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Statistical Approach to Light Scattering From Deformed Textured Heterogeneous Polymer Materials

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SYNOPSIS

A statistical theory of light scattering from deformed isotropic and textured heterogeneous polymer materials is formulated. Two types of textured structures are analyzed: assemblies of optically isotropic and anisotropic rods and a spatially anisotropic distribution of isotropic spherical inclusion centers. The small-angle H_v light-scattering patterns are calculated. The appearance of scattering from isotropic rods and spheres in deformed materials has been demonstrated. The changes of the H_v scattering patterns as a function of elongation and structure parameters are discussed. © 1993 John Wiley & Sons, Inc.

Keywords: light scattering • deformed heterogeneous networks • textured polymer materials • anisotropic correlation function of shear modulus • rodlike texture

INTRODUCTION

Structural inhomogeneity and a great variety of morphological formations are typical of polymer materials. This fact explains the effectiveness of the light-scattering technique as applied to the detailed analysis of structure.¹⁻³ At the same time, a quantitative interpretation of the experimental results runs into difficulties because of the ambiguity of the relation between the measured intensity distribution and polymer structure. In other words, the reciprocal problem of light scattering is not mathematically correct; and additional information provided by other physical methods (e.g., electron and polarizing microscopy, small-angle x-ray scattering, etc.) is necessary to construct an adequate structural model.

Model approaches perform well when applied to the study of various textured polymer systems. In particular, scattering patterns from isolated crystallites of various shapes, sizes, directions of optical axes, and orientations were studied.¹⁻⁹ In the case of highly ordered crystalline polymer films, the effects of interparticle interference on scattering patterns were found to be important.¹⁰⁻¹⁵ In particular, in the case of two-dimensional assemblies of closely packed crystalline rods, the interparticle interference resulted in an eight-leaf H_v light-scattering pattern.¹³ This effect was observed by Matsuo and

co-workers¹³ for poly(butylene terephthalate) and poly(tetramethylene terephthalate) films stretched at high temperature.

On the other hand, a similar eight-leaf H_v scattering pattern may appear in deformed polymer materials with elastic inhomogeneities.¹⁶⁻¹⁸ This effect is due to the external stress-induced inhomogeneous distribution of polarizability in the vicinity of regions of changing elastic modulus. In the systems discussed,¹³⁻¹⁵ the appearance of large-scale viscoelastic heterogeneities may be expected. For example, they can result from inhomogeneous distribution of amorphous layers between assemblies of rods. For this reason, the H_v scattering pattern can be interpreted as a superposition of two contributions: interparticle interference within the rod assemblies and additional scattering resulting from inhomogeneous distribution of local strains.

In this work, we focus our attention on the problem of a theoretical investigation of the effect of elastic inhomogeneities on light scattering in deformed, textured polymer systems. The analysis is carried out in terms of nonlinear elasticity theory.

The main results of this work are obtained within the statistical approach formulated by Debye and Bueche,¹⁹ Goldstein and Michalik,²⁰ and Stein and Wilson,²¹ and developed in various other works.^{1,2,11,22,23} In this approximation, interference effects are taken into account in terms of correlation functions of polarizability fluctuations. Of course,

$$\begin{aligned} \mathbf{O}_1^{(h)} &= -\frac{\sin \theta \sin \mu}{(\cos^2 \theta + \sin^2 \theta \sin^2 \mu)^{1/2}}, \\ \mathbf{O}_2^{(h)} &= \frac{\cos \theta}{(\cos^2 \theta + \sin^2 \theta \sin^2 \mu)^{1/2}}, \\ \mathbf{O}_3^{(h)} &= 0 \end{aligned} \quad (3)$$

and

$$\begin{aligned} \mathbf{O}_1^{(v)} &= -\frac{\sin \theta \cos \mu}{(\cos^2 \theta + \sin^2 \theta \cos^2 \mu)^{1/2}}, \quad \mathbf{O}_2^{(v)} = 0, \\ \mathbf{O}_3^{(v)} &= \frac{\cos \theta}{(\cos^2 \theta + \sin^2 \theta \cos^2 \mu)^{1/2}} \end{aligned} \quad (4)$$

According to the general theory of electromagnetic scattering^{24,25} the electric field strength of the light scattered by the ξ -th scattering element is given by

$$\mathbf{E}^{(\xi)} = \frac{k^2}{R_o} \exp(i\mathbf{k} \cdot \mathbf{R}_o) [\mathbf{F}^{(\xi)} - \mathbf{s}'(\mathbf{F}^{(\xi)} \cdot \mathbf{s}')], \quad (5)$$

where R_o is the distance from the center of the scattering volume V to the point of observation (far from the sample) and vector $\mathbf{F}^{(\xi)}$ is

$$\mathbf{F}^{(\xi)} = \mathbf{M}^{(\xi)} \int_V \chi^{(\xi)}(\mathbf{r}) \exp(-i\mathbf{q}\mathbf{r}) d\mathbf{r}. \quad (6)$$

Here $\mathbf{M}^{(\xi)}$ is the dipole moment induced by the electric field of the incident beam in the scattering element ξ . The components of $\mathbf{M}^{(\xi)}$ can be expressed in terms of the relative polarizability tensor $\hat{\alpha}^{(\xi)} = \hat{\beta}^{(\xi)} - \hat{\alpha}^{(s)}$ where $\hat{\beta}^{(\xi)}$ and $\hat{\alpha}^{(s)}$ are the polarizability tensors of the ξ -th scattering element and matrix in the laboratory frame:

$$M_k^{(\xi)} = \alpha_{kl}^{(\xi)} E_l^{(0)} = \alpha_{kl}^{(\xi)} t_l^{(p)} E_o. \quad (7)$$

(Here and below we imply summation over repeated indexes).

The function $\chi^{(\xi)}(\mathbf{r})$ in eq. (6) is the indication function of the region: $\chi^{(\xi)}(\mathbf{r}) = 1$ when the point given by vector \mathbf{r} belongs to the region occupied by the particle ξ and $\chi^{(\xi)}(\mathbf{r}) = 0$ otherwise. The vector \mathbf{r} can be represented by the sum of the vector giving the particle center $\mathbf{R}^{(\xi)}$ and the current vector ρ scanning over the volume V_ξ . Equation (6) can then be rewritten in the form:²

$$\begin{aligned} F_k^{(\xi)} &= f_k^{(\xi)} E_o \exp(-i\mathbf{q}\mathbf{R}^{(\xi)}), \\ f_k^{(\xi)} &= \alpha_{kl}^{(\xi)} t_l^{(p)} \chi(\mathbf{q}, \mathbf{n}_\xi), \end{aligned} \quad (8)$$

where

$$\chi(\mathbf{q}, \mathbf{n}_\xi) = \int_{V_\xi} \exp[i(-\mathbf{q}\mathbf{n}_\xi)\rho] d\rho \quad (9)$$

is the form factor.

The laboratory-frame polarizability tensor $\hat{\alpha}^{(\xi)}$ can be related to the polarizability tensor $\hat{\alpha}^{o(\xi)}$ in the system of the optical axis by the transformation matrix $\hat{\gamma}$

$$\alpha_{kl}^{(\xi)} = \gamma_{km}^{(\xi)} \gamma_{ln}^{(\xi)} \alpha_{mn}^{o(\xi)}. \quad (10)$$

The components of $\hat{\gamma}$ coincide with the projections of the unit vectors directed along the main optical axes of the particle on the axes of the laboratory coordinate system. In the case of the uniaxial rodlike crystallites with the optical axis along the rod axis ($\omega_o = 0$), the transformation matrix is given by⁷

$$\hat{\gamma} = \begin{pmatrix} \cos \alpha \sin \varphi & -\cos \varphi & \sin \alpha \sin \varphi \\ \cos \alpha \cos \varphi & \sin \varphi & \sin \alpha \cos \varphi \\ -\sin \alpha & 0 & \cos \alpha \end{pmatrix}. \quad (11)$$

We note also the orthogonality property of this matrix

$$\gamma_{im} \gamma_{km} = \delta_{ik}, \quad (12)$$

where δ_{ik} is the Kronecker delta ($\delta_{ik} = 1$ if $i = k$ and $\delta_{ik} = 0$ if $i \neq k$).

The polarizability tensor of a uniaxial crystallite is diagonal and can be presented in the form $\alpha_{mn}^{o(\xi)} = \alpha_{(m)}^{(\xi)} \delta_{mn}$ (the parentheses denote lack of summation over repeated indexes and $\alpha_1^{(\xi)} = \alpha_2^{(\xi)} = \alpha_t^{(\xi)}$, $\alpha_3^{(\xi)} = \alpha_l^{(\xi)}$). The difference between the longitudinal $\alpha_l^{(\xi)}$ and transverse $\alpha_t^{(\xi)}$ polarizabilities characterizes the optical anisotropy of the ξ -th particle. In this case, we have

$$\hat{\alpha}_{mn}^{(\xi)} = \Delta^{(\xi)} \delta_{m3} \delta_{n3} + \alpha_t^{(\xi)} \delta_{mn}, \quad (13)$$

Substituting eq. (13) into eq. (10) and taking into account eq. (12), we find that for a uniaxial crystallite

$$\alpha_{kl}^{(\xi)} = \Delta^{(\xi)} \gamma_{k3}^{(\xi)} \gamma_{l3}^{(\xi)} + \alpha_t^{(\xi)} \delta_{kl}. \quad (14)$$

In other words, the nondiagonal components of the $\alpha_{kl}^{(\xi)}$ in the laboratory reference system are proportional to the optical anisotropy of the ξ -th scattering element.

The intensity of the scattered light passed by the analyzer is given by:¹⁻³

$$I = \sum_{\xi, \zeta} (\mathbf{E}^{(\xi)} \cdot \mathbf{O})(\mathbf{E}^{(\zeta)*} \cdot \mathbf{O}) \\ = \frac{k^4}{R_0^2} \sum_{\xi, \zeta} (\mathbf{F}^{(\xi)} \cdot \mathbf{O})(\mathbf{F}^{(\zeta)*} \cdot \mathbf{O}). \quad (15)$$

Here $\mathbf{E}^{(\xi)*}$ and $\mathbf{F}^{(\xi)*}$ correspond to the complex conjugates of $\mathbf{E}^{(\xi)}$ and $\mathbf{F}^{(\xi)}$. In deriving the second equality of eq. (5) and the orthogonality of vectors, \mathbf{s}' and \mathbf{O} are taken into account. Substituting eq. (8) into eq. (15) and introducing the Rayleigh ratio \mathcal{R} , we obtain

$$\mathcal{R} = \frac{IR_0^2}{I_0 V} \\ = k^4 V^{-1} \sum_{\xi, \zeta} f^{(\xi)} f^{(\zeta)*} \exp[i\mathbf{q}(\mathbf{R}^{(\xi)} - \mathbf{R}^{(\zeta)})] \\ = k^4 N^{-1} c_s \left\{ \sum_{\xi} |f^{(\xi)}|^2 + \sum_{\substack{\xi, \zeta \\ (\xi \neq \zeta)}} f^{(\xi)} f^{(\zeta)*} \right. \\ \left. \times \exp[i\mathbf{q}(\mathbf{R}^{(\xi)} - \mathbf{R}^{(\zeta)})] \right\}, \quad (16)$$

where I and I_0 are scattering and incident light intensities, $f^{(\xi)} = f_k^{(\xi)} \cdot \mathbf{O}_k$ is the amplitude of the scattered light after it has passed through the analyzer, N and $c_s = N/V$ are number and concentration of the scattering elements, respectively.

When the distribution of particles in the volume of the sample is statistically homogeneous, the summation in eq. (16) can be substituted by averaging over the coordinates and orientations. We consider the simplest situation with no correlation between the orientation and position of a scattering element. In this case, individual averaging over positions and orientations gives

$$\mathcal{R} = k^4 c_s \left\{ \langle \overline{f(0) f^*(0)} \rangle \right. \\ \left. + c_s \int_V \langle \bar{f}(\mathbf{R}) \bar{f}^*(0) \rangle \exp(i\mathbf{q}\mathbf{R}) d\mathbf{R} \right\}, \quad (17)$$

Here the bar denotes averaging over orientations of the vector \mathbf{n} (see Fig. 1), and the function $\langle \bar{f}(\mathbf{R}) \bar{f}^*(0) \rangle$ denotes averaging over the coordinates of the particle centers under the condition that their relative positions are given by vector \mathbf{R} .

In the second term of eq. (17) the integration is carried out over the scattering volume V . Assuming that V is much greater than the average volume of scattering element and using Debye's trick,¹⁹ the integration can be extended over the whole space

and presented as a Fourier transform

$$\int_V \langle \bar{f}(\mathbf{R}) \bar{f}^*(0) \rangle \exp(i\mathbf{q}\mathbf{R}) d\mathbf{R} \\ \cong \int_{(\infty)} \langle \bar{f}(\mathbf{R}) \bar{f}^*(0) \rangle \exp(i\mathbf{q}\mathbf{R}) d\mathbf{R} \\ = \mathcal{F}_{\mathbf{q}} \{ \langle \bar{f}(\mathbf{R}) \bar{f}^*(0) \rangle \} \quad (18)$$

The function $\langle \bar{f}(\mathbf{R}) \bar{f}^*(0) \rangle$ can be written in the form²⁶

$$\langle \bar{f}(\mathbf{R}) \bar{f}^*(0) \rangle = \langle |f|^2 \rangle \psi(\mathbf{R}), \quad (19)$$

where $\psi(\mathbf{R})$ is the conditional probability density for the first particle center to be at a distance \mathbf{R} from the second one, provided that the position of the latter is fixed. This function can be related to the correlation coefficient $g(\mathbf{R})$ characterizing the probability density for finding particles simultaneously in two different volume elements with relative positions given by the vector \mathbf{R} ²⁷

$$\psi(\mathbf{R}) = g(\mathbf{R}) - c_s^{-1} \delta(\mathbf{R}) \quad (20)$$

Substituting eqs. (18)–(20) into eq. (17) we find

$$\mathcal{R} = k^4 c_s [\langle \overline{|f|^2} \rangle - \langle |f|^2 \rangle] \\ + c_s \mathcal{F}_{\mathbf{q}} \{ \langle \bar{f} \bar{f}^* \rangle_{\mathbf{R}} \}, \quad (21)$$

where

$$\langle \bar{f} \bar{f}^* \rangle_{\mathbf{R}} = \langle |f|^2 \rangle g(\mathbf{R}) \quad (22)$$

is the scattering-amplitude correlation function and $\langle |f|^2 \rangle = \langle \bar{f}(0) \bar{f}^*(0) \rangle$.

Equation (21) coincides with the known result¹¹ of light-scattering theory only if we introduce $\langle |f|^2 \rangle = \overline{|f|^2}$ and $\langle \overline{|f|^2} \rangle = \overline{|f|^2}$ (i.e., when we ignore the spatial average at $\mathbf{R} = 0$). In the considered case of light scattering in the deformed sample this cannot be done since, as shown below, the relation between the deformation polarizability and modulus of elasticity is not local and is defined by the distribution of elastic heterogeneities in the material.

Substituting eqs. (8) and (10) to eq. (21), we get an equation for the Rayleigh ratio applicable to the analysis of the light-scattering intensity from the deformed material:

$$\mathcal{R} = k^4 c_s [(\overline{h_{mn} h_{pq}^*} - \bar{h}_{mn} \bar{h}_{pq}^*) \times \langle \dot{\alpha}_{mn} \dot{\alpha}_{pq} \rangle + c_s \bar{h}_{mn} \bar{h}_{pq}^* \mathcal{F}_{\mathbf{q}} \{ \langle \dot{\alpha}'_{mn} \dot{\alpha}'_{pq} \rangle_{\mathbf{R}} \}], \quad (23)$$

where

$$h_{mn} = \gamma_{im} \gamma_{kn} O_i t_k^{(p)} \chi(\mathbf{q}, \mathbf{n}) \quad (24)$$

In the last term of eq. (23), the fluctuation part $\dot{\alpha}'_{mn} = \dot{\alpha}_{mn} - \langle \dot{\alpha}_{mn} \rangle$ is used instead of the polarizability tensor $\dot{\alpha}_{mn}$. This is due to the fact that the Fourier transform of the constant is zero at $\theta \neq 0$. This equation is valid for monodisperse scattering elements. To consider a distribution of particle sizes, the first term in eq. (23) should be averaged over the corresponding distribution function; and in the second term, the correlation between particles of different sizes should be taken into account.

The first term of eq. (23) corresponds to the so-called diffuse scattering, and the second term enables one to take into account interference effects with accuracy up to the correlation function of the polarizability fluctuations. Examples of calculations are given below for two typical heterogeneous structures: (1) material containing isotropic spherical inclusions and (2) material containing thin isotropic rods with a fixed orientation of the plane perpendicular to the incident beam.

Spherical Isotropic Scattering Elements

In this case, the polarizability tensor is $\dot{\alpha}_{mn} = \alpha \delta_{mn}$, $h_{mn} \dot{\alpha}_{mn} = \alpha \chi(\mathbf{q}) O_m t_m^{(p)}$, and the form-factor is³

$$\chi(\mathbf{q}) = \frac{4\pi a^3}{U^3} [\sin U - U \cos U], \quad (25)$$

where a is the radius of the sphere and $U = qa = 2ka \sin(\theta/2)$. The diffuse component is zero and from eq. (23) it follows that

$$\mathcal{R}^{(\alpha)} = k^4 c_s \langle \alpha^2 \rangle \chi^2(\mathbf{q}) D_{\alpha}(\mathbf{q}) (O_m t_m^{(p)})^2, \quad (26)$$

where

$$D_{\alpha}(\mathbf{q}) = \langle \alpha^2 \rangle^{-1} \mathcal{F}_{\mathbf{q}} \{ \langle \alpha' \alpha' \rangle_{\mathbf{R}} \} \quad (27)$$

is the Fourier transform of the correlation function of the polarizability fluctuations.

In the case of crossed polaroids, $\mathcal{R}_{H_v}^{(\alpha)}$ is zero since the vector $\mathbf{O}^{(h)}$ is orthogonal to the polarization direction $\mathbf{t}^{(p)}$ of the incident beam. For parallel polaroids we have $\mathbf{O}^{(v)} \cdot \mathbf{t}^{(p)} = O_3^{(v)}$ and from eqs. (4) and (26) we find

$$\mathcal{R}_{H_v}^{(\alpha)} = k^4 c_s \langle \alpha^2 \rangle \chi^2(\mathbf{q}) D_{\alpha}(\mathbf{q}) \cos^2 \theta \times (\cos^2 \theta + \sin^2 \theta \cos^2 \mu)^{-1}. \quad (28)$$

Rodlike Scattering Elements

To simplify the analysis we consider light scattering from an assembly of thin rods in the (x_2, x_3) -plane ($\varphi = 0$) and making angles $\pm\alpha$ with the x_3 -axis (see Fig. 1). We assume that the optical axis is parallel to the rod axis: that is, $\omega_o = 0$. From eqs. (14) and (24) we get

$$h_{mn} \dot{\alpha}_{mn} = (\Delta \gamma_{13} \gamma_{33} + \alpha_t \delta_{ik}) \chi(\mathbf{q}, \mathbf{n}) O_i, \quad (29)$$

where the unit vector $\mathbf{t}^{(p)}$ directed along the x_3 -axis is taken into account.

For very thin rods the form factor $\chi(\mathbf{q}, \mathbf{n})$ is given by⁴

$$\begin{aligned} \chi(\mathbf{q}, \mathbf{n}) &= \int_{-L/2}^{L/2} \exp[-i(\mathbf{q}\mathbf{n})\rho] d\rho \\ &= L \sin[(\mathbf{q}\mathbf{n})L/2] / [(\mathbf{q}\mathbf{n})L/2]. \end{aligned} \quad (30)$$

At $\varphi = 0$, from eqs. (2) and (8) it follows that⁴ $\mathbf{q}\mathbf{n} = q s_i n_i = \sin \theta \cos(\alpha - \mu)$. Substituting eqs. (29) and (30) into eq. (23) and assuming the following statistical independence of the optical anisotropy Δ and transverse polarizability α_t of the rod,²¹ we obtain

$$\begin{aligned} \mathcal{R}^{(\alpha)} &= k^4 c_s \{ X \langle (\Delta \gamma_{33} O_i \gamma_{i3} + \alpha_t O_3)^2 \rangle \\ &\quad + c_s |\bar{\chi}|^2 [(\gamma_{33} O_3 \gamma_{i3})^2 \langle \Delta^2 \rangle D_{\Delta}(\mathbf{q}) \\ &\quad + O_3^2 \langle \alpha_t^2 \rangle D_{\alpha_t}(\mathbf{q})] \}, \end{aligned} \quad (31)$$

where

$$\begin{aligned} D_{\Delta}(\mathbf{q}) &= \langle \Delta^2 \rangle^{-1} \mathcal{F}_{\mathbf{q}} \{ \langle \Delta' \Delta' \rangle_{\mathbf{R}} \} \quad \text{and} \\ D_{\alpha_t}(\mathbf{q}) &= \langle \alpha_t^2 \rangle^{-1} \mathcal{F}_{\mathbf{q}} \{ \langle \alpha'_t \alpha'_t \rangle_{\mathbf{R}} \} \end{aligned} \quad (32a)$$

are the Fourier transforms of the reduced correlation functions $\langle \Delta' \Delta' \rangle_{\mathbf{R}}$ and $\langle \alpha'_t \alpha'_t \rangle_{\mathbf{R}}$,

$$X = \overline{\chi^2(\mathbf{q}, \mathbf{n})} - [\bar{\chi}(\mathbf{q}, \mathbf{n})]^2 \quad (32b)$$

For crossed polaroids, $O_3^{(h)} = 0$ and $\gamma_{33} O_i^{(h)} \gamma_{i3} = O_2^{(h)} \sin \alpha \cos \alpha$. Putting these values into eq. (31) we obtain

$$\begin{aligned} \mathcal{R}_{H_v}^{(\alpha)} &= k^4 c_s (O_2^{(h)} \sin \alpha \cos \alpha)^2 \\ &\quad \times \langle \Delta^2 \rangle [X + c_s (\bar{\chi})^2 D_{\Delta}(\mathbf{q})]. \end{aligned} \quad (33a)$$

For parallel polaroids, $\gamma_{33}O_i^{(v)}\gamma_{i3} = O_3^{(v)}\cos^2\alpha$, whence we find

$$\mathcal{R}_{V_v}^{(\alpha)} = k^4 c_s (O_3^{(v)})^2 \{ X \langle (\Delta \cos^2\alpha + \alpha_t)^2 \rangle + c_s \chi^2 [\langle \Delta^2 \rangle \cos^4\alpha D_\Delta(\mathbf{q}) + \langle \alpha_t^2 \rangle D_{\alpha_t}(\mathbf{q})] \} \quad (33b)$$

(the values of $O_2^{(h)}$ and $O_3^{(v)}$ are given by eqs. (3) and (4)).

In the absence of spatial correlations of polarizabilities of scattering elements, eqs. (33a) and (34b) reduce to the known expressions derived in ref. 4.

THE POLARIZABILITY OF ELASTIC HETEROGENEOUS POLYMER MATERIALS

The light-scattering pattern from deformed inhomogeneous polymer materials changes because of three main factors: (1) changes in the shape and size of scattering elements, (2) redistribution of their positions and orientations, and (3) changes in the local polarizability tensor as a function of internal strain or stress (the effect of photoelasticity).

The first two factors result in changes of geometrical parameters of the structure and the appearance of additional anisotropy caused by the orientation of particles and different particle-to-particle distances in the directions parallel and orthogonal to the stretching vector. Changes in geometrical characteristics result in distortion of the SALS pattern as compared to that for the unloaded state. However, the main qualitative features are preserved.^{2,4,22} For instance, the X-type pattern produced by H_v scattering from thin rodlike crystallites is still observed in the case of a deformed sample, with the only difference that the angle between sharp leaf (streaks) is changed.

On the other hand, the last factor results in qualitative changes in the azimuthal distribution of light scattering intensity. For example, the presence of rigid spherical inclusions in the elastic matrix gives the well-known eight-leaf scattering pattern observed under stretching.¹⁶⁻¹⁸ Physically this is due to the inhomogeneous distribution of strains in the vicinity of inclusions, which results in additional inhomogeneity of polarizability. It seems that a full account of all the above noted factors makes it possible to explain a variety of SALS patterns observed from deformed inhomogeneous polymer materials.

First we consider the change of local polarizability in an elastic stress field:

$$\hat{\alpha}_{ik}(\mathbf{R}) = \alpha_{(i)}(\mathbf{R})\delta_{ik} + \eta_{ik}(\mathbf{R}). \quad (34)$$

Here $\alpha_i(\mathbf{R})$ is the local value of inherent polarizability of a scattering element relative to the matrix polarizability. In the absence of an external load the fluctuations of just these values alone define light scattering. The tensor $\eta_{ik}(\mathbf{R})$ is the local change in polarizability induced by the local stress $\sigma_{ik}(\mathbf{R})$, and is called the deformation polarizability tensor. Since stretching also causes change in the matrix polarizability, the tensor $\eta_{ik}(\mathbf{R})$ equals the difference in the scattering element and matrix $\eta_{ik}^{(s)}$ polarizabilities. Taking into account the linear dependence of $\eta_{ik}(\mathbf{R})$ on stress $\sigma_{ik}(\mathbf{R})$, we obtain

$$\eta_{ik}(\mathbf{R}) = A[\sigma_{ik}(\mathbf{R}) - \frac{1}{3}\sigma_{pp}(\mathbf{R})\delta_{ik}] - \eta_{ik}^{(s)}. \quad (35)$$

Here A is the stress-optical coefficient. We suppose for simplicity that A is constant and depends only on an average dielectric permeability of the medium. Equation (35) shows that additional optical anisotropy in material does not arise from hydrostatic stress.

The stress-strain relationship is determined by the elastic potential W , which in turn depends on the internal material structure. It can be represented as a polynomial in different invariants of the asymmetric strain tensor $\lambda_{ik} = \partial x_i / \partial x_k^0$, which we will call an elongation tensor (x_i^0 and x_i are coordinates of some material point relative to the free and deformed states of the sample).²⁸ In the present work we consider only the first term of the W expansion

$$W = \frac{1}{2}G\psi_1, \quad \psi_1 = \lambda_{pq}\lambda_{pq} - 3, \quad (36)$$

which is known as the elastic energy of a Gaussian network; G is a shear modulus. In the case of incompressible materials, the stress-strain relation can be written in the form

$$\sigma_{ik} = \lambda_{ip}\lambda_{kq} \frac{\partial \psi_1}{\partial e_{pq}} \frac{\partial W}{\partial \psi_1} - p\delta_{ik} = G\lambda_{ip}\lambda_{kp} - p\delta_{ik} \quad (37)$$

where $e_{pq} = (\frac{1}{2})(\lambda_{mp}\lambda_{mq} - \delta_{pq})$ is the strain tensor and p is a parameter determined from the incompressibility condition

$$\det \hat{\lambda} = 1. \quad (38)$$

It can be shown that eq. (37) results in Hooke's law at small deformations

$$\sigma_{ik} = 2Ge_{ik} - p\delta_{ik} \quad (39)$$

As follows from eqs. (34), (35) and (37), the local polarizability is characterized by two different ma-

terial parameters: the inherent polarizability $\alpha_i(\mathbf{R})$ and shear modulus $G(\mathbf{R})$. In the general case, these are random functions of the coordinates. Their fluctuation scales determine sizes of corresponding heterogeneity regions. The inherent polarizability and shear modulus are of a different physical nature. Therefore, their fluctuation regions can be described by various sizes and shapes. Polymer networks, in which α_i depends on the monomer density and G depends on the density of intermolecular covalent junctions, can be mentioned as an example. It is clear that their fluctuation scales are very diverse. Another example may be represented by highly crystalline polymers. In this case, the sizes of the fluctuation regions of inherent polarizability coincide with those of single crystallites. On the contrary, pronounced changes in the elasticity modulus can take place over a wide range. One of the reasons for this phenomenon is the strong dependence of apparent shear modulus on the thickness of intercrystalline amorphous layers.²⁹ They are comparable with the crystallite shear modulus at small intercrystalline distances. Hence, the range of elasticity modulus fluctuations will be determined by the assembly sizes of closely packed crystallites. At low concentration of crystallites or rigid inclusions the fluctuation regions of α_i and G coincide.

Statistical Characteristics of Deformation Polarizability

We split the shear modulus G and elongation tensor λ_{ik} in eq. (37) into average and fluctuation contributions:

$$G = \langle G \rangle + G' \quad \text{and} \quad \lambda_{ik} = \langle \lambda_{ik} \rangle + \lambda'_{ik}. \quad (40)$$

We assume that the stretching direction of the sample is parallel to the x_3 -axis. Then the average elongation tensor is diagonal and can be written as $\langle \lambda_{ik} \rangle = \lambda_{(i)} \delta_{ik}$.

We consider small fluctuations of shear modulus compared with the average one ($G' \ll \langle G \rangle$), which implies only small values of elastic strain fluctuations ($\lambda'_{ik} \ll \langle \lambda_{ik} \rangle$). This approach is suitable for two cases: (1) at small differences between local shear moduli and (2) at low concentration of small heterogeneities. It permits us to restrict the expansion of eqs. (35) and (37) with first-order accuracy of G' and λ'_{ik} . As a result we obtain

$$\eta'_{ik} = A \left\{ G' (\lambda_{(i)}^2 - \frac{1}{3} \sum_{p=1}^3 \lambda_p^2) \delta_{ik} + \langle G \rangle [(\lambda_{(i)} \lambda'_{ki} + \lambda_{(k)} \lambda'_{ik}) - \frac{2}{3} \sum_{p=1}^3 \lambda_p \lambda'_{pp} \delta_{ik}] \right\}. \quad (41)$$

This expression is simplified at small strain:

$$\eta'_{ik} = A[G'e_{(i)}\delta_{ik} + \langle G \rangle e'_{ik}], \quad (42)$$

where the diagonality of the mean strain tensor is taken into account, where $\langle e_{ik} \rangle = e_{(i)}\delta_{ik}$ together with the equation $e_{pp} = 0$, which follows from the incompressibility condition for linear media.³⁰ As can be seen from eqs. (41) and (42), in elastic homogeneous materials ($G' = 0$ and $\lambda'_{ik} = 0$), the fluctuation contribution to the deformation polarizability is zero.

We consider a correlation function of deformation polarizabilities $\langle \eta'_{ik} \eta'_{mn} \rangle_{\mathbf{R}}$. It is clear that these functions are presented as a combination of three correlation functions: $\langle \lambda'_{ik} \lambda'_{mn} \rangle_{\mathbf{R}}$, $\langle \lambda'_{ik} G' \rangle_{\mathbf{R}}$, and $\langle G' G' \rangle_{\mathbf{R}}$.¹⁸ The first two can be related to the correlation function for shear modulus fluctuations, owing to the dependence of local strain changes on the distribution of elastic moduli in a heterogeneous medium. These relations were obtained^{18,31} from the statistical theory of elasticity. (In Appendix 1 the derivation of these functions is presented for the particular case of small deformations). Here we give only the main results¹⁸ for the case of the Gaussian elastic potential:

$$\begin{aligned} \langle \lambda'_{ik} \lambda'_{mn} \rangle_{\mathbf{R}} &= \lambda_i \lambda_m Q_{,ik} * Q_{,mn} * A_i * A_m * K \\ \langle \lambda'_{ik} G' \rangle_{\mathbf{R}} &= \langle G \rangle \lambda_i Q_{,ik} * A_i * K, \\ A_i &= \delta(\mathbf{R}_o) + \lambda_i^{-2} \Phi_{,pp}, \end{aligned} \quad (43)$$

where $K(\mathbf{R}) = \langle G' G' \rangle_{\mathbf{R}} / \langle G \rangle^2$ is a measure of elastic inhomogeneity. The asterisk indicates the integral convolution:

$$f * g = \int f(\mathbf{R}_o - \mathbf{R}') g(\mathbf{R}') d\mathbf{R}'.$$

Values $Q_{,ik}$ and $\Phi_{,pp}$ are the second derivatives of the Green functions which satisfy the equations

$$Q_{,kk} = -\delta(\mathbf{R}_o) \quad \text{and} \quad \sum_{p=1}^3 \lambda_p^{-2} \Phi_{,pp} = -\delta(\mathbf{R}_o) \quad (45)$$

(the indices following the comma denote differentiation with respect to them).

Substituting eqs. (43) and (44) into the expression for the correlation function $\langle \eta'_{ik} \eta'_{mn} \rangle_{\mathbf{R}}$, which can be obtained from eq. (41),¹⁸ we obtain, after some algebra,

$$\langle \eta'_{ik} \eta'_{mn} \rangle_{\mathbf{R}} = A^2 \langle G \rangle^2 P_{ik} * P_{mn} * K \quad (46)$$

$$P_{ik}(\mathbf{R}_o) = (\lambda_{(i)}^2 - \frac{1}{3} \sum_{p=1}^3 \lambda_p^2) \delta_{ik} \delta(\mathbf{R}_o) + \lambda_i \lambda_k Q_{,ik} * (A_i + A_k) - \frac{2}{3} \delta_{ik} \sum_{p=1}^3 \lambda_p^2 Q_{,pp} * A_p \quad (47)$$

The dependence of the correlation function for the deformation polarizability on the measure of elastic inhomogeneity $K(\mathbf{R}_o)$ is the main result of eq. (46). This relation is nonlocal, owing to long-range elastic interactions between heterogeneities; in other words, the function $\langle \eta'_{ik} \eta'_{mn} \rangle_{\mathbf{R}}$ depends on the total shear modulus distribution in the volume of the material.

Finally, we note that the correlation function of the complete polarizabilities $\langle \alpha'_{ik} \alpha'_{mn} \rangle_{\mathbf{R}}$ [eq. (23)] can be written as

$$\langle \alpha'_{ik} \alpha'_{mn} \rangle_{\mathbf{R}} = \sum_{p=1}^3 \sum_{q=1}^3 \gamma_{ip} \gamma_{kp} \gamma_{mq} \gamma_{nq} \langle \alpha'_p \alpha'_q \rangle_{\mathbf{R}} + \langle \eta'_{ik} \eta'_{mn} \rangle_{\mathbf{R}} \quad (48)$$

as a result of the statistical independence between inherent (α_i) and deformation (η_{ik}) polarizabilities. The first term of eq. (48) depends only on geometrical parameters of the distribution of centers of scattering elements; and, moreover, the second term takes into account the strain distortions in the vicinity of elastic inclusions.

CALCULATION OF LIGHT-SCATTERING INTENSITY FROM DEFORMED POLYMER MATERIALS

Geometrical Parameters of Structure

According to eqs. (23) and (24), the light-scattering intensity depends on geometrical parameters that change during deformation of the sample. These are the shape, size, orientation, and spatial distribution of centers of scattering elements. We must pay attention to their strain dependence. The integral of the form factor $\chi(\mathbf{q}, \mathbf{n})$ in eqs. (9), (25), and (30) is taken over coordinates relative to the deformed state of the material. Transforming these to the coordinate system based on the undeformed (free) state we obtain

$$\chi(\mathbf{q}, \mathbf{n}) = \chi(\mathbf{Q}, \mathbf{n}_o) = \int_{V_i} \exp[-i(\mathbf{Q}\mathbf{n}_o)\rho_o] d\rho_o, \quad \mathbf{Q} = \mathbf{q}\hat{\lambda}. \quad (49)$$

The directions of the axial axis are degenerate for spherical heterogeneities. Therefore, after integration over solid angles in eq. (49), we get an expression similar to eq. (25), in which U must be replaced by:²

$$U_{\lambda} = s_{\lambda} U, \quad s_{\lambda} = \left(\sum_{p=1}^3 \lambda_p^2 s_p^2 \right)^{1/2}. \quad (50)$$

The projections of the unit vector \mathbf{s} are given by eq. (2).

When calculating the form factor of a rod, it is necessary to take into account the particle orientation with respect to the stretching-direction. For thin rods the expression suggested earlier⁴ should be considered

$$\chi(\mathbf{q}, \mathbf{n}) = \int_{-L_{\lambda}/2}^{L_{\lambda}/2} \exp[-i(\mathbf{q}\mathbf{n})\rho] d\rho, \quad (51)$$

where L_{λ} is the rod length after deformation of the sample. Making the transformation to a free-state system we obtain

$$\chi(\mathbf{Q}, \mathbf{n}_o) = L \left(\sum_{p=1}^3 \lambda_p^2 n_{op}^2 \right)^{1/2} \frac{\sin[(\mathbf{Q}\mathbf{n}_o)L/2]}{(\mathbf{Q}\mathbf{n}_o)L/2}. \quad (52)$$

Equation (52) coincides with the known formula⁴ when $\lambda_i = 1$ (free state).

We write, in addition, the relation between unit vectors \mathbf{n}_o and \mathbf{n} directed along the rod axis in free and deformed states:

$$n_i = \lambda_i n_{oi} \left(\sum_{p=1}^3 \lambda_p^2 n_{op}^2 \right)^{-1/2} \quad (53)$$

The components of the vector \mathbf{n} are given by eq. (1).

The interconnection of polar angles formed by the vectors \mathbf{n}_o and \mathbf{n} with respect to the x_3 -axis: may also be found:

$$\alpha = \arcsin \left[\sin \alpha_o \left(\sin^2 \alpha_o + \frac{\lambda_3^2}{\lambda_2^2} \cos^2 \alpha_o \right)^{-1/2} \right] \quad (53a)$$

In deriving eqs. (49)–(53), the incompressibility condition of eq. (38) and the approximation of affine deformation of scattering particles (which is fulfilled at the small degrees of inhomogeneity under consideration) are used.

Now we consider the Fourier transform $\mathcal{F}_q\{\mathbf{H}(\mathbf{R})\}$ of the correlation function $\mathbf{H}(\mathbf{R}) = \langle \hat{\alpha}'\hat{\alpha}' \rangle_{\mathbf{R}}$ of the tensor polarizability fluctuations introduced in eq. (23). The integration in eq. (23) is carried out over coordinates relative to the deformed state of the material in consequence of eqs. (17) and (18). Therefore the transformation to the coordinate system relative to the free-sample state gives the following sequence of equations:

$$\begin{aligned}\mathcal{F}_q\{\mathbf{H}(\mathbf{R})\} &= \int_{(\infty)} \mathbf{H}(\mathbf{R}) \exp(i\mathbf{q}\mathbf{R}) d\mathbf{R} \\ &= \int_{(\infty)} \mathbf{H}(\mathbf{R}_0) \exp(i\mathbf{Q}\mathbf{R}_0) d\mathbf{R}_0 \\ &= \mathcal{F}_Q\{\mathbf{H}(\mathbf{R}_0)\}\end{aligned}\quad (54)$$

where the incompressibility condition is used. It is also taken into account that the centers of scattering elements form a statistically homogeneous random field in the free state of the sample and retain homogeneity during deformation. Moreover, the field becomes more anisotropic. In other words, the correlation function of polarizability depends only on the distance between two arbitrary points in both free and deformed states.

The macroscopic optical anisotropy of the polymer material is caused not only by orientation of the particle axes, but also by the anisotropic spatial distribution of their centers (as may appear during high-temperature stretching or extrusion of polymer films, even if they contain spherical heterogeneities). The distribution of the centers is described by three correlation radii a_1 , a_2 , and a_3 . In the case of unidirectional stretching along the x_3 -axis ($a_3 > a_1 = a_2$), the material possesses axial symmetry; and the argument of the correlation function exhibits the characteristic ellipsoidal symmetry: $\sum_{p=1}^3 (x_p/a_p)^2 = \text{const.}$ With equal correlation radii, $a_1 = a_2 = a_3$, the distribution of centers is isotropic.

Light-Scattering Intensity Components

By introducing eq. (48) into eq. (23) it is easy to show that the Rayleigh ratio splits into two components

$$\mathcal{R} = \mathcal{R}^{(\alpha)} + \mathcal{R}^{(G)} \quad (55)$$

The first depends on the inherent polarizability fluctuations and the other on the deformation polarizability fluctuations. In the case of elastically

homogeneous media ($G' = 0$), the first term of eq. (55) determines the light-scattering intensity. It depends only on geometrical parameters of the structure and their relation to the average strain. The light scattering distribution can be calculated (i) for spherical particles from eqs. (25), (26), and (28), taking into account eq. (52), and (ii) for the rodlike crystallites from eqs. (31), (33), (34), (52), and (53a). The majority of these results have been confirmed.¹⁻³

When the polymer is optically homogeneous ($\alpha'_i = 0$), the elastic heterogeneity gives the main contribution to the light scattering in the deformed state of the material (see eqs. (41) and (42) for the deformation polarizability). In this case, the second term of eq. (55) determines the light scattering pattern. It depends on the Fourier transform of the correlation function $\mathcal{F}_q\{\langle \eta'_{ik}\eta'_{mn} \rangle_{\mathbf{R}}\}$ and dispersion $\langle \eta_{ik}\eta_{mn} \rangle$ of deformation polarizability, which relates to the correlation function of shear modulus fluctuations [see eqs. (46) and (47)]. In contrast to the first term of eq. (55), the Rayleigh ratio $\mathcal{R}^{(G)}$ depends not only on the geometrical parameters but also on inhomogeneous local strain distribution in the vicinity of elastic heterogeneities. It is the main reason for quantitative changes in the scattering pattern from the stretched material.

We consider the expression of $\mathcal{R}^{(G)}$ in more detail. First, note that the main optical axis of the average part of the deformation polarizability η_{ik} lies along the stretching axis. This means that the transform matrix $\hat{\gamma}$ [see eq. (11)] is equal to a unit matrix ($\gamma_{ik} = \delta_{ik}$) in the coordinate system under study (see Fig. 1). This permits us to write $\mathcal{R}^{(G)}$ from eqs. (23) and (24) as follows:

$$\begin{aligned}\mathcal{R}^{(G)} &= k^4 c_s [X \langle \eta_{ik}\eta_{mn} \rangle \\ &\quad + c_s |\bar{X}|^2 \mathcal{F}_Q\{\langle \eta'_{ik}\eta'_{mn} \rangle_{\mathbf{R}_0}\}] O_i O_m t_k^{(p)} t_n^{(p)},\end{aligned}\quad (56)$$

where X is given by eq. (32b). Below we consider the H_v light-scattering pattern only. The value of $\langle \eta_{ik}\eta_{mn} \rangle O_i^{(h)} O_m^{(h)} t_k^{(p)} t_n^{(p)}$ is calculated in Appendix 2:

$$\langle \eta_{ik}\eta_{mn} \rangle O_i^{(h)} O_m^{(h)} t_k^{(p)} t_n^{(p)} = A^2 \langle G \rangle^2 J K_o, \quad (57)$$

where

$$\begin{aligned}J &= \lambda_3^2 \lambda_2^2 \left(\frac{a_2}{a_3} \right)^2 \left[x^4 J_1 - \left(1 + \frac{\lambda_2^2}{\lambda_3^2} \right) x^2 y^2 J_3 \right. \\ &\quad \left. + \frac{1}{4} \left(1 + \frac{\lambda_2^2}{\lambda_3^2} \right)^2 y^4 J_2 \right]\end{aligned}\quad (58)$$

$$J_1 = -3 + \frac{3x^2 - 1}{2x} \ln \left| \frac{x+1}{x-1} \right|,$$

$$J_2 = -3 + \frac{3y^2 - 1}{2y} \ln \left| \frac{y+1}{y-1} \right|,$$

$$J_3 = (x^2 - y^2)^{-1} \left[x(x^2 - 1) \ln \left| \frac{x+1}{x-1} \right| - y(y^2 - 1) \ln \left| \frac{y+1}{y-1} \right| \right] - 2,$$

$$\begin{aligned} x^2 &= a_3^2(a_3^2 - a_2^2)^{-1}, \\ y^2 &= a_3^2\lambda_3^2(a_3^2\lambda_3^2 - a_2^2\lambda_2^2)^{-1} \end{aligned} \quad (59)$$

Here K_o is the shear-modulus dispersion.

Substituting eq. (46) into eq. (56) and taking into account the rules for the Fourier transform of the integral convolutions, we find:

$$\begin{aligned} \mathcal{R}_{H_v}^{(G)} &= A^2 \langle G \rangle^2 k^4 c_s [XJK_o \\ &+ c_s |\bar{\chi}|^2 O_i^{(h)} O_m^{(h)} P_{i3}(\mathbf{Q}) P_{m3}(\mathbf{Q}) K(\mathbf{Q})] \end{aligned} \quad (60)$$

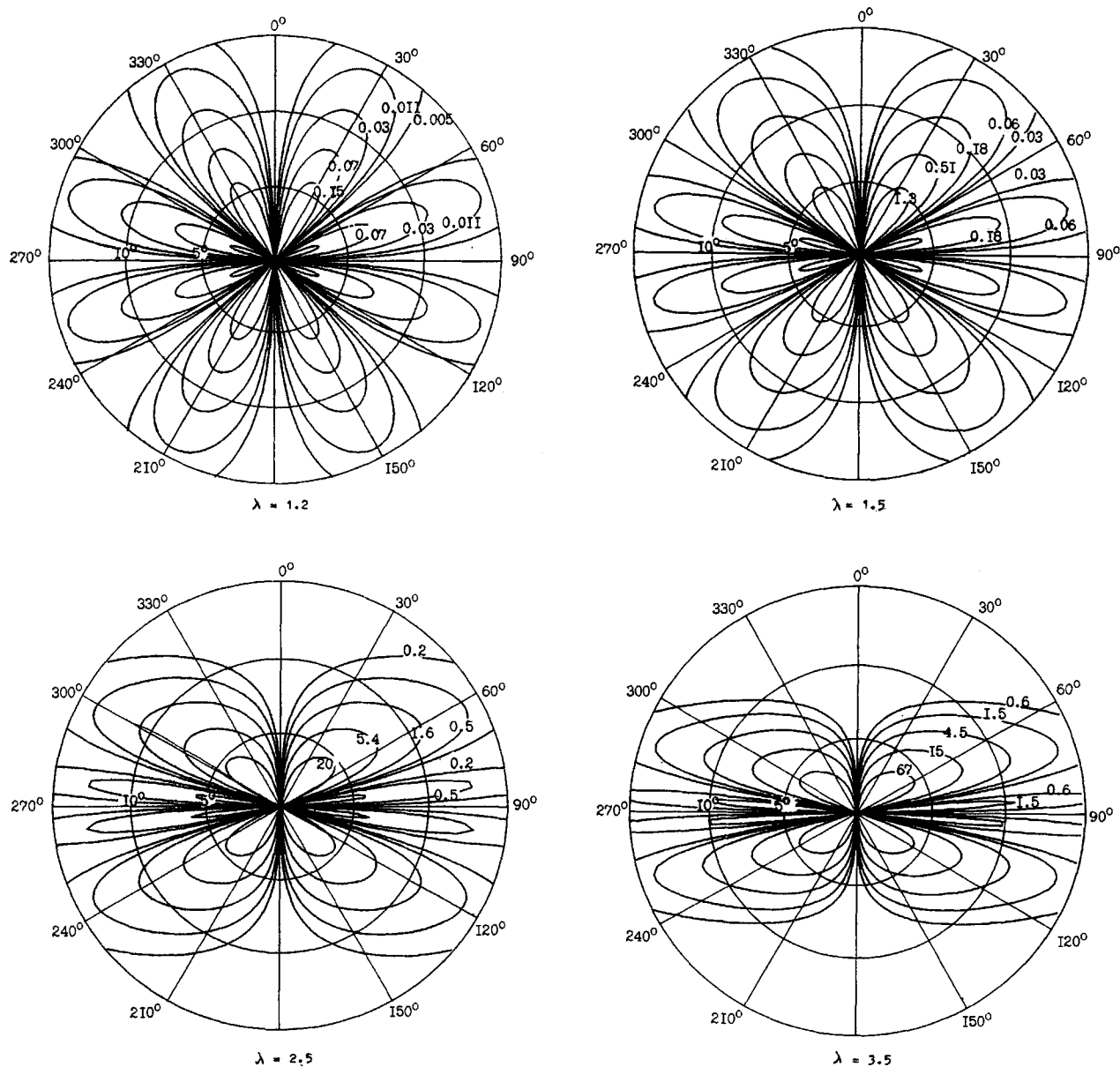


Figure 2. H_v light scattering patterns at various elongations λ (isotropic distribution of spherical inclusion centers).

where $P_{ik}(\mathbf{Q})$ is the Fourier transform of the function $P_{ik}(\mathbf{R}_0)$, which can be calculated from eq. (47):

$$P_{ik}(\mathbf{Q}) = \lambda_{(i)} \lambda_{(k)} B_{ik}(\mathbf{Q}) - \frac{1}{3} \delta_{ik} \sum_{p=1}^3 \lambda_p^2 B_{pp}(\mathbf{Q}) \quad (61)$$

$$B_{ik}(\mathbf{Q}) = \delta_{ik} - \frac{s_{(i)} s_{(k)}}{\lambda_{(i)} \lambda_{(k)}} \times [2\lambda_i^2 \lambda_k^2 (\sum_{p=1}^3 s_p^2 \lambda_p^2)^{-1} - \lambda_i^2 - \lambda_k^2] \quad (62)$$

The components of the unit vector \mathbf{s} are represented by eq. (2). Note that in the previous report¹⁸ it was not taken into account that the Fourier transformation was carried out over the coordinate system of the deformed media. Therefore the expression for $B_{ik}(\mathbf{Q})$ obtained there is true only for small strains of the material.

An interesting consequence follows from eq. (60). The Rayleigh ratio component $\mathcal{R}_{H_v}^{(\alpha)}$ is zero for materials containing isotropic rodlike particles [see eq. (33)]. However, additional scattering characterized by the term $\mathcal{R}_{H_v}^{(G)}$ appears if the sample is stretched. This property can be used to identify the shape and orientation of scattering elements.

DISCUSSION

The theory makes it possible to establish quantitative results between the scattered light intensity and the correlation functions of the inherent polarizability and shear modulus fluctuations. As shown above, because of the different physical nature of dielectric and elastic properties, fluctuations of the inherent polarizability and shear modulus can be characterized by different scales and geometry. This, together with the fact that SALS patterns are sensitive to the shape and orientation of the particles, may result in a great variety of azimuthal scattered light distributions from deformed polymers. A comprehensive discussion of the possible situations is beyond the scope of the present work, which is limited to the analysis of several typical structures and the corresponding H_v scattering patterns.

Consider the initial deformation dependence of SALS in macroscopically isotropic media with spherical heterogeneities. As we noted above [see eq. (26)], with crossed polaroids the Rayleigh ratio component relating to fluctuations of the inherent polarizability is zero. Owing to this fact, scattering in this case is observed only in deformed samples.

For this reason the scattering indicatrices are dependent only on the Fourier transform of the reduced correlation function of the shear modulus fluctuations $K(\mathbf{Q}) = \langle G \rangle^{-2} \mathcal{F}_{\mathbf{Q}} \{ \langle G' G' \rangle_{\mathbf{R}_0} \}$, where the vector \mathbf{Q} is related to the scattering vector \mathbf{q} by $\mathbf{Q} = \mathbf{q} \lambda$. Below, we consider the analysis of uniaxial stretching of filled composites with statistically independent inclusions. The corresponding correlation function in real space is exponential, $K(\mathbf{R}_0) = \exp(-R_0/a)$, where a is the correlation radius, with the Fourier transform equal to

$$K(\mathbf{Q}) = a^3 (\lambda \pi^{-1})^2 \{ \lambda + (2ka)^2 \sin^2 \left(\frac{\theta}{2} \right) \times [1 + (\lambda^3 - 1) \cos^2(\theta/2) \cos^2 \mu] \}^{-2}. \quad (63)$$

Here we put $\lambda_3 = \lambda$ and take into account the incompressibility condition $\lambda_3 \lambda_2^2 = 1$.

Figure 2 shows H_v contours calculated from eqs. (25), (50), and (57)–(63). One can see that the scattering is described by an eight-leaf pattern with four broad leaves (lobes) near the stretching axis and four narrow leaves (streaks) close to the equatorial direction orthogonal to the first one. The azimuthal position of these leaves depends on the ex-

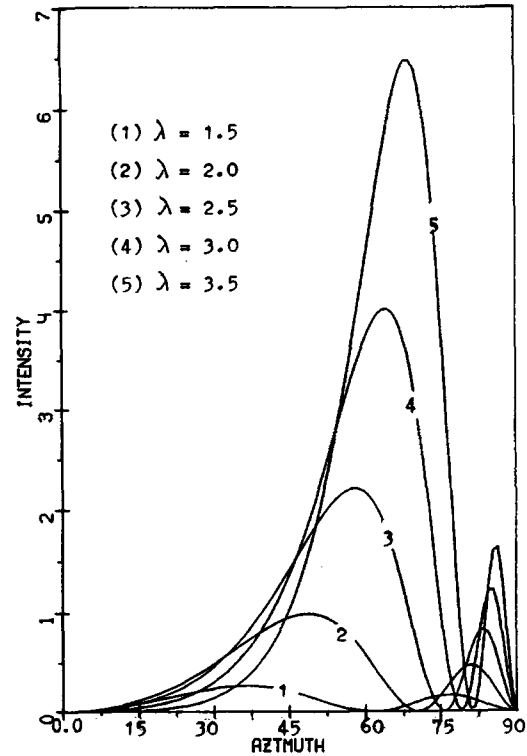


Figure 3. Azimuthal dependence of relative H_v light-scattering intensity for $\vartheta = 10^\circ$ at various elongations λ .

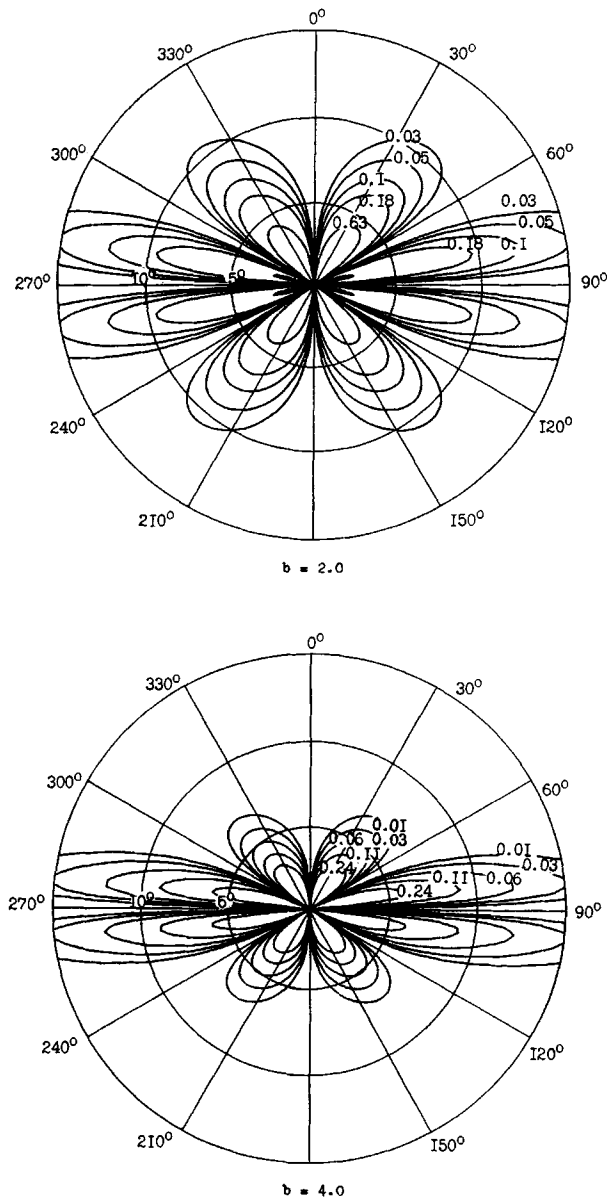


Figure 4. H_v light-scattering patterns for stretched, textured elastomer for $b > 1$ (spherical inclusions; $\lambda = 1.5$; $ak = 2\pi$)

tension ratio. The stretching results in deviation of the lobes and streaks from the stretching direction towards the equatorial line. Similar behavior was observed in experiment.^{14,16} We can see from Figures 2 and 3 that the azimuthal position μ_{\max} of the maximum H_v scattering intensity also depends on elongation; and increasing λ results in an increasing μ_{\max} with respect to the x_3 -axis. Hence, the azimuthal light scattering behavior is determined by the distribution of local elastic strains in a heterogeneous medium.

The inhomogeneous, macroscopically isotropic system considered before can be transformed to a macroscopically anisotropic one by high-temperature stretching or extrusion during preparation. In this case the position of the centers of spherical particles form a random anisotropic field with the texture axis directed along the stretching direction x_3 . This field, by definition, describes the distribution of local elastic moduli and is characterized by two different correlation radii a_3 and a_2 (the ratio $b = a_3/a_2$ is a measure of the anisotropy of the medium).

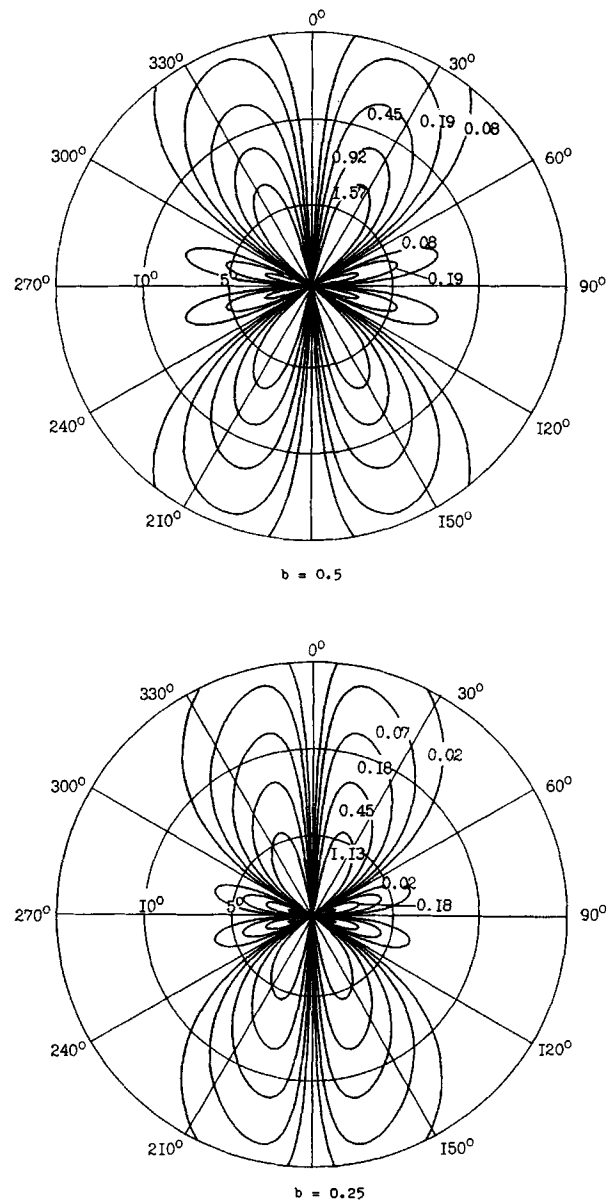


Figure 5. H_v light-scattering patterns from stretched textured elastomer for $b < 1$ (spherical inclusions; $\lambda = 1.5$; $a_2k = 2\pi$).

Then, in the case of statistically independent fluctuations of shear modulus, their correlation function is²⁶ $K(\mathbf{R}_0) = \exp\left\{-\sum_{p=1}^3 (x_p^0/a_p)^2\right\}^{1/2}$ with the Fourier transform

$$K(\mathbf{Q}) = ba_2^3(\lambda\pi^{-1})^2\left\{\lambda + (2ka_2)^2\sin^2\left(\frac{\theta}{2}\right) \times [1 + (\lambda^3b^2 - 1)\cos^2(\theta/2)\cos^2\mu]\right\}^{-2} \quad (64)$$

At $b = 1$, eq. (64) gives eq. (63).

Figures 4 and 5 show H_v contours calculated using eqs. (25), (50), (57)–(62), and (64) at a fixed value of $\lambda = 1.5$ for various values of the anisotropy parameter b . At $b > 1$, the intensity of lobes close to the equatorial line increases, whereas the intensity of lobes close to the texture axis decreases. At $b < 1$, the opposite behavior is observed. By comparing these patterns with the corresponding scattering for isotropic material, conclusions can be drawn on the character of the anisotropy of the spatial distribution of scattering elements.

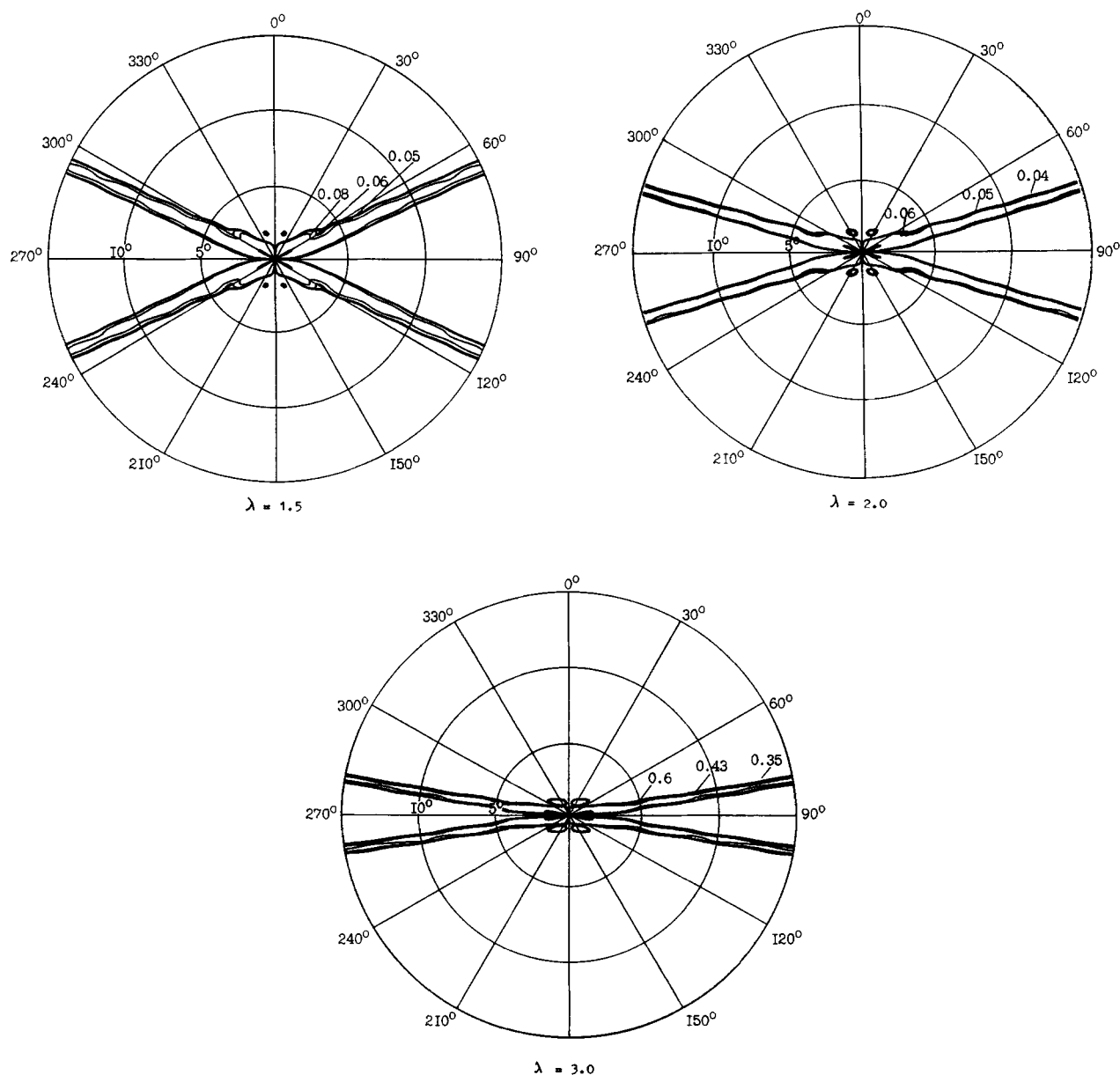


Figure 6. H_v light-scattering patterns at various elongations λ (thin isotropic rods; $\alpha_0 = \pm 40^\circ$; $Lk/2\pi = 40$).

We consider now the scattering from rodlike heterogeneous regions. In this case, probably, various experimental SALS patterns depend on the orientation of the optical axis vector \mathbf{d} relative to the rod axis and to the orientation of the latter. We restrict ourselves to the analysis of the simplest case of isotropic rods in the (x_2, x_3) -plane and the angle $\alpha_0 = \pm 40^\circ$ with respect to the x_3 -axis. According to eq. (33), H_v scattering is not observed in the undeformed state of the sample ($\mathcal{R}_{H_v}^{(\alpha)} = 0$). It appears only for loaded samples. We consider this simple model to analyze the effect of the particle shape on the scattering pattern. Figure 6 shows H_v contours for scattering from a system of thin rods of length $Lk/2\pi = 40$ for various extension ratios. The curves were calculated using eqs. (52) and (57)–(63) (for an isotropic distribution of rod centers). The calculated x -type SALS patterns are similar to those observed in scattering from isolated rodlike crystallites where the optical axis parallels the rod axis. One can see that the strain dependence of the scattering pattern is determined mainly by geometrical parameters of heterogeneities (shapes and polar angle α). The angle between streaks in the equatorial direction equals the current orientation of the rod axis. In this case the photoelastic effect produces only small changes in the SALS. The variation of the anisotropy parameter b has practically no effect on the angular position of the X -type streaks; but stretching can be used to make visible the H_v light scattering from the system of isotropic rods and to find the rod orientation.

Finally, we consider SALS from thin rodlike crystallites and spherical elastic heterogeneities. This situation is quite possible owing to the different physical nature of the inherent polarizability and shear modulus. In the case where the crystallites lie in the (x_2, x_3) -plane and their optical axes are parallel to the rod axes and make angles $\pm 40^\circ$ with the x_3 -axis. The calculations carried out by eqs. (25), (33), (50), (52), and (57)–(63) give scattering patterns shown in Figure 7. One can see that four leaves close to the equator split into eight and the H_v scattering pattern transforms into a 12-leaf pattern. A similar light scattering distribution has been observed.³³ The analysis shows that H_v scattering patterns may undergo marked changes, depending on variations of a number of parameters, such as rod orientations, anisotropy parameter b , the values of fluctuation amplitudes of the inherent polarizability anisotropy, shear modulus, correlation radii, and so on. A more detailed investigation could be carried out for some concrete polymer structures.

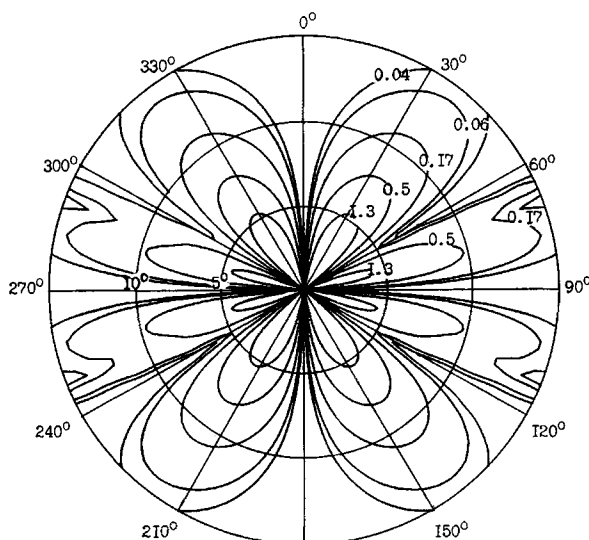


Figure 7. H_v light-scattering pattern from stretched elastomer containing rigid spherical assemblies of oriented rodlike crystallites ($\omega_0 = 0$; $\alpha_0 = \pm 40^\circ$; $Lk/2\pi = 40$; $ak = 2\pi$; $b = 1.0$)

CONCLUSION

Theoretical relations derived in this work permit study of light scattering of both isotropic and textured polymer materials with various structures. In particular, H_v scattering can be produced from optically isotropic heterogeneities in stretched materials. The light scattering pattern is determined by elongation and size, orientation, and spatial distribution of heterogeneities. The scattering indicatrix depends on azimuthal angle, the elasticity, and the correlation function for shear modulus fluctuations.

Calculated H_v contours form eight-leaf patterns for material containing spherical elastic heterogeneities. The pattern changes with increasing stretching and is in qualitative agreement with experimental data. This phenomenon depends on the specific distribution of local strains in a heterogeneous elastic medium. The H_v scattering pattern is determined also by the ratio of correlation radii along and orthogonal to the texture axis in the case of an anisotropic distribution of spherical particle centers.

The X -type H_v pattern appears from a deformed sample with optically isotropic thin rigid (or smooth) rods. The angle formed by streaks of scattered light with respect to equatorial direction corresponds to rod orientation for some material elongation. The light scattering azimuth distribution does not depend practically on the photoelastic effect

in this case, but is determined by geometrical parameters of the body.

There can appear various new H_v patterns when fluctuation regions of inherent polarizability and shear moduli are characterized by different forms. In particular, a 12-leaf pattern can appear if optical heterogeneities are rodlike and elastic ones are spherical.

The author is grateful to Prof. M. Matsuo for stimulating discussions and interest to this work. Thanks are also due to Dr. K. Summanen for useful comments and discussions.

APPENDIX 1. DERIVATION OF THE RELATION BETWEEN STRAIN AND SHEAR MODULUS CORRELATION FUNCTIONS: THE LINEAR CASE

Consider the equilibrium elastic equation of an inhomogeneous medium:

$$\sigma'_{ik,k} = 0, \quad (\text{A1.1})$$

where σ'_{ik} is the fluctuation part of the stress tensor. Splitting strain e_{ik} and shear modulus G in eq. (39) into average and fluctuation contributions gives

$$\sigma'_{ik} = 2\langle G \rangle e'_{ik} + 2G'e_{(i)}\delta_{ik} - p'\delta_{ik} \quad (\text{A1.2})$$

with account taken of the smallness e'_{ik} and G' . Putting eq. (A1.2) into eq. (A1.1) we find

$$u'_{k,ki} + u'_{i,kk} = -\langle G \rangle^{-1}(e_{(i)}G'_{,i} - \frac{1}{2}p'_{,i}), \quad (\text{A1.3})$$

where u_k is a displacement vector component ($e_{ik} = \frac{1}{2}(u_{i,k} + u_{k,i})$). The incompressibility condition in the case of linear elasticity theory has the form $u_{k,k} = 0$. Therefore, the first term in the left hand side of eq. (A1.3) is zero. Thus, we have

$$u'_{i,kk} = -\langle G \rangle^{-1}e_{(i)}\psi_{,i}; \quad \psi = G' - \frac{1}{2e_{(i)}}p' \quad (\text{A1.4})$$

This equation can be solved with the aid of Green's function method

$$\begin{aligned} u'_i(\mathbf{R}_o) &= \langle G \rangle^{-1}e_{(i)} \int Q(\mathbf{R}_o - \mathbf{R}'_o) \psi_{,i}(\mathbf{R}'_o) d\mathbf{R}'_o \\ &= \langle G \rangle^{-1}e_{(i)} Q * \psi_{,i} \end{aligned} \quad (\text{A1.5})$$

where $Q(\mathbf{R}_o)$ is Green's function satisfying eq. (45). After differentiation of the left and right hand sides

of eq. (A1.5) with respect to the x_k^o -coordinate, it follows that

$$u'_{i,k} = u'_{ik} = \langle G \rangle^{-1}e_{(i)}Q_{,ik} * \psi \quad (\text{A1.6})$$

From this we can obtain equations for some correlation functions:

$$\begin{aligned} \langle u'_{ik}u'_{mn} \rangle_{\mathbf{R}_o} &= \langle G \rangle^{-1}e_{(i)}Q_{,ik} * \left[\langle G'u'_{mn} \rangle_{\mathbf{R}_o} - \frac{1}{2e_i} \langle p'u'_{mn} \rangle_{\mathbf{R}_o} \right] \\ \langle u'_{ik}G' \rangle_{\mathbf{R}_o} &= \langle G \rangle^{-1}e_{(i)}Q_{,ik} * \left[\langle G'G' \rangle_{\mathbf{R}_o} - \frac{1}{2e_i} \langle p'G'_n \rangle_{\mathbf{R}_o} \right] \\ \langle u'_{ik}p' \rangle_{\mathbf{R}_o} &= \langle G \rangle^{-1}e_{(i)}Q_{,ik} * \left[\langle G'p' \rangle_{\mathbf{R}_o} - \frac{1}{2e_i} \langle p'p' \rangle_{\mathbf{R}_o} \right] \end{aligned} \quad (\text{A1.7})$$

Two additional equations are obtained from the incompressibility condition:

$$\langle u'_{pp}p' \rangle_{\mathbf{R}_o} = 0 \quad \text{and} \quad \langle u'_{pp}G' \rangle_{\mathbf{R}_o} = 0 \quad (\text{A1.8})$$

Excluding correlation functions $\langle p'p' \rangle_{\mathbf{R}_o}$, $\langle p'G' \rangle_{\mathbf{R}_o}$ and $\langle p'u'_{mn} \rangle_{\mathbf{R}_o}$ from eqs. (A1.7) and (A1.8), we obtain relations of interest:

$$\begin{aligned} \langle u'_{ik}G' \rangle_{\mathbf{R}_o} &= \langle G \rangle A_{ik} * K \quad \text{and} \\ \langle u'_{ik}u'_{mn} \rangle_{\mathbf{R}_o} &= A_{ik} * A_{mn} * K \end{aligned} \quad (\text{A1.9})$$

where

$$A_{ik}(\mathbf{R}_o) = [e_{(i)}\delta(\mathbf{R}_o) - \sum_{p=1}^3 e_p Q_{,pp}] * Q_{,ik} \quad (\text{A1.10})$$

APPENDIX 2. CALCULATION OF $\langle \eta_{ik}\eta_{mn} \rangle O_i^{(h)} O_m^{(h)} t_k^{(p)} t_n^{(p)}$ FOR CROSSED POLARIZATIONS

Taking into account the diagonal form of the average value of the deformation polarizability $\langle \eta_{ik} \rangle = \eta_{(i)}\delta_{ik}$ we obtain

$$\langle \eta_{ik}\eta_{mn} \rangle = \langle \eta'_{ik}\eta'_{mn} \rangle + \eta_{(i)}\eta_{(m)}\delta_{ik}\delta_{mn} \quad (\text{A2.1})$$

From this the value sought is found to have the form:

$$\langle \eta_{ik} \eta_{mn} \rangle O_i^{(h)} O_m^{(h)} t_k^{(p)} t_n^{(p)} = \langle \eta'_{i3} \eta'_{m3} \rangle O_i^{(h)} O_m^{(h)} \quad (\text{A2.2})$$

where the direction of the polarization unit vector $t^{(p)}$ parallel to the x_3 -axis is taken into account. The second term in eq. (A2.1) disappears after index convolutions. Substituting eq. (46) into eq. (A2.2), we obtain

$$\langle \eta'_{i3} \eta'_{m3} \rangle O_i^{(h)} O_m^{(h)} = A^2 \langle G \rangle^2 (P_{i3} * P_{m3} * K)_o O_i^{(h)} O_m^{(h)}. \quad (\text{A2.3})$$

The integral convolution in eq. (A2.3) at $\mathbf{R}_o = 0$ can be presented in the form:

$$(P_{i3} * P_{m3} * K)_o = \int P_{i3}(\mathbf{k}) P_{m3}(\mathbf{k}) K(\mathbf{k}) d\mathbf{k}, \quad (\text{A2.4})$$

where $P_{ik}(\mathbf{k})$ is a Fourier transform of the function $P_{ik}(\mathbf{R}_o)$. The argument of the correlation function $K(\mathbf{k})$ figures in the quadratic form $\sum_{p=1}^3 k_p^2 a_p^2 = l^2$ in the general case of anisotropic heterogeneous media (a_1, a_2 , and a_3 are correlation radii). Introducing new variables $l_i = k_{(i)} a_i$, and taking into account the properties of Green's functions $Q(\mathbf{l})$ and $\Phi(\mathbf{l})$, we come to the conclusion that $P_{ik}(\mathbf{l})$ depends on \mathbf{l} orientations in \mathbf{k} -space rather than on the magnitude of the vector \mathbf{l} : $P_{ik}(\mathbf{l}) = P_{ik}(\mathbf{v})$, where $\mathbf{v} = \mathbf{l}/l$. At the same time $K(\mathbf{l})$ depends only on the magnitude l . This permits us to write eq. (A2.4) as a product of two integrals:

$$\int P_{i3}(\mathbf{k}) P_{m3}(\mathbf{k}) K(\mathbf{k}) d\mathbf{k} = (a_1 a_2 a_3)^{-1} \times \int K(l) l^2 dl \int P_{i3}(\mathbf{v}) P_{m3}(\mathbf{v}) d\Omega_v \quad (\text{A2.5})$$

The first one is equal to $(4\pi)^{-1} a_1 a_2 a_3 K_o$, where $K_o = \langle G'^2 \rangle / \langle G \rangle^2$ is the dispersion of the shear modulus. Then from eqs. (A2.3)–(A2.5) we obtain

$$(P_{i3} * P_{m3} * K)_o O_i^{(h)} O_m^{(h)} = (4\pi)^{-1} K_o O_i^{(h)} O_m^{(h)} \times \int P_{i3}(\mathbf{v}) P_{m3}(\mathbf{v}) d\Omega_v \quad (\text{A2.6})$$

With help of eqs. (3) and (47) it is easy to show that the r.h.s. of eq. (A2.6) is proportional to the sum

$$(O_i^{(h)})^2 \int P_{13}^2(\mathbf{v}) d\Omega_v + (O_2^{(h)})^2 \int P_{23}^2(\mathbf{v}) d\Omega_v \quad (\text{A2.7})$$

since $\int P_{13}(\mathbf{v}) P_{23}(\mathbf{v}) d\Omega_v = 0$. But the integrals in eq. (A2.7) are equal. Hence, taking into account that $(O_i^{(h)})^2 + (O_2^{(h)})^2 = 1$ we obtain

$$\langle \eta_{ik} \eta_{mn} \rangle O_i^{(h)} O_m^{(h)} t_k^{(p)} t_n^{(p)} = A^2 \langle G \rangle^2 J K_o, \quad (\text{A2.8})$$

where $J = (4\pi)^{-1} \int P_{13}^2(\mathbf{v}) d\Omega_v$ and the result may be found in eqs. (58) and (59). As follows from eq. (A2.8), the diffuse contribution H_o scattering does not depend on the $\mathbf{O}^{(h)}$ vector.

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Received July 18, 1991

Accepted December 30, 1992