and anisotropic fluctuations of the dielectric constant, i.e., it describes the entire spectrum of the scattered light, including the so-called wing of the Rayleigh line. By integrating the expressions for the spectral intensities with respect to frequency we can obtain integrated intensities of the total spectrum, and of individual components (e.g., the non-displaced line, the doublet, etc.). In fact, a series of such integrated intensities can be obtained for any reasonable specification of the dispersion relations.

In the first part of the paper, Secs. 1 – 3, we obtain the general formulas (3.1) for the spectral intensities of the scattered light, observed at right angles to the primary wave, for four combinations of the polarization of the primary and scattered light. Then, in Sec. 4, we calculate the integrated intensity of the isotropic scattering I_{iso} under the following assumptions: (1) the mechanical and thermo-optical coefficients

$$Y = -\rho_0 (\partial\varepsilon / \partial\rho)_T, \qquad Z = T_0 (\partial\varepsilon / \partial T)_\rho,$$

and the coefficient of thermal expansion exhibit no dispersion, (2) the compression modulus $\overline{K}$ obeys a dispersion relation with a single relaxation time τ', and the shear modulus $\overline{\mu}$ depends on the frequency in an arbitrary way. In the case of liquids, the Einstein formula follows from Eq. (4.3) for I_{iso}, when Z is neglected and $\overline{K}$ is dispersionless. For slightly viscous fluids (Sec. 5) the dispersion correction to the Einstein formula simplifies considerably. It depends on the ratio of $1/\tau'$ to the frequency Ω_{MB} of the Mandel'stam-Brillouin doublet; however, it does not reduce, as might be expected, to the replacement of the static compressibility β_T in the Einstein formula by the compressibility $1/K(\Omega_{\mathrm{MB}})$ at the doublet frequency.

In the second part of the paper, we consider some further consequences of (3.1) under certain assumptions as to the dispersion relations: the separation of I_{iso} into components (central line, Mandelstam-Brillouin doublet, background), the dispersion correction to the Landau-Placzek relation, the frequency behavior of the intensity and the degree of depolarization in the wing of the Rayleigh line, etc.

1. SPECTRAL SOLUTION OF THE SCATTERING PROBLEM

Let us dwell briefly on the well-known spectral solution of the problem of the scattering of a plane monochromatic electromagnetic wave by weak optical irregularities of the medium (cf. Ref. 7), describing this solution in terms of the correlation theory for random fields.

Let the dielectric constant of the medium have the form

$$\varepsilon_0 \delta_{\alpha\beta} + \varepsilon_{\alpha\beta}(t, \mathbf{r}),$$

where the fluctuation $\epsilon_{\alpha\beta}$ from the mean value ϵ_0 is small enough so that in calculating the scattered field produced by the incident primary wave

$$\mathbf{E}_0 = \mathbf{A} e^{i(\omega t - \mathbf{k}_0 \mathbf{r})}, \quad (k_0 = \omega \sqrt{\varepsilon_0}/c),$$

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* The analogous problem in the case of a viscous fluid with no dispersion was solved earlier by Landau and Lifshitz.[6]

we can confine ourselves to the first perturbation-theory approximation. We seek a solution of Maxwell's equations in spectral form, i.e. we represent $\epsilon_{\alpha\beta}$ in the form

$$\varepsilon_{\alpha\beta}(t, \mathbf{r}) = \int\limits_{-\infty}^{+\infty} \varepsilon_{\alpha\beta}(\Omega, \mathbf{r}) e^{i\Omega t} d\Omega,$$

and the scattered field in the form

$$E_\alpha(t, \mathbf{r}) = \int\limits_{-\infty}^{+\infty} E_\alpha(\Omega, \mathbf{r}) e^{i(\omega+\Omega)t} d\Omega.$$

Then, at distances $R \gg k_0 l^2$, where l is a linear dimension of the scattering volume V, the spectral amplitude $E_\alpha(\Omega, \mathbf{r})$ is

$$E_\alpha(\Omega, \mathbf{r}) = \frac{k^2 e^{-ikR}}{4\pi\varepsilon_0 R} \int\limits_V e^{-i\mathbf{q}\mathbf{r}} p_\alpha(\Omega, \mathbf{r}) d\mathbf{r},$$

where $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$, $\mathbf{k}$ is the wave vector of the scattered wave $[k = (\omega + \Omega)\sqrt{\epsilon_0}/C \approx k_0$, since only $\Omega \ll \omega$ is important$]$, and $\mathbf{p}$ is the component of the polarization perpendicular to the direction of observation (multiplied by 4π):

$$\mathbf{p} = 4\pi \{\mathbf{P} - \mathbf{k}(\mathbf{k}\,\mathbf{P})/k^2\} \quad P_\alpha = \varepsilon_{\alpha\beta} A_\beta / 4\pi. \tag{1.1}$$

As a measure of the intensity of the scattered light we take $J_{\omega+\Omega}$, the ratio of the average Poynting vectors of the scattered and direct waves, multiplied by $V^{-1}(2\pi\epsilon_0 R/k^2)^2$. An elementary calculation gives

$$J_{\omega+\Omega} = \frac{1}{VA^2} \int\limits_V \int\limits_V \overline{p_\alpha(\Omega, \mathbf{r}) p_\alpha^*(\Omega, \mathbf{r}')} e^{-i\mathbf{q}\boldsymbol{\rho}} d\mathbf{r}\, d\mathbf{r}', \quad \boldsymbol{\rho} = \mathbf{r} - \mathbf{r}'. \tag{1.2}$$

Thus, the intensity at the frequency $\omega + \Omega$ is determined by the spatial autocorrelation of the spectral amplitude of the vector $\mathbf{p}$. Because of the statistical homogeneity of the fluctuation field of $\mathbf{p}$ the correlation function depends on the vectors $\mathbf{r}$ and $\mathbf{r}'$ only through their difference $\boldsymbol{\rho}$.

Equation (1.2) is limited only by two initial assumptions: the first approximation with respect to $\epsilon_{\alpha\beta}$, and observation in the Fraunhofer zone. Now let (in agreement with actual experimental conditions) the dimensions of the volume V be very large with respect to the correlation distance of the optical inhomogeneities of the medium. The integration over $\mathbf{r}'$ can then be replaced by integration over $\boldsymbol{\rho}$, with the limits of integration extended to infinity:

$$J_{\omega+\Omega} = \frac{1}{VA^2} \int\limits_V d\mathbf{r} \int\limits_{-\infty}^{+\infty} \overline{p_\alpha(\Omega, \mathbf{r}) p_\alpha^*(\Omega, \mathbf{r}')} e^{-i\mathbf{q}\boldsymbol{\rho}} d\boldsymbol{\rho} = \frac{1}{A^2} \int\limits_{-\infty}^{+\infty} \overline{p_\alpha(\Omega, \mathbf{r}) p_\alpha^*(\Omega, \mathbf{r}')} e^{-i\mathbf{q}\boldsymbol{\rho}} d\boldsymbol{\rho}. \tag{1.3}$$

If we represent $p_\alpha(\Omega, \mathbf{r})$ as a spatial Fourier integral

$$p_\alpha(\Omega, \mathbf{r}) = \int\limits_{-\infty}^{+\infty} p_\alpha(\Omega, \mathbf{q}) e^{i\mathbf{q}\mathbf{r}} d\mathbf{q}$$

and bear in mind that because of the spatial homogeneity of the fluctuations the correlation function of the $\Omega\mathbf{q}$-amplitude has the form

$$\overline{p_\alpha(\Omega, \mathbf{q}) p_\alpha^*(\Omega, \mathbf{q}')} = \overline{|p_\alpha(\Omega, \mathbf{q})|^2}\, \delta(\mathbf{q} - \mathbf{q}'),$$

it is apparent that

$$\overline{p_\alpha(\Omega, \mathbf{r}) p_\alpha^*(\Omega, \mathbf{r}')} = \int\limits_{-\infty}^{+\infty} \overline{|p_\alpha(\Omega, \mathbf{q})|^2} e^{i\mathbf{q}\boldsymbol{\rho}} d\mathbf{q}. \tag{1.4}$$

The integral appearing in (1.3) is the inverse of the Fourier integral (1.4), multiplied by $(2\pi)^3$, i.e.,

$$J_{\omega+\Omega} = (2\pi)^3 A^{-2} \overline{|p_\alpha(\Omega, \mathbf{q})|^2}. \tag{1.5}$$

Thus, the intensity of the light at frequency $\omega + \Omega$, scattered in the direction $\mathbf{k}$, is to within a constant factor the Ωq-intensity of the vector $\mathbf{p}$, where $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$.

Let us now fix the conditions of observation. We take the x-axis to be the direction of propagation of the primary wave and restrict ourselves to the case of perpendicular observation (along the y-axis). Then

$$\mathbf{q} = (k_0, -k_0, 0), q^2 = 2k_0^2. \tag{1.6}$$

Moreover, we consider two polarizations of the primary wave, vertical ($A_z = A$) and horizontal ($A_y = A$); these will be denoted by the symbols ↑ and →. We also consider two polarizations of the observed scattered light, along z and x. Then, from (1.1), (1.5) and (1.6) we obtain the following expressions for the intensities, corresponding to the four polarization combinations (in what follows we omit the index $\omega + \Omega$ on J):

$$J_x^{\uparrow} = (2\pi)^3 \overline{|\varepsilon_{13}(\Omega, \mathbf{q})|^2}, \quad J_z^{\uparrow} = (2\pi)^3 \overline{|\varepsilon_{33}(\Omega, \mathbf{q})|^2}, \quad J_x^{\rightarrow} = (2\pi)^3 \overline{|\varepsilon_{12}(\Omega, \mathbf{q})|^2}, \quad J_z^{\rightarrow} = (2\pi)^3 \overline{|\varepsilon_{32}(\Omega, \mathbf{q})|^2}. \tag{1.7}$$

Thus, the problem reduces to calculation the $\Omega\mathbf{q}$-intensities of the four components of the tensor $\epsilon_{\alpha\beta}$, where the vector $\mathbf{q}$ is fixed in accordance with (1.6).

2. THE RELATION BETWEEN $\epsilon_{\alpha\beta}$ AND THE FLUCTUATIONS IN DEFORMATION AND TEMPERATURE OF THE MEDIUM

For the mechanical and thermal quantities which give a spectral description of the fluctuations in the scattering medium we take the Ω-amplitudes of the fluctuational deformations $u_{\alpha\beta}$ and the deviation of the temperature T from its equilibrium value T_0. In this connection, it is convenient to divide $u_{\alpha\beta}$ into a pure volume deformation $u'_{\alpha\alpha} \equiv u = -\rho/\rho_0$ (ρ is the deviation of the density from the equilibrium value ρ_0) and a pure shear deformation $u'_{\alpha\beta} = u_{\alpha\beta} - u\delta_{\alpha\beta}/3$. Because the fluctuations are small the relation between $\epsilon_{\alpha\beta}$ and the quantities $u'_{\alpha\beta}$, u, and $\vartheta = T/T_0$ is linear and the spectral-amplitude relations are, by hypothesis, purely algebraic:

$$\varepsilon_{\alpha\beta}(\Omega, \mathbf{r}) = X(i\Omega)\, u'_{\alpha\beta}(\Omega, \mathbf{r}) + Y(i\Omega)\, u(\Omega, \mathbf{r})\, \delta_{\alpha\beta} + Z(i\Omega)\, \vartheta(\Omega, \mathbf{r})\, \delta_{\alpha\beta}. \tag{2.1}$$

The coefficients X, Y, and Z are, in general, complex and describe the mechanical-optical and thermo-optical properties of the medium at the frequency Ω.*

In the case in which these coefficients and the mechanical and thermal parameters of the medium are dispersionless (and consequently are real), Eq. (2.1) is valid even for the quantities which are not resolved spectrally, i.e.,

$$\varepsilon_{\alpha\beta}(t, \mathbf{r}) = Xu'_{\alpha\beta}(t, \mathbf{r}) + Yu(t, \mathbf{r})\,\delta_{\alpha\beta} + Z\vartheta(t, \mathbf{r})\,\delta_{\alpha\beta}.$$

Contracting this expression, we obtain ($u'_{\alpha\alpha} = 0$)

$$\varepsilon_{\alpha\alpha} \equiv 3\varepsilon = 3Yu + 3Z\vartheta,$$

whence it follows that in the absence of dispersion

$$Y = (\partial\varepsilon/\partial u)_{\vartheta} = -\rho_0(\partial\varepsilon/\partial\rho)_T, \quad Z = (\partial\varepsilon/\partial\vartheta)_u = T_0(\partial\varepsilon/\partial T)_{\rho}. \tag{2.2}$$

Equation (2.1) is, of course, also valid for the $\Omega\mathbf{q}$-amplitudes

$$\varepsilon_{\alpha\beta}(\Omega, \mathbf{q}) = X(i\Omega)\, u'_{\alpha\beta}(\Omega, \mathbf{q}) + Y(i\Omega)\, u(\Omega, \mathbf{q})\,\delta_{\alpha\beta} + Z(i\Omega)\,\vartheta(\Omega, \mathbf{q})\,\delta_{\alpha\beta}. \tag{2.3}$$

It follows from (1.7) and (2.3) that

$$J_x^{\uparrow} = (2\pi)^3 |X|^2 \overline{|u'_{13}|^2}, \quad J_z^{\uparrow} = (2\pi)^3 \overline{|Xu'_{33} + Yu + Z\vartheta|^2}, \quad J_x^{\rightarrow} = (2\pi)^3 |X|^2 \overline{|u'_{12}|^2}, \quad J_z^{\rightarrow} = (2\pi)^3 |X|^2 \overline{|u'_{32}|^2}. \tag{2.4}$$

All the intensities, except $J_z^{\uparrow}$, are due to anisotropic fluctuations; only $J_z^{\uparrow}$ contains the isotropic part, which is proportional to $\overline{|Yu + Z\vartheta|^2}$.

3. SPECTRAL INTENSITIES OF THE SCATTERED LIGHT

In accordance with Eq. (2.4), the determination of the spectral intensities of the scattered light reduces to a search for the $\Omega\mathbf{q}$-intensities for deformation and temperature fluctuations. This problem has been

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*Since the spectral amplitudes of the fluctuations of any internal parameters can be expressed linearly in terms of $u_{\alpha\beta}(\Omega, \mathbf{r})$ and $\vartheta(\Omega, \mathbf{r})$ (in the absence of spatial dispersion, cf. Ref. 5), there are no grounds in our spectral theory for introducing in (2.1) an isotropic term of the form $\epsilon'\delta_{\alpha\beta}$ which does not reduce to fluctuations of density and temperature, as was done in Ref. 8.

solved in Ref. 5 and we now make use of the results obtained there.

In Secs. 4 and 5 of the work cited formulas are given for the following Ωq-intensities (in the notation of Ref. 5 these are called ωk-intensities):

$$\overline{u'_{\alpha\beta}u'^{*}_{\mu\nu}},\ \overline{u'_{\alpha\beta}u^{*}},\ \overline{u'_{\alpha\beta}\vartheta^{*}},\ \overline{uu^{*}},\ \overline{u\vartheta^{*}},\ \overline{\vartheta\vartheta^{*}}.$$

In these general formulas, in accordance with Eq. (1.6), we set $q_1 = q_2 = q/\sqrt{2}$, and $q_3 = 0$ whence the expressions which appear in (2.4) are obtained. As a result we find

$$J_x^{\rightarrow} = \frac{\Theta\,|X|^2}{8\pi i\Omega}\left\{\frac{1}{\overline{\mu}^*}\left(1+\frac{d_1\overline{\mu}q^2}{\Delta}\right)-\text{compl. conj.}\right\},\qquad J_z^{\rightarrow} = J_x^{\uparrow} = \frac{\Theta\,|X|^2}{16\pi i\Omega}\left\{\frac{1}{\overline{\mu}^*}\left(1+\frac{\rho_0^2\Omega^4}{|A_4|^2}\right)-\text{compl. conj.}\right\},$$

$$J_z^{\uparrow} = \frac{\Theta}{2\pi i\Omega}\left\{\frac{|X|^2}{3\overline{\mu}^*}\left(1+\frac{d_1\overline{\mu}q^2}{3\Delta}\right)+\left(XY^*C^*+X^*YC\frac{\overline{\mu}}{\overline{\mu}^*}\right)\frac{C\overline{K}q^2}{3\Delta}-\left(XY^*\frac{\overline{K}}{\overline{K}^*}+X^*Y\frac{\overline{\mu}}{\overline{\mu}^*}\right)\frac{dq^2}{3\Delta}+\left(XZ^*+X^*Z\frac{\overline{\mu}}{\overline{\mu}^*}\right)\frac{C\overline{K}q^2}{3\Delta}\right. \tag{3.1}$$

$$\left.+\frac{|Y|^2}{\Delta}\left(\frac{d_1A_3}{\overline{K}^*}-CC^*\overline{K}q^2\right)-\left[YZ^*C\overline{K}q^2-Y^*Z\left(C^*A_1-C\frac{\overline{K}}{\overline{K}^*}A_3\right)\right]\frac{1}{\Delta}+\frac{|Z|^2}{\Delta}A_1-\text{compl. conj.}\right\}.$$

For brevity we use the same notation as in Ref. 5, in particular

$$d = D+\varkappa T_0q^2/i\Omega,\ d_1 = d-C^2\overline{K} = D_1+\varkappa T_0q^2/i\Omega,\quad D_1 = D-C^2\overline{K},\ \Delta = dA_1-C^2\overline{K}A_3 = d_1A_3-dKq^2,$$

$$A_1 = \rho_0\Omega^2-\left(\overline{K}+\frac{4}{3}\overline{\mu}\right)q^2,\ A_3 = \rho_0\Omega^2-\frac{4}{3}\overline{\mu}q^2,\ A_4 = \rho_0\Omega^2-\overline{\mu}q^2.$$

Thus, in the final analysis, all quantities are expressed in terms of $\overline{K}$, $\overline{\mu}$, κ, C and D which have the following significance: $\overline{K}$ and $\overline{\mu}$ are the complex elastic moduli, i.e.,

$$\overline{K} = K(\Omega^2)+i\Omega\zeta(\Omega^2);\ \overline{\mu} = \mu(\Omega^2)+i\Omega\eta(\Omega^2),$$

where K is the compression modulus, μ is the shear modulus, ξ and η are respectively the volume and shear viscosity, κ is the complex heat conductivity, and C and D are complex coefficients in the equations which relate the spectral amplitudes of the fluctuations to the specific (per unit mass) entropy S, the volume deformation u and the temperature $\vartheta = T/T_0$:

$$\rho_0T_0S(\Omega,\mathbf{r}) = C\overline{K}u(\Omega,\mathbf{r})+D_1\vartheta(\Omega,\mathbf{r}).$$

In the absence of dispersion $\overline{K}$, $\overline{\mu}$, κ, C, D and D_1 are real constants where

$$K = 1/\beta_T,\ C = \alpha T_0,\ D = \rho_0T_0c_p,\ D_1 = \rho_0T_0c_v, \tag{3.2}$$

where β_T is the isothermal compressibility, α is the coefficient of heat expansion and c_p and c_v are respectively the heat capacities at constant pressure and constant volume.

Equations (3.1) have been written for a frequency which satisfies the condition $\hbar\Omega \ll \Theta = kT_0$. When this condition does not hold Θ must be replaced by the quantum expression for the mean energy of an oscillator.

Without carrying out a more detailed analysis of Eq. (3.1) we can make several general remarks as to the form of the spectra which are described.

As has been noted in Ref. 5 the dispersion equation can be broken up into two equations, namely $\Delta = 0$ and $A_4 = 0$ where the first refers to the compression wave and the thermal wave while the second refers to the shear wave. Correspondingly, the terms in Eq. (3.1) which contain Δ in the denominator give rise to a triplet in the spectrum—a central maximum and a Mandel'shtam-Brillouin doublet while those containing A_4 in the denominator (that term appears only in $J_z^{\rightarrow} = J_x^{\uparrow}$) give rise to a shear doublet.

The presence of dispersion in the medium leads, first of all, to a finite width in the maxima of both doublets. In the absence of loss these maxima become discrete lines (δ-peaks); this also occurs at the central maximum if the heat conductivity approaches zero. Secondly, dispersion leads to the appearance of a wide continuous background, the distribution of which depends on the dispersion relation. Terms which contain $\overline{\mu}$ in the denominator and which arise solely as a result of optical anisotropy (for X = 0 these all disappear) lead to the formation of the wing of the Rayleigh line which, in the case of a liquid, may extend far beyond the Mandel'shtam-Brillouin doublet. In a similar way terms with $\overline{K}$ in the denominator make a contribution to the continuous background. These terms will be considered in greater detail later on.

It is reasonable to assume that the ratio of the maxima to the background level itself depends, in an important way, on the values of the parameters. Thus, for example, the triplet in $J_X^{\rightarrow}$, which should be present because of the second term in the denominator which contains Δ, is practically unobservable in a slightly viscous fluid because μ is very small at the frequencies in question. If the value of the static shear modulus approaches zero (transition to the liquid case) the maxima of the shear doublet, described by the second term in $J_Z^{\rightarrow} = J_X^{\uparrow}$, contract about the central line and merge into the background, and so on.

Equations (3.1) represent the most information that can be reasonably expected from a purely phenomenological theory. These general expressions allow us to draw concrete conclusions which are necessarily based on certain assumptions as to the dispersion relations between the parameters X, Y, Z and $\overline{K}$, $\overline{\mu}$, κ, C, D. There are certain theoretical restrictions on the enumerated parameters. The dispersion of the mechanical and thermal parameters of the medium, $\overline{K}$, $\overline{\mu}$, C and D may be subject to rather general considerations—something like those which were introduced in the formulation of the relaxation theory for dispersion and absorption of sound in liquids in the work of Mandel'shtam and Leontovich.[9,10] The problem is somewhat more difficult for the heat conductivity κ. As for the parameters X, Y, Z there seems to be, as yet, no approach to a theory for setting up a frequency dependence for these parameters. However, Eqs. (3.1) make it possible to compare various assumptions with the experimental data on the scattering of light and can be useful in this respect.

We now turn to the results which follow from Eq. (3.1) when some particular assumptions as to the dispersion relations between the above-mentioned parameters are introduced.

4. INTEGRATED INTENSITY OF THE ISOTROPIC COMPONENT OF THE SCATTERED LIGHT

The intensity of the isotropic component, given by those terms in Eqs. (3.1) which do not contain X, is

$$J_{z\,\mathrm{iso}}^{\uparrow} = \frac{\Theta}{2\pi i\Omega}\left\{\frac{1}{\Delta}\left[|Y|^2\left(\frac{d_1 A_3}{\overline{K}^*} - CC^*\overline{K}q^2\right) - YZ^*C\overline{K}q^2 + Y^*Z\left(C^*A_1 - C\frac{\overline{K}}{\overline{K}^*}A_3\right) + |Z|^2 A_1\right] - \text{compl. conj.}\right\}. \tag{4.1}$$

The indices which indicate the vertical polarization of the primary and observed waves will be discarded in the following.

To compute the integrated intensity

$$I_{\mathrm{iso}} = \int\limits_{-\infty}^{+\infty} J_{\mathrm{iso}}\, d\Omega \tag{4.2}$$

we make use of (7.4) add (7.5) of Ref. 5, having made the following assumptions for this purpose:

(a) Y, Z and C are independent of Ω, that is, they have real thermodynamic values (2.2) and (3.2).

(b) The compression modulus $\overline{K}$ obeys a simply dispersion relation characterized by a single relaxation time τ'

$$\overline{K} = \frac{K_\infty z + K_0/\tau'}{z + 1/\tau'} = K_\infty \frac{z+a}{z+1/\tau'} \quad \left(z = i\Omega,\ a = \frac{K_0}{K_\infty \tau'}\right).$$

Then,

$$J_{\mathrm{iso}} = \frac{\Theta}{2\pi i\Omega}\left\{\frac{1}{\Delta}\left[-Y^2C^2\overline{K}q^2 + YZC\left(A_1 - \overline{K}q^2\right) + Z^2A_1 + \left(Y^2 d_1 - YZC\right)\frac{A_3(z - 1/\tau')}{K_\infty(z-a)}\right] - \text{compl. conj.}\right\}.$$

Substituting this relation in (4.2) and using (7.5) of Ref. 5 in the first three terms (and their complex conjugates) and (7.4) in the last term (and its complex conjugate) we obtain

$$I_{\mathrm{iso}} = \Theta\left\{Y^2\left(\frac{1}{K_\infty} - \frac{4\mu_0/3}{K_0\left(K_0 + \frac{4}{3}\mu_0\right)}\right) + \frac{Z^2}{D_{1\infty}} + \frac{2\left(K_\infty - K_0\right)}{K_0 K_\infty \Delta_a} Y\left(Y d_{1a} - ZCK_a\right)\right\}. \tag{4.3}$$

The subscript 0 and ∞ here denote values of the parameters which obtain at $z \rightarrow 0$ and $z \rightarrow \infty$; these can be shown to be real from general considerations. The subscript a denotes values for $z = a = K_0/K_\infty \tau'$ (also real).

For a liquid ($\mu_0 = 0$), neglecting the dependence of ϵ on temperature ($Z = 0$), in the absence of dispersion in the compression modulus ($K_\infty = K_0 = 1/\beta_T$) the Einstein thermodynamic formula[11] is obtained from Eq. (4.3)

$$I_{\text{iso}} = \Theta Y^2/K_0 = \Theta\beta_T\,[\rho_0\,(\partial\varepsilon/\partial\rho)_T]^2.$$

Equation (4.3) describes both a highly viscous liquid and a solid body, depending on the degree to which the assumptions made above apply. In any case, in Eq. (4.3) we have not assumed that the dispersion differential $K_\infty - K_0$ is small; for the shear modulus $\bar{\mu}$ there is, in general, no limitation other than the general requirement that the limiting values μ_0 and μ_∞ be finite. As an example we now consider the case of a slightly viscous liquid.*

Let us consider first the assumption that the coefficient Y is constant. The measurements of Fabelinskii and Motulevich have shown[12] in a number of liquids that even at supersonic frequencies (10^7) the square of the modulus of $Y(i\Omega)$ is about 10 — 12 percent lower than at 50 cps; this result is in good agreement with the values obtained from the intensity of the scattered light. It is difficult to interpret this result even when we compare the frequency at which the liquid parameters change Ω, not with the frequency of light ω, but with the reciprocal values of the time required for establishing the index of refraction. This time should be determined, at least in terms of order of magnitude, by the width of the absorption band and not by its location in the spectrum. Thus, for example, the index of refraction of a gas through which passes a wave front with an associated frequency of approximately 10^{15} is established not in 10^{-15} sec but approximately 10^{-9} sec, corresponding to the width of the spectral line of the gas ($\Delta\lambda \sim 0.01$ A). If the line (or band) has a width of 1 — 10 A the corresponding time is $10^{-11} - 10^{-12}$ sec. Thus one expects a certain dispersion effect in $Y(i\Omega)$ for frequencies of the order of 10^{10} but under the condition that the light frequency is close to that of the absorption line or band. This is precisely what is not found in scattering observations and thus the index of refraction should follow the density oscillations almost quasistatically if the medium parameters very in a sinusoidal manner.

Thus, it is difficult to explain dispersion in $Y(i\Omega)$ even at frequencies of the order of 10^{10}, let alone 10^7. In view of these considerations the assumption that Y is constant is a reasonable one; however, the contradictory experimental results force us to leave this assumption open to question.

5. CASE OF SLIGHTLY VISCOUS LIQUID

Turning now to the case of a liquid ($\mu_0 = 0$) with rather small dispersion we need keep in (4.3) only terms of first order in the dispersion corrections, that is, in the coefficient for $K_\infty - K_0$ we take values of all parameters for $z \to 0$.† Furthermore, since the value of Z is itself small, in general it is possible to neglect the dispersion corrections in terms which contain Z. Then Eq. (4.3) assumes the form

$$I_{\text{iso}} = \Theta\left\{Y^2\left(\frac{1}{K_\infty} + \frac{2\,(K_\infty - K_0)\,s}{K_0^2\,(1+s)}\right) + \frac{Z^2}{D_{10}}\right\}, \tag{5.1}$$

where

$$s = -\frac{d_{1a}A_{3a}}{d_aK_aq^2} \approx -\frac{d_{10}A_{30}}{d_0K_0q^2} = \frac{1+\gamma\chi q^2\tau'}{1+\chi q^2\tau'}\,\frac{1}{\Omega_{\text{MB}}^2\tau'^2} \approx \frac{1}{\Omega_{\text{MB}}^2\tau'^2}, \tag{5.2}$$

$K = \kappa_0T_0/D_0 = \kappa_0/\rho_0c_p$ is the heat conductivity of the liquid, $\gamma = D_0/D_{10} = c_p/c_v$ and $\Omega_{\text{MB}}^2 = \gamma K_0q^2/\rho_0$ (Ω_{MB} is the frequency of the Mandel'shtam-Brillouin doublet). It is apparent that the parameter s is a measure of the degree to which the compression modulus relaxes at the doublet frequency. If the relaxation region for K is already reached when $\Omega = \Omega_{\text{MB}}$, ($\Omega_{\text{MB}}\tau' \gg 1$), s is small and the corresponding dispersion correction in (5.1) is unimportant.

In the three liquids for which Fabelinskii and his colleagues[13,14] either measured or estimated the values of τ', if it is assumed that $q^2 = 4.15 \times 10^{10}$ (light wave length 4368 A) we have:

Liquid	$\tau'\cdot 10^{10}$	γ	$\chi q^2\tau'$	$\Omega^2_{\text{MB}}\cdot 10^{-20}$	s
Carbon tetrachloride	0.67	1.44	0.0021	4.31	0.52
Benzol	2.44	1.44	0.0092	7.89	0.021
Carbon bisulfide	21.8	1.56	0.114	5.59	0.00038

Thus the dispersion correction given by the second

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*In solid bodies information concerning the dispersion of elastic moduli, or even the order of magnitude of the relaxation time is not available, to the best of the author's knowledge.

†It is obvious that the quasi-static values coincide with the thermodynamic values (dispersionless); hence, for these, as for the parameters which were earlier assumed to be dispersionless, we will frequently use the notation of (3.2).

term in (5.1) is important in carbon tetrachloride but is extremely small in the other two liquids.

In those cases in which s ≪ 1 Eq. (5.1) reduces to the following:

$$I_{\text{iso}} = \Theta\left(\frac{Y^2}{K_\infty} + \frac{Z^2}{D_{10}}\right) = \Theta\beta_T\left\{\rho_0^2\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T^2\frac{K_0}{K_\infty} + \frac{\gamma-1}{\alpha^2}\left(\frac{\partial\varepsilon}{\partial T}\right)_\rho^2\right\}. \tag{5.3}$$

If K_∞ could be measured independently, using Eq. (5.3) it would be possible to verify the assumption that the coefficient Y is dispersionless. But dispersion measurements in the propagation of compression waves do not give direct information as to the magnitude of K_∞.

Actually, it follows from Eq. (6.5) of Ref. 5 that the square of the complex velocity of propagation of longitudinal waves v is given as follows:

$$v^2 = \frac{P+R}{2\rho_0 D_1}, \quad P = i\Omega\varkappa\rho_0 T_0 + D\overline{K} + \frac{4}{3}D_1\overline{\mu}, \quad R = \sqrt{P^2 - 4i\Omega\varkappa\rho_0 T_0 D_1(\overline{K} + 4\overline{\mu}/3)}. \tag{5.4}$$

The parameters D, D_1, and K reach their limiting values D_∞, $D_{1\infty}$ and K_∞ at frequencies $\Omega \gg 1/\tau'$, that is, when $\Omega \approx 10^{11}$. But in the case of a slightly viscous fluid these frequencies are very small as compared with $1/\tau$ (τ is the relaxation time for the shear modulus), since $\tau'/\tau \sim 10^3$. Furthermore, at the frequencies indicated the quantity $\Omega\kappa\rho_0 T_0$ is very small as compared with D_0K_0 since these quantities can become comparable (i.e., comparable thermal and longitudinal wave length) only when

$$\Omega = D_0K_0/\varkappa\rho_0T_0 = 1/\rho_0\beta_T\chi \sim 10^{13}.$$

Thus, in Eq. (5.4) we can neglect $4\overline{\mu}/3$ and $\Omega\kappa\rho_0T_0$ not only when $\Omega \to 0$ but also for those frequencies $\Omega \gg 1/\tau'$ at which the velocity has already reached value v_∞. Then

$$v^2 = D\overline{K}/D_1\rho_0, \tag{5.5}$$

Whence it follows that from the dispersion differential in the velocity v we can find the limiting value ($\Omega\tau' \gg 1$) of the "adiabatic" modulus $K_{\text{ad}} = D\overline{K}/D_1$

$$\frac{v_0^2}{v_\infty^2} = \frac{D_0K_0}{D_{10}} : \frac{D_\infty K_\infty}{D_{1\infty}} = \frac{1}{\beta_S}\,\frac{D_{1\infty}}{D_\infty K_\infty} \qquad \left(\beta_S = \frac{\beta_T}{\gamma}\right), \tag{5.6}$$

whereas in (5.3) we have the limiting value K_∞ of the "isothermal" modulus $\overline{K}$.

We wish to take this opportunity to thank M. A. Leontovich and I. L. Fabelinskii for their interest in this work and for very valuable discussion of the results.

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Translated by H. Lashinsky