RELAXATION THEORY OF RAYLEIGH SCATTERING

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A theory of equilibrium thermal fluctuations in an isotropic continuous medium is developed, in which the state of incomplete equilibrium is described by deformations, a temperature, and an arbitrary number of scalar and symmetric tensor relaxation parameters. The spectral densities of these variables which depend on the complex elastic and thermal heat moduli with definite dispersion laws are obtained with the help of the fluctuation-dissipation theorem. Formulas for the spectral and integral intensities of the light scattered by the medium are derived in the general case where the fluctuations of the dielectric constant depend on all the above-mentioned parameters. It is shown that these formulas include as special cases the results of various other relaxation theories of Rayleigh scattering.[9-13] The incorrect formulation and solution of the problem in previous papers of the author,[2-4] pointed out in[1], are analyzed. The analysis shows that the earlier critical remarks[7] of the author about the theory of Mountain[11,12] are completely invalid.

1. INTRODUCTION

ROMANOV, Solov'ev, and Filatova[1] have pointed out that in my paper[2] on the thermal fluctuations in a visco-elastic medium with dispersion, an incorrect transition from stresses to deformations has been made in the application of the fluctuation-dissipation theorem (FDT): such a transformation is not valid in a so-called incomplete description of the system, i.e., in a description where the number of generalized coordinates determining the state of the system do not include the internal relaxation parameters, and the dispersion is formally taken into account by introducing complex frequency dependent elastic moduli, heat capacities, and thermal expansion coefficients.

The error in the spectral deformation densities arising from this transformation, of course, showed up also in my theory of Rayleigh scattering[3,4] which is based on the results of[2]. Moreover, my endeavor not to go beyond the limits of an incomplete description led me[3,4] to the incorrect assumption that the fluctuations of the dielectric constant of the medium do not depend explicitly on the internal parameters.

My objections against some of the assertions about the applicability of the FDT in[1] are of secondary importance, and I intend to come back to these in another place. The main assertion, to which I must fully agree, is that a complete description of the thermal fluctuations in the medium is required for the construction of a theory of Rayleigh scattering. This means that one must dismiss the possibility, which seemed so attractive to me, of describing the spectrum of the scattered light without any concrete assumption about the dispersion mechanism, requiring only that the Kramers-Kronig relation be fulfilled.

I am grateful to Romanov, Solov'ev, and Filatova, whose paper[1] induced me to reconsider carefully my papers[2-4] and which inspired me to obtain a solution of the problem of the thermal fluctuations in a relaxing medium, and of the scattering of light on such fluctuations with the same generality as in the complete description. The corresponding theory of thermal fluctuations is presented in Secs. 1 to 3 of the present paper, and the theory of Rayleigh scattering, in Sec. 4. In Sec. 5 it is shown that this theory contains as special cases the results of a number of papers on the scattering of light in a relaxing medium which have come to my attention.

In the present paper we use, as before, the spectral description of the fluctuations and the FDT, since, in my view, there are no reasons why one should prefer the temperal description to the spectral one. In principle, both are equivalent, but the spectral description operates with the ωq fluctuation amplitudes, i.e., with those quantities whose correlations are directly determined by the scattering. Moreover, the spectral description reduces the problem at once to linear algebraic equations and, owing to the FDT, leads more "automatically" to the final result than the temporal description.

2. COMPLETE DESCRIPTION OF THE FLUCTUATIONS. CHOICE OF COORDINATES AND FORCES. BASIC EQUATIONS

Let us assume that the complete description of the thermal fluctuations in the medium is given in terms of the following coordinates: the displacement vector s_α [or the deformation tensor $u_{\alpha\beta} = (\partial s_\alpha/\partial x_\beta + \partial s_\beta/\partial x_\alpha)/2$], the temperature T, and a certain number of internal relaxation parameters, scalar, $\zeta^{(j)}$ ($j = 1, 2, \ldots$), or of the symmetric tensor type, $\zeta^{(k)}_{\alpha\beta}$ ($k = 1, 2, \ldots$); i.e., the free energy Ψ of the unit volume depends only on these variables.

Since the correlation theory of equilibrium thermal fluctuations requires only linearized equations of motion, it suffices to give Ψ in the quadratic approximation. Hence, Ψ can be constructed solely from pair products of the scalar quantities $u = u_{\alpha\alpha}$, $T_1 = T - T_0$, and $\zeta^{(j)}$ and bilinear invariants of the tensor quantities $u_{\alpha\beta}$ and $\zeta^{(k)}_{\alpha\beta}$. If, as usual, we divide the deformations

$u_{\alpha\beta}$ into pure shears $\tilde{u}_{\alpha\beta} = u_{\alpha\beta} - u\delta_{\alpha\beta}/3$ and the compression u, and the tensors $\zeta^{(k)}_{\alpha\beta}$ into pure anisotropy tensors $\tilde{\zeta}^{(k)}_{\alpha\beta} = \zeta^{(k)}_{\alpha\beta} - \zeta^{(k)}\delta_{\alpha\beta}/3$ and the traces $\zeta^{(k)} = \zeta^{(k)}_{\alpha\alpha}$, these invariants are given by the contractions $(\tilde{u}_{\alpha\beta})^2$, $\tilde{u}_{\alpha\beta}\tilde{\zeta}^{(k)}_{\alpha\beta}$, and $\tilde{\zeta}^{(k)}_{\alpha\beta}\tilde{\zeta}^{(l)}_{\alpha\beta}$. The traces $\zeta^{(k)}$ are equivalent to scalar parameters and can be included in the set of these, $\xi^{(j)}$, i.e., one can assume that Ψ does not depend explicitly on the $\zeta^{(k)}$. Clearly, in our quadratic approximation no invariant combinations of scalars and tensors occur; this implies the statistical independence of the scalar and tensor quantities.

In writing down the equations for the above-enumerated coordinates, we introduce at once the fluctuation forces, i.e., the usual forces with the volume density F_α (or the stresses $\Sigma_{\alpha\beta}$ where $F_\alpha = \partial\Sigma_{\alpha\beta}/\partial x_\beta$), the "external" entropy $S^e = q/T_0$ (q is the volume density of the intensity of the external heat sources), and the forces $\Xi^{(j)}$ and $\tilde{Z}^{(k)}_{\alpha\beta} = Z^{(k)}_{\alpha\beta} - Z^{(k)}_{\gamma\gamma}\delta_{\alpha\beta}/3$, connected with $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$ in the same Lagrangian sense.

The equations of motion are

$$\rho_0\ddot{s}_\alpha = \frac{\partial\sigma^{tot}_{\alpha\beta}}{\partial x_\beta} = \frac{\partial}{\partial x_\beta}(\sigma_{\alpha\beta} + \sigma_{\alpha\beta}' + \Sigma_{\alpha\beta}) = \frac{\partial}{\partial x_\beta}(\sigma_{\alpha\beta} + \sigma_{\alpha\beta}') + F_\alpha. \quad (1)$$

Here ρ_0 is the average density of the medium, $\sigma'_{\alpha\beta} = 2\eta\dot{\tilde{u}}_{\alpha\beta} + \zeta\dot{u}\delta_{\alpha\beta}$ is the viscous stress tensor due to constant viscosities: the shear, η, and the bulk viscosities, ζ, and $\sigma_{\alpha\beta} = \partial\Psi/\partial u_{\alpha\beta}$ are the elastic stresses. Furthermore, we have the linearized equation for the heat transfer:

$$T_0\dot{S}^{tot}_1 = T_0(\dot{S}_1 + \dot{S}^e) = \varkappa\partial^2 T_1/\partial x_\beta^2, \quad (2)$$

where κ is the heat conductivity, and $S_1 = S - S_0 = -\partial\Psi/\partial T_1$ is the volume density of the "internal" entropy. Equations (1) and (2) must be complemented by kinetic equations for the relaxation parameters, which, neglecting inertia and choosing these parameters appropriately, can always be written in the form[5]

$$\theta_j\frac{\partial^2\Psi}{\partial\xi^{(j)2}}\dot{\xi}^{(j)} = -\frac{\partial\Psi}{\partial\xi^{(j)}} + \Xi^{(j)}, \quad (3)$$

$$\theta_k\frac{\partial^2\Psi}{\partial\tilde{\zeta}^{(k)2}_{\alpha\beta}}\dot{\tilde{\zeta}}^{(k)}_{\alpha\beta} = -\frac{\partial\Psi}{\partial\tilde{\zeta}^{(k)}_{\alpha\beta}} + \tilde{Z}^{(k)}_{\alpha\beta}, \quad (4)$$

where no summation over the indices is implied, and θ_j and θ_k are the relaxation times which (in analogy to the normal and partial frequencies in coupled vibrational systems) may be called "partial" times, since they characterize the relaxation of each of the parameters when all others are held fixed. The "normal" relaxation times will be needed in the following.

First of all we verify that the fluctuation forces just introduced are indeed connected with the chosen coordinates such as required for the application of the FDT. To this end we multiply (1) to (4) by $\dot{s}_\alpha$, T_1/T_0, $\dot{\xi}^{(j)}$, and $\dot{\tilde{\zeta}}^{(k)}_{\alpha\beta}$, respectively, and add them up. Introducing the instantaneous power dissipated per unit volume,

$$Q = \sigma'_{\alpha\beta}\dot{u}_{\alpha\beta} + \frac{\varkappa}{T_0}\left(\frac{\partial T_1}{\partial x_\beta}\right)^2 + \sum_j\theta_j\frac{\partial^2\Psi}{\partial\xi^{(j)2}}\dot{\xi}^{(j)2} + \sum_k\theta_k\frac{\partial^2\Psi}{\partial\tilde{\zeta}^{(k)2}_{\alpha\beta}}\dot{\tilde{\zeta}}^{(k)2}_{\alpha\beta}$$

and the energy current density,

$$P_\beta = \dot{s}_\alpha(\sigma_{\alpha\beta} + \sigma_{\alpha\beta}') + \frac{\varkappa T_1}{T_0}\frac{\partial T_1}{\partial x_\beta},$$

and using, furthermore,

$$\sigma_{\alpha\beta}\dot{u}_{\alpha\beta} - S_1\dot{T}_1 + \sum_j\frac{\partial\Psi}{\partial\xi^{(j)}}\dot{\xi}^{(j)} + \sum_k\frac{\partial\Psi}{\partial\tilde{\zeta}^{(k)}_{\alpha\beta}}\dot{\tilde{\zeta}}^{(k)}_{\alpha\beta} = \frac{d\Psi}{dt},$$

we find for the sum

$$\frac{d}{dt}(E_k + E + S^e T_1) + Q = \\ = \frac{\partial P_\beta}{\partial x_\beta} + F_\alpha\dot{s}_\alpha + \dot{S}^e T_1 + \sum_j\Xi^{(j)}\dot{\xi}^{(j)} + \sum_k\tilde{Z}^{(k)}_{\alpha\beta}\dot{\tilde{\zeta}}^{(k)}_{\alpha\beta}. \quad (5)$$

Here $E_k = \rho_0\dot{s}_\alpha^2/2$ and $E = \Psi + T_1S_1$ are the volume densities of the kinetic and internal energies. When averaging (5) over the ensemble, the time derivative vanishes owing to the stationarity of the fluctuations, and in the integration over space with the usual assumptions at infinity ($s_\alpha = 0$, $\partial T_1/\partial x_\beta = 0$) the integral over the divergence of the current is zero. As a result we obtain for the average power dissipated in the medium

$$\int\langle Q\rangle dV = \int\left\{\langle F_\alpha\dot{s}_\alpha\rangle + \langle\dot{S}^e T_1\rangle + \sum_j\langle\Xi^{(j)}\dot{\xi}^{(j)}\rangle + \sum_k\langle\tilde{Z}^{(k)}_{\alpha\beta}\dot{\tilde{\zeta}}^{(k)}_{\alpha\beta}\rangle\right\}dV, \quad (6)$$

which proves the correctness of the fluctuation forces introduced above.

If, instead of s_α, we use the deformations $u_{\alpha\beta}$ as coordinates, we have, assuming symmetric fluctuation stresses $\Sigma_{\alpha\beta}$

$$\int\langle F_\alpha\dot{s}_\alpha\rangle dV = \int\left\langle\frac{\partial\Sigma_{\alpha\beta}}{\partial x_\beta}\dot{s}_\alpha\right\rangle dV = -\int\left\langle\Sigma_{\alpha\beta}\frac{\partial\dot{s}_\alpha}{\partial x_\beta}\right\rangle dV = -\int\langle\Sigma_{\alpha\beta}\dot{u}_{\alpha\beta}\rangle dV,$$

i.e., the fluctuation forces corresponding to $u_{\alpha\beta}$ are $-\Sigma_{\alpha\beta}$; these will be used in the following.

The form of the equations (3) and (4) presupposes already that the dissipative function Q is reduced to a sum of squares, but it does not yet imply the statistical independence of the relaxation parameters $\xi^{(j)}$ of each other, and of the quantities $\tilde{\zeta}^{(k)}_{\alpha\beta}$ of each other. We now make this assumption, since it simplifies considerably the calculation and the final result. On the other hand, this does not restrict the generality, since the simultaneous reduction of the two symmetric quadratic forms $Q(\dot{\xi}^{(j)})$ and $\Psi(\xi^{(j)})$ and (or) $Q(\dot{\tilde{\zeta}}^{(k)}_{\alpha\beta})$ and $\Psi(\tilde{\zeta}^{(k)}_{\alpha\beta})$ to a sum of squares can always be effected via a linear transformation of the variables. Of course, if one is considering a model for which the introduction of dependent relaxation parameters is natural, the application of the more general formulas given below is complicated by the rather intricate preliminary transformation of the corresponding parts Q and Ψ to sums of squares.

We note in this connection that going beyond the limits of the relaxation theory, for example by taking account of inertia, (involving the appearance of second time derivatives in the equations for $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$), introduces a third quadratic form ("kinetic energy"), so that a complete separation of the variables becomes impossible in general.

In writing down Ψ, we must further take account of

$$\frac{\partial^2\Psi}{\partial u\,\partial T} = -K_\infty\alpha_\infty, \quad \frac{\partial^2\Psi}{\partial T^2} = -\frac{\rho_0 c_{v\infty}}{T}. \quad (7)$$

The index ∞ refers to the values of the moduli (the isothermal compressibility K, the thermal expansion coefficient α, and heat capacity c_V) corresponding to constant $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$, i.e., to sufficiently rapid processes (in the spectral language, to frequencies which are much higher than the largest of the inverse relaxation times). Besides the coefficients (7), Ψ contains also the shear modulus μ_∞ and the coefficients

$$L_j = \frac{\partial^2\Psi}{\partial u \partial \xi^{(j)}}, \quad M_j = \frac{\partial^2\Psi}{\partial T \partial \xi^{(j)}}, \quad N_k = \frac{\partial^2\Psi}{\partial \tilde{u}_{\alpha\beta} \partial \tilde{\zeta}^{(k)}_{\alpha\beta}}$$

[no summation over α and β is implied in the expression for N_k, since N_k is the scalar coefficient of the contraction $\tilde{u}_{\alpha\beta}\tilde{\zeta}^{(k)}_{\alpha\beta}$]. The free energy has thus the following form:

$$2\Psi = 2\mu_\infty (\tilde{u}_{\alpha\beta})^2 + \sum_k (\tilde{\zeta}^{(k)}_{\alpha\beta})^2 + 2\tilde{u}_{\alpha\beta} \sum_k N_k \tilde{\zeta}^{(k)}_{\alpha\beta} + \sum_j \xi^{(j)2}$$
$$+ 2u \sum_j L_j \xi^{(j)} + 2T_1 \sum_j M_j \xi^{(j)} + K_\infty u^2 - 2K_\infty \alpha_\infty u T_1 - \frac{\rho_0 c_{V\infty}}{T_0} T_1^2 \quad (8)$$

Calculating from (8) the derivatives $\sigma_{\alpha\beta} = \partial\Psi/\partial u_{\alpha\beta}$, $S_1 = -\partial\Psi/\partial T_1$, $\partial\Psi/\partial\xi^{(j)}$, and $\partial\Psi/\partial\zeta^{(k)}_{\alpha\beta}$, we find from (1) to (4) the following system of equations:

$$\rho_0 \ddot{s}_\alpha = \frac{\partial}{\partial x_\beta}\Big\{2\mu_\infty \tilde{u}_{\alpha\beta} + K_\infty u \delta_{\alpha\beta} + 2\eta \dot{\tilde{u}}_{\alpha\beta} + \zeta \dot{u} \delta_{\alpha\beta}$$
$$- K_\infty \alpha_\infty T_1 \delta_{\alpha\beta} + \sum_j L_j \xi^{(j)} \delta_{\alpha\beta} + \sum_k N_k \tilde{\zeta}^{(k)}_{\alpha\beta}\Big\} + F_\alpha,$$
$$\frac{\partial}{\partial t}\Big(K_\infty \alpha_\infty u + \frac{\rho_0 c_{V\infty}}{T_0} T_1 - \sum_j M_j \xi^{(j)}\Big) = \frac{\varkappa}{T_0} \frac{\partial^2 T_1}{\partial x_\beta^2} - \dot{S}^e, \quad (9)$$
$$\tau_j \dot{\xi}^{(j)} = -\xi^{(j)} - L_j u - M_j T_1 + \Xi^{(j)},$$
$$\tau_k \dot{\tilde{\zeta}}^{(k)}_{\alpha\beta} = -\tilde{\zeta}^{(k)}_{\alpha\beta} - N_k \tilde{u}_{\alpha\beta} + \tilde{Z}^{(k)}_{\alpha\beta}.$$

The relaxation times for the independent ones of the parameters $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$, i.e., the "normal" times, are here denoted by τ_j and τ_k.

3. SPECTRAL DESCRIPTION OF THE FLUCTUATIONS

Taking the Fourier transform of (9) ($\partial/\partial t \to i\omega$, $\partial/\partial x_\beta \to iq_\beta$), we obtain

$$F_\alpha = a s_\alpha + b q_\alpha q_\gamma s_\gamma + i q_\alpha \Big(K_\infty \alpha_\infty T_1 - \sum_j L_j \xi^{(j)}\Big)$$
$$- i q_\gamma \sum_k N_k \Big(\frac{\tilde{\zeta}^{(k)}_{\alpha\gamma} + \tilde{\zeta}^{(k)}_{\gamma\alpha}}{2} - \frac{\tilde{\zeta}^{(k)}}{3}\delta_{\alpha\gamma}\Big),$$
$$S^e = -i q_\gamma K_\infty \alpha_\infty s_\gamma - c T_1 + \sum_j M_j \xi^{(j)} \quad (10)$$
$$\Xi^{(j)} = i q_\gamma L_j s_\gamma + M_j T_1 + \lambda_j \xi^{(j)},$$
$$\tilde{Z}^{(k)}_{\alpha\beta} = i N_k \Big(\frac{q_\beta s_\alpha + q_\alpha s_\beta}{2} - \frac{q_\gamma s_\gamma}{3}\delta_{\alpha\beta}\Big) + \lambda_k \tilde{\zeta}^{(k)}_{\alpha\beta}$$

where we have introduced the notation

$$a = (\mu_\infty + i\omega\eta) q^2 - \rho_0 \omega^2, \quad b = K_\infty + i\omega\zeta + \frac{\mu_\infty + i\omega\eta}{3}$$
$$c = \frac{1}{T_0}\Big(\rho_0 c_{V\infty} + \frac{\varkappa q^2}{i\omega}\Big), \quad \lambda_j = 1 + i\omega\tau_j, \quad \lambda_k = 1 + i\omega\tau_k. \quad (11)$$

The coefficients in the equations (10) form the inverse generalized susceptibility matrix $\hat{\alpha}^{-1}$,[6] with the help of which one can, in accordance with the FDT, write down the matrix of the ωq densities of the fluctuation forces F_α, S^e, $\Xi^{(j)}$, and $\tilde{Z}^{(k)}_{\alpha\beta}$ (it is, of course, diagonal, i.e., the spectral amplitudes of the forces are mutually uncorrelated).

However, for the scattering theory we need the ωq densities, not of the forces, but of the coordinates, and of these not the displacements s_α, but the deformations $u_{\alpha\beta}$. Solving (10) for s_α, T_1, $\xi^{(j)}$, and $\tilde{\zeta}^{(k)}_{\alpha\beta}$, we obtain the susceptibility matrix $\hat{\alpha}$ and thus the ωq densities of these coordinates. With the help of these we can easily calculate also the ωq densities for the $u_{\alpha\beta}$, using

$$u_{\alpha\beta} = {}^1/_2 i (q_\beta s_\alpha + q_\alpha s_\beta). \quad (12)$$

However, with the help of (12), one can also go over to the coordinates $u_{\alpha\beta}$, T_1, $\xi^{(j)}$, and $\tilde{\zeta}^{(k)}_{\alpha\beta}$ in the equations themselves. We are speaking here of the transformation of the first equation in (10) only, since the remaining three already contain $\tilde{u}_{\alpha\beta}$ and u.

In any of these fashions we arrive at expressions for the coordinates $u_{\alpha\beta}$, T_1, $\xi^{(j)}$, $\tilde{\zeta}^{(k)}_{\alpha\beta}$ in terms of the corresponding fluctuation forces $-\Sigma_{\alpha\beta}$, S^e, $\Xi^{(j)}$, and $\tilde{Z}^{(k)}_{\alpha\beta}$, and thus obtain the matrix $\hat{\alpha}$:

$$\begin{array}{c|cccc} & -\Sigma_{\gamma\delta} & S^e_\cdot & \Xi^{(j')} & \tilde{Z}^{(k')}_{\gamma\delta} \\ \hline u_{\alpha\beta} & a_1 & a_2 & a_3 & a_4 \\ T_1 & b_1 & b_2 & b_3 & b_4 \\ \xi^{(j)} & c_1 & c_2 & c_3 & c_4 \\ \tilde{\zeta}^{(k)}_{\alpha\beta} & d_1 & d_2 & d_3 & d_4 \end{array}, \quad (13)$$

where

$$a_1 = \frac{\nu_{\alpha\beta\gamma\delta}}{A} + \frac{C q_\alpha q_\beta q_\gamma q_\delta}{\Delta q^2}, \quad a_2 = -\frac{K\alpha}{\Delta} q_\alpha q_\beta,$$
$$a_3 = \frac{U_{j'} q_\alpha q_\beta}{\Delta \lambda_{j'}}, \quad a_4 = -\frac{N_{k'}}{\lambda_{k'}}\Big(\frac{\nu_{\alpha\beta\gamma\delta}}{A} + \frac{C q_\alpha q_\beta \pi_{\gamma\delta}}{\Delta q^2}\Big),$$
$$b_1 = -\frac{K\alpha}{\Delta} q_\gamma q_\delta, \quad b_2 = -\frac{A + Bq^2}{\Delta}, \quad b_3 = \frac{V_{j'}}{\Delta \lambda_{j'}},$$
$$b_4 = \frac{N_{k'} K\alpha}{\Delta \lambda_{k'}} \pi_{\gamma\delta}, \quad c_1 = \frac{U_j q_\gamma q_\delta}{\Delta \lambda_j}, \quad c_2 = \frac{V_j}{\Delta \lambda_j},$$
$$c_3 = \frac{1}{\lambda_j}\Big(\delta_{jj'} - \frac{W_{jj'}}{\Delta \lambda_{j'}}\Big), \quad c_4 = -\frac{N_{k'} U_j}{\lambda_{k'} \Delta \lambda_j} \pi_{\gamma\delta},$$
$$d_1 = -\frac{N_k}{\lambda_k}\Big(\frac{\nu_{\alpha\beta\gamma\delta}}{A} + \frac{C q_\gamma q_\delta \pi_{\alpha\beta}}{\Delta q^2}\Big), \quad d_2 = \frac{N_k K\alpha}{\Delta \lambda_k} \pi_{\alpha\beta},$$
$$d_3 = -\frac{N_k U_{j'}}{\lambda_k \Delta \lambda_{j'}} \pi_{\alpha\beta}, \quad d_4 = \frac{\delta_{kk'}}{\lambda_k} \mu_{\alpha\beta\gamma\delta} + \frac{N_k N_{k'}}{\lambda_k \lambda_{k'}}\Big(\frac{\nu_{\alpha\beta\gamma\delta}}{A} + \frac{C \pi_{\alpha\beta} \pi_{\gamma\delta}}{\Delta q^2}\Big).$$

Here we have introduced the tensors

$$\nu_{\alpha\beta\gamma\delta} = {}^1/_4 (\delta_{\alpha\gamma} q_\beta q_\delta + \delta_{\alpha\delta} q_\beta q_\gamma + \delta_{\beta\gamma} q_\alpha q_\delta + \delta_{\beta\delta} q_\alpha q_\gamma) - q_\alpha q_\beta q_\gamma q_\delta / q^2,$$
$$\pi_{\alpha\beta} = q_\alpha q_\beta - {}^1/_3 q^2 \delta_{\alpha\beta}, \quad \mu_{\alpha\beta\gamma\delta} = {}^1/_2 (\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\beta\gamma}\delta_{\alpha\delta}) - {}^1/_3 \delta_{\alpha\beta}\delta_{\gamma\delta} \quad (14)$$

and the notation

$$A = \mu q^2 - \rho_0 \omega^2, \quad B = K + \frac{\mu}{3}, \quad C = \frac{1}{T_0}\Big(\rho_0 c_V + \frac{\varkappa q^2}{i\omega}\Big),$$
$$\Delta = (A + Bq^2) C + K^2 \alpha^2 q^2,$$
$$U_j = K\alpha M_j - C L_j, \quad V_j = (A + Bq^2) M_j + K\alpha q^2 L_j, \quad (15)$$
$$W_{jj'} = M_j V_{j'} + L_j U_{j'} q^2,$$

where μ, K, $K\alpha$, and c_V are the complex moduli:

$$\mu = \mu_\infty - \frac{1}{2}\sum_k \frac{N_k^2}{\lambda_k}, \quad K = K_\infty - \sum_j \frac{L_j^2}{\lambda_j},$$
$$K\alpha = K_\infty \alpha_\infty + \sum_j \frac{L_j M_j}{\lambda_j}, \quad c_V = c_{V\infty} + \frac{T_0}{\rho_0}\sum_j \frac{M_j^2}{\lambda_j}. \quad (16)$$

The dispersion of the shear modulus is determined solely by the tensor parameters $\tilde{\zeta}^{(k)}_{\alpha\beta}$, while the dispersion of the other quantities connected with the compression waves are determined only by the scalar parameters $\xi^{(j)}$. The expressions (16) for K, $K\alpha$, and c_V have already been obtained and discussed in[7].

The frequency independent viscosities η and ζ which violate the Kramers-Kronig condition, also do not conform with the meaning of the constants with index ∞ (the values of the moduli for $\omega \gg 1/\tau_{\min}$). If many relaxation times are taken into account explicitly, the constants η and ζ need not be introduced and have therefore been discarded in (16). When we introduced them above (introducing, accordingly, the viscous stresses $\sigma'_{\alpha\beta}$), we did this only for greater clarity in the separation of the dissipative terms in the energy balance equation (5). According to (16), the static values of the moduli, and for μ and K also the coefficients of $i\omega$ in the imaginary parts, i.e., the viscosities η_0 and ζ_0, are the following:

$$\mu_0 = \mu_\infty - \frac{1}{2}\sum_k N_k^2, \quad \eta_0 = \frac{1}{2}\sum_k N_k^2 \tau_k, \tag{16'}$$

$$K_0 = K_\infty - \sum_j L_j^2, \quad \zeta_0 = \sum_j L_j^2 \tau_j,$$

$$K_0 a_0 = K_\infty a_\infty + \sum_j L_j M_j, \quad c_{V0} = c_{V\infty} + \frac{T_0}{\rho_0}\sum_j M_j^2.$$

In accordance with the FDT the generalized susceptibility matrix $\hat{\alpha}$ which connects the coordinates **x** with corresponding forces **F** ($\mathbf{x} = \hat{\alpha}\mathbf{F}$) directly determines the matrix of the spectral coordinate densities:[6,8]

$$\langle x_i x_k^* \rangle_\omega = H(\alpha_{ik} - \alpha_{ki}^*), \tag{17}$$

where

$$H = -\Theta / (2\pi)^4 i\omega, \tag{18}$$

in the classical region of frequencies, where $\theta = k_B T_0$ is the temperature of the medium in energy units. Separating the pure shears $\tilde{u}_{\alpha\beta}$ and the compression u, we obtain, with the help of (13) and (17), the following spectral coordinate densities $\tilde{u}_{\alpha\beta}$, u, T_1, $\xi^{(j)}$, and $\zeta^{(k)}_{\alpha\beta}$:

$$\langle \tilde{u}_{\alpha\beta}\tilde{u}_{\gamma\delta}^* \rangle_\omega = H\left(\frac{\nu_{\alpha\beta\gamma\delta}}{A} + \frac{C}{\Delta q^2}\pi_{\alpha\beta}\pi_{\gamma\delta} - \text{c.c.}\right),$$

$$\langle \tilde{u}_{\alpha\beta} u^* \rangle_\omega = H\pi_{\alpha\beta}\left(\frac{C}{\Delta} - \text{c.c.}\right), \quad \langle \tilde{u}_{\alpha\beta} T_1^* \rangle_\omega = -H\pi_{\alpha\beta}\left(\frac{K\alpha}{\Delta} - \text{c.c.}\right),$$

$$\langle \tilde{u}_{\alpha\beta}\xi^{(j)*} \rangle_\omega = H\pi_{\alpha\beta}\left(\frac{U_j}{\Delta\lambda_j} - \text{c.c.}\right),$$

$$\langle \tilde{u}_{\alpha\beta}\tilde{\zeta}^{(k)*}_{\gamma\delta} \rangle_\omega = -HN_k\left[\frac{1}{\lambda_k}\left(\frac{\nu_{\alpha\beta\gamma\delta}}{A} + \frac{C}{\Delta q^2}\pi_{\alpha\beta}\pi_{\gamma\delta}\right) - \text{c.c.}\right], \tag{19}$$

$$\langle uu^* \rangle_\omega = Hq^2\left(\frac{C}{\Delta} - \text{c.c.}\right), \quad \langle uT_1^* \rangle_\omega = -Hq^2\left(\frac{K\alpha}{\Delta} - \text{c.c.}\right),$$

$$\langle u\xi^{(j)*} \rangle_\omega = Hq^2\left(\frac{U_j}{\Delta\lambda_j} - \text{c.c.}\right), \quad \langle u\tilde{\zeta}^{(k)*}_{\gamma\delta} \rangle_\omega = -HN_k\pi_{\gamma\delta}\left(\frac{C}{\Delta\lambda_k} - \text{c.c.}\right),$$

$$\langle T_1T_1^* \rangle_\omega = -H\left(\frac{A + Bq^2}{\Delta} - \text{c.c.}\right), \quad \langle T_1\xi^{(j)*} \rangle_\omega = -H\left(\frac{V_j}{\Delta\lambda_j} - \text{c.c.}\right),$$

$$\langle T_1\tilde{\zeta}^{(k)*}_{\gamma\delta} \rangle_\omega = HN_k\pi_{\gamma\delta}\left(\frac{K\alpha}{\Delta\lambda_k} - \text{c.c.}\right),$$

$$\langle \xi^{(j)}\xi^{(j')*} \rangle_\omega = H\left[\frac{1}{\lambda_j}\left(\delta_{jj'} - \frac{W_{jj'}}{\Delta\lambda_{j'}}\right) - \text{c.c.}\right],$$

$$\langle \xi^{(j)}\tilde{\zeta}^{(k)*}_{\gamma\delta} \rangle_\omega = -HN_k\pi_{\gamma\delta}\left(\frac{U_j}{\Delta\lambda_j\lambda_k} - \text{c.c.}\right),$$

$$\langle \tilde{\zeta}^{(k)}_{\alpha\beta}\tilde{\zeta}^{(k')*}_{\gamma\delta} \rangle_\omega = H\left[\frac{\delta_{kk'}}{\lambda_k}\mu_{\alpha\beta\gamma\delta} + \frac{N_kN_{k'}}{\lambda_k\lambda_{k'}}\left(\frac{\nu_{\alpha\beta\gamma\delta}}{A} + \frac{C}{\Delta q^2}\pi_{\alpha\beta}\pi_{\gamma\delta}\right) - \text{c.c.}\right],$$

where c.c. means "complex conjugate."

We note that in (19), the original quantities and their complex conjugates never enter in the same term, as was found in[2] owing to the transition from the stresses $\sigma_{\alpha\beta}$ to the coordinates $u_{\alpha\beta}$, which is not permitted in an incomplete description. As a result, the spatial correlation functions are here local (delta correlation for all integral (with respect to ω) quantities, i.e., those considered at one and the same instant.

If we eliminate the parameters $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$ from (10) i.e., if we go over to an incomplete description in the coordinates $u_{\alpha\beta}$ and T_1, then the forces $\Xi^{(j)}$ and $\tilde{Z}^{(k)}_{\alpha\beta}$ enter linearly in the new set of fluctuation forces $-\Sigma'_{\alpha\beta}$ and S^e through which $u_{\alpha\beta}$ and T_1 will be expressed in the previous manner. In other words, the susceptibility matrix in the incomplete ($u_{\alpha\beta}$, T_1) description coincides with the submatrix indicated in (13) by the dotted lines, and the ωq densities of the deformations and the temperature remain the same as in the complete description. Of course, the ωq densities of the forces $-\Sigma'_{\alpha\beta}$ and $S^{e\prime}$ are different from those for $-\Sigma_{\alpha\beta}$ and S^e; this does not mean that one can say that the incomplete description leads to <u>incorrect</u> forces.[1]

In the complete description one can choose any linear combinations of the original coordinates as the new coordinates. In particular, one may go from the deformations $u_{\alpha\beta}$ to the stresses $\sigma_{\alpha\beta}$ and (or) from T_1 to S_1.[1)] But the incomplete ($u_{\alpha\beta}$, T_1) and ($\sigma_{\alpha\beta}$, T_1) descriptions are not equivalent to each other, since the transformation $\sigma_{\alpha\beta} = -\partial\Psi/\partial u_{\alpha\beta} \to u_{\alpha\beta}$ (like the transformation $T_1 \to S_1 = -\partial\Psi/\partial T_1$) contains also the parameters $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$ which are eliminated in the transition from the complete ($u_{\alpha\beta}$, T_1, $\xi^{(j)}$, $\tilde{\zeta}^{(k)}_{\alpha\beta}$) and ($\sigma_{\alpha\beta}$, T_1, $\xi^{(j)}$, $\tilde{\zeta}^{(k)}_{\alpha\beta}$) descriptions to the corresponding incomplete ones. Equivalent are only those incomplete descriptions which are obtained from one another by a transformation which does not contain $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$. An example are the ($s_\alpha$, T_1) and ($u_{\alpha\beta}$, T_1) descriptions, which are connected by (12).

4. RAYLEIGH SCATTERING

The deviations $\epsilon_{\alpha\beta}$ of the dielectric constant of the medium from the average value $\epsilon_0\delta_{\alpha\beta}$ depend in general on the deformation and on the temperature, as well as on relaxation parameters $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$:

$$\varepsilon_{\alpha\beta} = x\tilde{u}_{\alpha\beta} + yu\delta_{\alpha\beta} + zT_1\delta_{\alpha\beta} + \sum_j m_j\xi^{(j)}\delta_{\alpha\beta} + \sum_k n_k\tilde{\zeta}^{(k)}_{\alpha\beta}. \tag{20}$$

The coefficients x, y, z, m_j, and n_k are naturally considered real, since we assume a complete description of the system.

If we eliminate $\xi^{(j)}$ and $\tilde{\zeta}^{(k)}_{\alpha\beta}$ from (20) with the help of the last two equations (10), we obtain

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1)The coordinate S_1 corresponds to the fluctuation force T^e, the "external temperature."

$$\varepsilon_{\alpha\beta}=X\tilde{u}_{\alpha\beta}+Yu\delta_{\alpha\beta}+ZT_1\delta_{\alpha\beta}+\sum_j\frac{m_j}{\lambda_j}\Xi^{(j)}\delta_{\alpha\beta}+\sum_k\frac{n_k}{\lambda_k}\tilde{Z}^{(k)}_{\alpha\beta},\quad(20')$$

where

$$X=x-\sum_k\frac{n_kN_k}{\lambda_k},\quad Y=y-\sum_j\frac{m_jL_j}{\lambda_j},\quad Z=z-\sum_j\frac{m_jM_j}{\lambda_j}.\quad(21)$$

It is seen directly from (20′) why one cannot restrict oneself to the incomplete ($u_{\alpha\beta}$, T_1) description for the scattering theory: for nonvanishing m_j and (or) n_k, i.e., if $\epsilon_{\alpha\beta}$ depends explicitly on the relaxation parameters, the spectral density $\epsilon_{\alpha\beta}$ is determined by the spectral densities not only of the deformations and the temperature, but also of the fluctuation forces $\Xi^{(j)}$ and $\tilde{Z}^{(k)}_{\alpha\beta}$, and of the cross densities of these forces and the conserved coordinates. If $m_j=0$, $n_k=0$, then the incomplete description is sufficient, but then X, Y, and Z do not have dispersion (they are equal to x, y, and z, respectively) and (20′) does not—when the spectral deformation densities are calculated correctly—give a true description of the wings of the spectral line.

In this connection the natural question arises why in[4], where the fluctuations of the dielectric constant were assumed to be given only by the first three terms of (20′), the Leontovich theory[9] was obtained as a limiting case and why the correct relations for the anisotropic wing (in particular, a depolarization coefficient equal to 6/7) could be derived. The explanation is that the deformations were determined in[2] not by (12), but as the quantities $\hat{u}_{\alpha\beta}=u_{\alpha\beta}-U_{\alpha\beta}$, where the $U_{\alpha\beta}$ are the "external" deformations, i.e., the fluctuation forces corresponding to the stresses $\sigma_{\alpha\beta}$. Thus the expression for $\epsilon_{\alpha\beta}$ is in fact

$$\varepsilon_{\alpha\beta}=X\tilde{u}_{\alpha\beta}+Yu\delta_{\alpha\beta}+ZT_1\delta_{\alpha\beta}-X\tilde{U}_{\alpha\beta}-YU\delta_{\alpha\beta}.\quad(20'')$$

The additional term with $\tilde{U}_{\alpha\beta}$, which has the necessary symmetry, is responsible for the "imitation" of the correct spectrum in the anisotropic wing. This situation can also be described differently, as shown by Volterra.[10] Since in[2] the stresses $\sigma_{\alpha\beta}$ were, as usual, related to $\hat{u}_{\alpha\beta}$ and not to $u_{\alpha\beta}$, the transformation (20″) to $\sigma_{\alpha\beta}$ gives

$$\varepsilon_{\alpha\beta}=X\frac{\tilde{\sigma}_{\alpha\beta}}{2\mu}+Y\frac{\sigma}{3K}\delta_{\alpha\beta}+(Z+\alpha Y)T_1\delta_{\alpha\beta}.$$

Therefore one can say that the anisotropic scattering has been calculated in[3,4] for shear deformations defined as $\tilde{\sigma}_{\alpha\beta}/2\mu$.

Formulas (21) show that the dispersion of the magneto-optical and thermo-optical coefficients X, Y, Z is determined by the same processes in the medium as the dispersion of the moduli (16), and is characterized, in particular, by the same relaxation times. It is thus impossible to assume, as was done in[3,4], that the dispersion laws for X, Y, and Z can be taken as arbitrary, independently of the dispersion laws for the moduli μ, K, etc.

If one is dealing not with the thermal fluctuations, but with the determining processes, then the fluctuation forces must be set equal to zero and the shear term in $\epsilon_{\alpha\beta}$ will, according to (20′), be equal to $X\tilde{u}_{\alpha\beta}$. For $\omega \ll 1/\tau_{k\,\max}$ the coefficient X can be written in the form $X=X_0+i\omega X_0'$, where

$$X_0=x-\sum_k n_kN_k=4\sqrt{\varepsilon_0}\,\mu_0c,\quad X_0'=\sum_k n_kN_k\tau_k=2\varepsilon_0\eta_0M,$$

and c and M are coefficients which are usually introduced in the empirical formulas for the anisotropy caused by the low-frequency stresses—which are elastic in solid matter (c is the so-called relative optical stress coefficient) and viscous in liquids (M is the Maxwell constant).

For the calculation of the spectral densities of the components of the dielectric constant it is, of course, not necessary to return formula (20′) which contains the coordinates as well as the fluctuation forces. It is simpler to start from (20), using (19). As a result we obtain the following cross ωq density for the components $\epsilon_{\alpha\beta}$ and $\epsilon_{\gamma\delta}$:

$$\langle\varepsilon_{\alpha\beta}\varepsilon_{\gamma\delta}^*\rangle_\omega=\Pi\Big\{X^2\Big(\frac{\nu_{\alpha\beta\gamma\delta}}{A}+\frac{C\pi_{\alpha\beta}\pi_{\gamma\delta}}{\Delta q^2}\Big)+\frac{X}{\Delta}(YC-ZK\alpha)(\delta_{\alpha\beta}\pi_{\gamma\delta}+\delta_{\gamma\delta}\pi_{\alpha\beta})+\sum_k\frac{n_k^2}{\lambda_k}\mu_{\alpha\beta\gamma\delta}$$
$$+\Big[\frac{1}{\Delta}(Y^2Cq^2-2YZK\alpha q^2-Z^2(A+Bq^2))+\sum_j\frac{m_j^2}{\lambda_j}\Big]\delta_{\alpha\beta}\delta_{\gamma\delta}-\text{c.c.}\Big\}.\quad(22)$$

According to (22), the appearance of the relaxation parameters affects the dielectric tensor in three ways: first, through the dispersion of the elastic and thermal moduli μ, K, α, and c_V, second, through the dispersion of the coefficients (21) owing to these relaxation parameters, and third, through the terms $\sum_j m_j^2/\lambda_j$ and $\sum_k n_k^2/\lambda_k$, which give (cf. below) a direct contribution to the wings of the spectral line (the compression wing and the shear wing).

Spectral intensities. Formula (22) allows one to calculate the spectral intensities of the scattered light for different polarizations of the initial wave and the observed light, and for various scattering angles. If the initial wave propagates along the x axis and the direction of observation lies in the (x, y) plane with angle θ with respect to the x axis, then the intensities of the scattered light for four combinations of polarizations are[3]

$$J_z^z(\omega,\mathbf{q})=(2\pi)^3\langle|\varepsilon_{33}|^2\rangle_\omega,\quad J_{\mathrm{r}}^z(\omega,\mathbf{q})=(2\pi)^3\langle|\varepsilon_{13}\sin\theta-\varepsilon_{23}\cos\theta|^2\rangle_\omega,$$
$$J_z^y(\omega,\mathbf{q})=(2\pi)^3\langle|\varepsilon_{32}|^2\rangle_\omega,\quad J_{\mathrm{r}}^y(\omega,\mathbf{q})=(2\pi)^3\langle|\varepsilon_{12}\sin\theta-\varepsilon_{22}\cos\theta|^2\rangle_\omega.\quad(23)$$

The upper index refers to the polarization of the initial light wave, the lower to the observed polarization (h—horizontal). Here q is the scattering vector which is equal to the difference of the wave vectors of the initial (k) and the scattered waves (k′):

$$\mathbf{q}=\mathbf{k}-\mathbf{k}'=\{k_0(1-\cos\theta),-k_0\sin\theta,0\},\quad q=2k_0\sin\frac{\theta}{2}.$$

Calculating the spectral densities from (22), we obtain from (23) using (18)[2)]

2)Calculating the vertex $J^{\mathbf{p}}_{\mathbf{p}'}(\omega,\theta)=(2\pi)^3\langle\varepsilon_{\alpha\beta}\varepsilon_{\gamma\delta}^*\rangle_\omega p_\alpha p_\beta' p_\gamma p_\delta'$, with the help of (22), where p and p′ are the polarizations of the incident and observed waves, it is easy to expand $J^{\mathbf{p}}_{\mathbf{p}'}$ into the canonical "modes" considered by Volterra. [10] We restrict ourselves, however, to the special choice of polarizations corresponding to the usual experimental conditions.

$$J_z^z = -\frac{\Theta}{2\pi i\omega}\left\{\frac{1}{\Lambda}\left[\frac{Xq^2}{3}\left(\frac{XC}{3} - 2YC + 2ZK\alpha\right) + Y^2Cq^2 - 2YZK\alpha q^2 - Z^2(A + Bq^2)\right] + \sum_j \frac{m_j^2}{\lambda_j} + \frac{2}{3}\sum_k \frac{n_k^2}{\lambda_k} - \text{c.c.}\right\},$$

$$J_h^z = J_z^y = -\frac{\Theta}{2\pi i\omega}\left\{\frac{X^2q_2^2}{4A} + \frac{1}{2}\sum_k \frac{n_k^2}{\lambda_k} - \text{c.c.}\right\}, \tag{24}$$

$$J_h^y = -\frac{\Theta}{2\pi i\omega}\left\{\frac{q_2^2}{\Delta}\left[\frac{X^2C}{2}\left(1 - \frac{\cos\theta}{3}\right) + 2X(YC - ZK\alpha)\cos\theta\right] + \frac{1}{2}\sum_k \frac{n_k^2}{\lambda_k}\sin^2\theta - \text{c.c.}\right\} + J_z^z\cos^2\theta.$$

In the general case of an arbitrary ratio of the relaxation times τ_j and τ_k the effects due to the tensor parameters $\tilde{\zeta}^{(k)}_{\alpha\beta}$ which determine the dispersion of X and μ (and also affect B and Δ, via μ) and the effects due to the scalar parameters $\xi^{(j)}$ which determine the dispersion of Y, Z, K, α, c_V, B, C, and Δ are interwined in a complicated manner. The relaxation of $\xi^{(j)}$ does not affect only the intensities of the depolarized scattering $J_k^z = J_z^y$.

The dispersion equation has the form $A\Delta = 0$. The terms of (24) which contain the determinant Δ in the denominator describe the fine structure (the central line and the Mandel'shtam-Brillouin doublet) and the term with A in the denominator, which enters only in $J_h^z = J_z^y$ describes the shear doublet which occurs under certain conditions. The terms of both kinds give a certain contribution also to the relaxation background (line wings), but this background also arises from terms containing $\lambda_j = 1 + i\omega\tau_j$ and $\lambda_k = i + i\omega\tau_k$ in the denominator:

$$-\frac{\Theta}{2\pi i\omega}\sum_j m_j^2\left(\frac{1}{\lambda_j} - \frac{1}{\lambda_j^*}\right) = \frac{\Theta}{\pi}\sum_j \frac{m_j^2\tau_j}{1 + \omega^2\tau_j^2},$$
$$-\frac{\Theta}{2\pi i\omega}\sum_k n_k^2\left(\frac{1}{\lambda_k} - \frac{1}{\lambda_k^*}\right) = \frac{\Theta}{\pi}\sum_k \frac{n_k^2\tau_k}{1 + \omega^2\tau_k^2}. \tag{25}$$

Depolarization in the anisotropic wing. If the relaxation times are so short that the anisotropic wing reaches sufficiently far beyond the limits of the fine structure line, then $\Delta \approx -\rho_0^2 c_V \omega^2/T_0$, $A \approx -\rho_0\omega^2$ in this region of frequencies, and the terms with Δ and A in the denominator become small compared with the terms of the form (25). Thus, in this spectral region

$$J_z^z = \frac{\Theta}{\pi}\left\{\sum_j \frac{m_j^2\tau_j}{1 + \omega^2\tau_j^2} + \frac{2}{3}\sum_k \frac{n_k^2\tau_k}{1 + \omega^2\tau_k^2}\right\},$$
$$J_h^z = J_z^y = \frac{\Theta}{2\pi}\sum_k \frac{n_k^2\tau_k}{1 + \omega^2\tau_k^2},$$
$$J_h^y = \frac{\Theta}{2\pi}\sum_k \frac{n_k^2\tau_k}{1 + \omega^2\tau_k^2}\sin^2\theta + J_z^z\cos^2\theta,$$

and the depolarization coefficient is

$$\Delta_k = \frac{J_r^z + J_r^y}{J_z^z + J_z^y} = \frac{6}{7}\frac{1}{1 + \delta}\left(1 + \frac{1 + 7\delta}{6}\cos^2\theta\right),$$
$$\delta = \frac{6}{7}\sum_j \frac{m_j^2\tau_j}{1 + \omega^2\tau_j^2} \Big/ \sum_k \frac{n_k^2\tau_k}{1 + \omega^2\tau_k^2}. \tag{26}$$

The quantity Δ_k increases linearly with $\cos^2\theta$, changing from the value $(1 + \delta)6/7$ at $\theta = 90°$ to unity at $\theta = 180°$, going through the value 6/7 for $\cos^2\theta = 6\delta/(1 + 7\delta)$. Usually the parameter δ, which differs from zero only to the extent that the compression wing is noticeable, is small. With increasing frequency it changes from

$$\delta_0 = 6\sum_j m_j^2\tau_j \Big/ 7\sum_k n_k^2\tau_k$$

to

$$\delta_\infty = 6\sum_j \frac{m_j^2}{\tau_j} \Big/ 7\sum_k \frac{n_k^2}{\tau_k}.$$

In any case, the fact that Δ_k is close to 6/7 is connected with the presence of the coefficients n_k, i.e., with the explicit dependence of $\epsilon_{\alpha\beta}$ on the anisotropy tensors $\tilde{\zeta}^{(k)}_{\alpha\beta}$, at least on one such tensor, as for example, in the theory of Leontovich.[9]

Integral intensities. All spectral intensities (24) consist of terms of the form

$$J = -\frac{\Theta}{2\pi z}\left\{\frac{g(z)}{f(z)} - \frac{g(-z)}{f(-z)}\right\}, \quad z = i\omega,$$

where g(z) and f(z) are polynomials in z; the poles in the left half-plane of z come only from the first term, and the point z = 0 is not singular. Hence, the integral (with respect to the spectrum) intensities can be calculated using the theorem [cf.[2], formula (6.7)]

$$\frac{1}{2\pi i}\oint_\Gamma\left\{\frac{g(z)}{f(z)} - \frac{g(-z)}{f(-z)}\right\}\frac{dz}{z} = \frac{g(\infty)}{f(\infty)} - \frac{g(0)}{f(0)},$$

where the contour Γ encloses the left half-plane. It is easy to see that $g(\infty)/f(\infty) = 0$ for all intensities (24), so that the integral intensity I is expressed through the corresponding spectral intensity J according to the formula

$$I = \int_{-\infty}^{+\infty} J\,d\omega = -\frac{\Theta}{2\pi i}\oint_\Gamma\left\{\frac{g(z)}{f(z)} - \frac{g(-z)}{f(-z)}\right\}\frac{dz}{z} = \Theta\frac{g(0)}{f(0)}. \tag{27}$$

Applying this formula to the spectral intensities (24), we obtain

$$I_z^z = \Theta\left\{\frac{(Y_0 - {}^1/_3 X_0)^2}{K_0 + {}^4/_3\mu_0} + \sum_j m_j^2 + \frac{2}{3}\sum_k n_k^2\right\}, \tag{28}$$
$$I_h^z = I_z^y = \Theta\left\{\frac{X_0^2 q_2^2}{4\mu_0 q^2} + \frac{1}{2}\sum_k n_k^2\right\},$$
$$I_h^y = \Theta\left\{\frac{X_0 q_2^2}{2(K_0 + {}^4/_3\mu_0)q^2}\left[X_0\left(1 - \frac{\cos\theta}{3}\right) - 4Y_0\cos\theta\right] + \frac{1}{2}\sum_k n_k^2\sin^2\theta\right\} + I_z^z\cos^2\theta.$$

The index 0 refers to the value for z = 0, i.e., according to (16′)

$$\mu_0 = \mu_\infty - \frac{1}{2}\sum_k N_k^2, \quad K_0 = K_\infty - \sum_j L_j^2, \tag{29}$$

and by (21),

$$X_0 = x - \sum_k n_k N_k, \quad Y_0 = y - \sum_j m_j L_j \quad (X_\infty = x,\ Y_\infty = y). \tag{30}$$

It is seen from expression (28) for $I_h^z = I_z^y$ that in the case of liquids ($\mu_0 = 0$) these intensities remain finite only if the ratio X_0^2/μ_0 is finite. The requirement $X_0 = 0$ for $\mu_0 = 0$ means according to (29) and (30) that

$$2\mu_\infty = \sum_k N_k^2, \quad X_\infty = \sum_k n_k N_k.$$

Hence the shear modulus μ and the mechano-optical coefficient X must have the following form for liquids:

$$\mu=\frac{i\omega}{2}\sum_k\frac{N_k{}^2\tau_k}{1+i\omega\tau_k},\quad X=i\omega\sum_k\frac{n_kN_k\tau_k}{1+i\omega\tau_k}. \tag{31}$$

It is clear from this that the ratio X/μ can show dispersion if there are two or more relaxation times of the anisotropy. This ratio will be constant either if there is only one relaxation time—the case considered by Leontovich[9]—or when the conditions

$$n_k=\text{const}\cdot N_k\quad (k=1,2,\ldots),$$

are satisfied, which, however, cannot be derived from anywhere. It is for this reason that it is impossible to justify the extension of the Leontovich relation $X = \text{const}\cdot\mu$ to the general case of many relaxation times. Other arguments concerning this point have been given in[4].

The expressions (31) not only give $\mu_0 = 0$, $X_0 = 0$ for liquids but also imply $X_0^2/\mu_0 = 0$, so that the integral intensities (28) for liquids take the form

$$I_z{}^z=\Theta\left(\frac{Y_0{}^2}{K_0}+\sum_j m_j{}^2+\frac{2}{3}\sum_k n_k{}^2\right),$$

$$I_h{}^z=I_z{}^y=\frac{\Theta}{2}\sum_k n_k{}^2,\quad I_h{}^y=\frac{\Theta}{2}\sum_k n_k{}^2\sin^2\theta+I_z{}^z\cos^2\theta. \tag{32}$$

In the present paper we do not intend to give a detailed analysis of the various consequences of (24), (28), and (32), and to compare these with the available data or with the experimental possibilities. In concluding, we only compare the spectral intensities (24) with the results of a few other relaxation theories of scattering.

5. COMPARISON WITH OTHER RELAXATION THEORIES

One might simply state that the other theories are contained in the one delt with in the present paper as special cases, and leave it at that. However, we regard it of interest to analyze the transition to these special cases in some detail. In this way one may also obtain a better idea of the contents of formulas (24).

Mountain's Theory[11-13]. We do not follow the chronological order and begin with these papers because they are concerned with the relaxation of a scalar internal parameter. Mountain is interested in the isotropic scattering in a liquid arising only from density fluctuations. He assumes only one relaxation parameter ξ, where $\epsilon_{\alpha\beta}$ does not depend on it explicitly, i.e., (20) has the form $\epsilon_{\alpha\beta} = yu\,\delta_{\alpha\beta}$, the coefficients x, z, m_j, and n_k are equal to zero and, according to (21), $X = 0$, $Y = y$, $Z = 0$.

As a result, the only term remaining from the intensity of the non-depolarized scattering in (24) is

$$J_z{}^z=(2\pi)^3Hy^2q^2\left(\frac{C}{\Delta}-\frac{C^*}{\Delta^*}\right). \tag{33}$$

In the absence of tensor parameters $\tilde{\zeta}^{(k)}_{\alpha\beta}$ the coefficients N_k in the free energy are also zero, and hence the shear modulus has no dispersion: $\mu_\infty = \mu_0 = 0$ (liquid). Introducing, following Mountain, the frequency independent viscosities ζ and η, we obtain from (16)

$$\mu=i\omega\eta,\quad K=K_\infty+i\omega\zeta-\frac{L^2}{\lambda},$$

$$K\alpha=K_\infty\alpha_\infty+\frac{LM}{\lambda},\quad c_V=c_{V\infty}+\frac{T_0M^2}{\rho_0\lambda},$$

where $\lambda = 1 + i\omega\tau$. As shown in[7], the formulation in the papers[11,12] of Mountain, where the case of a frequency dependent volume viscosity is considered, corresponds to the model where $M = \partial^2\Psi/\partial T\partial\xi = 0$. These restrictions are removed in[13], but only two limiting cases are considered: "thermal relaxation" for which $(\partial\xi/\partial\rho)_T = 0$, and of course $\partial^2\Psi/\partial\rho\partial\xi = 0$ (in our formulas this means $L = 0$), and "structural relaxation" for which $(\partial\xi/\partial T)_\rho = 0$ and hence, $\partial^2\Psi/\partial T\partial\xi = M = 0$. Thus the "structural relaxation" is identical with the dispersion of the bulk viscosity, as noted in[13]. In both limiting cases $K\alpha$ has no dispersion: $K\alpha = K_\infty\alpha_\infty = K_0\alpha_0$.

For $M = 0$, formula (33) is easily reduced to the result of Mountain,[11,12] in its simplest form[7] [cf. formulas (36), (37a), and (38) of this paper]. My objections, expressed in the last section of[7], are completely groundless: the difference between this result of Mountain and my formula in[3] is due to the faultiness of the latter.

For $L = 0$, when only c_V has dispersion, formula (33) agrees with the result of[13].

Theory of Leontovich.[9] In order to make the transition to this theory, one must discard in the free energy (8) and in the fluctuations of the dielectric constant (20) all terms containing the temperature (we assume isothermal fluctuations) and the scalar parameters $\xi^{(j)}$ (we consider only the fluctuations of the anisotropy), i.e., we must set α_∞, $c_{V\infty}$, L_j, M_j, z, and m_j equal to zero, Of only the anisotropy tensor $\tilde{\zeta}_{\alpha\beta}$ is present, we have then

$$2\Psi=2\mu_\infty\tilde{u}_{\alpha\beta}{}^2+K_\infty u^2+\tilde{\zeta}_{\alpha\beta}{}^2+2N\tilde{u}_{\alpha\beta}\tilde{\zeta}_{\alpha\beta},$$

$$\varepsilon_{\alpha\beta}=x\tilde{u}_{\alpha\beta}+yu\delta_{\alpha\beta}+n\tilde{\zeta}_{\alpha\beta},$$

while the basic formulas of Leontovich have the form

$$2\Psi=2\mu_\infty(\tilde{u}_{\alpha\beta}-\xi_{\alpha\beta})^2+K_\infty u^2,$$

$$\varepsilon_{\alpha\beta}=A_L(\tilde{u}_{\alpha\beta}-\xi_{\alpha\beta})+yu\delta_{\alpha\beta},$$

where $\xi_{\alpha\beta}$ is the pure anisotropy tensor ($\xi_{\alpha\alpha} = 0$). Comparison shows that

$$\tilde{\zeta}_{\alpha\beta}=\sqrt{2\mu_\infty}\,\xi_{\alpha\beta},\quad N=-\sqrt{2\mu_\infty},\quad x=A_L,\quad n=-A_L/\sqrt{2\mu_\infty}.$$

For such values of N, x, and n we find from (16) and (21)

$$X=x-\frac{Nn}{\lambda}=A_L\frac{i\omega\tau}{1+i\omega\tau},\quad \mu=\mu_\infty-\frac{N^2}{2\lambda}=\mu_\infty\frac{i\omega\tau}{1+i\omega\tau}$$

and hence, $X/\mu = A_L/\mu_\infty = \text{const}$.

Using the notation introduced in[9],

$$\Omega_L{}^2=\frac{K_\infty q^2}{\rho_0},\quad \Omega_T{}^2=\frac{\mu_\infty q^2}{\rho_0},\quad \Omega_S{}^2=\Omega_L{}^2+\frac{4}{3}\Omega_T{}^2$$

it is easy to see that with the above-named restrictions and for scattering angle $\theta = 90°$, formulas (24) go over into the expressions for the intensities obtained in[9]. In particular, for $\omega^2 \gg \Omega_S^2$ they yield

$$J_x{}^z=J_z{}^y=J_x{}^y=\frac{3}{4}J_z{}^z=\frac{\Theta A_L{}^2\tau}{4\pi\mu_\infty(1+\omega^2\tau^2)},\quad \Delta_h=\frac{6}{7}.$$

Theory of Volterra.[10] As in the theory of Leontovich, this theory contains no scalar relaxation parameters (therefore $L_j = M_j = m_j = 0$ and $K = K_\infty$, $\alpha = \alpha_\infty$, $c_V = c_{V\infty}$ show no dispersion) but the fluctuations of the temperature are taken into account (c_V and α are different from zero). The main difference is that two tensor parameters are introduced, and, correspondingly, two relaxation times.

The derivation of the relaxation equations is in[10] based on the "pseudo-crystalline lattice;" one of the tensors, $\zeta_{\alpha\beta}$, describes macroscopically the result of the deviation of the orientation of the anisotropic molecules from the isotropic equilibrium distribution, and the other, $H_{\alpha\beta}$, describes the shear deformations of the pseudo-lattice of the equilibrium positions of the molecules. Of course, $\zeta_{\alpha\alpha} = 0$ and $H_{\alpha\alpha} = 0$. The instantaneous shear deformation is $s_{\alpha\beta} = \tilde{u}_{\alpha\beta} - H_{\alpha\beta}$ and the free energy of the shears is equal to

$$\begin{aligned} 2\Psi_{sh} &= 2\mu_\infty s_{\alpha\beta}^2 + 2bs_{\alpha\beta}\zeta_{\alpha\beta} + a\zeta_{\alpha\beta}^2 = \\ &= 2\mu_\infty\tilde{u}_{\alpha\beta}^2 + 2\mu_\infty H_{\alpha\beta}^2 - 2bH_{\alpha\beta}\zeta_{\alpha\beta} + a\zeta_{\alpha\beta}^2 + 2\tilde{u}_{\alpha\beta}(b\zeta_{\alpha\beta} - 2\mu_\infty H_{\alpha\beta}). \end{aligned} \tag{34}$$

The fluctuations of the dielectric tensor are assumed to depend only on $\zeta_{\alpha\beta}$ and on the compression u, but not on the temperature $(x = 0, z = 0)$:

$$\varepsilon_{\alpha\beta} = yu\delta_{\alpha\beta} + B\zeta_{\alpha\beta}. \tag{35}$$

Under these assumptions Eq. (8) for Ψ takes the form

$$2\Psi = Ku^2 - 2K\alpha uT_1 - \frac{\rho_0 c_V}{T_0}T_1^2 + 2\Psi_{sh},$$

where

$$2\Psi_{sh} = 2\mu_\infty(\tilde{u}_{\alpha\beta})^2 + (\tilde{\zeta}^{(1)}_{\alpha\beta})^2 + (\tilde{\zeta}^{(2)}_{\alpha\beta})^2 + 2\tilde{u}_{\alpha\beta}(N_1\tilde{\zeta}^{(1)}_{\alpha\beta} + N_2\tilde{\zeta}^{(2)}_{\alpha\beta}), \tag{36}$$

and formula (20) gives

$$\varepsilon_{\alpha\beta} = yu\delta_{\alpha\beta} + n_2\tilde{\zeta}^{(1)}_{\alpha\beta} + n_2\tilde{\zeta}^{(2)}_{\alpha\beta}. \tag{37}$$

However, a direct comparison of (34) with (36) and (35) with (37) is impossible, since (34) contains the contraction $H_{\alpha\beta}\zeta_{\alpha\beta}$. We are encountering here a case where we must first transform (34) and (35) to the independent parameters $\tilde{\zeta}^{(1)}_{\alpha\beta}$ and $\tilde{\zeta}^{(2)}_{\alpha\beta}$ in order to make use of the general formulas obtained above.

The coefficients ρ_i of this transformation,

$$\zeta_{\alpha\beta} = \rho_1\tilde{\zeta}^{(1)}_{\alpha\beta} + \rho_2\tilde{\zeta}^{(2)}_{\alpha\beta}, \qquad H_{\alpha\beta} = \rho_3\tilde{\zeta}^{(1)}_{\alpha\beta} + \rho_4\tilde{\zeta}^{(2)}_{\alpha\beta}$$

are determined by the requirement that the form $2\mu_\infty H^2_{\alpha\beta} - 2bH_{\alpha\beta}\zeta_{\alpha\beta} + a\zeta_{\alpha\beta}^2$ in (34) is reduced to $(\zeta^{(1)}_{\alpha\beta})^2 + (\tilde{\zeta}^{(2)}_{\alpha\beta})^2$ and the form $c\theta_1\dot{\zeta}^2_{\alpha\beta} + 2\mu_\infty\theta_2\dot{H}^2_{\alpha\beta}$ in the dissipative function $(c = a - b^2/2\mu_\infty)$ to the form $\tau_1(\tilde{\zeta}^{(1)}_{\alpha\beta})^2 + \tau_2(\tilde{\zeta}^{(2)}_{\alpha\beta})^2$.[3)]

Thus ρ_i and $\tau_{1,2}$ are known functions of the original parameters (we do not write down the corresponding formulas for lack of space), and (34) and (35) take the form

$$\begin{aligned} 2\Psi_{sh} &= 2\mu_\infty\tilde{u}^2_{\alpha\beta} + (\tilde{\zeta}^{(1)}_{\alpha\beta})^2 + (\tilde{\zeta}^{(2)}_{\alpha\beta})^2 \\ &+ 2\tilde{u}_{\alpha\beta}[(b\rho_1 - 2\mu_\infty\rho_3)\tilde{\zeta}^{(1)}_{\alpha\beta} + (b\rho_2 - 2\mu_\infty\rho_4)\tilde{\zeta}^{(2)}_{\alpha\beta}], \end{aligned} \tag{34'}$$

$$\varepsilon_{\alpha\beta} = yu\delta_{\alpha\beta} + B\rho_1\tilde{\zeta}^{(1)}_{\alpha\beta} + B\rho_2\tilde{\zeta}^{(2)}_{\alpha\beta}. \tag{35'}$$

Comparison with (36) and (37) gives now

$$N_1 = b\rho_1 - 2\mu_\infty\rho_3, \quad N_2 = b\rho_2 - 2\mu_\infty\rho_4, \quad n_1 = B\rho_1, \quad n_2 = B\rho_2.$$

It remains to express the intensity $J^p_{p'}$ [cf. footnote 2] through the original parameters a, b, $2\mu_\infty$, and $\theta_{1,2}$, which leads to the formulas of Volterra for the spectral densities of the compression u and the five independent combinations of the components $\zeta_{\alpha\beta}$.

In summarizing, one can say that the Volterra theory is a certain special case of the theory with two tensor relaxation parameters, but the author's interpretation of the tensors $\zeta_{\alpha\beta}$ and $H_{\alpha\beta}$ is hardly the only one possible. We note in this connection that Leontovich[9] especially points out the general character of his theory and emphasizes that the interpretation of the tensor $\zeta_{\alpha\beta}$ as a quantity describing the effect of the orientation of the molecules is a possible but not necessary model concept.

6. CONCLUSION

The construction of a relaxation theory of scattering with an arbitrary number of relaxation parameters is formally no more complicated for two or three parameters, but the meaning of the results does not, of course, rest in the possibility of an infinite increase in the number of such parameters.

The use of Rayleigh scattering as one of the methods for investigating the structure of real matter is fruitful to the extent to which it (1) helps explain particular (and not extremely numerous) relaxation processes which determine a whole range of phenomena, including the temperature dependence of the various components of the spectrum under different conditions of observation (this is the intent of the Volterra theory) or (2) allows one to establish that the observed laws (or at least part of them) go beyond the limitations of the relaxation theory and require a different explanation.

In both these respects, so it seems to me, the results provided by the relaxation theory in its general form are not without interest. This refers to the general form of the dispersion laws for various quantities describing the medium [the moduli (16), the coefficients (21)], the type of connection between these laws, and also to the type of relation between the complex parameters of the medium and the components of the spectrum of the scattered light.

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3)The appearance of the coefficient c is connected with the fact that Volterra writes the kinetic equation for $\zeta_{\alpha\beta}$ not in the form where

$$a\tilde{\theta}_1\dot{\zeta}_{\alpha\beta} = -(\partial\Psi_{sh}/\partial\zeta_{\alpha\beta})_{s_{\alpha\beta}},$$

$a = (\partial^2\Psi_{sh}/\partial\zeta^2_{\alpha\beta})_{s\alpha\beta}$, Ψ_{sh} i.e., the derivative for constant deformations

$$c\theta_1\dot{\zeta}_{\alpha\beta} = -(\partial\Psi_{sh}/\partial\zeta_{\alpha\beta})_{s_{\alpha\beta}},$$

(which would be natural), but in the form where $c = (\partial^2\Psi_{sh}/\partial\zeta_{\alpha\beta}^2)$ $\tilde{\sigma}_{\alpha\beta}$, i.e., the derivative for constant stresses $\tilde{\sigma}_{\alpha\beta} = -2\mu_\infty s_{\alpha\beta} - b\zeta_{\alpha\beta}$. Incidentally, this change leads simply to a renormalization of the partial relaxation time θ_1 $[\theta_1 = (a/c)\tilde{\theta}_1]$.

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