Theory of depolarized molecular light scattering

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The theoretical studies on depolarized molecular light scattering are reviewed. Chapter 2 is devoted to the phenomenological theories, mainly the relaxation theories of M. A. Leontovich and S. M. Rytov. The general symmetry properties of the scattering cross sections are treated. The theory of the depolarized component $I_{VH}(\omega)$ is presented in detail on the basis of the fluctuation-dissipation theorem, with account taken of two internal relaxation parameters. This theory permits one to explain the experimentally observed fine structure of the tail of the Rayleigh line. A generalization of the theory for taking account of the antisymmetric part of the tensor of the dielectric-constant fluctuations is discussed. Chapter 3 is devoted to statistical-mechanical methods. The development is traced of ideas on the molecular mechanisms of scattering and depolarization of light, and methods are treated of determining the scattering cross sections in terms of the characteristics of individual particles or groups of them. The results of Mori's linear reaction theory are briefly presented, and it is used to establish the form of the equations that determine the evolution of the parameters that enter into the scattering cross section. It is shown that the statistical theories give results that agree with the phenomenological theory of S. M. Rytov, and they permit one to give a molecular-kinetic interpretation of the relaxation parameters that figure in it.

CONTENTS

1. INTRODUCTION

Less than ten years have elapsed since the publication of Fabelinskii's book[1], in which he gave a thorough presentation of the problems of molecular light scattering. Yet, owing to the widespread use of precision laser technique, these are precisely the years that have brought a number of major advances in the experimental study of scattered light.

Fabelinskii, Starunov, and Tiganov discovered[2] and then studied[3–10, 147] the fine structure of the tail of the Rayleigh line (the depolarized component of the scattered light), which has the form of a doublet in liquids of low viscosity. As is well known (see[1]), the fine structure of the polarized component of the light scattered in an isotropic medium (the Mandel'shtam-Brillouin doublet) is closely associated with the characteristics of propagation of longitudinal hypersound (of frequencies $\sim 10^{10}$ Hz). Thus, the displacement of the components of the doublet from the frequency of the exciting light determines (according to the Bragg condition) the speed of hypersound, and their half-width determines the absorption coefficient. M. A. Leontovich has shown that depolarization of scattered light in a liquid can involve shear deformations that thermal fluctuations generate in it. A theory[11] based on the hypothesis that one can describe both the shear viscosity and the anisotropy responsible for the scattering by a single relaxation time has indicated the existence of a fine structure in the depolarized spectrum as well. However, detailed experimental studies of the fine structure of the tail region in liquids of low viscosity have shown[3–9] that the latter is produced by a more complex mechanism than that treated in[11], and one can explain it by assuming at least two relaxation times.[5, 6, 23, 31, 32]

Intensive study of depolarized light scattering by systems of spherically-symmetrical particles has been conducted in recent years. This was started by the studies of Thibeau, Oksengorn, and Vodar[12] and of McTague and Birnbaum[13], which involved scattering in argon and krypton. Depolarization of light scattered by such systems had been observed long ago.[14] However, before the invention of lasers, not only did it seem impossible to study it quantitatively, owing to the small size of the effect, but there was no assurance that the phenomenon of depolarization itself had been actually observed. The situation was also aggravated by the fact that the depolarization could not be ascribed to optical anisotropy of the scattering particles (owing to the absence of the latter). In order to explain it, the theoretical studies[15–18] treated an interaction that was poorly amenable to calculation between the dipole moments induced by the wave of the incident light in different particles.

Experimental advances stimulated interest in further development of the theory of molecular light scattering. First we should mention the studies[23, 31, 32], which critically reexamined and generalized the known phenomenological theory[11, 30] in line with the attained experimental results. Other studies[36, 53, 58, 59, 62, 96–99, 121–128, 141, 142] have paid their major attention to further development of molecular-statistical concepts of light scattering.

Yet no studies are currently known in which the above-mentioned investigations have been generalized and the advances in the phenomenological and statistical theories have been correlated. Moreover, the results of some studies that have been performed by using the methods of non-equilibrium statistical me-

chanics are sometimes contrasted without adequate grounds with the conclusions of the phenomenological theory. This explains why it now seems expedient to give a review of the new studies on molecular light scattering that would be useful to a broad set of physicists interested in molecular optics, molecular acoustics, and statistical physics.

This review does not aim to encompass the entire set of problems of molecular light scattering. Fundamental attention will be paid to depolarized scattering, however, the polarized component will be treated only insofar as it is needed for determining the depolarization coefficient. The fine structure of this component and the contour of the Mandel'shtam-Brillouin lines will not be discussed, and all the more, since Mountain and other authors (see[19-21] and the literature cited there) have presented these questions in rather full detail. We have also not deemed it possible to take up such important problems as the effect on light scattering of critical phenomena and concentration fluctuations, or light scattering by crystals, liquid crystals, and macromolecules. Moreover, the review covers only effects that are linear with respect to the primary field, and hence, it does not treat phenomena of frequency multiplication of the incident light upon scattering, etc. (see, e.g.[22]).

The conceptual basis of the review is the idea of the scattering cross-section, both in the phenomenological and in the statistical theories, in terms of space-time correlation functions, whose analysis in turn is based on the fluctuation-dissipation theorem. This permits one systematically to establish the relationship between the different approaches in studying light scattering, and to evaluate the final results from unified viewpoints, broadly adducing here symmetry considerations.

The first part of the review is devoted to the phenomenological theories, mainly the relaxation theory of Leontovich[11] and Rytov's theory[12], which permits a correct description of the experimental data with account of only two relaxation processes. A generalization of the theory is also treated here to the case in which the internal rotational degrees of freedom are taken into account in the hydrodynamics of the medium. This makes it possible, while remaining within the framework of the phenomenological theory, to study the effect on light scattering of a possible asymmetry of the tensor of the fluctuations of the dielectric constant.

The second part reviews the statistical theories, which treat the scattering medium as a system of many particles, and which permit one to establish the relation of the scattering cross-sections to the characteristics of the individual particles and of groups of them. It discusses how one can establish the form of the relaxation equations for the parameters that figure in the scattering cross-section by using the methods of modern non-equilibrium statistical mechanics. It discusses the relationship between these statistical methods and the relaxational phenomenological theories of M. A. Leontovich and S. M. Rytov.

2. PHENOMENOLOGICAL THEORIES

The interest that arose in the thirties in sound absorption in liquids involved, in particular, the possibility of comparing the results of acoustic measurements with the fine structure of the Rayleigh light-scattering line. Mandel'shtam and Leontovich developed

a relaxational theory of sound absorption[24, 25] based on introducing internal parameters that characterize the deviation of the state of the material from equilibrium. A natural extension of it was the theory that Leontovich devised on Rayleigh light scattering[11], which used as its basis the idea of thermal fluctuations as the cause of scattering, and which was the first theory that permitted one to describe from a unified standpoint the spectra of both the polarized and the depolarized components of the scattered light by taking account of one relaxing internal parameter and assuming that the fluctuations are isothermal.

The early fifties were marked by the appearance of general and extremely powerful methods of calculating thermal fluctuations. They led Kallen and Welton to prove the fluctuation-dissipation theorem (FDT),[26] which is one of the most important theorems of nonequilibrium statistical thermodynamics (see[27]). The extension of the FDT, which was initially proved for systems having a finite number of degrees of freedom, to a continuous medium[28, 29] made it possible to formulate the equations of fluctuational hydrodynamics. On this basis Rytov[30] generalized Leontovich's scattering theory by extending it to the case not only of liquids, but also of a solid isotropic medium with account taken of temperature fluctuations, and with an arbitrary number of relaxing parameters.

This initial theory of Rytov assumed that the frequency dispersion that arises from the kinetics of the internal parameters can be accounted for formally simply by assuming that the thermal and elastic moduli of the medium are frequency-dependent. It did not explicitly introduce equations for the relaxing parameters, nor assume the tensor of the dielectric-constant fluctuations to be explicitly dependent on them. The theory was reflected in this form also in Fabelinskii's book[1]. However, subsequently Romanov, Solov'ev, and Filatova[31] pointed out that the theory of light scattering requires a so-called complete description of the thermal fluctuations in the scattering medium. That is, one must account explicitly for all the internal parameters on which the fluctuations of the dielectric constant are assumed to depend. The effect of these parameters on light scattering only in terms of the dispersion of the hydrodynamic and mechanooptical coefficients does not exhaust their role. The first detailed experimental studies[3, 5-7] pointed out the difficulties of interpreting the temperature-dependence of the characteristics of the fine structure of the tail of the Rayleigh line, and attempts were quickly undertaken to eliminate them[5, 6, 32]. Then Rytov[23] (and in a somewhat less general form, Romanov and Solov'ev[33]) constructed a general relaxation theory of molecular light scattering that satisfied the requirement for a complete description of the fluctuations.

Let us examine the fundamental concepts and simplifications that permit one to derive a general expression for the light-scattering cross-section. In describing the scattered light one usually restricts the treatment to the dipole approximation. Then the solution of Maxwell's equations for the Fraunhofer zone, i.e., at distances $R \gg l^2/\lambda$, where l is the dimension of the scattering volume and λ is the wavelength of the light, with also the condition that $l \gg \lambda$, gives the following expression for the field intensity $E(R, \Omega)$ of the scattered wave:

$$E(R, \Omega) = \frac{\Omega^2}{2\pi R c^2} \left(I - \frac{RR}{R^2} \right) \cdot \int_V dq \int_{-\infty}^{\infty} dt p(q, t) \exp\left[i\Omega \left(t + \frac{R}{c} - \frac{qR}{R^2} \right) \right];$$
(1)

Here q is the radius vector of a point within the scattering volume V, R is the radius vector of the point at which the field of the scattered wave is observed (the origin of the coordinate system is usually set within the scattering volume), Ω and c are respectively the frequency of the scattered wave and the velocity of propagation of light, and I is the unit tensor. The scalar product is denoted by the dot.

Eq. (1) is an approximate solution of the purely electrodynamic problem. Of course, one can use it both in the statistical and the phenomenological treatment of light scattering. The distinction between these approaches consists primarily in the methods of finding the volume density of the dipole moment $p(q,t)$.

The fundamental idea of the phenomenological theory, which was used already in the studies of Smoluchowski and Einstein[34], and then also in the studies of Leontovich[11] and Rytov[23, 30], consists in representing the fluctuating part of the dipole-moment density that is of interest to us in terms of the tensor of the dielectric-constant fluctuations (as is well known, this is precisely the part of the dipole moment that governs light scattering[1]). In turn, this is determined by the fluctuations in the parameters that describe the thermodynamic state of the medium (see (10)). This idea has proved fruitful, precisely because the complex problem of determining the fluctuations of the dielectric constant has been reduced to the far simpler problem of calculating the fluctuations of the thermodynamic parameters. Accordingly, we shall write the following expression for the density of the induced dipole moment:

$$p_\alpha(q, t) = p_{0\alpha}(q, t) + \Delta p_\alpha(q, t),$$
$$p_{0\alpha} = (\epsilon - 1) E_{0\alpha}(q, t), \quad \Delta p_\alpha = \Delta \epsilon_{\alpha\beta} E_{0\beta}(q, t),$$
(2)

Here ϵ is the equilibrium dielectric constant, $\Delta\epsilon_{\alpha\beta}$ is the tensor of the dielectric-constant fluctuations, and $E_0(q, t)$ is the field intensity of the incident light wave:

$$E_0(q, t) = E_0 \exp[i(k_i q - \Omega_0 t)]i;$$
(3)

Here i, k_i, and Ω_0 are respectively the polarization unit vector, the wave vector, and the frequency of the incident wave.

Consequently, the spectral intensity of the scattered light having the polarization s can be determined in terms of the space-time correlation function of the dielectric-constant fluctuations:

$$I_{is}(R, \Omega) = \langle |E(R, \Omega) \cdot s|^2 \rangle =$$
$$= C s_\alpha s_\gamma^* i_\beta i_\delta^* \int_V dq \int_{-\infty}^{\infty} dt \langle \Delta\epsilon_{\alpha\beta}(0, 0) \Delta\epsilon_{\gamma\sigma}^*(q, t) \rangle \exp[i(kq - \omega t)],$$
(4)

Here

$$k = \frac{\Omega}{c} \frac{R}{R} - k_l = k_s - k_l, \quad \omega = \Omega - \Omega_0, \quad C = \frac{\Omega^4 I_0 V}{4\pi^2 c^4 R^2},$$

where k_S is the wave vector of the scattered light, and the angle brackets denote averaging over the ensemble. The differential (in terms of frequency) scattering cross-section[1)] is determined by the ratio $I_{is}(R, \Omega)/I_0$.

In deriving (4), we assumed statistical homogeneity of the medium and fluctuations that are steady-state in time, so that the correlation function of the dielectric-constant fluctuations depends only on the distance between the points $Q = q' - q'$ at which the tensors $\Delta\epsilon_{\gamma\delta}^*$

and $\Delta\epsilon_{\alpha\beta}$ are determined, and only on the interval between the instants of time $t = t'' - t'$. We have also used the transverse nature of the scattered wave, $s \cdot R = 0$. Thus, the intensity of the scattered light in the phenomenological theory is fully determined by the scattering tensor:

$$\sigma_{\alpha\beta\gamma\delta}(\omega, k) = C \int_V dq \int_{-\infty}^{\infty} dt \langle \Delta\epsilon_{\alpha\beta}(0, 0) \Delta\epsilon_{\gamma\delta}^*(q, t) \rangle \exp[i(kq - \omega t)].$$
(5)

One can derive a number of useful results by analyzing the symmetry properties of the scattering cross-section. Placzek[35] has studied the symmetry properties of the integral scattering cross-section for an arbitrary form of the tensor $\Delta\epsilon_{\alpha\beta}$, but without accounting for the spatial dispersion of the medium. Ben-Reuven and Gershon[36] have studied the symmetry properties of the differential scattering cross-section by using an expression for it in terms of symmetric polarizability tensors of the particles of the medium (see (58)). Subsequently the symmetry properties of magnetic dipole[37,38] and electric quadrupole[39] scattering have been studied, as well as scattering by multipoles of arbitrary order[40]. The symmetry properties of the scattering cross-section of (4) were studied in[41] by expanding the symmetric tensor $\Delta\epsilon_{\alpha\beta}$ in terms of irreducible representations of the rotation group. For the sake of brevity, we shall use here the well-known representations of the tensors (up to the fourth order inclusive) in terms of invariants of the corresponding symmetry group[42].

If we restrict the treatment to the symmetric tensor $\Delta\epsilon_{\alpha\beta}$, then the fourth-order tensor $\sigma_{\alpha\beta\gamma\delta}^{(s)}(\omega, k)$ must be symmetric with respect to permutation of indices within the pairs $\alpha\beta$ and $\gamma\delta$, owing to Onsager's symmetry principle. For an isotropic medium having a center of symmetry, the tensor $\sigma_{\alpha\beta\gamma\delta}^{(s)}$ also satisfies the symmetry properties of group $\infty \cdot m$ (according to Shbunikov;[43] there is a unique direction determined by the vector k). Hence it can be represented as a linear combination with five independent coefficients. It is convenient to select this representation in the form

$$\sigma_{\alpha\beta\gamma\delta}^{(s)}(\omega, k) = \sigma_1 \delta_{\alpha\beta}\delta_{\gamma\delta} + \sigma_2 \mu_{\alpha\beta\gamma\delta} + \sigma_3(\delta_{\alpha\beta}\pi_{\gamma\delta} + \delta_{\gamma\delta}\pi_{\alpha\beta}) + \sigma_4 \pi_{\alpha\beta}\pi_{\gamma\delta} + \sigma_5 \nu_{\alpha\beta\gamma\delta},$$
(6)

where

$$\sigma_j = \sigma_j(\omega, k^2) \quad (j = 1, 2, \ldots, 5), \quad \pi_{\alpha\beta} = k_\alpha k_\beta - \frac{1}{3} k^2 \delta_{\alpha\beta},$$
$$\mu_{\alpha\beta\gamma\delta} = \frac{1}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) - \frac{1}{3}\delta_{\alpha\beta}\delta_{\gamma\delta},$$
$$\nu_{\alpha\beta\gamma\delta} = \frac{1}{4}(\delta_{\alpha\gamma}k_\beta k_\delta + \delta_{\alpha\delta}k_\beta k_\gamma + \delta_{\beta\gamma}k_\alpha k_\delta + \delta_{\beta\delta}k_\alpha k_\gamma) - \frac{k_\alpha k_\beta k_\gamma k_\delta}{k^2}.$$
(7)

Naturally, the number of independent coefficients here is the same as in[41], although the representation of the tensor $\sigma_{\alpha\beta\gamma\delta}^{(s)}$ in itself differs. The conditions that the incident and scattered waves are transverse can reduce the number of independent coefficients in Eq. (4) as compared with the representation in (6). However, substitution of $k = k_S - k_l$ and Eq. (6) into (4) and application of the conditions $k_S \cdot s = 0$ and $k_i \cdot i = 0$ show that all five independent coefficients are preserved. Light scattering in an isotropic medium lacking a center of symmetry (which corresponds to the symmetry group ∞) with a symmetric $\Delta\epsilon_{\alpha\beta}$ tensor is characterized by six independent coefficients[41].

The symmetric tensor of the dielectric-constant fluctuations can be represented as the sum of a spherically-symmetric part and of one having zero trace:

$$\Delta\epsilon_{\alpha\beta} = \Delta\epsilon \delta_{\alpha\beta} + \tilde{\Delta}\epsilon_{\alpha\beta}.$$
(8)

In Eq. (6), the coefficient σ_1 arises from the fluctuations

of the scalar part of (8), and it describes pure polarized scattering; σ_3 describes the correlational coupling between the scalar and tensor components, and the rest of the coefficients arise only from the tensor component. The results of direct calculation of $\sigma^{(s)}_{\alpha\beta\gamma\delta}$ in [23] are represented precisely in the form of (6). This permits one to find the important relation of the independent coefficients σ_j that describe the light scattering to the hydrodynamic characteristics of the medium.

The basis of the phenomenological calculation [11,23] of the scattering tensor $\sigma^{(s)}_{\alpha\beta\gamma\delta}$ is the hypothesis that the thermodynamic description of the state of the medium is complete [25,44]. According to this hypothesis, any state of the medium that differs from the initial equilibrium state that is defined by the density ρ_0 and the temperature T_0 can be fully described in quasistatic processes by the deformation tensor $u_{\alpha\beta}$ referred to the equilibrium values, by the temperature change T_1 = $(T - T_0)/T_0$, and by a certain set of internal parameters, which can have different tensor dimensions. In other words, all of the thermodynamic functions are fully determined by assigning $u_{\alpha\beta}$, T_1, and the stated set of internal parameters. One assumes that the dielectric constant is also determined by the thermodynamic state of the medium, and hence, its variation upon small deviations from equilibrium is expressed as a linear combination of all the stated parameters. Evidently, when one describes depolarized scattering, one must include in the treatment at least one tensor parameter. This is just the problem that Leontovich [11] first solved.

Leontovich's theory implies that the frequency interval between the displaced components of the triplet (the low-temperature branch of the fine structure of the tail of the Rayleigh line), which is

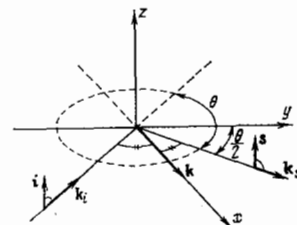$$2\Delta\omega_m \approx 2V\overline{\mu_\infty/\rho_0 k}, \qquad (9)$$

must decline with increasing temperature. This is because theoretical considerations and direct statistical estimates [45] show that the high-frequency shear modulus μ_∞ slowly declines with increasing temperature. Observation of the fine structure of the tail in highly-viscous liquids ($\sim 10-10^9$ poise) reveals just this relationship [5,9]. However $\Delta\omega_m$ slowly increases with temperature at low viscosities ($\sim 10^{-2}-10^{-3}$ poise), in spite of the theoretical predictions. They pointed out in [5] that the features of behavior of $\Delta\omega_m$ at any viscosity can be explained by introducing two relaxation times (a Maxwellian one, and one for the anisotropy). The theories [6,32] that take account of two relaxation processes (although not in most general form) have confirmed this possibility.

Rytov's study [23] introduced a set comprising an arbitrary number of relaxing scalars ($\xi^{(i)}$) and of zero-trace symmetric tensor ($\tilde{\zeta}^{(j)}_{\alpha\beta}$) parameters that define the state of the medium. Here one takes the following expression for the dielectric constant fluctuations (without accounting for spatial dispersion):

$$\Delta\varepsilon = yu + zT_1 + \sum_i m_i\xi^{(i)},$$
$$\Delta\varepsilon_{\alpha\beta} = x\tilde{u}_{\alpha\beta} + \sum_j n_j\tilde{\zeta}^{(j)}_{\alpha\beta}, \qquad (10)$$

Here x, y, z, m_j, and n_j are real constants, while the tensor $\sigma^{(s)}_{\alpha\beta\gamma\delta}$ is expressed as a superposition of the correlation functions of the parameters u, $\tilde{u}_{\alpha\beta}$, T_1, $\xi^{(i)}$, and $\tilde{\zeta}^{(j)}_{\alpha\beta}$. In calculating the latter, one assumes, in line with Onsager's hypothesis, that the evolution of the fluctuations in the medium obeys the macroscopic equations of motion: the equations of hydrodynamics (balance of mass, momentum, and energy or entropy) and additional equations of relaxational nature (see (12)), which by assumption describe the variation of the internal parameters $\xi^{(i)}$ and $\tilde{\zeta}^{(j)}_{\alpha\beta}$. Of course, the equations for the additional parameters need not be relaxational, [2] and ultimately, their form is determined by the formulation of the problem. Thus, when one is studying light scattering by solutions of macromolecules, liquid crystals, or by concentration fluctuations, one uses equations of the diffusional type. In turn, the relaxation equations can have a more complex structure than that used below, e.g., when one accounts for inertia effects (see [90]).

It is essential to emphasize the important circumstance that the equations of motion are not homogeneous. [23,30] These are the equations of fluctuational hydrodynamics, which contain on the right-hand side the fluctuational (Langevin) forces, so that the obtained spectrum of fluctuational parameters corresponds to induced motion of the medium under the action of this type of forces. Although this fact is somewhat obvious, it has been treated in detail in a recent methodological note [46].

Calculation of the scattering tensor $\sigma^{(s)}_{\alpha\beta\gamma\delta}$ does not require introduction of any special coordinate system (see [23,30]). However, for describing the scattered-light spectrum that corresponds to certain experimental conditions, it is convenient to use the system of coordinates shown in Fig. 1. The x axis lies along the scattering vector $\mathbf{k} = \mathbf{k}_s - \mathbf{k}_i$, and the xy plane coincides with the scattering plane defined by the vectors $\mathbf{k}_i$ and $\mathbf{k}_s$.

For illustration of the application of the FDT in Rytov's theory and comparison of it with the following statistical theories, it suffices to examine the description of the depolarized component I_{VH} (the first subscript indicates the polarization (vertical) of the incident light, and the second indicates the polarization (horizontal) of the scattered light). If we take account of the fact that $\mathbf{k} = \{k, 0, 0\}$, $\mathbf{l} = \{0, 0, 1\}$, and $\mathbf{s} = \{-\cos\theta/2, \sin\theta/2, 0\}$, then in agreement with (4) we find that

$$I_{VH}(\omega) \sim \langle\Delta\varepsilon_{xz}\Delta\varepsilon^*_{xz}(\omega)\rangle\cos^2\frac{\theta}{2} + \langle\Delta\varepsilon_{yz}\Delta\varepsilon^*_{yz}(\omega)\rangle\sin^2\frac{\theta}{2} \qquad (11)$$
$$+ (\langle\Delta\varepsilon_{xz}\Delta\varepsilon^*_{yz}(\omega)\rangle - \langle\Delta\varepsilon_{yz}\Delta\varepsilon^*_{xz}(\omega)\rangle)\sin\frac{\theta}{2}\cos\frac{\theta}{2}.$$

In line with Eq. (6), the expression in the round parentheses vanishes. Hence,

$$I_{VH}(\omega) \sim \langle\Delta\varepsilon_{xz}\Delta\varepsilon^*_{xz}(\omega)\rangle\cos^2\frac{\theta}{2} + \langle\Delta\varepsilon_{yz}\Delta\varepsilon^*_{yz}(\omega)\rangle\sin^2\frac{\theta}{2}.$$

Then we should take account of the fact that $\tilde{u}_{yz} = 0$, and in order to find the second term in (11), we need only write the equations for the internal parameters. According to [23], the latter acquire in this case the form

$$\tau_j\dot{\tilde{\zeta}}^{(j)}_{yz} = -\tilde{\zeta}^{(j)}_{yz} + \tilde{Z}^{(j)}_{yz}, \qquad (12)$$

where $\tilde{Z}^{(j)}_{yz}$ is the fluctuational force that is coupled energetically with $\tilde{\zeta}^{(j)}_{yz}$.

Further, let us restrict the treatment to the case of two tensor internal parameters (j = 1, 2), for which the

FIG. 1. The system of coordinates used for calculating the scattered-light spectrum.

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spectrum of the fluctuations $\tilde{\zeta}_{yz}^{(1)}$ and $\tilde{\zeta}_{yz}^{(2)}$, according to (12), is the sum of two undisplaced Lorentzians of half-widths τ_1^{-1} and τ_2^{-1}.

In order to calculate the first term in (11), we must also write down the equation for momentum transport, in addition to the relaxation-type equations for the internal parameters:

$$\rho_0 \ddot{s}_z = \frac{\partial}{\partial x}(2\mu_\infty \tilde{u}_{zx} + 2\eta \dot{\tilde{u}}_{zx} + N_1 \tilde{\zeta}_{zx}^{(1)} + N_2 \tilde{\zeta}_{zx}^{(2)}) + F_z,$$

$$\tau_1 \dot{\tilde{\zeta}}_{zx}^{(1)} = -\tilde{\zeta}_{zx}^{(1)} - N_1 \tilde{u}_{zx} + \tilde{Z}_{zx}^{(1)}, \qquad \tau_2 \dot{\tilde{\zeta}}_{zx}^{(2)} = -\tilde{\zeta}_{zx}^{(2)} - N_2 \tilde{u}_{zx} + \tilde{Z}_{zx}^{(2)}; \tag{13}$$

Thus we obtain here a system of three equations. In order to determine the spectrum of the fluctuations, according to the FDT[47], we must transform in Eq. (13) to the $(\omega, \mathbf{k})$-representation $(\partial/\partial q \rightarrow ik, \partial/\partial t \rightarrow i\omega)$, and solve the equations thus derived with respect to the generalized coordinates. The components of the matrix that expresses the generalized coordinates in terms of the fluctuational forces (the so-called generalized susceptibility matrix) determine the spectral density of the corresponding generalized coordinates.

We should note that introduction of a frequency-independent viscosity into the equations of relaxational hydrodynamics implies violation of the Kramers-Kronig relation[23]. When such a viscosity exists, the integral intensities diverge. Hence, its existence can only have the meaning that actually it arises from one or several relaxing parameters, but they have relaxation times so short that dispersion has not yet set in in the frequency range of interest to us $(\omega\tau \ll 1)$. In other words, in a theory that doesn't restrict the number of relaxing internal parameters, introduction of frequency-independent viscosities (either shear or volume viscosity) is not necessary, and hence we can set $\eta = 0$ in (13).

To go over to an incomplete description, i.e., to omit from the system of equations like (13) all or part of the internal parameters, gives rise to frequency-independent coefficients in the remaining equations (after transforming to the $(\omega, \mathbf{k})$-representation). The derived new system of equations can be used to study light scattering, provided that we have also eliminated these parameters in advance from Eq. (10) by using their equations of motion. Then the tensor $\Delta\epsilon_{\alpha\beta}$ will be determined not only by the fluctuations of the remaining parameters, but also by the fluctuational forces associated with the eliminated parameters. The correlation functions of the fluctuations of the rest of the parameters do not depend on whether one uses a complete or incomplete description[23], but one cannot restrict the treatment in the scattering tensor to them alone, precisely because the fluctuational forces now enter into the expression for $\Delta\epsilon_{\alpha\beta}$. However, we should emphasize that generally one can introduce into a light-scattering theory frequency-dependent characteristics of the medium without explicitly specifying the internal parameters that cause this dispersion. Such an incomplete description of the thermal fluctuations in the medium is admissible whenever the set of internal parameters determining the deviations of the medium from an equilibrium state contains some that do not enter into the tensor of the dielectric-constant fluctuations. These parameters[3] can be eliminated from the complete system of equations of relaxational hydrodynamics. The effect on the scattering of these "optically passive" parameters is reduced to the dispersion that they cause in the hydrodynamic and mechanooptical characteristics of the medium.

As has been shown in[23], the vanishing of the low-frequency limit of the shear modulus for a liquid implies the condition

$$2\mu_\infty = N_1^2 + N_2^2. \tag{14}$$

Moreover, the requirement of a finite integral intensity of the scattered light leads in this case to the following relationship among the mechanooptical (x, n_j) and hydrodynamic coefficients:

$$x = n_1 N_1 + n_2 N_2. \tag{15}$$

If we take two relaxing parameters into account, according to (11)–(13), we get the following expression[48] for the spectral intensity I_{VH} of the scattered light:

$$I_{VH}(\omega, \mathbf{k}) \sim$$

$$\sim -\frac{k_B T}{2\pi i\omega}\left[\frac{X^2}{4(\mu k^2 - \rho_0 \omega^2)} k^2 \cos^2\frac{\theta}{2} + \frac{1}{2}\left(\frac{n_1^2}{1+i\omega\tau_1} + \frac{n_2^2}{1+i\omega\tau_2}\right) - \text{c.c.}\right], \tag{16}$$

where

$$\mu = \frac{i\omega}{2}\left(\frac{N_1^2\tau_1}{1+i\omega\tau_1} + \frac{N_2^2\tau_2}{1+i\omega t_2}\right), \quad X = i\omega\left(\frac{n_1 N_1 \tau_1}{1+i\omega\tau_1} + \frac{n_2 N_2 \tau_2}{1+i\omega\tau_2}\right).$$

The structure of the spectrum of (16) in the general case with various relationships among the parameters has not been examined explicitly. An example of the results obtained with a computer has been given in[33] in the form of graphs that show the change in the nature of the spectrum $I_{VH}(\omega)$ at the scattering angle $\theta = \pi/2$ as a function of the low-frequency viscosity $\eta_0 = 1/2(N_1^2\tau_1 + N_2^2\tau_2)$. These results show that the theory explains the appearance of a doublet at low viscosities and a triplet at high viscosities. Moreover, we must note that the dependence on the viscosity η_0 of the spacing $2\Delta\omega_m$ between the fine-structure maxima in the doublet region does not correspond with that experimentally found. This defect can be eliminated with a more suitable choice of parameters (see[147]).

Now we shall take up some general relationships concerning the depolarization coefficients and the ratios of the integral intensities of the different components of the scattered light. If we assume that $\theta = \pi/2$ and use the system of coordinates indicated in Fig. 1, then after convolution of the general expression (6) with the unit vectors of the incident and scattered light according to (4), we find the corresponding components of the scattered light:

$$\left.\begin{array}{l} I_{VV}(\omega, k^2) = \sigma_1 + \dfrac{2}{3}\sigma_2 - \dfrac{2}{3}k^2\sigma_3 + \dfrac{1}{9}k^4\sigma_4, \\[2mm] I_{VH}(\omega, k^2) = I_{HV}(\omega, k^2) = \dfrac{1}{2}\sigma_2 + \dfrac{1}{8}k^2\sigma_5, \\[2mm] I_{HH}(\omega, k^2) = \dfrac{1}{2}\sigma_2 + \dfrac{1}{12}k^4\sigma_4. \end{array}\right\} \tag{17}$$

In back-scattering $(\theta = \pi)$ we find that

$$I_{VV}(\omega, k^2) = I_{HH}(\omega, k^2) = \sigma_1 + \frac{2}{3}\sigma_2 - \frac{2}{3}k^2\sigma_3 + \frac{1}{9}k^4\sigma_4,$$

$$I_{VH}(\omega, k^2) = I_{HV}(\omega, k^2) = \frac{1}{2}\sigma_2. \tag{18}$$

In an isotropic liquid having a negligibly small radius a of spatial dispersion (as compared with the parameter $\lambda = k^{-1}$; most studied objects fulfill this condition, at least at low viscosities and at scattering angles that are not too small), the integral scattering cross-section should not depend on the scattering vector $\mathbf{k}$ (see, e.g.[41]). Actually

$$\int_{-\infty}^{\infty} \sigma_{\alpha\beta\gamma\delta}^{(s)}(\omega, \mathbf{k})\,d\omega = C\int_V \langle\Delta\epsilon_{\alpha\beta}(0, 0)\,\Delta\epsilon_{\gamma\delta}^*(0, q)\rangle\, e^{-i\mathbf{k}\mathbf{q}}\,d\mathbf{q} = \sigma_{10}\delta_{\alpha\beta}\delta_{\gamma\delta} + \sigma_{20}\mu_{\alpha\beta\gamma\delta}. \tag{19}$$

The expression is valid to an accuracy of terms of the

order of a/λ. The quantities σ_{10} and σ_{20} are the integrals with respect to the frequency of $\sigma_1(\omega,\,k^2)$ and $\sigma_2(\omega,k^2)$, and they no longer depend on k^2. Moreover, $\sigma_{30} = \sigma_{40} = \sigma_{50} = 0$, so that we have the following expressions for the integral intensities:

$$I_{VV}=\sigma_{10}+\tfrac{2}{3}\sigma_{20}, \quad I_{HH}=I_{VH}=I_{HV}=\tfrac{1}{2}\sigma_{20}\left(\theta=\tfrac{\pi}{2}\right), \qquad (20)$$

$$I_{VV}=I_{HH}=\sigma_{10}+\tfrac{2}{3}\sigma_{20}, \quad I_{VH}=I_{HV}=\tfrac{1}{2}\sigma_{20}\,(\theta=\pi). \qquad (21)$$

This implies that, when the tensor of the dielectric-constant fluctuations is symmetric and we neglect spatial dispersion in the expressions (10), the depolarization coefficient calculated from the integral intensities is

$$\Delta_u=\frac{I_{VH}}{I_{VV}}=\frac{I_{HH}}{I_{VV}}=\frac{3\sigma_{20}}{6\sigma_{10}+4\sigma_{20}}, \qquad (22)$$

while the component I_{VV} of the scattered light can be expressed in terms of the coefficient σ_{10} that describes the purely polarized scattering, with account taken of the correction of Cabannes

$$I_{VV}=\sigma_{10}\left(1-\tfrac{4}{3}\Delta_u\right)^{-1}. \qquad (23)$$

Any theory that includes both of the stated assumptions should lead to Eqs. (22) and (23).

As eq. (19) implies, the integral intensities of the light scattered by the spherical and the zero-trace parts of the tensor $\Delta\epsilon_{\alpha\beta}$ can be treated independently of one another, while the depolarization coefficient of the asymmetric scattering proves to be $\tilde{\Delta}_u = 3/4$.

Moreover, Eq. (17) implies that the depolarization coefficient in spectral regions whose structure depends substantially on k will differ from (22), and we can no longer isolate $\tilde{\Delta}_u$ in the general case. Evidently, dependence on the scattering vector k is manifested at $\omega \sim \omega^* = kc$ (c is the characteristic velocity of propagation of mechanical perturbations in the medium). Hence, in the spectral region $\omega \gg \omega^*$, Eqs. (17) and (18) must acquire the form of (20) and (21) (σ_1 and σ_2 will be functions of ω, but not of k^2). This in turn leads to (22) and (23). The depolarization coefficient Δ_u will not equal $3/4$ even in the spectral region $\omega \gg \omega^*$, if scalar internal parameters exist (and contribute to σ_1) that have short enough relaxation times. Analogous conclusions were drawn in[23] concerning the depolarization coefficient for natural light, as based on explicit expressions for the coefficients $\sigma_j(\omega,\,k^2)$ found in this study.

The expressions derived in [23] permit one to find the relationship between the integral intensities of the narrow and broad components of the depolarized spectrum. Since the total integral intensity (for liquids) is

$$I_{VH} \sim \tfrac{1}{2}k_BT\sum n_j^2, \qquad (24)$$

then in the case of two relaxing parameters we get

$$\frac{I_{\text{broad}}}{I_{\text{narrow}}}=\frac{n_2^2}{n_1^2} \quad (\tau_1>\tau_2). \qquad (25)$$

Rytov[23] showed that the previously proposed relaxation theories[19,20,32] are special cases of his more general theory. We note that a theory[49] that has subsequently appeared is also a special case of the general theory that accounts for two relaxation processes.

Further development of the phenomenological theory can proceed in various directions. In particular, one could use a more complex model of the relaxation process. As we know, a spatially unlocalized model of a liquid[51] has been proposed to explain the features of dispersion and absorption of hypersound in liquids at high viscosities (see[50]). Perhaps this very model of a liquid will prove useful also in studying depolarized scattering in highly viscous liquids[9].

Another interesting aspect of the light-scattering problem consists in the fact that the tensor of the dielectric-constant fluctuations $\Delta\epsilon_{\alpha\beta}$ in the general case need not satisfy a priori any symmetry conditions (see[52], Sec. 81). Hence a formal generalization of the theory that accounts for an antisymmetric part of $\Delta\epsilon_{\alpha\beta}$ is quite admissible. Such a generalization leads to interesting physical consequences[53].

The physical basis for introducing an antisymmetric part of $\Delta\epsilon_{\alpha\beta}$ is the existence in a medium consisting of nonspherical particles of an antisymmetric part of the deformation tensor[54,55]. The latter also can lead to light scattering (as we know, an antisymmetric part of the deformation tensor that does not take account of the internal rotational degrees of freedom, but describes a rotation of the medium as a whole, cannot cause light scattering[52]).

The tensor of the dielectric-constant fluctuations is expressed in[53] in terms of the deformation tensor. The effect of the additional parameters that cause the fluctuations in the dielectric constant is taken into account only in terms of the dispersion of the hydrodynamic and mechanooptical coefficients. With this formulation of the problem, the spectrum of the scattered light will lack terms caused by an explicit dependence of the dielectric constant on the additional parameters that lead to the dispersion of the coefficients. That is, an incomplete description has been used. However, this does not affect the general conclusions drawn in this study.

First of all, we should note the increase in the number of independent coefficients that characterize the scattering tensor:

$$\sigma_{\alpha\beta\gamma\delta}(\omega,\,k)=\sigma^{(s)}_{\alpha\beta\gamma\delta}(\omega,\,k)+\sigma_6(\delta_{\alpha\gamma}\delta_{\beta\delta}-\delta_{\alpha\delta}\delta_{\beta\gamma})+\sigma_7(\overline{s_{\alpha\beta}{}^a{}_{\gamma\delta}}+\overline{a_{\alpha\beta}{}^s{}_{\gamma\delta}})+\sigma_8\overline{a_{\alpha\beta}{}^a{}_{\gamma\delta}},$$

$$(26)$$

where

$$\overline{s_{\alpha\beta}{}^a{}_{\gamma\delta}}=\tfrac{1}{4}(k_\alpha k_\gamma\delta_{\beta\delta}-k_\alpha k_\delta\delta_{\beta\gamma}+k_\beta k_\gamma\delta_{\alpha\delta}-k_\beta k_\delta\delta_{\alpha\gamma}),$$

$$a_{\alpha\beta}\begin{cases} {}^s{}_{\gamma\delta} \\ a_{\gamma\delta} \end{cases}=\tfrac{1}{4}(k_\alpha k_\gamma\delta_{\beta\delta}\pm k_\alpha k_\delta\delta_{\beta\gamma}-k_\beta k_\gamma\delta_{\alpha\delta}\mp k_\beta k_\delta\delta_{\alpha\gamma}).$$

In these expressions, s and a denote the symmetric and antisymmetric parts of the tensor with respect to the corresponding pair of subscripts. The integral scattering cross-section is determined by three independent coefficients:

$$\sigma^{(0)}_{\alpha\beta\gamma\delta}=\sigma_{10}\delta_{\alpha\beta}\delta_{\gamma\delta}+\sigma_{20}\mu_{\alpha\beta\gamma\delta}+\sigma_{60}(\delta_{\alpha\gamma}\delta_{\beta\delta}-\delta_{\alpha\delta}\delta_{\beta\gamma}). \qquad (27)$$

We find from (27) the following expressions for the integral intensities in scattering at a right angle ($\theta = \pi/2$):

$$I_{VV}=\sigma_{10}+\tfrac{2}{3}\sigma_{20}, \quad I_{HH}=\tfrac{1}{2}\sigma_{20}+\sigma_{60}, \quad I_{VH}=I_{HV}=\tfrac{1}{2}(\sigma_{20}+\sigma_{60}), \qquad (28)$$

and for backscattering ($\theta = \pi$):

$$I_{VV}=I_{HH}=\sigma_{10}+\tfrac{2}{3}\sigma_{20}, \quad I_{VH}=I_{HV}=\tfrac{1}{2}(\sigma_{20}+\sigma_{60}). \qquad (29)$$

A difference already appears here in the polarization properties of the scattered light. In contrast to (20), we have from (28), i.e., at $\theta = \pi/2$:

$$I_{HH} - I_{VH} = \frac{1}{2}\sigma_{80} \neq 0. \tag{30}$$

Evidently, the depolarization coefficient also increases in terms of the integral intensities, since the antisymmetric part of the dielectric-constant tensor, while contributing to the depolarized scattering, does not alter the polarized component.

Interesting consequences are also derived for the differential scattering cross-section in the spectral range that depends on the scattering vector $\mathbf{k}$. We note here the relationship that was derived in[53], which indicates a violation of the reversibility principle in optics in its commonly-used treatment:[56]

$$I_{VH}(\omega) = I_{HV}(\omega). \tag{31}$$

Equation (26) implies that

$$I_{VH}(\omega) - I_{HV}(\omega) = \frac{1}{2}\sigma_7(\omega, k^2). \tag{32}$$

However, there is actually no evident contradiction of the principle of microscopic reversibility, since consistent application of this principle to light scattering leads to an expression that differs from (31). At high enough temperatures and with $\omega \ll \Omega_0$, such that $[(\Omega_0 + \omega)/\Omega_0]^4 \exp(\hbar\omega/k_BT) \approx 1$, the reversibility principle in optics takes on the form[52]

$$I_{VH}(\Omega_0, \omega) = I_{HV}(\Omega_0 + \omega, -\omega), \tag{33}$$

As before, Ω_0 on the left-hand side here is the frequency of the incident light, while $\Omega_0 + \omega$ is that of the scattered light. The expressions (33) and (31) are equivalent if the intensity of the scattered light depends weakly on Ω_0. As Landsberg and Mandelstam[57] have shown, the intensity of the scattered light depends strongly on Ω_0 when the frequency of the incident light lies in a region close to an absorption band of the scattering material. The equality (31) then loses force. Expansion of the right-hand side of Eq. (33) in a series in the neighborhood of Ω_0 indicates that in general the intensities $I_{VH}(\omega)$ and $I_{HV}(\omega)$ are not equal, and moreover, they are not symmetrical with respect to the point $\omega = 0$.

By comparing (32) with Eq. (19) of[53], we can express $\sigma_7(\omega, k^2)$ in terms of the hydrodynamic characteristics of the medium. The integral of the coefficient σ_7 with respect to the frequency is zero, and hence the integral intensities of I_{VH} and I_{HV} are identical.

An unsymmetrical tensor of the dielectric-constant fluctuations has been treated in[58], where the scattering theory was constructed on the basis of the equations of motion of a continuous medium having internal rotational degrees of freedom. However, errors entered into the calculations, and the authors of the study state that Eq. (31) continues to hold, which contradicts the general symmetry properties of the scattering tensor of (26). In a later study,[59] the antisymmetric part of the tensor $\Delta\epsilon_{\alpha\beta}$ is not treated, although the hydrodynamic equations are written with account taken of the antisymmetric part of the deformation tensor, and they are supplemented by the balance equation for the angular momentum. We shall take up the results obtained in[59] in Sec. b of Chap. 3.

3. STATISTICAL THEORIES

Naturally, the phenomenological theories of scattering have given rise to the attempt to develop a molecular theory of this phenomenon, and primarily, to elucidate the molecular-kinetic meaning of the concepts that it introduces. For the discussed relaxation theories of Leontovich and Rytov, the most important topic from this standpoint is to establish the microscopic meaning of the phenomenological internal parameters. The fundamental problems of the statistical theory include the derivation of equations resting on a concrete molecular model of the substance that will determine the kinetics of these parameters, and the derivation of explicit expressions for the relaxation times and kinetic coefficients that enter into the equations. In addition, the statistical methods must make it possible to treat other optical phenomena on the basis of the same molecular model (the Kerr effect, the Maxwell effect, the Cotton-Mouton effect; see, e.g.[1, 60-63]), and hence to reveal the essential connections among their characteristics.

a) **Mechanisms of light scattering and its depolarization.** The fundamental concepts upon which the statistical theory of molecular light scattering has grown have been developed by Kirkwood[64] and especially by Yvon.[16] Kirkwood derived an expression for the static dielectric constant of a system of nonspherical, polarizable particles, while Yvon has treated light scattering in a system of optically isotropic molecules.

The concept of molecules as the polarizable structural elements of a medium had been widely used even earlier in treating light scattering. Thus, from the moment of its discovery in gases[65] and liquids[66], depolarization of scattered light has been considered to be due to the optical anisotropy of the particles of the medium. Rayleigh[67] expressed the depolarization coefficient in terms of the principal values of the polarizability tensor of the molecules under the assumption that their orientational distributions are equally probable and mutually independent. On the basis of this calculation, Cabannes[68] introduced a correction for depolarized scattering into the Einstein formula for the integral intensity of scattered light. The form of the correction remains invariant upon taking account of both the rotation of the particles[69] and of orientational correlation among them.[70] The phenomenological theories of Leontovich and Rytov give the same form of correction factor. This is understandable, since the correction of Cabannes (see (23)) is implied by the general symmetry properties of the scattering tensor of (6), and it cannot vary in line with any particular concretization of the depolarization mechanism.

The depolarization of light scattered by a system of optically isotropic particles cannot be explained within the framework of the above-stated mechanism, and hence it requires special discussion.

Rayleigh[14] and Cabannes[68] had already observed a depolarized component of the light scattered in methane, carbon tetrachloride, and even in the inert gases. However, until very recently, experimental difficulties did not permit one to say with assurance that a depolarization effect had actually been observed in these substances (see[1], p. 224). Broad experimental studies of depolarization of light in inert gases have become possible owing to the development of laser technology. As was noted in the Introduction, they were started in[12,13], and a rather extensive material has accumulated up to now.[71-79] A detailed study of the spectrum of depolarized light scattering in carbon tetrachloride, whose molecules are isotropic has been taken up in[80].

Depolarization of light scattered by a system of optically isotropic particles has been treated theoretically in[16]. The appearance of a depolarized component was explained by the interaction of dipoles induced in the particles by the wave of the incident light. Gans[15] had pointed out this mechanism earlier (see also[81]). However, apparently, people didn't grant the requisite significance to these studies in their own time, and they sometimes tried to explain depolarization by the Rayleigh mechanism, i.e., by the anisotropy of the particles.

Development of the theory of molecular light scattering has shown that one must take account of many factors for a complete description of this phenomenon. The first theoretical studies starting with[67,68] treated a very simple mechanism of scattering and depolarization of light in which each molecule of the medium was represented as a polarizable particle subject to the action of the light wave, and emitting light independently of the rest of the particles of the system. The effect of the environment on a given particle was taken into account indeed only in terms of expressions like the Lorentz-Lorenz formula for the internal field in the medium. Various correlation effects were taken into account later. Thus, Yvon[16] devised a general theory of the integral intensity of polarized and depolarized light scattering of a system of optically isotropic particles, with account taken of correlation among their spatial positions and interaction among the dipole moments induced in the particles. The latter leads to fluctuations of the local field acting on the particle, and it gives rise to anisotropic scattering in the system of spherically symmetrical particles. The new feature was that the spatial correlation was described by the particle distribution functions.

A number of studies have been concerned with investigating only the spatial correlations of isotropic particles. Davydov[82] has developed a theory in which he expressed the characteristics of the integral intensity of the scattered light as a series in Mayer group integrals. The result obtained in this study might be represented as an expansion in terms of the density. However in this case he was able to sum the series and obtain the Einstein formula for ordinary states of the scattering medium and the Ornstein-Zernike formula to describe the scattering near a critical point. In Zimm's study,[83] as in[16], particle distribution functions were also used to describe spatial correlations, but without taking account of the fluctuations of the local field. A study by Komarov and Fisher[84] borders in its theme on[82,83]. These authors treated the more general problem of determining the spectral composition of the scattered light, and they expressed the final result in terms of Van Hove space-time functions.

Ansel'm[70] has examined the effect of orientational correlations of nonspherical particles on light scattering. A rather large number of studies has subsequently been devoted to this effect (see, e.g.,[85-87]). Buckingham and Stephen[18] calculated the integral-intensity of the scattered light and its depolarization, with account taken of both orientational and spatial correlations of a system of nonspherical, polarizable particles, and also of fluctuations of the local field. Kielich (see[88]) has carried out a number of studies in the development along this line.

Determination of the spectrum of the scattered light

has attracted broad interest relatively recently. Initially the calculations were based on studying the Brownian movement of mutually-independent scattering particles.[89-91] Essentially these theories are phenomenological, although they use the concept of the polarizability tensor of the molecule. The role of the statistical methods is reduced here to justifying the Langevin equations for the Brownian movement of a nonspherical particle and to calculating the frictional coefficients (see[91-93]).

Pecora and Steele[94] have generalized the approach of[84] in which a system of spherical particles is treated, and they studied the spectrum of the scattered light from a system of nonspherical particles. The differential scattering cross-section was expressed in terms of generalized Van Hove space-time functions that take account of the orientation of the particles. Thus, attention was paid in[94] only to the effect of spatial and orientational correlations of the particles on the spectrum of the scattered light, but not to that of fluctuations of the local field. Hellwarth[62] took account also of the interaction between the dipole moments induced in the particles, and he treated the Kerr effect as well as light scattering. He derived a relationship between the Kerr constant and the scattering and depolarization coefficients, but the insufficient accuracy of the experimental data did not permit him to draw reliable conclusions on the validity of the assumptions used.

All of the cited studies on the statistical theory of molecular light scattering have used the concept of the polarizability tensor of a particle in a medium, which is usually identified with the polarizability tensor of the particle in a vacuum, but sometimes is treated as a tensor parameter that must be determined experimentally. Moreover, the concept of the polarizability of a molecule in a medium faces serious difficulties caused by the interaction of the given particle with the others.

Mazur and his associates[95] have shown that one can introduce the polarizability tensor of an individual particle, but only with a dependence on the positions of all the rest of the particles of the system, whereby it becomes a fluctuating quantity. Hence one must take account in the scattered-light spectrum also of the contribution from the fluctuations of the polarizability tensor of the molecule caused by the action of the surrounding particles. People have widely adduced this effect, in addition to the local-field fluctuations, to explain the depolarization of the light scattered by systems of spherically-symmetrical particles.[12,13,71-79,96-100] The number of studies that have subsequently tried to calculate the polarizability tensor of a particle in a medium is small (see[101-105]).

The polarizability tensor also depends on the internal state of the molecule. One can neglect the excitation of electronic levels in the problem of molecular light scattering, while excitation of vibrational degrees of freedom is conveniently described by expanding the polarizability tensor in a series in the corresponding internal coordinates of the molecule:[62]

$$\alpha = \alpha^{(0)} + \sum_{\alpha,\beta} \left(\frac{\partial^2 \alpha}{\partial q_\alpha \, \partial q_\beta} \right)^{(0)} q_\alpha q_\beta + \cdots , \qquad (34)$$

Here the superscript (0) indicates the value of the quantity in the ground state of the molecule. The classical

variant of the theory of Raman scattering of light is based precisely on this expansion (see[106]). The possibility is not ruled out that the scattering caused by fluctuations in α arising from excitation of vibrational degrees of freedom can contribute appreciably in the studied region of the molecular scattering spectrum (0–150 cm^{-1}), but a discussion of this problem falls outside the limits of this review.

Excitation of internal degrees of freedom of the molecules can affect molecular light scattering in another way as well. The internal coordinates q_a of the molecule are among the internal parameters that determine the deviation of the scattering system from the equilibrium state. Hence, if we restrict the treatment in (34) to the first term $\alpha^{(0)}$ in the expansion, the vibrational degrees of freedom of the molecules will be manifested in the spectrum of the scattered light as a frequency dispersion of the hydrodynamic coefficients (in gases, the processes that cause such a dispersion are called Kneser processes). That is, they will effect the spectrum as "optically passive" parameters. The studies[107,148] are concerned with treating this effect on the spectrum of polarized light scattering.

The studies[95] considered precisely the polarizability tensor $\alpha^{(0)}$ that corresponds to the unexcited internal state of the particle. Henceforth we also shall assume that $\alpha = \alpha^{(0)}$; we shall denote the quantity α_0 as the polarizability of the particle in vacuo.

b) Isolation of the "optically active parameters." Let us assume that we can introduce the polarizability tensor of the i-th molecule α_i, which depends on the positions of the rest of the particles of the system. This means that the dipole moment induced in the particle will be determined by the local field $E_i(q_i)$ acting on the particle:

$$p_i = \alpha_i \cdot E_i(q_i). \tag{35}$$

In turn, the local field at the point q_i is determined by the external field $E(q_i)$ and by the fields induced by the rest of the particles of the system:

$$E_i(q_i) = E(q_i) + \sum_{j \neq i}^{N} T_{ij} \cdot p_j(q_j). \tag{36}$$

The tensor T_{ij} describes the interaction of the dipoles. If we neglect retardation, it is determined by the expression

$$T_{ij} = -\frac{1}{4\pi r_{ij}^3}\left(1 - 3\frac{r_{ij}r_{ij}}{r_{ij}^2}\right), \quad r_{ij} = q_j - q_i. \tag{37}$$

The dipole moment induced in an arbitrary particle can be found by solving the system of equations (35) and (36). We note that in the more general case of multipole interactions, the part of the dipole moment p_i that is linear in the imposed field $E(q_i)$ contains the hyperpolarizabilities of the particles.[18,88]

In order to justify the possibility of introducing the polarizability of an individual particle in a medium Jansen, Mazur, and Mandel[95] have used the quantum-mechanical perturbation theory, and they calculated in the adiabatic approximation the dipole moment of a particle in a medium upon imposing an external field. They were able to represent the result in the form of Eq. (35) and (36). This permitted them to derive an expression for the polarizability tensor α. This polarizability of a particle in a medium, as defined in the sense of Eq. (35) (i.e., from the ratio to the local field

acting on the particle), differs from the polarizability α_0 in vacuo, and it depends on the arrangement of the rest of the particles of the system. To simplify the calculation, they treated a system of monatomic molecules with a nondegenerate ground state. They assumed the distances between the particles to be not too small, so that they could restrict the treatment only to dipole-dipole interaction. In this case, the polarizability of the particle in the medium is represented as a power series in its polarizability in vacuo and in the tensor T.

Eqs. (35) and (36) can be solved for the dipole moment of the i-th particle

$$p_i = \sum_{j=1}^{N} Z_{ij} \cdot \alpha_j \cdot E(q_j, t), \tag{38}$$

Here the tensor Z_{ij} is given by the expression[62]

$$Z_{ij}^{-1} = I\delta_{ij} - \alpha_i \cdot T_{ij} \quad (T_{ij} = 0 \text{ when } i = j). \tag{39}$$

Let us assume that the distance at which the interaction of the dipole moments induced in the molecules appreciably begins to figure is considerably shorter than the wavelength of the light. Then we can set $E(q_j, t) \approx E(q_i, t)$ in Eq. (38), and write the expression for the fluctuations of volume density of the dipole moment (the polarization $\mathscr{P}$) of the system in the form

$$\Delta \mathscr{P}(q, t) = Q(q_1, q_2, \ldots, q_N; q) \cdot E(q, t). \tag{40}$$

The tensor Q for the polarizability fluctuations of the entire system has the form

$$Q(q_1, q_2, \ldots, q_N; q) = \sum_{i, j}^{N} Z_{ij} \cdot \alpha_j \delta(q - q_i) - \left\langle \sum_{i, j}^{N} Z_{ij} \cdot \alpha_j \delta(q - q_i) \right\rangle. \tag{41}$$

The way in which it depends on the mutual arrangement of the particles is determined by the form of the tensors Z_{ij} and α_j.

The second term on the right-hand side of (41) involves the dielectric constant of the system. Transformation of this term leads to the Lorentz-Lorenz and Clausius-Mosotti formulas, but with corrections that arise from the fluctuations of the local field (see, e.g.,[108,109]). As was stated above, we get additional corrections upon accounting for the difference between the polarizabilities of the particle in a vacuum and the medium. The contribution of these additional corrections to the dielectric constant and to the refractive index is of the same order of magnitude as that of the corrections for the fluctuation of the local field.[95]

The expression (40) for the polarization fluctuations corresponds to Eq. (2), so that the scattering cross-section is determined by the correlation function of the tensor $Q(q, t)$:

$$S_{is}(\omega, k) = s_\alpha s_\gamma^* i_\beta i_\delta^* \int_V dq \int_{-\infty}^{\infty} dt \langle Q_{\alpha\beta}(0, 0) Q_{\gamma\delta}^*(q, t) \rangle \exp[i(kq - \omega t)]. \tag{42}$$

This contains the correlation function of a quantity that depends on the dynamical variables of all the particles of the system.

We can represent the tensor Q in the form

$$Q = Q_1 + Q_2 + Q_3 + \ldots, \tag{43}$$

where Q_k is a sum of terms, each of which depends on the dynamical variables of a group of k particles, and which in turn is expanded in a power series in α_0. If we neglect the fluctuations of the polarizability tensor of the individual particle, and take account in the scattering cross-section of (42) of quantities up to the fourth order

in the polarizability, then the first two terms of the expansion (43) will take on the form

$$Q_1 = \sum_{i=1}^{N} \alpha_{0i} \delta (q - q_i) - \frac{N}{V} \alpha_0 I, \quad \alpha_0 = \frac{1}{3} Sp \, \alpha_0,$$

$$Q_2 = \sum_{i \neq j}^{N} (\alpha_{0i} \cdot T_{ij} \cdot \alpha_{0j} + \alpha_{0i} \cdot T_{ij} \cdot \alpha_{0j} \cdot T_{ji} \cdot \alpha_{0i} + \ldots) \delta (q - q_i) \quad (44)$$
$$- \left\langle \sum_{i \neq j}^{N} (\text{idem}) \delta (q - q_i) \right\rangle.$$

Taking account of the fluctuations of the polarizability tensor of the particle in the medium leads only to replacing the tensor T in (44) by some other, generally more complicated operator.

The quantities Q_k that enter into (43) can be interpreted as being the internal "optically active" parameters that govern light scattering.

M. A. Leontovich's relaxation theory uses only one internal parameter. One can naturally choose this parameter in the form $Q^\Phi = Q_1$, as was already noted in[11]. The results of Pecora and Steele's study[94] automatically stem from (42) if one restricts treatment in (43) to the first term of the expansion. We should emphasize that, although Q_1 is a one-particle operator, two-particle correlation functions enter into the scattering tensor of (42). This makes it possible, even in the first approximation, to account for the very substantial effects of two-particle spatial and orientational correlations. The studies[89-91], which are based on the concept of the Brownian movement of the particles of the medium, also do not exceed the framework of accounting for the parameter Q_1. Moreover, they restrict the treatment in the scattering cross-section of (42) to one-particle terms alone, i.e., to terms that include the polarizability of one given particle at different instants of time. In this approach, no account is yet taken of two-particle correlation functions (which contain the product of the polarizabilities of two different particles), nor of spatial and orientational correlations as well.

The subsequent terms of the expansion (43), which describe many-particle correlations, can be used as the internal relaxational parameters of Rytov's phenomenological theory, provided only that we neglect a possible correlational dependence among the parameters Q_k having different subscripts. In the converse case, one must either transform to normal coordinates, or take account of the correlation of parameters directly in the equations of motion.

The method under discussion of determining the scattering cross-sections for light arouses no doubts as applied to gases that are not very dense. However, in liquids, the very expansion of the interaction in terms of multipoles, or a fortiori the accounting only for dipole-dipole interaction, requires justification. This problem has not been discussed in the literature, although the discussed concepts have often been used in describing light scattering in liquids. Also there are grounds for thinking that an expansion in a power series in the polarizability is considerably more effective (in terms of convergence) than an expansion in terms of the density.[110] A number of additional assumptions were made in introducing the polarizability tensor of an individual particle. The existing calculations of this quantity have been performed in the adiabatic approximation, and far from the absorption bands of the molecular system. Consequently, the tensor Q

of the system of optically inactive molecules proves to be symmetric, and this causes the scattering tensor to be symmetric with respect to permutation of indices within the first and second pairs. Hence one can expect scattering effects by the antisymmetric part of the polarizability tensor only near absorption bands. This agrees with the conclusion derived in Chap. 1.

Another method[53] of calculating the scattering tensor is based on using Kubo's reaction theory.[111] This method can be conveniently used for studying the effect on light scattering of a given set of parameters. The effect on light scattering was studied in[53] of fluctuations of the deformation tensors of a medium possessing internal rotational degrees of freedom. In order to do this on the basis of Kubo's theory, the part of the dipole moment of the system was isolated that was bilinear in the deformation tensors and in the imposed field. Thus the tensor for the fluctuations of the dielectric constant was expressed in terms of the deformation tensors. The tensors of the mechanooptical coefficients that enter into this expression were represented in terms of the correlation functions of the operators for density of momentum flux and angular momentum dipole-moment density.[112] The main difficulty is that the theory does not permit one to isolate the "optically active" parameters. Hence, in the general case the mechanooptical coefficients are frequency-dependent, and the calculated spectrum of the scattered light corresponds to an incomplete description of the state of the medium.

The relation between the discussed methods of determining the cross-section for light scattering has not been studied. However, one can apparently arrive at the results of[53, 112] by isolating in Eq. (41) the terms that are linear in the deformation tensors. It has been reported in a brief note[113] that an attempt has been undertaken to make such a calculation of the elasto-optical coefficients.

c) **Methods of deriving the relaxation equations.**
At present, nonequilibrium statistical thermodynamics possesses a number of general methods for deriving equations to describe the evolution of functions of dynamical variables (generalized coordinates and momenta) of macroscopic systems.[27] Many of them have been applied specially to problems of molecular light scattering.

In[53], the balance equations of momentum and angular momentum of a system of nonspherical particles were used to determine the correlation functions of the deformation tensor. These equations had been derived earlier[114] by statistical averaging (using the Liouville equation) of the corresponding functions of the dynamical variables of the system. The form of the material equations and the expressions for the kinetic coefficients have been determined[55,114,115] within the framework of Kubo's[116] linear-reaction theory.

Many studies have been based on the theories of linear response developed by Mori[117,118] and by Oppenheim and his associates.[119,120] Some of them[59,121-126] have formally treated a single relaxing parameter (besides the variables associated with transport of momentum, angular momentum, and energy). This parameter is usually identified with the optical-anisotropy tensor of the particles of the medium. The other studies[124,127,128] have used a larger number of relaxing parameters.

The methods developed in[117-120] are similar to one another, and we have therefore restricted the treatment only to presenting briefly the results of Mori's theory that are necessary for the subsequent treatment.

Let us study a certain set of functions of the dynamical variables as represented by the column vector $A(t)$, which depends implicitly on the time, but only via the dynamical variables themselves.[117] The functions of the set A are conveniently referred to their equilibrium values. Acting in the spirit of the concepts of the theory of Brownian movement, let us (assuming it possible) isolate the part that is linear in A in the derivative $dA(t)/dt \equiv F(t)$ as determined over a certain time interval $[0, t]$, including memory effects over the stated interval: $F(t) = F_{lin}(t) + f(t)$. The additive term $f(t)$ contains the terms that are nonlinear in A, and it takes account of the explicit influence of the other variables that determine the microstate of the system in addition to the set A. The system of equations that govern the evolution of the set A over the time interval $[0, t]$ can be conveniently written in the form of Langevin's equations for Brownian movement. In matrix notation, they have the form:[4]

$$\frac{dA(t)}{dt} - i\omega \cdot A(t) + \int_0^t \varphi(t-s) \cdot A(s) \cdot ds = f(t). \qquad (45)$$

The additive term $f(t)$ is a random quantity. Consequently its properties differ considerably from those of the dynamical function $F(5)$. This difference has been studied in detail by Mori.

The solution of (45) is of the form

$$A(t) = \Theta(t) \cdot A + \int_0^t \Theta(t-s) \cdot A(s) \, ds, \qquad (46)$$

where the function $\Theta(t)$ is defined by the inverse Laplace transform:

$$\Theta(z) = \int_0^\infty \Theta(t) e^{-zt} \, dt, \quad \Theta(z) = [zI - i\omega + \varphi(z)]^{-1}. \qquad (47)$$

We have adopted here and below the notation $A = A_0$.

The formal solution of (46) as treated in the Hilbert space of the dynamical variables of the system has a pictorial geometric interpretation. Without as yet concretizing the scalar product in this space, we shall merely require that, at any arbitrary instant t of time, the second term on the right-hand side of (46) (it describes the effect of the random "force" f on the evolution of the parameters A) should be orthogonal to the initial value of the vector $A(0) = A$. The first term will then determine the projection of the vector $A(5)$ on the space A. This implies in addition the formal properties

$$\Theta(t) = (A(t) A^*) \cdot (AA^*)^{-1}, \qquad (48)$$

$$(f(t) A^*) = 0. \qquad (49)$$

The parentheses denote the scalar product.

In order to describe the averaged (secular) variation of the set A starting at some instant of time $t = 0$, we must select an ensemble. Let us make use of the extremal principle. At the initial instant of time, we require that the mean values of the functions of the set A and of the additive integrals of motion over the sought ensemble should be the most probable values and equal to the assigned initial values. As we know, an ensemble that satisfies these requirements is described by the distribution function (or density matrix) $\rho_0 = Z_0^{-1} \exp[-\beta(\mathcal{H} - AB^*)]$, where $\mathcal{H}$ is the Hamiltonian

of the system, and the B are the parameters conjugate to A, and $\beta = (k_B T)^{-1}$. We shall denote averaging over such an ensemble with a bar: $\overline{A(t)} = Sp[A(t)\rho_0]$. We shall retain the angle brackets to denote the averaging $\langle A(t)\rangle = Sp[A(t)\rho]$ over the equilibrium canonical ensemble $\rho = Z^{-1} \exp(-\beta\mathcal{H})$. We impose requirements on the latter only with respect to the mean values of the additive integrals of motion. Now we shall require that Eq. (45) without the right-hand side should describe in the linear approximation the averaged variation of the set $A(t)$ for an assigned initial value of A. That is, they should be the equations of motion for $\overline{A(t)}$. Since $Z_0 \rho_0 = Z\rho(1 + \beta AB^* \ldots)$, the condition $\overline{f(t)} = 0$ implies that

$$\langle f(t) A^* \rangle = 0. \qquad (50)$$

Combination of Eq. (50) with the orthogonality condition (49) permits us to concretize the scalar product as being the average over the canonical distribution ρ. Mori used the fact that the time derivative in the stated Hilbert space is determined by the Hermitian Liouville operator $d/dt = iL$, and thus obtained exact expressions for the matrices $i\omega$ and ϕ. The first of these is determined by the static correlators:

$$i\omega = (\dot{A}A^*) \cdot (AA^*)^{-1}. \qquad (51)$$

The aftereffect matrix ϕ describes the effects of retardation, and it is expressed in terms of time correlation functions:

$$\varphi(t) = (f(t) f^*) \cdot (AA^*)^{-1}. \qquad (52)$$

Exact solution of the system of equations (45) encounters difficulties that are usual in many-body problems. However, the practical value of Eqs. (45) is that they serve as a convenient basis for making use of various physical hypotheses. In particular, the system (45) is considerably simplified if one can isolate a group of the parameters of A that relax slowly as compared with the variation of the rest of the variables. Then the matrix $\phi(t)$ will differ from zero only within a certain time interval τ_f, which is considerably shorter than the characteristic time τ_A that is required for an appreciable variation of the function A. Then the system (45) for $t \gg \tau_f$ takes on the form

$$dA(t)/dt - (i\Omega - \gamma) \cdot A(t) = f(t). \qquad (53)$$

Such a system describes a steady-state Markov process, and the tensor of frictional coefficients γ and the tensor $i\Omega$ are determined by the relationships

$$\gamma = Re \, \Gamma, \quad \Omega = \omega - Im \, \Gamma,$$
$$\Gamma = \lim_{\varepsilon \to +0} \int_0^\infty \varphi(t) \exp[-(i\omega + \varepsilon I) t] dt. \qquad (54)$$

In the general case, if we impose no restrictions on the choice of parameters of A or on the studied time interval, Eqs. (45) can be reduced to a form determined by the correlation matrix $\langle A(t) A^* \rangle$. In order to do this it suffices to multiply (45) on the right by A^*, and to use the property (50):

$$\frac{d}{dt}\langle A(t) A^* \rangle - i\omega \cdot \langle A(t) A^* \rangle + \int_0^t \varphi(t-s) \cdot \langle A(s) \cdot A^* \rangle \, ds = 0. \qquad (55)$$

Upon applying the Laplace transform, we find the solution of Eq. (55)

$$\langle A(z) A^* \rangle = [zI - i\omega + \varphi(z)]^{-1} \cdot \langle AA^* \rangle, \qquad (56)$$

which, of course, corresponds to Eq. (48).

In Mori's method, the finding of $\phi(t)$ is reduced to

calculating the time-correlation function of the so-called reduced fluxes, which generally differ from the fluxes defined by the relationships[5] I_A = $\dot{A}$. Mori also proposed another procedure for calculating $\phi(t)$ based on expanding the right-hand side of (56) in a continued fraction.[118] In[119,120], the correlation function was also represented in the form of (56), while the matrix of the kinetic coefficients $M(k, z) = i\omega(k) - \phi(k, z)$ was calculated as a power series in the wave vector k. One can also find the matrix $M(k, z)$ by using the non-equilibrium statistical operator,[27] and in a number of cases of space and time dispersion, it is convenient from the physical standpoint to expand the matrix M^{-1} in a series in k and in $z = i\omega$.[130]

The system of equations (45) resembles in form and properties the system of equations of relaxational fluctuational hydrodynamics.[28,29] In particular, both systems lead to the same result (56) for the correlation matrix of the fluctuations of the parameters A. Ultimately, this brings about an agreement between the calculated spectra of the scattered light. The properties of the random forces used in these two systems of equations differ somewhat. This is understandable, since the equations of fluctuational hydrodynamics are defined over the time interval $[-\infty, t]$, while the initial instant of time is specified in Mori's equations. Hence, in correlating the properties of the random forces, one must account for the stated difference in the systems of equations.

d) One "optically active" parameter. If we know all of the "optically active" parameters and the system of equations (45) for them, then we can calculate the spectrum of the scattered light over the entire frequency range that is characteristic of molecular scattering (from 0 to ~100–150 cm^{-1}). In the phenomenological approach, in which the choice of parameters is physically not concretized, such a general approach remains justified. The shape of the spectrum in individual regions can be studied on the basis of the general expressions. Moreover, the existence in these general expressions of a large number of coefficients does not always permit one to determine their values unambiguously and with sufficient accuracy from the experimental data. Hence, it is convenient to dissect the structure of the statistical theory of the spectral composition of the scattered light into a set of narrower problems, while using from the outset certain physical assumptions. In this section we shall treat the close-lying region of the tail of the Rayleigh line, in which we can restrict treatment to accounting for only the parameters that vary relatively slowly.

In order to find the "optically active" parameters, one most often assumes that the theory treated in Sec. b also holds for the condensed state of matter. From among the set of parameters Q_k that enter into (43), one should primarily assign the first term Q_1 = Q^Φ to the region of the spectrum of the scattered light that is adjacent to the undisplaced line. This parameter is expressed as a sum of one-particle functions, and its role in light scattering has been repeatedly emphasized and studied (see[1,89-91]). Study of dipole relaxation and infrared absorption, as well as direct estimates of the statistical expressions (see[10,93,131]) have shown that the characteristic times associated with the orientational movement of the particles are of an order of magnitude that corresponds to the width of the close-lying region of the line of the scattered light.

Even the next term, Q_2, which is a two-particle function, varies considerably more rapidly. This is indicated by the great line widths of the light scattered by systems of optically isotropic particles for which the contribution of the parameter Q_2 to the scattering is not masked by the contribution of the one-particle functions Q_1.

In addition to the "optically active" parameters, one must also determine the "optically passive" parameters that affect the spectrum of the scattered light via the simultaneous system of relaxation equations. First of all, we should include here the quantities that enter into the equations of ordinary hydrodynamics: the number-density of particles Q^n, the momentum density Q^p, and the energy density Q^E. A number of studies[53, 58,59] have treated the density Q^s of the intrinsic angular momentum of the particles of the medium. The polarized component of the scattered light is also affected by the variables that describe excitation of internal degrees of freedom of the molecules (see[107]).

Let us return to determining the spectral composition of the scattered light, and we shall show that the results of the statistical and the phenomenological theories agree. We shall treat only the depolarized component $I_{VH}(\omega)$, and following[122,125], we shall include in the set of slowly varying parameters the polarizability density Q^Φ and the transverse component of the momentum density Q_1^p. As has been mentioned in Chap. 1, the scalar parameters Q^n and Q^E and the longitudinal component of the momentum density $Q_\parallel^p$ do not affect the studied component of the scattered light, while we shall neglect the effect of Q^s.

In the k-representation and in the system of coordinates shown in Fig. 1, the quantities of interest to us have the form

$$Q_\perp^p(k) = \sum_{i=1}^{N} p_{iz} \exp(ikx_i), \quad Q_{xz}^\Phi(k) = \sum_{i=1}^{N} \alpha_{ixz} \exp(ikx_i),$$

$$Q_{yz}^\Phi(k) = \sum_{i=1}^{N} \alpha_{iyz} \exp(ikx_i), \tag{57}$$

Here x_i is the projection of the radius vector of the i-th particle on the x axis.

In agreement with (11), the spectrum of the scattered light is determined by the expression

$$I_{VH}(\omega, k) = \langle Q_{yz}^\Phi(\omega, k) Q_{yz}^\Phi(-k) \rangle \sin^2 \frac{\theta}{2} + \langle Q_{xz}^\Phi(\omega, k) Q_{xz}^\Phi(-k) \rangle \cos^2 \frac{\theta}{2}. \tag{58}$$

Spatial-symmetry properties[122] (see also Chap. 1) imply that the parameter Q_{yz}^Φ varies independently of $Q_\perp^p$ and Q_{xz}^Φ, while the equation that governs its evolution according to Eq. (53), has the form

$$\dot{Q}_{yz}^\Phi(k, t) = -\Gamma Q_{yz}^\Phi(k, t) + f_{yz}^\Phi(k, t). \tag{59}$$

The static correlation function of quantities having differing time parity vanishes. Hence, $i\omega_{yz}$ = $\langle Q_{yz}^\Phi(k) Q_{yz}^\Phi(-k) \rangle$ = 0. According to (54), the decay coefficient Γ that determines the relaxation time $(\Gamma = \tau^{-1})$ has the form

$$\Gamma = \langle |Q_{yz}^\Phi(k)|^2 \rangle^{-1} \int_0^\infty \langle \dot{Q}_{yz}^\Phi(k, t) \dot{Q}_{yz}^\Phi(-k) \rangle dt. \tag{60}$$

In view of the smallness of the wave vector, we can restrict the treatment in calculating the kinetic coefficients to the lowest orders in k, and go in Eq. (60) to the limit $k \to 0$.

The parameters $Q_\perp^p$ and Q_{xz}^Φ are not independent, and in order to derive the equations of motion, we should take A in Eq. (53) to be the column vector composed of

these quantities. $Q_\perp^p$ and Q_{xz}^Φ have differing time pari-
ties. Hence the non-diagonal elements of the matrix
$i\omega$ will differ from zero. Moreover, if the studied set
of slowly varying parameters is complete, then, accord-
ing to the estimates of[122], we can neglect in the lowest
order in k the non-diagonal elements of the matrix γ
as compared with the corresponding elements of the
matrix $i\omega$. The resulting equations take on the form

$$\dot{Q}_\perp^p (k, t) = -k^2 \frac{\eta_2}{\rho} Q_\perp^p (k, t) + ik\delta_{xz} k_B T \langle \Phi^2 \rangle^{-1/2} Q_{xz}^\Phi (k, t) + f_\perp^p (k, t),$$

$$\dot{Q}_{xz}^\Phi (k, t) = ik \frac{\delta_{xz}}{m} \langle \Phi^2 \rangle^{1/2} Q_\perp^p (k, t) - \Gamma Q_{xz}^\Phi (k, t) + f_{xz}^\Phi (k, t). \tag{61}$$

The following relationship holds for systems having
short-range interparticle forces:

$$\lim_{k\to 0} \dot{Q}_\perp^p (k) = \lim_{k\to 0} ik \sum_{i=0}^N \left[\frac{d}{dt} (p_{iz} x_i) \right] \exp (ikx_i), \tag{62}$$

Hence, the coefficients of the system (26) can be written
in the form

$$\eta_2 = (Vk_B T)^{-1} \int_0^\infty \langle \Pi_{xz} (t) \Pi_{xz} \rangle \, dt,$$

$$\delta_{xz} = (Nk_B T \langle \Phi^2 \rangle^{1/2})^{-1} \langle \Pi_{xz} Q_{xz}^\Phi \rangle; \tag{63}$$

Here Π_{xz} is the operator for momentum flux density in
the long-wavelength limit:

$$\Pi_{xz} = \sum_{i=1}^N \frac{d}{dt} (p_{iz} x_i), \tag{64}$$

whose form has been repeatedly discussed in detail
(see[117,132]).

In deriving (61) and (63), we have also used the
theorem of uniform energy distribution

$$\langle Q_\perp^p Q_\perp^p \rangle = mNk_B T \tag{65}$$

and have introduced the notation

$$N \langle \Phi^2 \rangle = \langle Q_{xz}^\Phi Q_{xz}^\Phi \rangle = \langle Q_{yz}^\Phi Q_{yz}^\Phi \rangle. \tag{66}$$

The relationship between the two equations of the
system (61) arises from the parameter δ_{xz}. The need
of accounting for this parameter in explaining the fine
structure of the tail of the Rayleigh line was even
pointed out in[36] on the basis of studying the symmetry
properties of the scattering cross-section.

The equations of motion (61) are linear, and they can
be reduced to the form (13) that is used in Rytov's
phenomenological theory by a substitution of variables
(see[25]):

$$Q_\perp^p = \rho V s_z,$$

$$\frac{m}{V} \left(\frac{k_B T}{\rho m \langle \Phi^2 \rangle} \right)^{1/2} \left(Q_{xz}^\Phi - ik \frac{\delta_{xz}}{m} \langle \Phi^2 \rangle^{1/2} \rho V s_z \right) = \tilde{\zeta}_{xz}^{(1)}. \tag{67}$$

Owing to this substitution, Eqs. (61) acquire the form:

$$\left. \begin{array}{l} \rho \ddot{s}_z = -k^2 \mu_\infty s_z - k^2 \eta_2 \dot{s}_z + ik\mu_\infty^{1/2} \tilde{\zeta}_{xz}^{(1)} + f_z, \\[2mm] \tau_1 \dot{\tilde{\zeta}}_{xz}^{(1)} = -\tilde{\zeta}_{xz}^{(1)} - ik\mu_\infty^{1/2} s_z + f_{xz}^{(1)}, \\[2mm] \tau_1 = \Gamma^{-1}, \quad \mu_\infty = \frac{N}{V} \delta_{xz}^2 k_B T. \end{array} \right\} \tag{68}$$

The appearance of the viscosity constant η_2 in (68) is
quite understandable, since in the derivation we accoun-
ted only for the evolution of the slowly varying para-
meters, which determine the structure of the spectrum
at low frequencies. Hence, there is actually no break-
down of the Kramers-Kronig relationships owing to the
appearance of the frequency-independent viscosity,
since the equations (68) themselves are valid only in
the limit of low frequencies. In order to study the
higher-frequency regions of the scattered-light spec-

trum, one must either treat the frequency-dependence
of the coefficients of Eq. (61) in line with their rigorous
definition (52), or supplement the system (61) with
equations that will account for the faster relaxation
processes. Hence, the system of equations (68) corres-
ponds to the special case of Rytov's theory that con-
siders a single "optically active" parameter, while
assuming the "optically passive" parameters (of which
several can exist) to vary more rapidly and eliminating
them from the equations of motion. In the low-frequency
region, we can neglect the dispersion of the coefficients
caused by elimination of the rapidly-varying parameters
whereby the viscosity constant η_2 arises. This special
case has also been treated phenomenologically in[6].

The shape of the spectrum $I_{VH}(\omega)$ that was obtained
in[122,125] arises from Eq. (16) with the following values
of the parameters:

$$n_1 \neq 0, \quad n_2 = 0, \quad x = n_1 \delta_{xz} \left(\frac{Nk_B T}{V} \right)^{1/2},$$

$$N_1^2 = \mu_{1\infty} = \frac{Nk_B T}{V} \delta_{xz}^2, \quad N_2^2 \tau_2 = \eta_2, \quad N_1^2 \tau_1 = \eta_1. \tag{69}$$

Here the fraction of the viscosity η_2 arises from the
high-frequency relaxation processes, while η_1 arises
from the relaxation of the slowly-varying parameter
that governs the orientation of the particle. The resul-
tant spectrum in the low-frequency region can be con-
veniently described by a formula that contains three
independent parameters:[125]

$$I_{VH} \sim \frac{\Gamma^2}{\omega^2 + \Gamma^2} \sin^2 \frac{\theta}{2} + \frac{\omega^2 \Gamma^2 + \omega_T^4 (1-R)}{(\omega^2 - \omega_T^2)^2 + \omega^2 \Gamma^2 [1 + (\omega^2/\Gamma^2) (1-R)]^2} \cos^2 \frac{\theta}{2}, \tag{70}$$

where

$$R = \frac{\eta_1}{\eta}, \quad \eta = \eta_1 + \eta_2, \quad \omega_T^2 = \eta \frac{\Gamma}{\rho} k^2.$$

When the ratio ω_T is small enough, Eq. (70) ex-
plains[6,122] the appearance of a doublet in the spectrum
$I_{VH}(\omega)$. The local minimum at the point $\omega = 0$ disap-
pears and hence the spectrum is converted into a trip-
let or into a single undisplaced line when the quantity
ω_T reaches its critical value $\hat{\omega}_T$, which is given by the
expression[125]

$$\left(\frac{\hat{\omega}_T}{\Gamma} \right)^2 = \frac{(1-R) R + [(1-R)^2 + tg^2 (\theta/2)]^{1/2} R^{1/2}}{(1-R)^3 + tg^2 (\theta/2)}. \tag{71}$$

However, the analysis of the behavior of the spectrum
when $\omega_T > \hat{\omega}_T$ that was performed in[122] is not com-
plete enough. Thus, the doublet defined by Eq. (70)
goes over into a triplet in scattering at a right angle,
not only when R = 1, but even starting at R = 0.64. When
R = 0.64 and $\omega_T = 1.05$ ($\hat{\omega}_T \approx 1.02 \Gamma$), the triplet
structure in I_{VH} is barely marked, and it rapidly van-
ishes with increasing ω_T. The graphs in Fig. 2
imply that the triplet arises from the appearance of a
weak local maximum at the point $\omega = 0$ as ω_T passes its
critical value $\hat{\omega}_T$. With further increase in ω_T, the
undisplaced peak becomes more marked, but when
$R \lesssim 0.9$, the triplet rapidly vanishes. (Fig. 2a). For any
$R \ll 1$, there is a limiting value $\omega_{T\lim} = R^{1/4}(1 - R)$
$\times (1 - R^{1/2})]^{-1/2} \Gamma$ above which ($\omega_T > \omega_{T\lim}$) the second
term on the right-hand side of Eq. (70), and hence also
the spectrum I_{VH}, become monotonic functions of the
frequency (for $\omega > 0$). Only when R = 1 does the triplet
structure persist to arbitrarily large values of ω_T, and
here the maxima of the displaced components steadily
remain above the undisplaced maximum.

The expression (70) explains at least qualitatively
the behavior of the fine structure of the tail of the
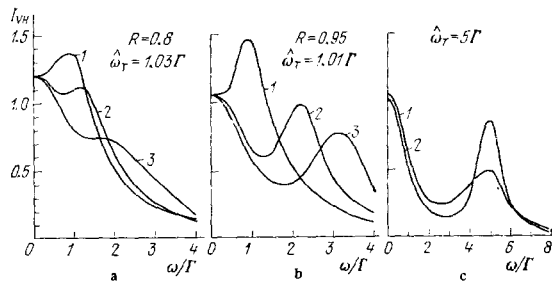Rayleigh line over a broad temperature range. The con-

FIG. 2. Structure of the spectrum I_{VH} for values of the parameters that give rise to a triplet.

dition of existence of a doublet (see (71)) at high temperatures and low viscosities imposes no special restrictions on the size of R. Thus, the inequality $R > 0.1$ must be satisfied when $\omega_T = 0.3\Gamma$. The authors of[122] concluded that R must increase with decreasing temperature in order to explain the temperature-dependence of the displacement of the doublet components when the strong inequality $\omega_T^2 \ll \Gamma^2$ is satisfied. However, the ratio ω_T/Γ itself depends strongly on R, and it substantially affects the positions of the maxima of the fine structure. A relation is given in[6] between the structure of the doublet and the viscosity η at constant $R = 0.5$ that matches that observed experimentally. The disappearance of the fine structure at intermediate temperatures considerably restricts the upper bound of possible values of R. The fine structure degenerates into a single undisplaced line if $R \lesssim 0.6$. Upon further decrease in temperature, R must increase (statistical estimates[122] confirm this behavior of R), and a clearly marked triplet appears in the spectrum of the scattered light at values $R \approx 0.9$ (see Fig. 2b, c). We can determine the positions of the maxima of the displaced components of the triplet approximately from the second term of Eq. (70):

$$\left(\frac{\omega_m}{\Gamma}\right)^2 = \left(\frac{\omega_T}{\Gamma}\right)^2 R^{1/2} - \left(\frac{\omega_T}{\Gamma}\right)^{1/4} (1-R)(1-R^{1/2}). \quad (72)$$

Stegeman and Stoicheff[10] have undertaken a detailed experimental study of depolarized scattering in liquids. In spite of painstaking treatment of the experimental material, the obtained values of ω_T and μ_∞ still could not be considered to be well-grounded enough. The trouble is that the determination of these characteristics is based on using the results of the theory that accounts for only a single relaxation process (the expression (70) was taken for the spectrum I_{VH} with $R = 1$). Moreover, this same study noted that the necessary condition for applicability of this theory ($\mu_\infty T/\eta = 1$) is not satisfied ($\mu_\infty T/\eta \approx 0.1-0.7$) This fact favors the theory having two relaxing parameters, and in particular, Eq. (70) with a value $R < 1$.

The appearance of a doublet is explained in[6,12] by the existence of an imaginary root of $\omega = \omega(k)$ of the dispersion equation of the system (68), i.e., by coupling of the parameter Q^Φ with purely dissipative shear modes. However, one may object to this viewpoint, since the light scattering does not arise from free waves in the liquid. The system of equations (45), just like the system of equations of fluctuational hydrodynamics (13), contains the quantities f, which play the role of external forces (in this regard see also p. 561 of this article). The thermal fluctuations in the medium are described by a superposition of waves with all possible relationships between ω and k. However, the ones that are essential in light scattering are not those that correspond to solutions of the dispersion equation, but those for which both the wave vector and the frequency are real, in line with the experimental conditions. Only in an ideal elastic medium can the wave vector and the frequency that satisfies the dispersion equation be simultaneously real. Then the spectrum of the scattered light degenerates into a set of monochromatic lines lying at the points $\omega_m = v_{sound}k$. The existence of dissipation in the medium brings about a mismatch between the positions of the maxima of the fine structure of the scattered light and of the speed of propagation of acoustic waves ($v_{sound} \neq \omega_m/k$). This mismatch for longitudinal waves has been discussed repeatedly,[19,133] although the reasons for it have not been pointed out very clearly. The large modulus of volume elasticity and the relatively small absorption coefficient for longitudinal sound lead only to a slight difference between the quantities v_{sound} and ω_m/k. However, the situation differs radically for transverse waves in a liquid, since the low-frequency shear modulus is zero. In this case one can compare the data of acoustic[6] and optical measurements only by directly calculating the coefficients that enter into the hydrodynamic equations. An attempt has been undertaken in[136] to make such a comparison of the data of optical and acoustic measurements on the basis of Rytov's theory.

In[122] they also calculated the depolarized component of the spectrum of scattered light $I_{HH}(\omega)$. The principle of choosing the parameters and constructing the system of equations for them remained the same as in calculating the component $I_{VH}(\omega)$. Analysis of the spatial-symmetry conditions showed that the components of the tensor Q^Φ that are essential for the spectrum I_{HH} involve the scalar parameters $Q_{\parallel}^p$, Q^E, and Q^n. Of course, the resultant spectrum that was calculated in[122] can also be obtained from the more general formula of Rytov[23] by using in the latter some simplifications analogous to Eq. (69). The relation of the "optically active" parameter Q^Φ to the propagation of longitudinal waves that is described by $Q_{\parallel}^p$ leads to the appearance in the spectrum I_{HH} of lines that correspond to the Mandel'shtam-Brillouin doublet, as Leontovich has also pointed out.[11] A study[137] has very recently appeared in which they studied the characteristics of the spectrum I_{HH} on the basis of the theory of[33].

Ben-Reuven and Gershon[121,123] have applied a variant of Mori's theory[118] for calculating the depolarized components I_{VH} and I_{HH}. Here they use an expansion of the correlation function (56) written for the parameter Q^Φ as a continued fraction. In these studies they also considered the momentum density Q^p as the quantity that modulates the orientational motion of the particles. Apparently, one should still prefer the approach of Keyes and Kivelson, since at least it rests on heuristic considerations in describing the interaction between Q^Φ and Q^p. The studies[122,125] take account of the mutual influence of these parameters, whereas Ben-Reuven and Gershon do not account for the effect of reorientation of the particles on the propagation of transverse and longitudinal modes in the liquid. Hence it is strange that the quantity γ_k that describes the attenuation was taken to be the same in[121] for both longitudinal and transverse modes, with a value of 2×10^9 rad/sec, which is characteristic of Kneser-type relaxation processes. In contradiction to this hypothesis, it is implied by[122] that the characteristic parameter for relaxation

of the shear viscosity must be substantially larger ($\Gamma \gtrsim 10^{10}$ rad/sec), even though here one can hardly obtain the correct order of magnitude of the spacings $\Delta \omega_m$ between the fine-structure maxima.

The density of the intrinsic angular momentum $\mathbf{Q}^s$ of the particles of the medium was also introduced in [59] in addition to the parameters $\mathbf{Q}^\Phi$, $\mathbf{Q}^p$, $\mathbf{Q}^\epsilon$, and $\mathbf{Q}^n$. As before, only the parameter $\mathbf{Q}^\Phi$ was considered to be "optically active." However, the calculations did not lead to fundamental differences in the spectrum of the scattered light from that found in [122]. In particular, they showed that the introduction of the parameter $\mathbf{Q}^s$ does not explain the existence of a broad background. Gershon and Oppenheim[126] have treated the same group of variables, and have obtained the spectra of I_{VH} and I_{HH} by using the method of calculating the matrix M of the kinetic coefficients that was developed in [119,120]. The structure of the spectra was not studied in detail in [128], but they noted that the nature of the fine structure of the two components corresponds to that observed experimentally (see also [149]).

Mori's method[117] has also been applied for constructing the equations of motion in [124]. The choice of the "optically active" parameters in this study was not based on any theoretical considerations. They took the stress tensor as the slowly varying "optically active" parameter to explain the fine structure of the spectrum of I_{VH}. The group properties of the stress tensor and the polarizability tensor $\mathbf{Q}^\Phi$ coincide. Hence, the spectrum obtained in [124] is formally almost identical with Eq. (70), which was derived in [122] (the use in these studies of not quite identical approximations led only to insignificant differences in the results). The tensor $\mu_\alpha \mu_\beta$ (μ is a unit vector along the axis of the molecule), to which was attributed a more rapid relaxation,[124] was chosen as being responsible for the appearance of the broad background in the spectrum. However, the possibility of choosing values of the parameters that make the calculated spectrum agree with the experimental data still tells nothing about whether the theory is correct, since in [124] they didn't develop methods of estimating the statistical expressions. The example of this study shows how important it is to base the treatment when choosing "optically active" parameters on definite theoretical hypotheses, if reliable methods are lacking for estimating the coefficients statistically.

3) Two relaxing parameters. The structure of the spectrum of the scattered light over a broad frequency range containing the broad background as well as the sharp central line[1,138,139] cannot be explained by introducing only one "optically active" parameter. This conclusion has been argued most convincingly in [23]. In fact, Eq. (25) implies that the integral intensity of the broad component is zero if $n_2 = 0$. Hence, introduction of rapidly relaxing "optically passive" parameters cannot explain the existence of narrow and broad undisplaced lines in the spectrum.

The studies[127,128] have dealt with the "optically active" parameter $\mathbf{Q}^\Phi$ and a second parameter $\mathbf{Q}^F$, which can be either "optically active" or "optically passive". As has been noted, until the parameters $\mathbf{Q}^\Phi$ and $\mathbf{Q}^F$ have been concretized, one cannot consider a theory based on the system of equations (53) to be any more statistical than the theory based on the equations of fluctuational relaxational hydrodynamics. This is just why the results of[127,128], which work with non-concre-

tized parameters $\mathbf{Q}^\Phi$ and $\mathbf{Q}^F$ prove to be a special case, in view of the less general formulation of the problem (the interaction of the parameters $\mathbf{Q}^\Phi$ and $\mathbf{Q}^F$ with the hydrodynamic variables $\mathbf{Q}^p$, $\mathbf{Q}^E$, and $\mathbf{Q}^n$ is not taken into account) than the results[23].

Only that part of[127] is of interest in which attempts were undertaken to concretize the choice of the parameters $\mathbf{Q}^\Phi$ and $\mathbf{Q}^F$. Bearing in mind the theory presented in Sec. b, we can naturally choose these parameters as follows:

$$Q^\Phi = Q_1, \quad Q^F = Q_2. \tag{73}$$

We recall that Q_2 accounts for two-particle interactions, but the structure of the formula (42) for the cross-section is such that it contains not only the two-particle functions $\alpha_i T_{ij} \alpha_j \alpha_j T_{ji} \alpha_i$ ($i \neq j$), but also the three- and four-particle functions of the forms $\alpha_i T_{ij} \alpha_j \alpha_j T_{jk} \alpha_k$ ($i \neq j \neq k$) and $\alpha_i T_{ij} \alpha_j \alpha_l T_{lk} \alpha_k$ ($i \neq j \neq l \neq k$).

If we do not take account of the relation of the parameters of (73) to the hydrodynamic parameters (as is justified in treating regions of the spectrum that do not depend on the wave vector k), their relaxation equations have the form of (12), with the difference that terms arise that describe the mutual correlation of $\mathbf{Q}^\Phi$ and $\mathbf{Q}^F$. When the characteristic relaxation times of these parameters differ considerably, the resultant spectrum consists of a sum of two Lorentzians with half-widths Γ_Φ and Γ_F, and with a ratio of integral intensities equal to

$$\frac{I_{broad}}{I_{narrow}} = \frac{\beta^2 f (\Gamma_\Phi/\Gamma_F)^2 + 2\beta\gamma (\Gamma_\Phi/\Gamma_F) + \gamma^2}{\beta^2 + \gamma^2 f^2 - 2\beta\gamma f} \quad (\Gamma_\Phi \ll \Gamma_F). \tag{74}$$

The coefficients β, γ, and f are determined by the static

$$\beta^2 = \langle Q_{xz}^\Phi Q_{xz}^\Phi \rangle, \quad \gamma^2 = \langle Q_{xz}^F Q_{xz}^F \rangle,$$
$$f = -(\gamma\beta)^{-1} \langle Q_{xz}^\Phi Q_{xz}^F \rangle, \tag{75}$$

while the half-widths of the lines are expressed in terms of time-integrals of the correlation functions:

$$\Gamma_\alpha = \langle Q_{xz}^\alpha Q_{xz}^\alpha \rangle^{-1} \int_0^\infty \langle \dot{Q}_{xz}^\alpha (t) \, \dot{Q}_{xz}^\alpha \rangle \, dt \quad (\alpha = \Phi, F). \tag{76}$$

Eq. (74) has been derived under the assumptions that $\Gamma_\Phi \ll \Gamma_F$, and $\Gamma/\Gamma_\Phi = 0$, where

$$\Gamma = (\alpha\beta)^{-1} \int_0^\infty \langle \dot{Q}_{xz}^\Phi (t) \, \dot{Q}_{xz}^F \rangle \, dt. \tag{77}$$

The statistical averaging in (75) is a complex problem for two reasons: we must know the distribution functions with account taken of the orientation of the particles, and we must know the three- and four-particle distribution functions, in addition to the two-particle functions. There are as yet no studies that have attempted to solve this problem in complete form. The problem was extremely simplified in[128] in estimating the coefficients β, γ, and f, and only two-particle point correlations were treated. Moreover the authors assumed that $\Gamma_\Phi/\Gamma_F \approx 0.1$, and they concluded that Eq. (74) does not contradict the experimental data.

More substantial results have been attained in studying systems of point particles. Buckingham and Stephen[18] had also estimated the depolarization coefficient of light scattered in liquid argon, and they obtained the very high value $\Delta_u = 0.12$, while restricting the treatment in calculating γ^2 to two-particle correlations, and using the radial distribution function that had been determined by neutron-scattering experiments. One cannot explain the sharp discrepancy with the currently existing experimental data by inaccuracy of the statistical averag-

ing (according to[71], $\Delta_u \sim 10^{-3}$ in liquid argon at 90°K). It was shown in[97] that the value of Δ_u calculated by the formula of Buckingham and Stephen deviates from the experimental data by no more than 50% at low densities ($\rho \lesssim 0.4$ g/cm^{-3}).

The reasons for such a sharp disagreement of the estimates of[18] with the experimental data at high densities has currently become understandable. Gelbart[140] approximated the three-particle distribution function with two-particle distributions, and he showed that taking account of three-particle correlations while calculating γ^2 considerably improves the agreement of theory with experiment.

A computer experiment was used in[141,142,150] for studying light scattering. A system of spherical, polarizable particles having pairwise interparticle interactions was treated. The fluctuations of the local field were determined in an approximation that corresponds to taking account of the term $\alpha_i \cdot T_{ij} \cdot \alpha_j$ in the expansion of the parameter Q_2 (see (44)). The authors[141] concluded on the basis of the difference between the results of the computer experiment and the experimental data that the polarizability fluctuations of the particles (these fluctuations were not taken into account in the study) must affect substantially the integral intensity of the scattered light. Specifically, they must reduce the effects of anisotropy caused by fluctuations of the local field. We find this view to be too categorical. First, the expressions that account for three- and four-particle correlations decline slowly (as r^{-3}) with increasing interparticle distance. These expressions should have been transformed in advance, so as to eliminate the dependence of the integrals on the form of the surface bounding the volume of the system (of course, under the condition that such a transformation is possible). Second, the depolarization coefficient was defined as a sum of terms whose absolute values exceeded the result by one or two orders of magnitude. (Insignificant variations in the values of the terms (and not so much because of inaccuracy of the calculations as because of the approximations used) can substantially change the result.)

The shape of the spectrum[142] agrees with the experimental data considerably better. Perhaps this arises from the fact that the long-range nature of the dipole-dipole interaction affects the integral intensity more than it does the spectrum of the scattered light (as we have stated, they didn't analyze in[141,142,150] the correctness of the account taken of long-range action).

One can draw interesting conclusions from analyzing the results given in[141] of calculating the contributions of two-, three-, and four-particle correlations to the integral scattering cross-section. Restriction to two-particle correlations alone gives a very high depolarization coefficient that is comparable with the depolarization coefficient in a system of nonspherical particles. To account for the three- and four-particle as well as two-particle correlations amounts to treating more symmetrical states of the medium, and it considerably diminishes the final value of the scattering cross-section. Hence, local-field fluctuations can per se make quite a substantial contribution to the scattering cross-section that is comparable with that from the fluctuations of density and orientation that are described by the parameter Q_1. In a system of nonspherical particles, owing to the non-central nature of the intermolecular

interactions, the many-particle distributions can no longer be so symmetrical as in a system of point particles. Hence it is quite probable that precisely the parameter Q_2 is responsible for the broad line in the spectrum of the scattered light. There are experimental estimates that indicate that the integral intensity of the broad line amounts to 0.2–0.5 of the intensity of the narrow line.[143]

The spectrum of the scattered light that is obtained from the relaxation theory with two "optically active" parameters is under certain assumptions close to a sum of Lorentzian curves.[128] Levine and Birnbaum[96] have calculated the spectrum of the light scattered by a system of spherical particles with account taken of polarizability fluctuations.[96] The excess fraction of the polarizability was assumed to be exponentially dependent on the square of the interparticle distance,[144] while the motion of the particles was assumed to be rectilinear. An analogous calculation of the scattered-light spectrum has been performed in[97], but here they treated fluctuations of the local field to an accuracy of quantities that are described by the part of the parameter Q_2 that is quadratic in α, rather than treating the polarizability fluctuations of the particles. As we should expect for a model of two-particle collisions, in both cases the integral intensity of the scattered light is proportional to the square of the density. The spectral intensity proved to be approximately exponential:[75]

$$I(\omega) \sim f(\omega) \exp(-\omega/\omega_0) \quad (\omega > \omega_0), \tag{78}$$

Here $f(\omega)$ is a function that depends weakly on the frequency. An attempt was made in[99] to account for the correlations between the perturbations of polarizability in successive collisions of the particles.

Experimental studies[12,13,71-79] have shown that the exponential form of the spectrum is maintained at any density, but the integral intensity of the scattered light is proportional to the square of the density only for gases that are not very dense ($\rho < 0.4$ g/cm^3). We can assuredly state on the basis of[140,141] that the decrease in intensity of the scattered light at high densities involves the increasing contribution to the scattering cross-section of three- and four-particle correlations.

The characteristic parameter in (78) that determines the width of the spectrum of scattered light is the quantity ω_0. For gases, ω_0 varies over the range 7–10 cm^{-1}, but on transition to a liquid phase, it increases up to ~ 20 cm^{-1}. In order to elucidate the nature of this increase in the width of the spectrum, Volterra, Bucaro, and Litovitz[77] measured the density-dependence of the intensity of scattered light at frequency shifts of 10 and 105 cm^{-1}. It turned out that at $\omega = 10$ cm^{-1} the intensity varies more slowly than the square of the density. However, at $\omega = 105$ cm^{-1} it was proportional to the square of the density. This is explained by the fact that the effect of fluctuations of the local field is manifested at great distances, and even at low densities, many-particle correlations begin to exert an effect. On the other hand, the fraction of the polarizability fluctuations of the particles that Levine and Birnbaum studied differs from zero only at small interparticle distances, and here the many particle correlations are not substantial up to appreciably higher densities. The fluctuations of the local field are slower than those of the polarizability of the particles. This leads ultimately to a considerable broadening of the line of the scattered light in a liquid as compared with its width in a gas.

Thus, study of depolarized light scattering in systems of optically isotropic particles permits one to draw some conclusions also on light scattering in systems consisting of nonspherical molecules. There are data in the literature that indicate that the shape of the outer region of the scattered-light spectrum perhaps is close to exponential even when the molecules of the liquid are not optically isotropic.[145,146] Apparently the mechanisms treated above are very important in the formation of the broad line in the scattered-light spectrum: the fluctuations of the local field and those of the polarizability of the particles. Both of these mechanisms can be accounted for by the parameter Q_2.

4. CONCLUSION

The phenomenological relaxation theory with two "optically active" parameters basically gives a correct description of the depolarized components of scattered light over a broad spectral range. We should expect the best agreement with the experimental data in describing the fine structure and the close region of the tail of the Rayleigh line in liquids of low viscosity. A broad experimental test of the simplified expression (70) and the general formula (16) is needed. It would permit us to elucidate to what extent and within what limits the concepts of the relaxation theory that takes account of only two relaxation processes are suitable for describing the non-equilibrium properties of matter. In order to elucidate the stated problems, further experimental study of transverse hypersound in liquids of low viscosity seems important, as well as comparison of the data of optical and acoustic measurements based on relaxation theory.

The relaxation theory in the existing variant explains at least qualitatively the existence of the broad background and the data that exist on depolarized light scattering in liquids in the range of shear viscosity from 10^{-2} to 10^9 poises. However, the details of the structure of the broad background and of the scattered-light spectrum in highly-viscous liquids apparently do not agree well enough with the theoretical predictions. As we know, a correct description of the propagation of longitudinal sound in highly-viscous liquids has required the use of a more complex relaxation mechanism. An analogous situation inevitably arises also in explaining the features of structure of the broad background, for whose existence processes are responsible that develop in very short (kinetic) intervals of time. In this regard, apparently, we must alter the concept of the nature of the relaxation mechanism. A number of experimental studies have noted that the spectrum in the outer region of the tail of the Rayleigh line resembles an exponential frequency-dependence more than it does a Lorentzian curve form. An exponential form of spectrum arises from certain models of the relaxation process.

The achievements of the statistical theory of molecular light scattering are highly significant. The most important success of the theory has been the representation of the scattering cross-section in terms of a set of correlation functions of one-, two-, and many-particle operators. This has made it possible to interpret on the molecular level the internal parameters that are introduced by the phenomenological theory, and to apply effective statistical methods for deriving the relaxation equations for them.

Nevertheless, many problems of the statistical theory still require further development. The stumbling block

continues to be the quantum-mechanical problem of finding the polarizability fluctuations of the system of molecules. The small number of studies in which the polarizability of the system has been expanded in a series in the particle functions have been noted in Sec. b of Chap. 3 of this review, but the convergence of this expansion has not been studied at all. Also, the calculation of the correlation function of the polarizability fluctuations is an essentially statistical problem. Even here the positive results involve expansion in terms of the particle functions. One must overcome special difficulties in concrete calculation of the particle correlation functions. At present, more or less reliable estimates of the two-particle static (and in some cases also the temporal) correlation functions have been obtained. However, we should not consider the existing estimates for the many-particle correlation functions to be well enough grounded. Yet it seems indubitable that, in spite of great difficulties, it is precisely the statistical theory that will permit us to reveal deeper relations between the spectrum of the scattered light and the molecular structure and kinetics of the material.

[1)]In this review we use everywhere the angular-differential scattering cross-section, but this is not stipulated specifically anywhere.
[2)]We shall denote as relaxation equations or equations of relaxational type those that contain only time derivatives of the internal parameters, and mainly, linear equations like (12). We shall also use such expressions as the mechanism of relaxation, relaxation process, and relaxation equations, when we are referring to an arbitrary process of establishment of equilibrium.
[3)]S. M. Rytov has proposed calling them the "optically passive" parameters, so as to avoid the term "optically inactive," which is usually used in a completely different sense.
[4)]All formulas in this section are written in the k-representation.
[5)]One can find a discussion of the problems involved in determining the matrix $\phi(t)$ in [27,117,129]. Studies to be cited below give more exact expressions for the coefficients used in this review.
[6)]The first acoustic measurements of the speed of propagation of transverse hypersound in liquids have recently appeared [134,135].

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