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THE POLARIZATION PROPERTIES OF LIGHT SPONTANEOUSLY SCATTERED IN A LIQUID (PHENOMENOLOGICAL ANALYSIS)

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The polarization structure of the double differential (with respect to angle and frequency) of the cross section for spontaneous scattering of light in a liquid is considered. In the general case the cross section is defined by six functions of the frequency shift $\delta\omega$ and of the change in the photon wave vector on scattering $q = [k_1 - k_2]$. For a medium which is invariant under the space inversion five functions are involved. A set of experiments which permit one to determine all these functions is indicated. The analysis is also necessary for describing spontaneous scattering of light in gases, although in a comparatively narrow pressure range: for $ql \sim 1$, where l is the mean free path of the molecules.

1. INTRODUCTION

IN the problem of molecular scattering of light in liquids, the main quantity to be theoretically calculated from the microscopic theory and to be measured in experiments on light scattering is the fourth-rank tensor

$$T_{iklm}(\delta\omega, \mathbf{q}) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\tau \int d^3\mathbf{r}\, e^{i\delta\omega\tau - i\mathbf{q}\mathbf{r}} \langle \delta\varepsilon_{ik}(\mathbf{R}, t)\, \delta\varepsilon_{lm}(\mathbf{R} + \mathbf{r}, t + \tau)\rangle. \tag{1}$$

Here $\delta\epsilon_{ik}(r, t)$ is the fluctuation of the dielectric tensor of the medium at a point r and at the instant of time t, and the angle brackets denote averaging over the statistical ensemble of the fluctuations. We assume that there is no absorption of light and that $\delta\epsilon_{ik} = \delta\epsilon^*_{ik} = \delta\epsilon_{ki}$ (i.e., we neglect scattering of the antisymmetrical type). If the fluctuations must be considered quantum-theoretically (for example, at low temperatures: $kT \lesssim \hbar\delta\omega$), the quantities $\delta\hat{\epsilon}_{ik} = \delta\hat{\epsilon}_{ki}$ must be regarded as Hermitian operators at each value of the indices k and i. The differential cross section for the scattering of an incident wave of frequency ω_1, wave vector $\mathbf{k}_1$, and electric-field polarization unit vector $\mathbf{e}_1$ (where $\mathbf{e}_1 \cdot \mathbf{e}_1^* = 1$) to form a wave with frequency $\omega_2 = \omega_1 - \delta\omega$, wave vector $\mathbf{k}_2 = \mathbf{k}_1 - \mathbf{q}$, and polarization $\mathbf{e}_2$, for a unit volume of the scattering medium, is given by

$$\frac{d^2R}{do\, d\omega} = \left(\frac{\omega_2}{c}\right)^4 \frac{1}{(4\pi)^2} M(\delta\omega, \mathbf{q}, \mathbf{e}_1, \mathbf{e}_2) \equiv \left(\frac{\omega_2}{c}\right)^4 \frac{1}{(4\pi)^2} T_{iklm}(\delta\omega, \mathbf{q})\, e_{2i}\, e_{1k}^*\, e_{2l}^*\, e_{1m}. \tag{2}$$

This paper deals with the dependence of the scattering cross section on the polarizations of the incident and scattered radiation and on the direction of the wave vector q transferred to the medium by scattering. The unit vector characterizing this direction is

$$\mathbf{n} = \frac{\mathbf{q}}{|\mathbf{q}|} = \frac{\mathbf{k}_1 - \mathbf{k}_2}{|\mathbf{k}_1 - \mathbf{k}_2|} \approx \frac{\mathbf{n}_1 - \mathbf{n}_2}{|\mathbf{n}_1 - \mathbf{n}_2|}. \tag{3}$$

(The last equation is written under the assumption that the frequency shift $|\delta\omega|$ due to scattering is much smaller than the light frequency ω_1 itself.) The analysis is phenomenological, without any concrete assumptions concerning the properties of the liquid.

2. FREQUENCY-INTEGRATED SCATTERING CROSS SECTION

In this section we introduce a number of symbols pertaining to a well-studied quantity, the scattering cross section integrated with respect to the frequency (see, e.g.,[1-3]). These symbols will be useful in the discussions of the results of Secs. 3 and 4. To calculate the frequency-integrated cross section it suffices to integrate (2) with respect to the frequency. Assuming approximately that $(\omega_1 - \delta\omega)^4 \approx \omega_1^4$, we find from (1) that the scattering cross section is determined by a correlator of the type

$$\int d^3\mathbf{r}\, \langle \delta\varepsilon_{ik}(\mathbf{R}, t)\, \delta\varepsilon_{lm}(\mathbf{R} + \mathbf{r}, t)\rangle\, e^{-i\mathbf{q}\mathbf{r}}. \tag{4}$$

For ordinary liquids far from the critical point, the correlator of the quantities $\delta\epsilon$, at equal times, differs from zero only over distances on the order of the molecule dimension a. Neglecting the quantities $-qa \lesssim 4\pi a/\lambda$, we find that the frequency-integrated scattering cross section does not depend at all on q (and by the same token on n), and its polarization dependence takes the form of a sum of terms connected with the scalar part of $\delta\epsilon_{ik}$ and the symmetrical part with zero trace:

$$\int M(\delta\omega, \mathbf{q}, \mathbf{e}_1, \mathbf{e}_2)\, d\delta\omega = G_{\text{scal}}|\mathbf{e}_1\mathbf{e}_2^*|^2 + G_{\text{symm}}[1 + |\mathbf{e}_1\mathbf{e}_2|^2 - {}^2/_3|\mathbf{e}_1\mathbf{e}_2^*|^2]. \tag{5}$$

This means that from the phenomenological point of view the frequency-integrated cross section with all its polarization structure is characterized by only two numbers, G_{scal} and G_{symm}. Two functions of the frequency do not suffice to determine this cross section, in view of the appearance of the additional vector q in the problem. The same pertains also to the frequency-integrated scattering cross section in the case of anomalously large correlation radii ($r_{corr} \gtrsim q^{-1}$), for example for liquid crystals[1].

3. POLARIZATION STRUCTURE OF FREQUENCY-DIFFERENTIATED SCATTERING CROSS SECTION

In the presence of a vector $q \neq 0$, the tensor $T_{ik l m}$ defined by formula (1) can contain not only structures of the type $\delta_{ik}\delta_{lm}$, $\delta_{il}\delta_{km}$, etc., but also expressions of the type $\delta_{ik}n_l n_m$ etc. To find the most general form of the tensor T_{iklm} it is necessary to consider the symmetry group of the problem (the group of rotations about the n axis) and expand the fluctuation $\delta\epsilon_{ik}$ in the irreducible representations of this group. We choose the z axis in the direction of the vector n. Then the irreducible parts of $\delta\epsilon_{ik}$ then include two scalar representations, $\delta\epsilon_{zz}$ and $(\delta\epsilon_{xx} + \delta\epsilon_{yy})$, one vector representation $(\delta\epsilon_{zx}, \delta\epsilon_{zy})$, and one tensor representation: a symmetrical tensor with zero two-dimensional trace $(\delta\epsilon_{xy}, (\delta\epsilon_{xx} - \delta\epsilon_{yy})/2$. It is possible to make up from the scalar representations any linear combination to obtain new scalar representations. We make use of this possibility to separate two scalar (with respect to rotations about the n axis) quantities of the type

$$S_1 = {}^1/_3(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \equiv {}^1/_3\varepsilon_{tt}, \tag{6}$$

$$S_2 = {}^1/_6(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}) \equiv {}^1/_6\varepsilon_{tt} - {}^1/_2\varepsilon_{pt}n_p n_t; \tag{7}$$

we shall henceforth omit the δ in the designation of the fluctuation $\delta\epsilon_{ik}$. The vector part of ϵ_{ik} is conveniently written in the following three-dimensional form:

$$(\varepsilon_{ik})_{\text{vect}} = V_i n_k + V_k n_i, \qquad V_i = \varepsilon_{ip}n_p - n_i\varepsilon_{pt}n_p n_t. \tag{8}$$

The final expansion of ϵ_{ik} into irreducible part takes the form[2]

$$\varepsilon_{ik} = S_1\delta_{ik} + S_2(\delta_{ik} - 3n_i n_k) + V_i n_k + V_k n_i + \tilde{\varepsilon}_{ik}, \tag{9}$$

where $\tilde{\epsilon}_{ik}$ corresponds to a symmetrical tensor in two-dimensional space (x, y) with zero trace.

As a result of the averaging over the ensemble of fluctuations, a nonzero contribution to the tensor T_{iklm} is made only by a product of contributions from irreducible representations of one and the same type. In the concrete calculation of the correlators it must be taken into account that the invariance of the properties of the medium against time reversal leads to the inequality

$$\langle S_1(t)S_2(t+\tau)\rangle = \langle S_2(t)S_1(t+\tau)\rangle. \tag{10}$$

In addition, a correlator of the type $\langle V_i V_k \rangle$ is equal in the general case to

$$\langle V_i(t)V_k(t+\tau)\rangle = c_4(\tau)(\delta_{ik} - n_i n_k) + c_7(\tau)e_{ikl}n_l, \tag{11}$$

where e_{ikl} is a unit antisymmetrical tensor, and the correlator $\langle \tilde{\epsilon}_{ik}\tilde{\epsilon}_{lm} \rangle$ is equal to

$$\langle \tilde{\varepsilon}_{ik}(t)\tilde{\varepsilon}_{lm}(t+\tau)\rangle = c_5(\tau)[\delta_{il}^{(2)}\delta_{km}^{(2)} + \delta_{im}^{(2)}\delta_{kl}^{(2)} - \delta_{ik}^{(2)}\delta_{lm}^{(2)}] + c_6(\tau)[e_{ilp}n_p\delta_{km}^{(2)}$$
$$+ e_{imp}n_p\delta_{kl}^{(2)} + e_{klp}n_p\delta_{im}^{(2)} + e_{kmp}n_p\delta_{il}^{(2)}], \tag{12}$$

where we have introduced the notation $\delta_{ik}^{(2)} = \delta_{ik} - n_i n_k$. The functions $c_6(\tau)$ and $c_7(\tau)$ are pseudoscalars and differ from zero only when the medium is invariant against space inversion (for example, a mixture of right- and left-hand molecules in different proportions).

Taking (8)--(12) into account, we can obtain the following expression for the dependence of the cross section for spontaneous scattering on the polarizations $\mathbf{e}_1$ and $\mathbf{e}_2$ and on the direction of the vector $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$:

$$M(\delta\omega, \mathbf{q}, \mathbf{e}_1, \mathbf{e}_2) = M_1|\mathbf{e}_1\mathbf{e}_2^*|^2 + M_2\{(\mathbf{e}_1\mathbf{e}_2^*)[(\mathbf{e}_1^*\mathbf{e}_2) - 3(\mathbf{e}_1^*\mathbf{n})(\mathbf{e}_2\mathbf{n})]$$
$$+ (\mathbf{e}_1^*\mathbf{e}_2)[(\mathbf{e}_2^*\mathbf{e}_1 - 3(\mathbf{e}_2^*\mathbf{n})(\mathbf{e}_1\mathbf{n})]\}$$
$$+ M_3|(\mathbf{e}_1\mathbf{e}_2^*) - 3(\mathbf{e}_1\mathbf{n})\ (\mathbf{e}_2^*\mathbf{n})|^2 + M_4\{\mathbf{a}_1(\mathbf{e}_2\mathbf{n}) + \mathbf{a}_2(\mathbf{e}_1\mathbf{n})\}\ \{\mathbf{a}_1^*(\mathbf{e}_2^*\mathbf{n})$$
$$+ \mathbf{a}_2^*(\mathbf{e}_1\mathbf{n})\} + M_5\{(\mathbf{a}_1\mathbf{a}_1^*)(\mathbf{a}_2\mathbf{a}_2^*) + |\mathbf{a}_1\mathbf{a}_2|^2 - |\mathbf{a}_1\mathbf{a}_2^*|^2\}$$
$$+ M_6 i\{\mathbf{n}[\mathbf{e}_2\mathbf{e}_2^*](\mathbf{a}_1\mathbf{a}_1^*) + \mathbf{n}[\mathbf{e}_1^*\mathbf{e}_1](\mathbf{a}_2\mathbf{a}_2^*) + \mathbf{n}[\mathbf{e}_2\mathbf{e}_1](\mathbf{a}_1^*\mathbf{a}_2^*)$$
$$+ \mathbf{n}[\mathbf{e}_1^*\mathbf{e}_2^*](\mathbf{a}_1\mathbf{a}_2)\} + M_7 i\{\mathbf{n}[\mathbf{e}_2\mathbf{e}_2^*](\mathbf{n}\mathbf{e}_1)(\mathbf{n}\mathbf{e}_1^*) + \mathbf{n}[\mathbf{e}_1^*\mathbf{e}_2^*](\mathbf{n}\mathbf{e}_1)(\mathbf{n}\mathbf{e}_2)$$
$$+ \mathbf{n}[\mathbf{e}_2\mathbf{e}_1](\mathbf{n}\mathbf{e}_1^*)(\mathbf{n}\mathbf{e}_2^*) + \mathbf{n}[\mathbf{e}_1^*\mathbf{e}_1](\mathbf{n}\mathbf{e}_2)(\mathbf{n}\mathbf{e}_2^*)\}. \tag{13}$$

In formula (13), the functions $M_1, \ldots, M_7$ are scalar functions of scalar arguments: $M_\alpha = M_\alpha(\delta\omega, |\mathbf{q}|)$ and does not depend on the vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{n}$. In addition, to shorten the notation we have introduced in (13) the symbol

$$\mathbf{a}_{1,2} = \mathbf{e}_{1,2} - \mathbf{n}(\mathbf{e}_{1,2}\mathbf{n}). \tag{14}$$

The following important remark should be made concerning the general expression (13). In the derivation of (13), no use is made of the transversality of the electromagnetic waves in the incident and scattered radiation:

$$(\mathbf{e}_1\mathbf{n}) = 0, \quad (\mathbf{e}_2\mathbf{n}) = 0. \tag{15}$$

On the other hand, if (15) is taken into account and it is recognized that $\mathbf{n} = (\mathbf{n}_1 - \mathbf{n}_2)/|\mathbf{n}_1 - \mathbf{n}_2|$, then the coefficient of M_7, made up of the vectors $\mathbf{n}$, $\mathbf{e}$, and $\mathbf{e}_2$, turns out to be identically equal to zero. The term proportional to M_7 can therefore be disregarded (this term stems from the pseudoscalar part of the correlator (11)).

The functions $M_\alpha(\delta\omega, |\mathbf{q}|)$ are defined by the following equations:

$$M_\alpha(\delta\omega, |\mathbf{q}|) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\tau\, e^{i\delta\omega\tau} \int d^3\mathbf{r}\, e^{-i\mathbf{q}\mathbf{r}}\,\Phi_\alpha(\mathbf{r}, \tau), \tag{16}$$

where

$$\Phi_1 = {}^1/_9\langle\varepsilon_{ss}(0)\varepsilon_{ll}(\mathbf{r}, \tau)\rangle, \tag{17.1}$$

$$\Phi_2 = {}^1/_{18}\langle\varepsilon_{ss}(0)(\varepsilon_{ll}(\mathbf{r}, \tau) - 3\varepsilon_{lm}(\mathbf{r}, \tau)n_l n_m)\rangle, \tag{17.2}$$

$$\Phi_3 = {}^1/_{36}\langle(\varepsilon_{ss}(0) - 3\varepsilon_{su}(0)n_s n_u)(\varepsilon_{ll}(\mathbf{r}, \tau) - 3\varepsilon_{lm}(\mathbf{r}, \tau)n_l n_m)\rangle, \tag{17.3}$$

$$\Phi_4 = {}^1/_2\langle V_p(0)V_p(\mathbf{r}, \tau)\rangle \equiv \langle\varepsilon_{xz}(0)\varepsilon_{xz}(\mathbf{r}, \tau)\rangle, \tag{17.4}$$

$$\Phi_5 = \langle\varepsilon_{xy}(0)\varepsilon_{xy}(\mathbf{r}, \tau)\rangle, \tag{17.5}$$

$$\Phi_6 = -\frac{i}{2}\left\langle\varepsilon_{xy}(0)\,\frac{\varepsilon_{xx}(\mathbf{r}, \tau) - \varepsilon_{yy}(\mathbf{r}, \tau)}{2}\right\rangle, \tag{17.6}$$

$$\Phi_7 = -i\langle\varepsilon_{xz}(0)\varepsilon_{yz}(\mathbf{r}, \tau)\rangle. \tag{17.7}$$

The expressions for the functions $\Phi_4 - \Phi_7$ are given

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[1] In the case of light scattering near the liquid-vapor critical point, the anomalous fluctuations occur in a scalar quantity, the density. The polarization dependence of the scattering cross section is therefore of the scalar type, and the cross section itself depends only on $|\mathbf{q}|$ and not on its direction $\mathbf{n}$.

[2] We note that an expansion of this type was used already by M. A. Lentovich in his paper on the theory of the spectral composition of the depolarized part of Rayleigh scattering.

here in a coordinate system in which the z axis is directed along n. (These functions are scalars and the no explicit invariant forms are written out for $\Phi_5 - \Phi_7$ only because they are too cumbersome.) The functions M_α defined by (16) and (17) turn out to be real; in addition, if the fluctuations can be described classically (i.e., if $\hbar\delta\omega \ll kT$), then they are even functions of the frequency. The functions M_α, $\alpha = 1, 3, 4, 5$ are non-negative:

$$M_1 \geqslant 0, \quad M_3 \geqslant 0, \quad M_4 \geqslant 0, \quad M_5 \geqslant 0, \tag{18}$$

and the functions M_α, $\alpha = 2, 6, 7$, satisfy the inequalities

$$|M_2| \leqslant \sqrt{M_1 M_3}, \quad |M_6| \leqslant M_5, \quad |M_7| \leqslant M_4. \tag{19}$$

If the radius of the equal-time correlation r_{corr} satisfies the inequality $r_{\text{corr}} \ll q^{-1}$, then the integrals of the functions M_α with respect to frequency are given by the following equations:

$$\int M_1(\delta\omega, |\mathbf{q}|)\,d\delta\omega = G_{\text{scal}}, \tag{20.1}$$

$$3\int M_3 d\delta\omega = \int M_4 d\delta\omega = \int M_5 d\delta\omega = G_{\text{symm}}, \tag{20.2}$$

$$\int M_2 d\delta\omega = \int M_6 d\delta\omega = \int M_7 d\delta\omega = 0, \tag{20.3}$$

and we obtain formula (5) for the cross section integrated over the frequency.

For a gas of non-interacting molecules we must put

$$M_2 = M_6 = M_7 = 0, \quad 3M_3 = M_4 = M_5 = F_{\text{symm}}(\delta\omega, |\mathbf{q}|),$$
$$M_1 = F_{\text{scal}}(\delta\omega, |\mathbf{q}|).$$

It is precisely in this approximation that one constructs usually the theory of Raman scattering of light, in which the transfer of vibrational excitation from molecule to molecule can be neglected.

4. POSSIBILITY OF DETERMINING THE FUNCTIONS $M_1, \ldots, M_6$ FROM LIGHT-SCATTERING EXPERIMENTS

Let us see what experiments on light scattering must be performed to measure the complete set of functions $M_\alpha(\delta\omega, |\mathbf{q}|)$, $\alpha = 1, \ldots, 6$. To this end, we write down the polarization unit vectors of the incident and scattered waves in the form

$$\mathbf{e}_1 = \sqrt{\frac{2}{1+\beta}}(\mathbf{n} - \mathbf{n}_1(\mathbf{n}\mathbf{n}_1))\sin\frac{\psi_1}{2} + \frac{1}{\sqrt{1-\beta^2}}[\mathbf{n}_1\mathbf{n}_2]e^{i\varphi_1}\cos\frac{\psi_1}{2}, \tag{21.1}$$

$$\mathbf{e}_2 = \sqrt{\frac{2}{1+\beta}}(\mathbf{n} - \mathbf{n}_2(\mathbf{n}\mathbf{n}_2))\sin\frac{\psi_2}{2} + \frac{1}{\sqrt{1-\beta^2}}[\mathbf{n}_1\mathbf{n}_2]e^{i\varphi_2}\cos\frac{\psi_2}{2}. \tag{21.2}$$

Formulas (21) allow us to describe light of arbitrary elliptical polarization, and contain explicitly the transversality condition (15). We have introduced here the notation

$$\beta = \mathbf{n}_1\mathbf{n}_2 = \cos\theta, \tag{22}$$

where θ is the scattering angle. Substitution of (21) in (13) yields

$$\begin{aligned}
&M(\delta\omega, \mathbf{q}, \mathbf{e}_1, \mathbf{e}_2)\\
&= {}^1\!/_4 M_1\{(1+\beta^2) + (1-\beta^2)(\cos\psi_1 + \cos\psi_2)\\
&+ (1+\beta^2)\cos\psi_1\cos\psi_2 + 2\beta\sin\psi_1\sin\psi_2\cos(\varphi_1 - \varphi_2)\}\\
&+ {}^1\!/_4 M_2\{(2-3\beta-\beta^2) + (2+3\beta+\beta^2)(\cos\psi_1 + \cos\psi_2)\\
&+ (2-3\beta-\beta^2)\cos\psi_1\cos\psi_2 + (\beta-3)\sin\psi_1\sin\psi_2\cos(\varphi_1-\varphi_2)\}\\
&+ {}^1\!/_{16} M_3\{(13+6\beta+\beta^2) - (5+6\beta+\beta^2)(\cos\psi_1+\cos\psi_2)\\
&+ (13+6\beta+\beta^2)\cos\psi_1\cos\psi_2 - 4(3+\beta)\sin\psi_1\sin\psi_2\cos(\varphi_1-\varphi_2)\}\\
&+ {}^1\!/_4 M_4(1+\beta)\{1 - \cos\psi_1\cos\psi_2 + \sin\psi_1\sin\psi_2\cos(\varphi_1+\varphi_2)\}\\
&+ {}^1\!/_{16} M_5\{(9-6\beta+\beta^2) + (3-\beta)(1+\beta)(\cos\psi_1+\cos\psi_2)\\
&+ (1+2\beta+\beta^2)\cos\psi_1\cos\psi_2 +\\
&+ 4(1-\beta)\sin\psi_1\sin\psi_2[\cos(\varphi_1-\varphi_2) - \cos(\varphi_1+\varphi_2)]\}\\
&+ 2^{-3/2}M_6(1-\beta)^{1/2}\{\sin\psi_1\sin\varphi_1[(3-\beta) + (1+\beta)\cos\psi_2]\\
&+ \sin\psi_2\sin\varphi_2[(3-\beta) + (1+\beta)\cos\psi_1]\} + M_7\cdot 0.
\end{aligned} \tag{23}$$

We note first that when plane-polarized incident light is used and one registers the component of the scattered light with the same polarization, the coefficient of the pseudoscalar term M_6 vanishes (since, in our notation, $\varphi_1 = 0$ and $\varphi_2 = 0$ for plane-polarized light).

It follows also from (23) that the results of measurement with arbitrary plane polarization, given the values of $|\mathbf{q}|$ and $\delta\omega$, are expressed in terms of only four linearly-independent combinations of the numbers M_1, M_2, M_3, M_4, and M_5 (their explicit form is immaterial in what follows). To determine experimentally these linear combinations (and by the same token to be able to predict the results of arbitrary experiments in which plane-polarized incident and scattered light is used) it suffices to carry out four essentially independent measurements; for example, the following set of experiments will suffice:

$$\begin{gathered}
\varphi_1 = \varphi_2 = 0,\\
(\psi_1 = 0,\ \psi_2 = 0), \quad (\psi_1 = 0,\ \psi_2 = \pi), \quad (\psi_1 = \pi,\ \psi_2 = \pi),\\
(\psi_1 = \pi/2,\ \psi_2 = \pi/2).
\end{gathered} \tag{24}$$

To determine all five scalars $M_1, \ldots, M_5$ it suffices to add to the set (24) a measurement of the scattering cross section, for example for right-circularly polarized incident and left-circularly polarized scattered radiation (R – L):

$$(\psi_1 = \pi/2,\ \varphi_1 = \pi/2,\ \psi_2 = \pi/2,\ \varphi_2 = -\pi/2) \tag{25}$$

(the letters R and L left will denote right- and left-circularly polarized radiation, respectively). We note that the pseudoscalar term $\sim M_6$ makes likewise no contribution to the scattering cross section measured in the experiment (25).

From the formal point of view, the determination of the pseudoscalar M_6 requires one more experiment, for example, measurement of a cross section of the (R → R) type, i.e.,

$$(\psi_1 = \pi/2,\ \varphi_1 = \pi/2,\ \psi_2 = \pi/2,\ \varphi_2 = \pi/2). \tag{26}$$

If we are interested just in the pseudoscalar M_6 and are not interested in the remaining quantities $M_1, \ldots, M_5$, then two experiments suffice instead of six. Namely, M_6 is proportional to the difference of the scattering intensities in the experiments (R → R) and (L → L):

$$M_6 \propto M(\psi_1 = \psi_2 = \varphi_1 = \varphi_2 = \pi/2) - M(\psi_1 = \psi_2 = \pi/2,\ \varphi_1 = \varphi_2 = -\pi/2). \tag{27}$$

We must make here one essential stipulation. All the formulas written out so far are based implicitly on the assumption that the refractive index of the liquid (or the wave vector of the light in the liquid) does not

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*$[\mathbf{n}_1\mathbf{n}_2] \equiv \mathbf{n}_1 \times \mathbf{n}_2$.

depend on the state of polarization. It is however precisely in media that are invariant against inversions, the only ones in which $M_6 \neq 0$ can occur, that definite wave vectors are possessed only by right- and left-circularly polarized waves, owing to the natural optical activity. For this reason, when molecular scattering of light is observed from sufficiently large volumes (with linear dimensions noticeably larger than the reciprocal constant of optical rotation), only experiments with circularly polarized incident and scattering light are possible.

It follows from (23) that the (R → L) and (L → R) cross section are equal to each other and do not depend on M_6. On the other hand, the difference between the (R → R) and (L → L) scattering cross sections yields a quantity proportional to the pseudoscalar $M_6(\delta\omega, |q|)$. We note that the (R → R) and (L → L) scattering cross section should be measured at slightly different scattering angles[3] in order that the arguments $|q|$ in the functions $M_\alpha(\delta\omega, |q|)$ be the same in both experiments.

The set of experiments (24)—(26) considered above is "complete" (i.e., it makes it possible to determine all six functions) at any scattering angle, with the exception of the cases $\theta = 0°$ and $\theta = 180°$. In particular, this set is "complete" for $\theta = 90°$, the parameter β from formulas (21)—(23) vanishes, and the formulas themselves assume a simpler form. We present here expressions for the complete set of experiments (24)—(26) in the notation used by Fabelinskiĭ in[3] for polarization measurements of spontaneous scattering of light at $\theta = 90°$:

$$I_{zz},\quad I_{zx} \equiv I_{yz},\quad I_{yx},\quad I_{45,\,45}; \tag{24a}$$

$$I_{\mathrm{RL}}; \tag{25a}$$

$$I_{\mathrm{RR}}. \tag{26a}$$

The first subscript in I_{ik} denotes here the polarization of the electric vector of the incident light, and the second the same for scattered light. It is assumed here that the incident radiation propagates in the positive x direction, and the scattered light in the negative y direction (see the figure). The subscript 45 denotes plane polarization inclined at an angle 45° to the scattering plane, and the subscripts R and L stand for right and left circular polarizations.

5. RELAXATION THEORY OF SPONTANEOUS SCATTERING OF LIGHT IN A LIQUID

We present a concrete example of the application of the formulas derived above. In the relaxation model of spontaneous scattering of light in a liquid, the functions $M_\alpha(\delta\omega, |q|$ $(\alpha = 1, \ldots, 5)$ are proportional to the functions $S_{\mathcal{E}}$, $S_\Phi + S_{\mathcal{E}\Phi}/3\mu\beta$, S_Φ, S_T, S_A, calculated in[4] (see also[3], Sec. 6). In the Leontovich notation, the following equations hold:

$$M_1(\delta\omega, q) = C\beta\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)^2 S_{\mathcal{E}}(\delta\omega, q), \tag{28}$$

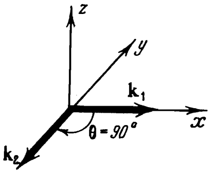
$$M_2(\delta\omega, q) = \frac{C}{2}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)A\left\{\frac{1}{2}\beta S_{\Phi\mathcal{E}}(\delta\omega, q) + \frac{1}{6\mu}S_{\mathcal{E}\Phi}(\delta\omega, q)\right\},$$

$$M_3(\delta\omega, q) = C\frac{A^2 S_\Phi(\delta\omega, q)}{12\mu},\quad M_4(\delta\omega, q) = C\frac{A^2 S_T(\delta\omega, q)}{4\mu},$$

$$M_5(\delta\omega, q) = C\frac{A^2 S_A(\delta\omega, q)}{4\mu},\quad M_6(\delta\omega, q) = 0.$$

The vanishing of the function M_6 is caused by the fact that in[3,4] the medium was implicitly assumed to be invariant against the inversion transformation. The explicit form of the functions $S_i(\delta\omega, q)$ is given in[3,4].

Thus, organization of the complete experiment (24) and (25) makes it possible (in principle) not only to measure definite combinations of the indicated functions (I_{zz}, I_{zx}, I_{yx}, which have been measured so far in most experiments), but also to determine each of the functions $M_\alpha(\delta\omega, q)$ separately. Of course, the question of the required experimental accuracy should be answered separately in each case.



6. RAYLEIGH SCATTERING OF LIGHT IN A GAS

The analysis given in Sec. 3 is in most cases too general for scattering of light in gases, and the number of essentially independent functions is equal to two.

Let us consider first in fact the limiting case of highly rarefied gases (or of large values of q), when $ql \gg 1$, where l is the molecule mean free path. In this case the form of the spectrum is the same for all the components of the scattered light: for the scalar part, for scattering by anisotropy fluctuations, and for lines of rotational Raman scattering[4]; this form corresponds to the Doppler curve

$$g(\omega - \omega_i) \sim \exp\{-m(\omega - \omega_i)^2/2q^2kT\}. \tag{29}$$

The anisotropy relaxation, the change of the molecule-velocity vector, and the transition to another rotational level all occur within a time on the order of the time between collisions $\tau_{\mathrm{col}} \sim l/v_T \sim (N\sigma v_T)^{-1}$, where N is the number of molecules per unit volume, σ the collision cross section, and $v_T \sim \sqrt{kT/m}$ the thermal velocity of the molecules. When $ql \gg 1$, therefore, the Doppler width $\delta\omega_{\mathrm{Dop}} \sim qv_T$ turns out to be much larger than the "relaxation" width $\delta\omega_{\mathrm{rel}} \sim \tau_{\mathrm{col}}^{-1} \sim l^{-1}v_T$. Thus, at $ql \gg 1$ the collisions play no role whatever in the formation of the spectrum. Nor do they influence at $ql \gg 1$ the polarization structure; the latter can therefore be described by two functions of the frequency, corresponding to the symmetrical and scalar parts of the scattering.

In the case $ql \ll 1$, the anisotropy relaxation and the transitions between the relaxational levels occur as before within a time τ_{rel} of the order of the free-path time; $\tau_{\mathrm{rel}} \sim v_T^{-1}l$. The corresponding width of the anisotropic (symmetrical) part of the scattering $\delta\omega_{\mathrm{rel}} \sim l^{-1}v_T$ does not depend on q; the same pertains also

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[3] The resultant small change of the coefficients in (23), which depend on $\beta \equiv \cos\theta$, should be neglected together with the other effects, proportional to qa, which were discarded by us. At the same time, neglect of the difference in the argument $|q|$ in the functions $M_\alpha(\delta\omega, |q|)$ may not be permissible.

[4] See, e.g., [2], Sec. 96, concerning resolution into such components.

to the widths of the individual lines of the rotational Raman scattering. At the same time, the density fluctuations, corresponding to the Mandel'shtam-Brillouin doublet and to the entropy peak, result in scattering of the scalar type with width $\delta\omega_{\text{scal}} \sim qv_T \ll \delta\omega_{\text{rel}}$ (see also[5]). Thus when $ql \ll 1$ the polarization structure of the frequency-differentiated light-scattering cross section can be characterized also in the case $ql \ll 1$ by two functions of the frequency, corresponding to the symmetrical and scalar parts of the scattering.

When $ql \sim 1$, however, the form of the spectrum is determined by the joint action of the collisions both on the translational motion of the molecules and on their rotation and orientation. In the theory of broadening of emission lines, the region $ql \sim 1$, where the so-called collision narrowing of the Doppler contour begins, has been well investigated (see, e.g.,[6]).

In our case, an important role is played in the Doppler shift $\delta\omega = \mathbf{q}\cdot\mathbf{v}$ by the projection of the molecule velocity on the direction of the vector $\mathbf{q}$. At the same time, the molecule collision cross section depends on the orientation of its axes relative to the direction of the velocity vector $\mathbf{v}$. Taking this circumstance into account, and since the changes of the velocity and of the orientation occur at the same instants of time, namely the instants of collision (cf.[6]), different components of the anisotropy tensor (relative to the vector $\mathbf{q}$) will produce a different scattered-light spectrum. It is precisely in such a situation that we need the more general phenomenological analysis of the polarization structure, as given in Sec. 3.

Thus, for gases of anisotropic molecules, at $ql \sim 1$, the complete experiment discussed here on the polarization properties of spontaneously scattered light can yield information on the dependence of the cross section of the molecule collisions on the orientation.

7. CONCLUSION

We have examined above which quantities can be measured with the aid of spontaneous scattering of light in a liquid, and which independent measurements must be made to determine the complete set of functions $M_\alpha(\delta\omega, \mathbf{q})$, $\alpha = 1, \ldots, 6$. Such a set yields apparently the most complete information on the properties of molecular motion, obtainable from experiment on spontaneous scattering of light.

We note here one more aspect of the problem, one more closely connected with optics proper. We have tacitly assumed throughout that the frequency of the incident light is fixed and that variation of the argument $|\mathbf{q}|$ of the functions M_α is effected by varying the scattering angle. Simultaneous variation of both the frequency ω_1 and the scattering angle θ, subject to the condition

$$2\frac{\omega_1}{c}n(\omega_1)\sin\frac{\theta}{2} = |\mathbf{q}| = \text{const} \tag{30}$$

(where $n(\omega)$ is the refractive index), makes it possible to measure the values of the correlator (1) corresponding to fixed $|\mathbf{q}|$ and $\delta\omega$, but to different values of the frequency ω_1 on which the fluctuation of the dielectric tensor $\delta\epsilon_{ik}$ can depend as a parameter. This procedure can be used to investigate such problems as the dispersion of the optical axes of a molecule in a liquid, the connection between the effective field with the macroscopic field, etc. We emphasize that to this end it is necessary to compare values of the functions $M_\alpha(\omega_1, \delta\omega, |\mathbf{q}|)$ pertaining to different ω_1. The determination of these functions from the experimental data can be based on the results obtained in the present article.

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