$K = 0.49$. This value is close to the observed value, 0.44, and agrees with the value due to the relation $K = g_{13}{}^0 g_{23}{}^0$ and eq 12. Since the average values of the characteristic quantities for the two solvent components are used to estimate the values of f and f', the value of $K = 0.49$ could be also compared with the value for the system BuCl + BuOH + PMMA. In view of the parallel behavior of $g_{12}(u_2)$, $\alpha(u_2)$, and $\beta(u_2)$ shown in Figure 5 the system BuCl + BuOH + PMMA appears to be better explained by Horta's theory. Thus, according to Horta's theoretical calculation the observed ternary function g_T could not be attributed to the specific properties of the solvent mixture but was due to the equation-of-state effect.

Registry No. PMMA, 9011-14-7; BuOH, 78-92-2; BuCl, 109-69-3; AcN, 75-05-8.

References and Notes

(1) Deb, P. C.; Palit, S. R. *Macromol. Chem.* **1973**, *166*, 277.
(2) Wolf, B. A.; Blaum, G. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1115.
(3) Cowie, J. M. G.; McCrindle, J. T. *Eur. Polym. J.* **1972**, *8*, 1185.
(4) Horta, A.; Fernandez-Pierola, I. *Macromolecules* **1981**, *14*, 1519.
(5) Prolongo, M. G.; Masegosa, R. M.; Hernandez-Fuentes, I.; Horta, A. *Macromolecules* **1981**, *14*, 1526.
(6) Masegosa, P. M.; Prolongo, M. G.; Hernandez-Fuentes, I.; Horta, A. *Macromolecules* **1984**, *17*, 1181.
(7) Chu, S. G.; Munk, P. *Macromolecules* **1978**, *11*, 879.
(8) Aminabhavi, T. M.; Munk, P. *Macromolecules* **1979**, *12*, 607.
(9) Katime, I.; Strazielle, C. *Makromol. Chem.* **1977**, *178*, 2295.
(10) Gavara, R.; Celda, B.; Campos, A. *Eur. Polym. J.* **1986**, *22*, 373.
(11) Read, B. E. *Trans. Faraday Soc.* **1960**, *56*, 382.
(12) Pouchlý, J.; Ziviny, A.; Šolc, K. *J. Polym. Sci., Part C* **1968**, *23*, 245.
(13) Dondos, A.; Patterson, D. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 209.
(14) Pouchlý, J.; Zivny, A. *Makromol. Chem.* **1982**, *183*, 3019.
(15) Pouchlý, J.; Zivny, A. *Makromol. Chem.* **1983**, *184*, 2081.
(16) Figueruelo, J. E.; Celda, B.; Campos, A. *Macromolecules* **1985**, *18*, 2504.
(17) Figueruelo, J. E.; Campos, A.; Celda, B. *Macromolecules* **1985**, *18*, 2511.
(18) Nakata, M.; Nakano, H.; Kawate, K. *Macromolecules*, preceding paper in this issue.
(19) Nakata, M.; Numasawa, N. *Macromolecules* **1985**, *18*, 1741.
(20) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; 3rd ed.; McGraw-Hill: New York, 1977.
(21) Fortier, J.-L.; Benson, G. C. *J. Chem. Thermodyn.* **1976**, *8*, 411.
(22) Olabisi, O.; Shimha, R. *Macromolecules* **1975**, *8*, 206.
(23) Scatchard, G.; Ticknor, L. B. *J. Am. Chem. Soc.* **1952**, *74*, 3724.
(24) Goates, J. R.; Snow, R. L.; James, M. R. *J. Phys. Chem.* **1961**, *65*, 335.
(25) Fernández-Piérola, I.; Horta, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1980**, *77*, 271.
(26) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 268.
(27) Horta, A. *Macromolecules* **1979**, *12*, 785.
(28) Horta, A. *Macromolecules* **1985**, *18*, 2498.
(29) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7.

Statistical Theory of Rayleigh Scattering of Light in Deformed and Swollen Heterogeneous Amorphous Polymer Networks

S. A. Patlazhan

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, Moscow Region, 142432 USSR. *Received April 13, 1987; Revised Manuscript Received September 4, 1987*

ABSTRACT: A statistical theory of Rayleigh scattering of light in heterogeneous Gaussian amorphous polymer networks, subjected to deformation or swelling, is developed. The scattered intensity is shown to depend on the mean square of fluctuations of the shear modulus and increases in a nonlinear way with the degree of network elongation or swelling. Results of the calculation agree with experimental data on the angle distribution of scattered intensity on the screen.

1. Introduction

Knowledge of light-scattering characteristics in a condensed medium provides one of the main sources of information about the structure of the medium.[1–3] Such a method of diagnosis is being widely used in scientific research and applications. At the same time there is an imperative of further development of theoretical concepts of the light scattering. A problem of this kind arises, in particular, when analyzing optical properties of deformed polymers. This is caused by several factors. One of them is that polymer materials are characterized by complex inhomogeneities of various types.[4] For example, in amorphous networks there are random spatial fluctuations of the cross-link concentration which produce regions with different elastic properties (namely, different values of the elastic modulus). Such inhomogeneities do not have abrupt borders. Their spatial distribution reflects conditions of network formation. Experiments show that deformation or swelling of such systems results in qualitative changes in the light-scattering pattern. Therefore the main objective of theory in reconstruction of basic structural characteristics of inhomogeneous networks based upon the light-scattering data.

Two main approaches have been developed for studying properties of heterogeneous materials, namely, the "regular" approach and the statistical approach.[2] The former treats inhomogeneity regions as inclusions having specific geometric form (sphere, rod, disk). The resultant scattering intensity is thus determined by a sum of contributions of different inclusions to the scattering. This approach was successfully applied to describe the small-angle light scattering from spherulites[2–5] and from assemblies of oriented rods and plates.[6–9] The regular approach made it possible to interpret observable patterns of polarized light scattering in swelled and deformed polymer films filled with solid spheres.[10–12] It was shown, in particular, that an additional scattering in deformed media is caused by a nonuniform distribution of dielectric permeability, induced by elastic stress fields in the vicinity of inclusions.

It should be noted that within the framework of the regular approach one has to invoke data on the structure

0024-9297/88/2221-2520$01.50/0

of heterogeneous medium studied. In many cases, however, one encounters the inverse problem, i.e., determining the internal structure of a body based upon the scattering light pattern. Such a problem, as applied to heterogeneous polymer networks, is of fundamental importance, and it can be solved with the use of statistical analysis. This method comprises a search for a relation between the scattering intensity and the correlation function of dielectric permeability fluctuations in the medium. The method was successfully used to describe the light scattering in materials with nonuniform distributions of density[13] and polarizability anisotropy.[14-15] However, all the work done in this field has been restricted to the study of optical properties of an undeformed polymer, hence they do not take into account a number of factors contributing to additional light scattering.

Because of the photoelastic effect, dielectric permeability of deformed networks depends on the degree of extension and on the network elasticity. Therefore it might be expected a priori that the light-scattering intensity in heterogeneous networks will also depend upon the correlation functions of elastic moduli (or correlation functions of fluctuations of the cross-link concentration). It is with this matter that the present work is concerned. Namely, we develop a statistical theory of Rayleigh scattering of light in amorphous heterogeneous Gaussian networks, deformed or swelled. With this objective in view, we start in the next section with basic relations of the general theory of electromagnetic wave scattering which are necessary for our further analysis. In section 3 the dependence of dielectric permeability on the local values of the shear moduli and strain of the network is considered. In section 4 we study the dependence of dielectric permeability correlation function on correlators of elastic fields and moduli of the network. Sections 5 and 6 treat the problem of interrelation between strain correlation functions and the structural function of the shear modulus of dry and swell networks, which characterize the degree of inhomogeneity of the medium. The dependence of the light-scattering intensity on the uniaxial extension and on the swelling degree is analyzed in sections 7 and 8. The main results of the work are listed in section 9.

2. Theory of Electromagnetic Wave Scattering: Basic Equations

The intensity I of a scattered electromagnetic wave depends upon the amplitude of the electric field intensity $\mathbf{E}$:

$$I = \langle E_i E^*_i \rangle \tag{1}$$

The asterisk stands for complex conjugate; the angular brackets denote averaging over the volume of a body. Besides, in (1), summation over repeating indices is meant. In what follows we deal with the Rayleigh ratio $R = I r_0^2 l^4 / I_0 V$ where r_0 is the distance between observation point and scattering volume V, $I_0 = \langle E_{0i} E^*_{0i} \rangle$ is the intensity of incident light corresponding to electric field intensity $\mathbf{E}_0$, $l = 2c\pi^{1/2}/\omega$.

According to the Born approximation, the electric field intensity of a scattered wave is given by the following equation:[1]

$$E_i = (4\pi r_0 \langle \epsilon \rangle)^{-1} (M_i + k_i k_m M_m) \exp(i\mathbf{k}\mathbf{r}_0) \tag{2}$$

$$M_i = \int \tilde{\epsilon}_{ik} E_{0k} \exp(i\mathbf{q}\mathbf{r})\, \mathrm{d}^3 r$$

Here $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors of the incident and scattered waves, respectively. Their wavenumbers are $k = k_0 = (\omega/c)\langle \epsilon \rangle^{1/2}$, where ω and c are the frequency and the velocity of light in a vacuum. The scattering vector is $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$. In (2) the difference $\tilde{\epsilon}_{ik} = \epsilon_{ik} - \langle \epsilon_{ik} \rangle$ means local deviation of the dielectric permeability tensor from its average value. If the wavelength of the electromagnetic wave exceeds characteristic dimensions of the inhomogeneity element, the vector $\mathbf{M}$ corresponds to the dipole moment of the region. In the case of discrete inclusions uniformly distributed over the sample, it is equal to the sum of dipole moments of particles in a volume unit, the tensor $\tilde{\epsilon}_{ik}$ being proportional to the polarizability tensor of the inclusion. The problem of light scattering is thus reduced to either the statistical, or the "regular" approach, according to the form chosen for the vector $\mathbf{M}$. In this work we will consider inhomogeneous materials with the small random spatial fluctuations of dielectric permeability.

In experiments on light-scattering monochromatic sources of linearly polarized light (such as lasers) are commonly used. A standard scheme of optical setup involved is given, for example, in ref 2. Let the x_1-axis of a coordinate system be parallel to electric field intensity vector $\mathbf{E}_0$ of the incident wave and the x_3-axis coincides with the direction of the wave vector $\mathbf{k}_0$. Then the scattering angle θ (i.e., the angle between directions of vectors $\mathbf{k}$ and $\mathbf{k}_0$) will be counted from the x_3-axis, while the azimuth angle φ (lying in the plane orthogonal to the wave vector of the incident wave) will be counted from the x_1-axis. In this coordinate system the wave vector of scattered light is equal to $\mathbf{k} = k_0 \mathbf{n}$, where $\mathbf{n}$ is the unit vector. Projections of the vector $\mathbf{n}$ are

$$n_1 = \sin\theta \cos\varphi \qquad n_2 = \sin\theta \sin\varphi \qquad n_3 = \cos\theta \tag{3}$$

Projections of the scattering vector are equal to $q_i = q_0 m_i$, $q_0 = 2\omega c^{-1} \sin\theta/2$

$$m_1 = \cos\frac{\theta}{2}\cos\varphi \qquad m_2 = \cos\frac{\theta}{2}\sin\varphi \qquad m_3 = -\sin\frac{\theta}{2} \tag{4}$$

It is seen that small absolute values of the vector $\mathbf{q}$ can be due to either large wavelength of the light or small-angle scattering. In what follows we treat the case of arbitrary scattering angles. In this case the Rayleigh ratio takes the form

$$R = \langle \overline{\tilde{\epsilon}_{i1}\tilde{\epsilon}_{i1}} \rangle - n_i n_j \langle \overline{\tilde{\epsilon}_{i1}\tilde{\epsilon}_{j1}} \rangle \tag{5}$$

The straight line on the top denotes the Fourier transformation with the wave vector $\mathbf{q}$.

If a polarizer is installed between the sample and the screen, different light-scattering patterns will be formed on the screen depending on the orientation of the polarizer. When polarizers are crossed, the Rayleigh ratio has the form

$$R_{\mathrm{H_v}} = \langle \overline{\tilde{\epsilon}_{21}\tilde{\epsilon}_{21}} \rangle + \langle \overline{\tilde{\epsilon}_{31}\tilde{\epsilon}_{31}} \rangle + (1 - n_1^2) n_p n_q \langle \overline{\tilde{\epsilon}_{p1}\tilde{\epsilon}_{q1}} \rangle + 2n_p (n_2 \langle \overline{\tilde{\epsilon}_{p1}\tilde{\epsilon}_{21}} \rangle + n_3 \langle \overline{\tilde{\epsilon}_{p1}\tilde{\epsilon}_{31}} \rangle) \tag{6}$$

while when they are parallel, it is of the form

$$R_{\mathrm{V_v}} = \langle \overline{\tilde{\epsilon}_{11}\tilde{\epsilon}_{11}} \rangle + \langle \overline{\tilde{\epsilon}_{31}\tilde{\epsilon}_{31}} \rangle + (1 - n_2^2) n_p n_q \langle \overline{\tilde{\epsilon}_{p1}\tilde{\epsilon}_{q1}} \rangle + 2n_p (n_1 \langle \overline{\tilde{\epsilon}_{p1}\tilde{\epsilon}_{11}} \rangle + n_3 \langle \overline{\tilde{\epsilon}_{p1}\tilde{\epsilon}_{31}} \rangle) \tag{7}$$

As follows from (5)–(7), in order to calculate the angle dependence of scattered intensity it is necessary to find the correlation function of fluctuations of dielectric permeability of the medium.

3. Dielectric Permeability of Inhomogeneous Polymer Networks

Dielectric permeability of undeformed (unswelled) polymers depends generally on the concentration of monomers and on anisotropy of their polarizability.[14,15] Optical properties of extended (or swelled) elastomers depend on cross-link concentration as well. We will suppose that the cross-link concentration is small compared to the concentration of monomers and does not affect dielectric permeability of the polymer in the absence of elastic fields.

Let us write down the following expression for dielectric permeability of the network:

$$\epsilon_{ik}(\mathbf{r}) = \epsilon_0(\mathbf{r})\delta_{ik} + \eta_{ik}(\mathbf{r}) \quad (8)$$

where $\epsilon_0(\mathbf{r})$ is a free-state value of dielectric permeability of a dry network, taken in the vicinity of the point which the radius vector is $\mathbf{r}$. Tensor $\eta_{ik}(\mathbf{r})$ determines a change in dielectric permeability resulting from imposing external actions such as deformation or swelling. Let us consider effects of each of them separately.

Dry Deformed Network. In this case an anisotropic component of dielectric permeability arises which can be expressed in terms of the strain tensor components.[16]

$$\eta_{ik}(\mathbf{r}) = B_0(\mathbf{r})G_0(\mathbf{r})[\lambda_{ip}(\mathbf{r})\lambda_{kp}(\mathbf{r}) - \tfrac{1}{3}\lambda_{pq}(\mathbf{r})\lambda_{pq}(\mathbf{r})\delta_{ik}] \quad (9)$$

Here $B_0(\mathbf{r}) = 4\pi[\epsilon_0(\mathbf{r}) + 2]^2\Delta\alpha/(45k_BT)$ is a coefficient depending on dielectric characteristics of a dry network, $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ is the anisotropy parameter of a macromolecule segment ($\alpha_\parallel$ and $\alpha_\perp$ being its longitudinal and transverse polarizabilities), $\lambda_{ik} = \partial x_i/\partial x_{0k}$ is the elongation tensor (x_i and x_{0k} are projections of radius vectors of a point of the body in the deformed and the free states, respectively), and δ_{ik} is the Kroneker symbol. The shear modulus $G_0(\mathbf{r})$ of a Gaussian network is related to the cross-link concentration $\nu_0(\mathbf{r})$ by a formula

$$G_0(\mathbf{r}) = \tfrac{1}{2}f\nu_0(\mathbf{r})k_BT\frac{\langle r^2\rangle}{\langle r^2\rangle_0} \quad (10)$$

where $\langle r^2\rangle/\langle r^2\rangle_0$ is the front factor of the network, $\langle r^2\rangle$ and $\langle r^2\rangle_0$ being mean-square distances between chain ends in the network and in the melt, respectively. It is seen that random variations in local values of the cross-link concentration result in fluctuations of the shear modulus and thus in random variations in dielectric permeability.

In order to calculate the fluctuations of dielectric permeability let us represent in the form of a sum of average and fluctuation parts quantities ϵ_0, G_0, and tensor λ_{ik} entering eq 8 and 9

$$\epsilon_0 = \langle\epsilon_0\rangle + \tilde{\epsilon}_0 \qquad G_0 = \langle G_0\rangle + \tilde{G}_0$$
$$\lambda_{ik} = \langle\lambda_{ik}\rangle + \tilde{\lambda}_{ik} \quad (11)$$

The average elongation tensor $\langle\lambda_{ik}\rangle$ can be chosen to be diagonal in the coordinate system considered: $\langle\lambda_{ik}\rangle = \lambda_{(i)}\delta_{ik}$ (summation is not performed over the indices in brackets). Then, to an accuracy of terms of the first order with respect to $\tilde{\epsilon}_0$, $\tilde{G}_0$, and $\tilde{\lambda}_{ik}$, we obtain from (8) and (9) the following expression for fluctuations of dielectric permeability tensor of a dry deformed network:

$$\tilde{\epsilon}_{ik} = \tilde{\epsilon}_0\langle\epsilon_0\rangle^{-1}T_{ik} + \langle B_0\rangle[\tilde{G}_0\Lambda_{(i)}\delta_{ik} + \langle G_0\rangle(\lambda_{(i)}\tilde{\lambda}_{ki} + \lambda_{(k)}\tilde{\lambda}_{ik}) - \tfrac{2}{3}\sum_p\lambda_p\tilde{\lambda}_{pp}\delta_{ik})] \quad (12)$$

$$T_{ik} = \langle\epsilon_0\rangle(1 + A\langle G_0\rangle\Lambda_{(i)})\delta_{ik}$$

$$\Lambda_i = \lambda_i^2 - \tfrac{1}{3}\sum_p\lambda_p^2, \qquad A = 2\langle B_0\rangle(\langle\epsilon_0\rangle + 2)^{-1}$$

Note that because of distortion of elastic deformation field in the vicinity of inhomogeneity elements, the fluctuation part of the tensor λ_{ik} may, in general, be nondiagonal.

Swollen Network. In the absence of binary interactions of macromolecules in the volume, a change in dielectric permeability of polymer networks caused by swelling in Θ-solvent can be represented in the following form

$$\eta_{ik}^{(s)}(\mathbf{r}) = v_s(\epsilon_s - \epsilon_0)\delta_{ik} + B(\mathbf{r})G(\mathbf{r})[\lambda_{ip}^{(s)}(\mathbf{r})\lambda_{kp}^{(s)}(\mathbf{r}) - \tfrac{1}{3}\lambda_{pq}^{(s)}(\mathbf{r})\lambda_{pq}^{(s)}(\mathbf{r})\delta_{ik}] \quad (13)$$

Here $B(\mathbf{r})$ is a coefficient similar to that in (9) but depending on dielectric properties of the swollen network, whose dielectric permeability is equal to $\epsilon = \epsilon_0 + v_s(\epsilon_s - \epsilon_0)$ in the absence of cross-links (v_s and ϵ_s are the concentration and dielectric permeability of the solvent, respectively). Tensor $\lambda_{ik}^{(s)}(\mathbf{r})$ characterizes the strain of the swollen polymer in some point, the local shear modulus being related to that of corresponding dry network by

$$G(\mathbf{r}) = (\det \lambda^{(s)})^{-1/3}G_0(\mathbf{r}) \quad (14)$$

Using (14) we arrive immediately at a relationship between average and fluctuation values of shear moduli of dry and swollen networks. Indeed, the substitution of expansion (11) for $\lambda_{ik}^{(s)}$ and G_0 in (14) with allowance made for the fact that the swelling is, on the average, isotropic, $\langle\lambda_{ik}^{(s)}\rangle = \varkappa\delta_{ik}$, we obtain

$$\langle G\rangle = \varkappa^{-1}\langle G_0\rangle, \qquad \tilde{G}(\mathbf{r}) = \varkappa^{-1}\tilde{G}_0(\mathbf{r}) - \tfrac{1}{3}\varkappa^{-2}\langle G_0\rangle\tilde{\lambda}_{pp}^{(s)}(\mathbf{r}) \quad (15)$$

where $\tilde{\lambda}_{pp}^{(s)}(\mathbf{r})$ is the fluctuation part of the sum of diagonal elements of the tensor $\tilde{\lambda}_{ik}^{(s)}(\mathbf{r})$. Using these relations we obtain from (8) and (13) the following expression for local changes in dielectric permeability tensor of the swollen network:

$$\tilde{\epsilon}_{ik}^{(s)} = v_p\tilde{\epsilon}_0\delta_{ik} + \langle B\rangle\langle G_0\rangle(\tilde{\lambda}_{ik}^{(s)} + \tilde{\lambda}_{ki}^{(s)} - \tfrac{2}{3}\delta_{ik}\tilde{\lambda}_{pp}^{(s)}) \quad (16)$$

where $v_p = 1 - v_s$ is the volume concentration of the polymer.

4. Spatial Correlations of Dielectric Permeability of Heterogeneous Networks

Equations 12 and 16 enable one to construct expressions for correlation functions of dielectric permeability fluctuations of deformed and swollen networks. In general they depend upon correlators of all random variables entering eq 12 and 16. However, since the monomer concentration in elastomers greatly exceeds the cross-link concentration, we may regard random fluctuations of ϵ_0 and G_0 as statistically independent. Mathematically, this can be written as $\langle\tilde{\epsilon}_0\tilde{G}_0\rangle = 0$. Besides, fluctuations of the strain field are determined by variations of the shear modulus and, hence, do not depend on ϵ_0: $\langle\tilde{\epsilon}_0\tilde{\lambda}_{ik}\rangle = 0$. Based on these considerations and using eq 12 we find the correlation function of fluctuations of dielectric permeability of a dry inhomogeneous network:

$$\begin{aligned}\langle\tilde{\epsilon}_{ik}\tilde{\epsilon}_{mn}\rangle = {} & T_{ik}T_{mn}D_\epsilon(\mathbf{r}) + \langle B_0\rangle^2\{\langle G_0\rangle^2\Lambda_{(i)}\Lambda_{(m)}\delta_{ik}\delta_{mn}D_G(\mathbf{r}) + \langle G_0\rangle[(\lambda_{(i)}\langle\tilde{\lambda}_{ki}\tilde{G}_0\rangle + \lambda_{(k)}\langle\tilde{\lambda}_{ik}\tilde{G}_0\rangle - {} \\ & \tfrac{2}{3}\sum_{p=1}^{3}\lambda_p\langle\tilde{\lambda}_{pp}\tilde{G}_0\rangle\delta_{ik})\Lambda_{(m)}\delta_{mn} + (\lambda_{(m)}\langle\tilde{\lambda}_{nm}\tilde{G}_0\rangle + \lambda_{(n)}\langle\tilde{\lambda}_{mn}\tilde{G}_0\rangle \\ & - \tfrac{2}{3}\sum_{p=1}^{3}\lambda_p\langle\tilde{\lambda}_{pp}\tilde{G}_0\rangle\delta_{mn})\Lambda_{(i)}\delta_{ik}] + \langle G_0\rangle^2[\lambda_{(i)}\lambda_{(m)}\langle\tilde{\lambda}_{ki}\tilde{\lambda}_{nm}\rangle + {} \\ & \lambda_{(i)}\lambda_{(n)}\langle\tilde{\lambda}_{ki}\tilde{\lambda}_{mn}\rangle + \lambda_{(k)}\lambda_{(m)}\langle\tilde{\lambda}_{ik}\tilde{\lambda}_{nm}\rangle + \lambda_{(k)}\lambda_{(n)}\langle\tilde{\lambda}_{ik}\tilde{\lambda}_{mn}\rangle - {} \\ & \tfrac{2}{3}\sum_{p=1}^{3}\lambda_p(\lambda_{(m)}\langle\tilde{\lambda}_{pp}\tilde{\lambda}_{nm}\rangle\delta_{ik} + \lambda_{(n)}\langle\tilde{\lambda}_{pp}\tilde{\lambda}_{mn}\rangle\delta_{ik} + {} \\ & \lambda_{(i)}\langle\tilde{\lambda}_{pp}\tilde{\lambda}_{ki}\rangle\delta_{mn} + \lambda_{(k)}\langle\tilde{\lambda}_{pp}\tilde{\lambda}_{ik}\rangle\delta_{mn}) + {} \\ & \tfrac{4}{9}\sum_{p=1}^{3}\sum_{q=1}^{3}\lambda_p\lambda_q\langle\tilde{\lambda}_{pp}\tilde{\lambda}_{qq}\rangle\delta_{ik}\delta_{mn}]\}\end{aligned} \quad (17)$$

Expressions for tensor T_{ik} and Λ_i are given in (12), while $D_\epsilon(\mathbf{r}) = \langle\epsilon_0\rangle^{-2}\langle\tilde{\epsilon}_0(\mathbf{r})\tilde{\epsilon}_0(0)\rangle$ and $D_G(\mathbf{r}) = \langle G_0\rangle^{-2}\langle\tilde{G}_0(\mathbf{r})\tilde{G}_0(0)\rangle$

are structural functions of dielectric permeability and shear modulus of a dry network in free state, respectively. These functions characterize the degree of inhomogeneity of the body.

Using relation 16 we can also write down an expression for the correlation function of dielectric permeability of a swollen network:

$$\langle\tilde{\epsilon}_{ik}^{(s)}\tilde{\epsilon}_{mn}^{(s)}\rangle = v_p^2\langle\epsilon_0\rangle^2 D_\epsilon(\mathbf{r})\delta_{ik}\delta_{mn} + \langle B\rangle^2\langle G_0\rangle^2[\langle\tilde{\lambda}_{ik}^{(s)}\tilde{\lambda}_{mn}^{(s)}\rangle + \langle\tilde{\lambda}_{ki}^{(s)}\tilde{\lambda}_{mn}^{(s)}\rangle + \langle\tilde{\lambda}_{ik}^{(s)}\tilde{\lambda}_{nm}^{(s)}\rangle + \langle\tilde{\lambda}_{ki}^{(s)}\tilde{\lambda}_{nm}^{(s)}\rangle - \tfrac{2}{3}(\langle\tilde{\lambda}_{pp}^{(s)}\tilde{\lambda}_{ik}^{(s)}\rangle\delta_{mn} + \langle\tilde{\lambda}_{pp}^{(s)}\tilde{\lambda}_{ki}^{(s)}\rangle\delta_{mn} + \langle\tilde{\lambda}_{pp}^{(s)}\tilde{\lambda}_{mn}^{(s)}\rangle\delta_{ik} + \langle\tilde{\lambda}_{pp}^{(s)}\tilde{\lambda}_{nm}^{(s)}\rangle\delta_{ik} + \tfrac{4}{9}\langle\tilde{\lambda}_{pp}^{(s)}\tilde{\lambda}_{qq}^{(s)}\rangle\delta_{ik}\delta_{mn})] \quad (18)$$

It can be seen from (17) and (18) that in order to solve the problem formulated above, it is necessary to express the correlators of elastic fields in terms of the structural function $D_G(\mathbf{r})$ of shear moduli. The problem of calculating the local strains which result from loading of inhomogeneous network without solvent differs from a similar problem for a swollen network, mainly by constraints imposed on change of the volume of polymer. In the first case the network deformation proceeds without any change of the volume. In the second case change of the volume because of network swelling results in emergence of internal strains. That is why we have to consider these cases separately.

5. Calculation of Correlation Functions of Elastic Fields of Dry Networks

Local elastic properties of amorphous incompressible Gaussian networks are described by the high elasticity equation:

$$\sigma_{ik}(\mathbf{r}) = G_0(\mathbf{r})\lambda_{ip}(\mathbf{r})\lambda_{kp}(\mathbf{r}) - p(\mathbf{r})\delta_{ik} \quad (19)$$

Here σ_{ik} is the stress tensor, p is a parameter with dimension of pressure (the latter is to be determined from incompressibility condition).

Let us consider the equation of equilibrium of inhomogeneous medium in the absence of volume forces:

$$\partial\sigma_{ik}/\partial x_k = 0 \quad (20)$$

It is clear that under uniform external deformation of a sample the average stress will be also uniform, its divergence with respect to the coordinates connected with undeformed state of a body being equal to zero identically. Therefore, instead of the full value of σ_{ik} we may substitute in (20) its fluctuation part only. Using eq 19 we can find local changes in stress. With an accuracy of terms of the first order in $\tilde{G}_0$ and $\tilde{\lambda}_{ik}$ these take the form

$$\tilde{\sigma}_{ik}(\mathbf{r}) = \tilde{G}_0(\mathbf{r})\lambda_{(i)}\delta_{ik} + \langle G_0\rangle[\lambda_{(i)}\tilde{\lambda}_{ki}(\mathbf{r}) + \lambda_{(k)}\tilde{\lambda}_{ik}(\mathbf{r})] - \tilde{p}(\mathbf{r})\delta_{ik} \quad (21)$$

Substituting (21) in (20) and transforming this to underformed body coordinates, we arrive at the equation[16]

$$\sum_{k=1}^{3}(\lambda_{(i)}^{-1}\tilde{\lambda}_{ik,k} + \lambda_k^{-1}\tilde{\lambda}_{ki,k}) = -\psi_{(i),i}$$

$$\psi_i = \langle G_0\rangle^{-1}(\tilde{G}_0 - \lambda_i^{-2}\tilde{p}) \quad (22)$$

which relates fluctuations of the elastic field to fluctuations of the shear modulus of the network. Indices after commas stand for differentiation with respect to coordinates of points of undeformed media. The incompressibility condition $\lambda_1\lambda_2\lambda_3 = 1$ is followed by an equality

$$\sum_{p=1}^{3}\lambda_p^{-1}\tilde{\lambda}_{pp} = 0$$

which is true with an accuracy of terms of the first order in fluctuations $\tilde{\lambda}_{ik}$. Using the equality we can simplify eq 22:

$$\tilde{\lambda}_{ik,k} = -\lambda_i\psi_{i,i} \quad (23)$$

A solution for this equation can be represented in the form of an integral convolution:

$$\tilde{\lambda}_{ik}(\mathbf{r}) = \lambda_i\int Q_{,ik}(\mathbf{r}-\mathbf{r}')\psi_i(\mathbf{r}')\,d^3r' \quad (24)$$

where $Q(\mathbf{r})$ is the Green function obeying the equation $Q_{,kk} = -\delta(\mathbf{r})$.

Multiplying the left and right sides of (24) by $\tilde{\lambda}_{mn}(0)$, $\tilde{G}_0(0)$ and $\tilde{p}(0)$ and performing averaging over the volume, we obtain a system of integro-differential equations, which, after being Fourier transformed, is reduced to a system of algebraic equations. If we exclude functions which contain the quantity $\tilde{p}$ we will find Fourier transforms of correlation functions sought of elastic strains:

$$\overline{\langle\tilde{\lambda}_{ik}\tilde{\lambda}_{mn}\rangle} = \lambda_i\lambda_m m_{ikmn}(1-\lambda_i^{-2}b)(1-\lambda_m^{-2}b)\bar{D}_G(\mathbf{q}) \quad (25)$$

$$\overline{\langle\tilde{\lambda}_{ik}\tilde{G}_0\rangle} = -\lambda_i\langle G_0\rangle m_{ik}(1-\lambda_i^{-2}b)\bar{D}_G(\mathbf{q}) \quad (26)$$

Here $\bar{D}_G(\mathbf{q})$ is the Fourier transform of the structural function $D_G(\mathbf{r})$, $m_{ij...k} \equiv m_im_j...m_k$, $b = (\sum_p m_p^2\lambda_p^{-2})^{-1}$, $\mathbf{q}$ is the wave vector of the Fourier transform. Values of components of the vector $\mathbf{m}$ are given in (4).

Equations 25 and 26 describe a relationship between correlation functions of elastic fields resulting from deformation of dry polymer network and the structural function of the shear modulus fluctuations.

6. Calculations of Correlation Functions of Elastic Fields of Swollen Networks

Let us consider now statistical characteristics of elastic fields of heterogeneous linked polymers that are swelled in Θ-solvent. The choice of Θ-solvent makes it possible to neglect the volume interaction between macromolecules. In Θ-solvent network conformations obey Gaussian statistics which simplifies essentially calculations of the network stress as a function of the swelling degree. In this case the free energy of an arbitrary volume of the sample can be written as

$$F(\mathbf{r}) = \frac{f}{4}k_BT\nu(\mathbf{r})\left[(J_1(\mathbf{r})-3) - \frac{2}{f}\ln J_3(\mathbf{r})\right] \quad (27)$$

$$J_1 = \lambda_{pq}^{(s)}\lambda_{pq}^{(s)} \qquad J_3 = \det(\lambda_{pi}^{(s)}\lambda_{pk}^{(s)})$$

where f is the functionality of nodes of the network and $\nu(\mathbf{r})$ is the local cross-link concentration in swollen polymer. The tensor $\lambda_{ik}^{(s)}$ in (27) is written down in a general form, since local combined stresses may arise in heterogeneous medium during its swelling. At the same time, the network swelling is, on the average, isotropic, the fact being expressed by equality $\langle\lambda_{ik}^{(s)}\rangle = \varkappa\delta_{ik}$.

In order to calculate the local stress tensor let us follow[17] and differentiate the free energy (27) with respect to the tensor of strains $e_{ik}^{(s)} = \tfrac{1}{2}(\lambda_{pi}^{(s)}\lambda_{pk}^{(s)} - \delta_{ik})$. Then we have

$$\sigma_{ik}^{(s)} = (\det\lambda^{(s)})^{-4/3}G_0[\lambda_{ip}^{(s)}\lambda_{kp}^{(s)} - \delta_{ik}] \quad (28)$$

Here we have used eq 14 which interrelates shear moduli of dry and swollen networks. Representing G_0 and $\lambda_{ik}^{(s)}$ in (28) as a sum of the average and fluctuation parts (with an accuracy of terms of first order in $\tilde{G}_0$ and $\tilde{\lambda}_{ik}^{(s)}$) we obtain an expression for fluctuations of the stress tensor of a swollen network:

$$\tilde{\sigma}_{ik}^{(s)}(\mathbf{r}) = \varkappa^{-3}\{\varkappa(1-\varkappa^{-2})\tilde{G}_0(\mathbf{r})\delta_{ik} - \langle G_0\rangle[\tfrac{4}{3}(1-\varkappa^{-2})\tilde{\lambda}_{pp}^{(s)}(\mathbf{r})\delta_{ik} + \tilde{\lambda}_{ik}^{(s)}(\mathbf{r}) + \tilde{\lambda}_{ki}^{(s)}(\mathbf{r})]\} \quad (29)$$

Substituting (29) in equilibrium equation (20) and taking into account a relation $\lambda_{ik}^{(s)} = \tilde{u}_{i,k}^{(s)}$ between the tensor $\tilde{\lambda}_{ik}^{(s)}$ and displacement vector $u_i = x_i - x_{0i}$ we arrive at the equation

$$\tilde{u}_{i,pp}^{(s)} + \frac{1}{3}\left(\frac{4}{\varkappa^2} - 1\right)\tilde{u}_{p,pi}^{(s)} = \left(\frac{1}{\varkappa^2} - 1\right)\varkappa\frac{\tilde{G}_{0,i}}{\langle G_0\rangle} \quad (30)$$

Applying the Fourier transformation to the right and left parts of the equation, we find, after some algebra, the following relation between Fourier transforms of fluctuations of elastic strains and shear moduli:

$$\overline{\tilde{\lambda}_{ik}^{(s)}}(\mathbf{q}) = am_{ik}\bar{\tilde{G}}_0(\mathbf{q})\langle G_0\rangle^{-1} \qquad a = \tfrac{3}{2}\varkappa(\varkappa^2 - 1)(\varkappa^2 + 2)^{-1} \quad (31)$$

($\mathbf{q}$ is the wave vector of the Fourier transformation). Multiplying the left and the right parts of (31) by $\overline{\tilde{\lambda}_{mn}^{(s)}}(0)$ and $\tilde{G}_0(0)$, and performing averaging over the volume of the body we can easily find the Fourier transforms of correlation functions sought:

$$\overline{\langle\tilde{\lambda}_{ik}^{(s)}\tilde{\lambda}_{mn}^{(s)}\rangle} = a^2 m_{ikmn}\bar{D}_G(\mathbf{q}) \quad (32)$$

$$\overline{\langle\tilde{\lambda}_{ik}^{(s)}\tilde{G}_0\rangle} = -am_{ik}\bar{D}_G(\mathbf{q}) \quad (33)$$

Equations 32 and 33 provide relations between correlation functions of elastic strains of a swollen polymer and the structural function of shear moduli of corresponding dry network.

Let us consider now optical properties of inhomogeneous networks.

7. Intensity of Rayleigh Light Scattering in Dry Deformed Heterogeneous Networks

Intensity of scattered light which is incident on the screen depends on the correlation function of fluctuations of the dielectric permeability tensor of the medium (see (5)–(7)). In the case of a dry deformed network the Fourier transform of this function can be found with the use of eq 17, 25, and 26. It has the form

$$\langle\overline{\tilde{\epsilon}_{ik}\tilde{\epsilon}_{mn}}\rangle = T_{ik}T_{mn}\bar{D}_\epsilon(\mathbf{q}) + P_{ik}P_{mn}\bar{D}_G(\mathbf{q}) \quad (34)$$

The expression for the tensor T_{ik} is given in (12), while

$$P_{ik} = \langle B_0\rangle\langle G_0\rangle(\lambda_{(i)}\lambda_{(k)}B_{ik} - \tfrac{1}{3}\delta_{ik}\sum_{p=1}^{3}\lambda_p^2 B_{pp})$$

$$B_{ik} = \delta_{ik} - m_{ik}[2 - (\lambda_{(i)}^{-2} + \lambda_{(k)}^{-2})(\sum_p m_p^2\lambda_p^{-2})^{-1}] \quad (35)$$

It can be seen from (34) that the correlation function of fluctuations or dielectric permeability of heterogeneous polymer network is determined by two structural functions, D_ϵ and D_G, which characterize the degree of inhomogeneity of the medium according to its density and elastic properties.

If cross-links are distributed uniformly in the medium, the structural function of the shear moduli is $D_G = 0$ and the light scattering is determined by fluctuations of monomer concentration (the first term in (34)). It is seen from (12) and (34) that in the case of a constant value of the shear modulus the scattered intensity will also depend on the degree of deformation of the material, although the angle distribution of scattered light is determined solely by the form of the structural function $\bar{D}_\epsilon(\mathbf{q})$. Indeed, substituting (12) and (34) in expression 5 we obtain the Rayleigh ratio for polarized light scattering from density fluctuations:

$$R^\epsilon = (1 - n_1^2)\langle\epsilon_0\rangle^2[1 + \tfrac{1}{3}A_0\langle G_0\rangle(2\lambda_1^2 - \lambda_2^2 - \lambda_3^2)]^2\bar{D}_\epsilon(\mathbf{q}) \quad (36)$$

When polarizers are crossed, the scattered intensity from density fluctuations is given by the formula

$$R_{H_v}^{\epsilon} = n_1^2 R^\epsilon \quad (37)$$

while when they are parallel,

$$R_{V_v}^{\epsilon} = [1 - (4 - n_2^2)(1 - n_1^2)^{-1}]R^\epsilon \quad (38)$$

where the values of n_1, n_2, and n_3 are given by (3).

In the absence of strains (or when compression or extension is uniform) eq 36 coincides with a well-known result by Debye.[13]

When the monomer concentration is constant, the light scattering in a deformed polymer network can be induced by random variations in local elastic properties which, as was mentioned above, may result from spatial fluctuations of the cross-link concentration. Unlike the previous example, the angular distribution of scattered light on the screen will be more complicated in this case. This fact is explained, in the final analysis, by a nonuniform distribution of local elastic strains in heterogeneous media. It seems relevant to consider light-scattering patterns in cases of crossed and parallel analyzers, as is usually done in experiment. When polarizers are crossed, the Raleigh ratio can be found from eq 6, 34, and 35:

$$R_{H_v}^{G} = S_{H_v}(\theta,\varphi)\bar{D}_G(\mathbf{q}) \quad (39)$$

The function $S_{H_v}(\theta,\varphi)$ has the form[18]

$$S_{H_v}(\theta,\varphi) = (n_2 n_i P_{i1} - P_{21})^2 + (n_3 n_i P_{i1} - P_{31})^2 \quad (40)$$

When polarizers are parallel, eq 7, 34, and 35 provide the following relation

$$R_{V_v}^{G} = S_{V_v}(\theta,\varphi)\bar{D}_G(q) \quad (41)$$

where $S_{V_v}(\theta,\varphi)$ has the form[18]

$$S_{V_v}(\theta,\varphi) = (n_1 n_i P_{i1} - P_{11})^2 + (n_3 n_i P_{i1} - P_{31})^2 \quad (42)$$

It can be seen from (39)–(41) that the angle dependence of the scattered intensity is determined by functions $S_{H_v}(\theta,\varphi)$ and $S_{V_v}(\theta,\varphi)$ and by the Fourier transform of the structural function of shear moduli of the network $\bar{D}_G(\mathbf{q})$. Note that in the case of isotropic material this function depends solely on the absolute value of the scattering vector $q_0 = 2(\omega/c)\sin(\theta/2)$ and, hence, on the angle θ only. Thus asimuthal distribution of scattered light intensity is determined by the form of the function $S_{H_v}(\theta,\varphi)$ or $S_{V_v}(\theta,\varphi)$.

At small-angle scattering and under uniaxial extension directed along the x_1-axis, the function $S_{H_v}(\theta,\varphi)$ can be simplified. Neglecting terms of the order of θ^2 in (40) we obtain the following expression[19]

$$S_{H_v} = \tfrac{1}{16}\lambda(\lambda^3 - 1)^2\sin^2 4\varphi[1 + (\lambda^3 - 1)\sin^2\varphi]^{-2} \quad (43)$$

where we put $\lambda_1 = \lambda$, $\lambda_2 = \lambda_3 = \lambda^{-1/2}$, the azimuth angle being counted from the x_1-axis in the plane orthogonal to the wave vector k_0 of the incident wave.

As an example let us consider the scattering pattern from heterogeneous network, uniaxially extended along the x_1-axis. The structural function of shear moduli of the network is supposed to have the following form: $D_G(\mathbf{r}) = (\pi^2/\xi^3)\exp(-(r/\xi))$. Such a network is similar to a matrix composite material filled with statistically independent dispersive inclusions with radii of ξ. The Fourier transform of the structural function chosen has the form $\bar{D}_G(\mathbf{q}) = (1 + q_0^2\xi^2)^{-2}$. In Figure 1 we present contour plots of equal intensity of scattered light which arise in crossed polarizers at sample extension $\lambda = 1.5$. The calculations were done with eq 39 and 40. The correlation radius was supposed

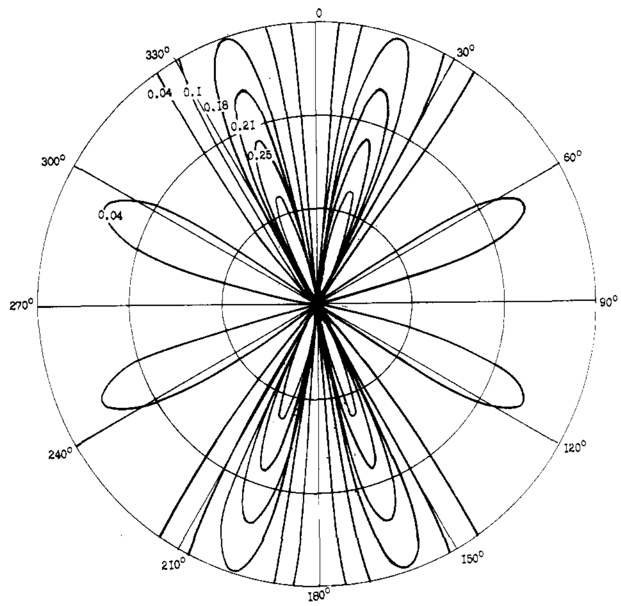

Figure 1. Contour plots of equal intensity of scattered light from uniaxially extended networks: crossed polarizers ($\lambda = 1.5$, $D_G(\mathbf{r}) = (\pi^2/\xi^3)\exp(-r/\xi)$.

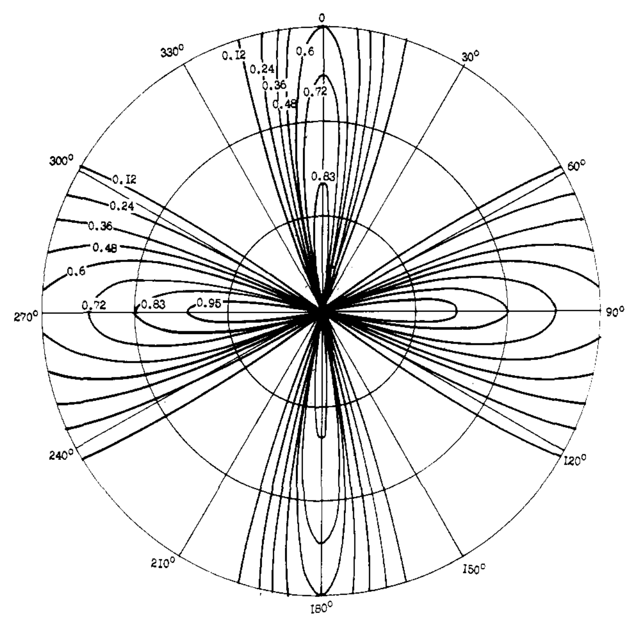

Figure 2. Contour plots of equal intensity of scattered light from uniaxially extended networks: parallel polarizers ($\lambda = 1.5$, $D_G(\mathbf{r}) = (\pi^2/\xi^3)\exp(-r/\xi)$).

to be equal to the wavelength of the light ($\xi = 2\pi c/\omega$). It can be seen from Figure 1 that an eight-lobe pattern arises on the screen. The scattered intensity is nonuniform, the lobes close to the extension axis being brighter. This theoretical pattern agrees well with experimental data (see, e.g., ref 11, 12).

Contour plots of equal intensities of the light scattering for the same material and the same value of $\lambda = 1.5$, but arising in parallel polarizers, are shown in Figure 2. The calculations were done with eq 41 and 42. It can be seen that maximum energy lies in the sector close to the x_2-axis. This results in efficient elongation of the scattering pattern along this axis and agrees with experiment.[18]

The main problem emerging when studying heterogeneous media by the light scattering method is determination of structural parameters of a sample (such as inhomogeneity dimensions, their mutual arrangements, etc.). Photometric measurements of scattering patterns arising at different values of azimuth angles show that scattering

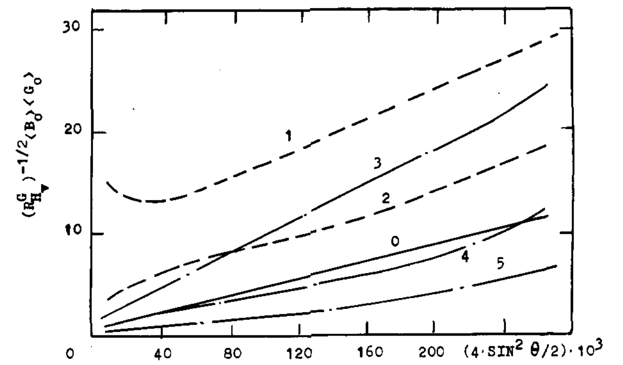

Figure 3. Scattering indicatrices from uniaxially extended networks: crossed polarizers. The straight line (0) corresponds to the function $\bar{D}_G(\mathbf{q}) = (1 + q_0{}^2\xi_0{}^2)^{-2}$. Dotted lines corresponds to $\varphi = 0$: (1) $\lambda = 1.5$; (2) $\lambda = 2.0$. Dash–dot lines corresponds to $\varphi = 20°$: (3) $\lambda = 1.5$; (4) $\lambda = 2.0$; (5) $\lambda = 3.0$.

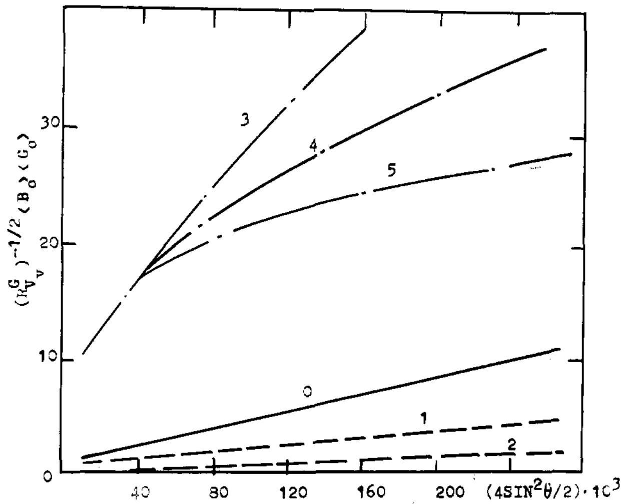

Figure 4. Scattering indicatrices from uniaxially extended networks: parallel polarizers. The straight line (0) corresponds to the function $\bar{D}_G(\mathbf{q}) = (1 + q_0{}^2\xi_0{}^2)^{-2}$. Dotted lines corresponds to $\varphi = 90°$: (1) $\lambda = 2.0$; (2) $\lambda = 3.0$. Dash–dot lines correspond to $\varphi = 45°$: (3) $\lambda = 2.0$; (4) $\lambda = 2.5$; (5) $\lambda = 3.0$.

indicatrices differ from one another. This fact presents difficulties when determining structural characteristics. The situation differs radically from that studied by Debye and Bueche[13] and characterized by an isotropic distribution of the scattered intensity with respect to the central ray.

The theory we have developed interprets the abovementioned behavior of intensity in terms of the character of dependence of the functions S_{H_v} and S_{V_v} on the angles φ and θ.[18] In Figures 3 and 4 we present theoretical scattering indicatrices in crossed and parallel polarizers. The scatterers are uniaxially extended heterogeneous networks whose structural function is $D_G(\mathbf{r}) = (\pi^2/\xi^3)\exp(-r/\xi)$. The Debye coordinates are used in Figures 3 and 4. The straight line 0 corresponds to the Fourier transform of the function $D_G(\mathbf{r})$. From its slope we can calculate the inhomogeneity size ξ, which is supposed to coincide with the wavelength of the light in the case considered. A comparison of scattering indicatrices of deformed networks with this straight line shows their more complicated behavior. This behavior is determined by the value of azimuth angle φ and extension degree of the network λ. In particular, at fixed φ the curvature and slope of indicatrices is controlled by the value of λ (see Figures 3 and 4). In addition, intensity redistribution over different values of the azimuth angle takes place when the scattering angle increases.[18] All these factors lead to mentioned behavior of scattering indicatrices. In order to determine the form of the structural function of the shear

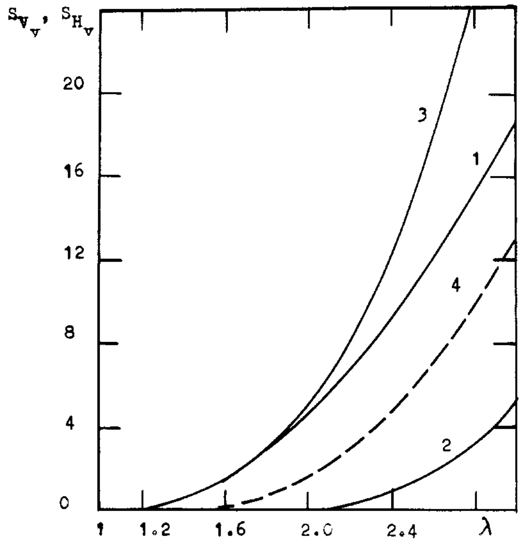

Figure 5. Dependence of functions S_{H_v} and S_{V_v} on elongation λ. For S_{V_v}: (1) $\varphi = 0$; (2) $\varphi = 27°$; (3) $\varphi = 87°$. For S_{H_v}: (4) $\varphi = 12°$.

moduli one has to divide the value of the scattering indicatrix experimentally found by the function S_{H_v} or S_{V_v} according to specific experimental conditions:

$$\bar{D}_G(\mathbf{q}) = S_{H_v}^{-1}(\theta,\varphi)R_{H_v}^{G} \quad \text{or} \quad \bar{D}_G(\mathbf{q}) = S_{V_v}^{-1}(\theta,\varphi)R_{V_v}^{G} \tag{44}$$

Equations 39–42 indicate that the scattered intensity essentially depends on the degree of network deformation. Physically, it can be explained by increase of fluctuations of the dielectric permeability of a heterogeneous network with degree of orientation of macromolecules under extension of the sample. While deriving these formulas no restriction was imposed on the degree of deformation. Therefore they might be valid in a rather wide range of extensions λ.

In Figure 5 functions S_{H_v} and S_{V_v} are plotted against the degree of uniaxial extension of the network at different values of the angle φ. It is seen that scattered intensity is a nonlinear function of λ. This means that at large extensions the light-scattering method can be used to investigate weak elastic inhomogeneities arising in polymer networks.

8. Light-Scattering Intensity in Swollen Heterogeneous Networks

In this section we restrict ourselves, for simplicity, to consideration of networks in which the monomer concentration is constant in the absence of solvent. In this case fluctuations of dielectric permeability are caused by nonuniform swelling of the network owing to random changes in cross-link concentration. The correlation functions of the fluctuations (18), (32), and (33) are

$$\langle \overline{\tilde{\epsilon}_{ik}^{(s)}\tilde{\epsilon}_{mn}^{(s)}} \rangle = P_{ik}^{(s)}P_{mn}^{(s)}\bar{D}_G(\mathbf{q}) \tag{45}$$

$$P_{ik}^{(s)} = 2a\langle B\rangle\langle G_0\rangle(m_i m_k - \tfrac{1}{3}\delta_{ik}) \tag{46}$$

Substituting these in (6) and (7), we find the Rayleigh ratios for swollen networks in crossed and parallel polarizers:

$$R_{H_v}^{G} = 4a^2 S_{H_v}^{(s)}(\theta,\varphi)\bar{D}_G(\mathbf{q}) \tag{47}$$

$$R_{V_v}^{G} = 4a^2 S_{V_v}^{(s)}(\theta,\varphi)\bar{D}_G(\mathbf{q}) \tag{48}$$

where functions $S_{H_v}^{(s)}(\theta,\varphi)$ and $S_{V_v}^{(s)}(\theta,\varphi)$ have the form similar to that of (40) and (42), the only difference being in the fact that one should replace P_{ik} by $P_{ik}^{(s)}$ from (46).

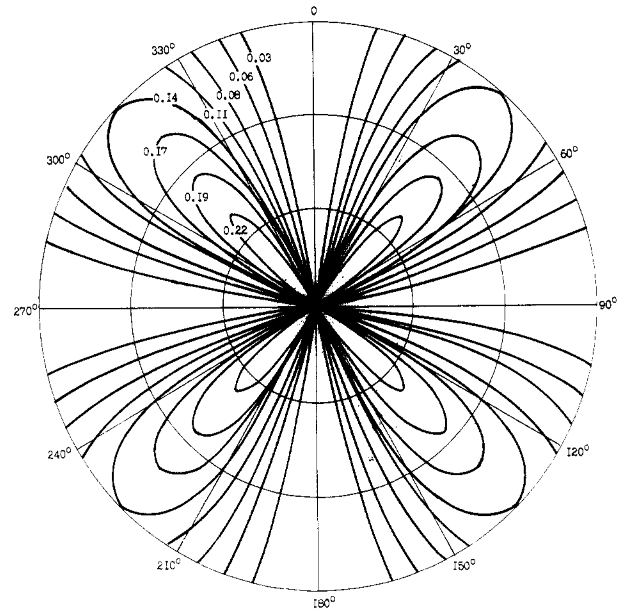

Figure 6. Contour plots of equal intensity of the light scattering from swollen networks: crossed polarizers.

Equations 47 and 48 are valid at arbitrary values of scattering angles θ, provided the wavelength of the light exceeds average dimensions of inhomogeneities. In the case of small-angle scattering the expressions for functions $S_{H_v}^{(s)}$ and $S_{V_v}^{(s)}$ can be simplified. Indeed, neglecting terms quadratical in θ we find

$$S_{H_v}^{(s)} = \tfrac{1}{12}\sin^2 2\varphi \tag{49}$$

$$S_{V_v}^{(s)} = \tfrac{1}{36}(1 + 3\cos 2\varphi)^2 \tag{50}$$

These follow simple estimates of possible scattering patterns. In crossed polarizers the pattern will have the form of a cross with four identical lobes at the angle of 45° with respect to the x_1 and x_2-axes. This result agrees with experimental data[11,20] concerning swollen polymer networks filled with small glass spheres. Note that solutions obtained here are also valid for filled systems with small concentration of rigid inclusions.

In Figure 6 equal intensity contours of the light scattering from swollen networks are plotted in the case of cross polarizers. The correlation function is supposed to be equal to $D_G(\mathbf{r}) = (\pi^2/\xi^3)\exp(-r/\xi)$ as in the previous section. The energy distribution of the light in the plane x_1x_2 becomes asymmetric as the scattering angle increases. This is due to behavior of the function $S_{H_v}^{(s)}(\theta,\varphi)$ whose values increase with θ in the vicinity of the azimuth angle $\varphi = 0$. Dependence of $S_{H_v}^{(s)}$ on φ is shown in Figure 7 at various scattering angles. It also follows from eq 40 and 46 that back-scattering intensity ($\mathbf{k} = -\mathbf{k}_0$) from swollen networks is zero when cross polarizers are used.

Theoretical contours of equal intensity of light scattering from networks considered are shown in Figure 8 as viewed with parallel polarizers. Calculations were done with eq 46 and 48. In this case positions of maximum intensity correspond to the x_1- and x_2-axes of the coordinate system chosen and are completely determined by direction of the light polarization. Dependence of $S_{V_v}^{(s)}$ on azimuth angle φ is shown in Figure 9 at various values of the scattering angle θ. Redistribution of scattered intensity with an increase of θ occurs here as well.

Equations 47 and 48 indicate that dependence of the Rayleigh ratios on the swelling degree of a network is determined by the form of the function $a(\varkappa)$ (see eq 31).

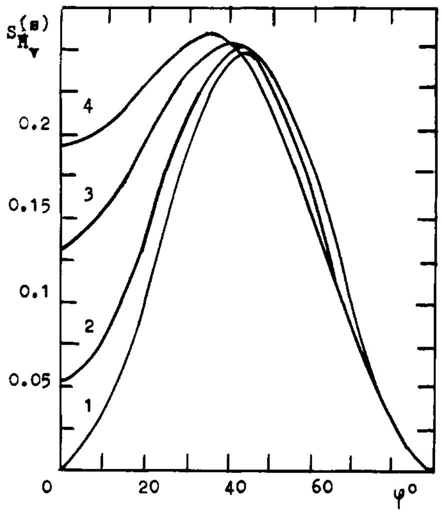

Figure 7. Dependence of the function $S_{H_v}^{(s)}$ on the azimuth angle φ: (1) $\theta = 5°$; (2) $\theta = 20°$; (3) $\theta = 35°$; (4) $\theta = 45°$.

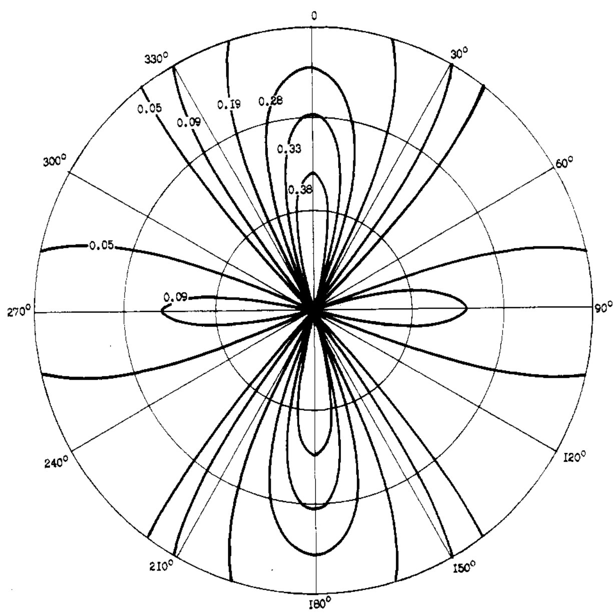

Figure 8. Contour plots of equal intensity of the light scattering from swollen networks: parallel polarizers.

Scattered intensity increases with $\varkappa$ in a nonlinear way. As in the case of deformed dry networks, this fact can be used for investigation of weak elastic inhomogeneities (for instance, such as spatial fluctuations of the cross-link concentration).

9. Conclusion

A statistical theory of Rayleigh scattering of light in deformed and swollen heterogeneous Gaussian polymer networks has been developed. Analytic expressions have been found which interrelate scattering intensity and structural functions characterizing degree of inhomogeneity from the viewpoint of monomer concentration and elastic properties of the medium. It has been shown that scattered intensity grows nonlinearly with degree of extension and swelling of the sample. This fact makes it possible to investigate weak fluctuations of elastic properties of polymer networks.

The theory developed enables one to find the form of structural functions of a heterogeneous network on the basis of scattering intensity distribution. In particular, the structural function of shear moduli can be estimated from the scattering indicatrix, measured at an arbitrary azimuth angle and an arbitrary degree of deformation, with allowance made for the form of functions $S_{H_v}(\theta,\varphi)$ and $S_{V_v}(\theta,\varphi)$ at the same values of φ and λ (see eq 44).

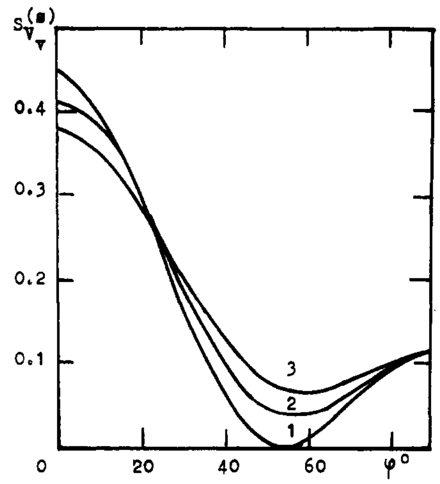

Figure 9. Dependence of the function $S_{V_v}^{(s)}$ on the azimuth angle φ: (1) $\theta = 5°$; (2) $\theta = 30°$; (3) $\theta = 45°$.

Note in conclusion that this theory can be easily generalized to describe networks, the elastic properties of which differ from those considered above.

Acknowledgment. I thank V. E. Zgaevskii for valuable discussions and V. B. Andreichenko for his assistance in computer calculations.

References and Notes

(1) Landau, L. D.; Lifshitz, E. M. *Electrodynamics of Continuous Media*; Nauka: Moscow, 1984.
(2) Stein, R. S. *Polymer Blends*; Academic: New York, 1978; Vol. 1, Chapter 8.
(3) Rytov, S. M.; Kravtsov, Yu. A.; Tatarskii, V. I. *An Introduction to Statistical Radiophysics*; Nauka: Moscow, 1978; Vol. 2.
(4) Dušek, K.; Prins, W. *Adv. Polym. Sci.* **1969**, *6*, 1.
(5) Volkov, T. I.; Baranov, V. G. *New Methods of Investigations of Polymers*; Himiya: Moscow, 1968.
(6) Stein, R. S.; Rhodes, M. B. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *27*, 1539.
(7) Hashimoto, T.; Murakami, Y.; Hayashi, N.; Kawai, H. *Polym. J.* **1974**, *6*, 132.
(8) Matsuo, M.; Nomura, S.; Hashimoto, T.; Kawai, H. *Polym. J.* **1974**, *6*, 151.
(9) Iida, M.; Sawatary, C.; Matsuo, M. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1599.
(10) Stein, R. S.; Wilkes, G. L. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1696.
(11) Ong, C. S. M.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1899.
(12) Pokrovskii, V. L.; Dolgova, I. F. *Opt. Spectrosk.* **1979**, *46*, 971.
(13) Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 518.
(14) Goldstein, M.; Michalik, E. R. *J. Appl. Phys.* **1955**, *26*, 1450.
(15) Stein, R. S.; Wilson, P. R. *J. Appl. Phys.* **1962**, *33*, 1914.
(16) Zgaevskii, V. E.; Patlazhan, S. A. *Opt. Spectrosk.* **1982**, *52*, 515.
(17) Green, A. E.; Adkins, J. E. *Large Elastic Strains and Nonlinear Mechanics of Continuous Medium*; Clarendon: Oxford, 1960.
(18) Patlazhan, S. A. "Physics and Chemistry of Rubber"; Preprints of the International Rubber Conference, Moscow, 1984; Vol. 2.
(19) Patlazhan, S. A.; Zgaevskii, V. E. *Visokomolekulyarnije Soedinenija, Part A* **1985**, *27*, 1446.
(20) Picot, C.; Fukuda, M.; Chou, C.; Stein, R. S. *Polymer Network Structural and Mechanical Properties*; Plenum: New York, 1971; p 293.