Microscopic theory of anisotropic scattering by deformed polymer networks

S. V. Panyukov

P. N. Lebedev Physics Institute, Russian Academy of Sciences, Moscow

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In modern experiments on neutron scattering by deformed polymer networks unusual iso-intensity lines of the "butterfly" and "diamond" type have been obtained. A microscopic approach is used here to calculate the correlation functions of the network-density fluctuations, which determine the intensity of such scattering. It is shown that the observed scattering anisotropy, which differs from the prediction of the classical theory of high elasticity, is due to defects of the topological structure of the network.

1. INTRODUCTION

One of the most sensitive methods for studying the structure of polymer networks on microscopic scales is neutron scattering. In neutron-scattering experiments one examines systems containing long deuterated chains cross-linked with chains of the matrix—the polymer network.[1] For visual observation of the scattering one uses a two-dimensional multiple detector placed at an angle of 90° to the incident beam. In the case of uniaxially deformed networks the classical theory,[2,3] based on the assumption that the stretching of the network is affine in character, predicts that the iso-intensity curves are elliptical in shape.[4-6]

Experimentally, one observes curves of the "butterfly" and "diamond" type (see Fig. 1), which differ substantially from this prediction.[1,7] An explanation of these effects can be given only on the basis of a microscopic approach that takes into account the nonaffine character of the stretching of the polymer networks. The study of these effects involving nonaffine character is also important for numerous practical applications of real polymer networks, which always have defects of the topological structure. The corresponding theory, describing structurally inhomogeneous networks, has been developed in Refs. 8–10.

In this article we shall give a theoretical description, on the basis of the replica approach of Refs. 8 and 9, of networks that are obtained by statistical cross-linking of long chains; such networks have been investigated experimentally in Refs. 1 and 7. We obtain the dependence of the intensity of the scattering of neutrons by deuterated chains on the volume fraction Φ of these chains. When the deuterated chains and the chains of the matrix are identical, this dependence has the form

$$I_{\mathbf{q}}=\Phi(1-\Phi)S_{\mathbf{q}}+\Phi^2(G_{\mathbf{q}}+C_{\mathbf{q}}). \qquad (1)$$

Here the form factor $S_{\mathbf{q}}$ has the classical anisotropy of an ellipse with its long axis perpendicular to the stretching. The form factors $G_{\mathbf{q}}$ and $C_{\mathbf{q}}$ have the butterfly anisotropy, with their respective maxima in the directions perpendicular and parallel to the stretching. For finite values of Φ the resulting scattering intensity (1) has the anisotropy of a rhombus.

2. THE CHOICE OF MODEL

Since the effects that we are discussing are due to structural disorder, in describing them theoretically we should first of all determine the probability measure on the configuration space $\{G\}$ of the system. Besides the topological structure Γ of the network, the configuration $G=(\Gamma,D)$ should include the "marking out" D of the chains of the network into deuterated and undeuterated chains. Correspondingly, the probability measure of configuration G is defined by the expression

$$P(G)=P(\Gamma)P(D/\Gamma), \qquad (2)$$

where $P(\Gamma)$ is the probability of synthesis of a network with the given topological structure Γ. In the case of networks obtained in conditions of equilibrium with respect to the formation and breaking of chemical bonds, we have

$$P(\Gamma)=\frac{z^N}{N!}\frac{w^K}{K!}Z^{(0)}(\Gamma,0)\Big/\sum_{\Gamma}\frac{z^N}{N!}\frac{w^K}{K!}Z^{(0)}(\Gamma,0), \qquad (3)$$

where N is the total number of monomer links of the chains of the network and K is the number of cross links of these chains in a network with the specified structure Γ. The parameters z and w are, respectively, the activities of the links and cross links, and $Z^{(0)}(\Gamma,0)$ is the partition function of a network with structure Γ at the synthesis temperature $T^{(0)}$.

The quantity $P(D/\Gamma)$ in (2) determine the conditional probability of a given way D of marking out the chains of a network with structure Γ. Regarding it as a Markovian process, we can set

$$P(D/\Gamma)=\prod_i \nu_{\alpha_i\alpha_{i+1}}, \qquad (4)$$

where the product is taken over all links i of the chains, and $\nu_{\alpha\beta}$ is the conditional probability of finding that the next link along the chain is of a given type $\beta=H,D$ (H for nondeuterated, and D for deuterated) if the preceding link was of type α. The matrix ν is normalized by the obvious condition

$$\sum_\beta \nu_{\alpha\beta}=1, \qquad (5)$$

and its nondiagonal elements determine the average length l of the deuterated chains and the fraction Φ of their links:

$$l=(\nu_{HD}+\nu_{DH})^{-1}, \quad \Phi=\nu_{HD}/(\nu_{HD}+\nu_{DH}). \qquad (6)$$

The scattering intensity (1) of interest to us is propor-

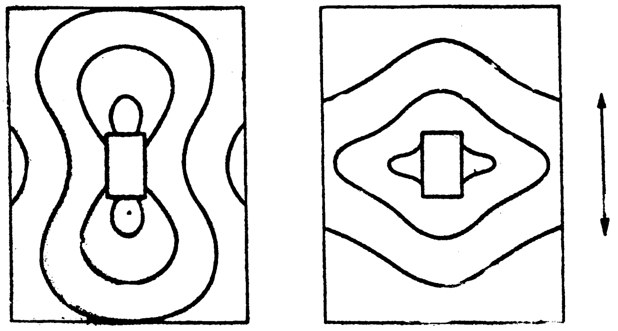
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FIG. 1. Experimentally observed[1,7] iso-intensity curves for neutron scattering through small wave vectors $\mathbf{q}$ in networks subjected to uniaxial stretching (in the direction indicated by the arrows). (a) Scattering by fluctuations of the total density of the network ("butterfly"); (b) scattering by deuterated fragments of chains of the network ("diamond").

tional to the Fourier component of the density-density correlation function

$$\overline{\langle\rho(\mathbf{x})\rho(\mathbf{x}')\rangle}=T^2\frac{\delta^2}{\delta h(\mathbf{x})\delta h(\mathbf{x}')}\sum_G P(G)Z^{-1}(\Gamma,0)Z(\Gamma,\{h\})\big|_{h=0}, \tag{7}$$

where the angular brackets denote the Gibbs average and the bar denotes averaging over all configurations G with the weight (2). The quantity $Z(\Gamma,\{h\})$ is the partition function of the polymer network under the experimental conditions at temperature T, and $h(\mathbf{x})$ is the external field acting on the links of the deuterated chains of the polymer network.

As shown in Ref. 11, when effects of topological restrictions are neglected the partition function of the polymer with allowance for the interaction between its links can be represented in the form of a functional integral over the fluctuating field $u(\mathbf{x})$:

$$Z(\Gamma,\{h\})=\int Du\exp\{-\Omega^*\{u\}/T\}\prod_i\int d\mathbf{x}_i u(\mathbf{x}_i)\lambda(\mathbf{x}_i-\mathbf{x}_{i+1})\times\exp\Big[-\frac{1}{T}\sum_i{}' h(\mathbf{x}_i)\Big], \tag{8}$$

where we associate a factor $\lambda(\mathbf{x}_i-\mathbf{x}_{i+1})$ with each bond between links with coordinates $\mathbf{x}_i$ and $\mathbf{x}_{i+1}$, and the prime indicates that the summation is only over the links of the deuterated chains. The functional Ω^* in (8) takes account the way the interaction of the chain links in the network contributes.

The free energy of the network under consideration is given by the expression[3]

$$F=-T\sum_G P(G)\ln Z(\Gamma,0). \tag{9}$$

3. THE FIELD THEORY

To perform the averaging (7), (9) over the configurations G, we make use of the method of replicas,[3,8] by means of which the correlator (7) can be represented in the form

$$\overline{\langle\rho(\mathbf{x})\rho(\mathbf{x}')\rangle}=T^2\frac{\delta^2}{\delta h^{(1)}(\mathbf{x})\delta h^{(1)}(\mathbf{x}')}\ln Z_m\{h^{(k)}\}\big|_{m=h=0}, \tag{10}$$

where the functional Z_m is given by the expression

$$Z_m\{h^{(k)}\}=\sum_G\frac{z^N}{N!}\frac{w^K}{K!}P(D/\Gamma)Z^{(0)}(\Gamma,0)\prod_{k=1}^m Z(\Gamma,\{h^{(k)}\}). \tag{11}$$

The free energy (9) of the network is also expressed in terms of the functional (11):

$$F=-T\frac{d}{dm}\ln Z_m\{0\}\big|_{m=0}. \tag{12}$$

Substituting the expression (8) for the partition function into (11), we find

$$Z_m\{h^{(k)}\}=\int Du^{(k)}\exp\Big\{-\frac{1}{T}\Big[\sum_k\Omega^*(u^{(k)})+\Omega_m\{u^{(k)},h^{(k)}\}\Big]\Big\}. \tag{13}$$

The functional Ω_m can be represented compactly in the form of a functional integral over the fields $\overline{\varphi}$ and φ:

$$\exp\{-\Omega_m/T\}=\int D\bar\varphi\,D\varphi\exp[-H\{\bar\varphi,\varphi\}],$$

$$H(\bar\varphi,\varphi)=\sum_{\alpha,\beta}\nu_{\alpha\beta}^{-1}\int d\mathbf{X}\,d\mathbf{X}'\lambda^{-1}(\mathbf{X}-\mathbf{X}')\bar\varphi_\alpha(\mathbf{X})\varphi_\beta(\mathbf{X}') \tag{14}$$

$$-z\int d\mathbf{X}u(\mathbf{X})[\exp(-h(\mathbf{X})/T)\bar\varphi_D(\mathbf{X})\varphi_D(\mathbf{X})+\bar\varphi_H(\mathbf{X})\varphi_H(\mathbf{X})]-(w/2)\int d\mathbf{X}\Big[\sum_\alpha^2\bar\varphi_\alpha(\mathbf{X})\varphi_\alpha(\mathbf{X})\Big]^2, \tag{15}$$

the validity of which can be seen without difficulty by expanding the integral (15) in a perturbation-theory series in the parameters z and w. The integration in (15) is performed over the coordinates $\mathbf{X}=(\mathbf{x}^{(0)},\mathbf{x}^{(1)},...,\mathbf{x}^{(m)})$ of the replica space, and ν^{-1} and λ^{-1} are the inverses, in the matrix sense, to the matrix ν and to the function

$$\lambda(\mathbf{X}-\mathbf{X}')=\prod_{k=0}^m\lambda(\mathbf{x}^{(k)}-\mathbf{x}'^{(k)}). \tag{16}$$

The fields $h(\mathbf{X})$ and $u(\mathbf{X})$, as in Ref. 11 too, are given by the expressions

$$h(\mathbf{X})=\sum_{k=1}^m h^{(k)}(\mathbf{x}^{(k)}),\qquad u(\mathbf{X})=\prod_{k=0}^m u^{(k)}(\mathbf{x}^{(k)}). \tag{17}$$

For $h=0$ the quadratic part of the effective action H (15) is diagonalized by going over to the new variables

$$\bar\psi(\mathbf{X})=\bar\varphi(\mathbf{X})S,\qquad\psi(\mathbf{X})=S^{-1}\varphi(\mathbf{X}),\qquad S=\begin{pmatrix}1-\Phi, & 1\\ -\Phi, & 1\end{pmatrix}. \tag{18}$$

Performing the gradient expansion of the Hamiltonian (15) and confining ourselves to the terms linear in the fields $h(\mathbf{X})$ and $v(\mathbf{X}) = \Delta u(\mathbf{X})$, we find

$$\begin{aligned} H(\bar\psi,\psi)=\int d\mathbf{X}\Big\{ & [l^{-1}+\tau+(1-\Phi)h+v]\bar\psi_1\psi_1 \\ & +h[\bar\psi_1\psi_2+\Phi(1-\Phi)\bar\psi_2\psi_1] \\ & +[\tau+\Phi h+v]\bar\psi_2\psi_2+a^2\sum_{i=1}^{2}\nabla\bar\psi_i\nabla\psi_i \\ & -\frac{w}{2}\Big[\sum_{i=1}^{2}\bar\psi_i\psi_i\Big]^2\Big\}, \end{aligned} \tag{19}$$

where the parameter $\tau = 1 - z$ determines the average length $\bar N = \tau^{-1}$ of a chain of the network between two cross-links, and a is the characteristic bond length.

4. MEAN-FIELD THEORY

When fluctuations of the fields $\bar\psi$ and ψ are neglected, the values of these fields can be found by minimizing the Hamiltonian (19). The polymer networks are described by a solution of these equations with spontaneously broken symmetry—a solution characterized by a well-defined direction in the replica space[8] (λ_μ are the coefficients of stretching of the network along the axes μ):

$$\mathbf{e}_\mu=(1,\lambda_\mu,\ldots,\lambda_\mu)/(1+m\lambda_\mu^2)^{1/2},\quad \mu=x,\ y,\ z, \tag{20}$$

the displacement along which corresponds to an affine deformation of the network:

$$x_\mu^{(0)}\to x_\mu^{(0)}+u_\mu,\quad x_\mu^{(k)}\to x_\mu^{(k)}+\lambda_\mu u_\mu. \tag{21}$$

It is convenient to introduce the components $\mathbf{R}^{(k)}$ of the vector $\mathbf{X}$ that are parallel to this direction:

$$R_\mu^{(0)}=(\mathbf{X}_\mu\mathbf{e}_\mu)=\sum_{k=1}^{m}X_\mu^{(k)}e_\mu^{(k)} \tag{22}$$

and perpendicular to it:

$$\mathbf{R}_\mu^\perp=\mathbf{X}_\mu-\mathbf{e}_\mu(\mathbf{X}_\mu\mathbf{e}_\mu). \tag{23}$$

Because of the conservation [for $h(\mathbf{X}) = 0$] of the rotational symmetry about the direction of the vector $\mathbf{e}_\mu$, the solution $\psi(\mathbf{X})$ of the equation for the minimum depends only on the quantity

$$z=(\mathbf{R}^\perp)^2/2={}^1/_2\sum_\mu\sum_{k=1}^{m}(R_\mu^{(k)})^2. \tag{24}$$

As a result, we find $\bar\psi_1 = \psi_1 = 0$, and the equation for the function $\bar\psi_2 = \psi_2 \equiv \psi$ in the limit $m\to 0$ takes the form

$$\tau\psi(z)-2a^2z\partial^2\psi(z)/\partial z^2=w\psi^3(z),\quad \psi(z\Rightarrow\infty)=0. \tag{25}$$

Making Eq. (25) dimensionless, we find

$$\begin{gathered}\psi(z)=(\tau/w)^{1/2}\chi(\tau z/2a^2),\\ x\chi''(x)=\chi(x)-\chi^3(x),\quad \chi(0)=1,\quad \chi(x\Rightarrow\infty)=0.\end{gathered} \tag{26}$$

The function $\chi(x)$ decreases rapidly as $x\to\infty$:

$$\chi(x)\sim x^{1/4}\exp(-2x^{1/2}); \tag{27}$$

and we have calculated it numerically using Eq. (26). This function describes thermal fluctuations $\delta\mathbf{x}_i = \mathbf{x}_i - \langle\mathbf{x}_i\rangle$ of the positions of the monomer links. The moments of $\delta\mathbf{x}_i$ can be expressed in terms of the corresponding moments of the function $\chi^2(x)$:

$$R^2=\overline{\langle\delta\mathbf{x}_i^2\rangle}=(2a^2/\tau)\int dx\chi^2(x)=1{,}44a^2/\tau. \tag{28}$$

Substituting the resulting solution (26) into (19) and (12), for the elastic contribution to the free energy we find the following expression from the classical theory:

$$F_{el}=\frac{T\tau^2}{4w}V^{(0)}(\lambda_x^2+\lambda_y^2+\lambda_z^2), \tag{29}$$

where $V^{(0)}$ is the volume of the system under the conditions under which the network is synthesized.

5. GENERAL APPROACH

To determine the correlation functions (10) of the density fluctuations it is sufficient to find the solution of the equations for the minimum of the Hamiltonian (19) to within terms linear in h and v. For this we go over to the mixed, Fourier–coordinate, representation:

$$h(\mathbf{X})=\int\frac{d\mathbf{q}}{(2\pi)^3}h_\mathbf{q}(\mathbf{R}^\perp)\exp\Big(i\sum_\mu p_\mu^{(0)}R_\mu^{(0)}\Big), \tag{30}$$

where, by means of the equality $(\mathbf{pR}) = (\mathbf{qX})$, we have introduced new wave vectors $\mathbf{p}$, corresponding to the coordinates (22) and (23). The quantities $p_\mu^{(0)} = \lambda_\mu q_\mu$, which are the zeroth components of these vectors, are chosen to be the same for the fields $h^{(k)}$ in all the replicas $k = 0, 1,\ldots,m$. It can be shown that, under this condition, the components $\mathbf{p}^\perp$ perpendicular to $\mathbf{p}^{(0)}$ are normalized, in the limit $m\to 0$, by the expressions

$$\begin{gathered}(\mathbf{p}_{0\mu}^\perp\mathbf{p}_{0\mu}^\perp)=0,\quad (\mathbf{p}_{0\mu}^\perp\mathbf{p}_{k\mu}^\perp)=-\lambda_\mu^2q_\mu^2,\quad k\neq 0\\ (\mathbf{p}_{k\mu}^\perp\mathbf{p}_{l\mu}^\perp)=(\delta_{kl}-\lambda_\mu^2)q_\mu^2,\quad k,\ l\neq 0,\end{gathered} \tag{31}$$

where δ_{kl} is the Kronecker symbol. The function $h_q(\mathbf{R}^\perp)$ in (30) is given by the expression

$$\begin{gathered}h_\mathbf{q}(\mathbf{R}^\perp)=\sum_{k=0}^{m}\tilde h_\mathbf{q}^{(k)}\exp\Big[i\sum_\mu(\mathbf{p}_{k\mu}^\perp\mathbf{R}_\mu^\perp)\Big],\\ \tilde h_\mathbf{q}^{(0)}=\lambda_x\lambda_y\lambda_z h_\mathbf{q}^{(0)},\quad \tilde h_\mathbf{q}^{(k)}=h_\mathbf{q}^{(k)},\quad k\neq 0.\end{gathered} \tag{32}$$

The formal solution of the equations for the minimum in the mixed representation (30) has the form

$$\begin{gathered}\psi_{i\mathbf{q}}(\mathbf{R}^\perp)=-\int d\mathbf{R}^{\perp\prime}D_{i\mathbf{q}}(\mathbf{R}^\perp,\mathbf{R}^{\perp\prime})h_{i\mathbf{q}}(\mathbf{R}^{\perp\prime})\psi(z'),\\ \bar\psi_{1\mathbf{q}}(\mathbf{R}^\perp)=\Phi(1-\Phi)\psi_{1\mathbf{q}}(\mathbf{R}^\perp),\quad \bar\psi_{2\mathbf{q}}(\mathbf{R}^\perp)=\psi_{2\mathbf{q}}(\mathbf{R}^\perp),\\ h_{1\mathbf{q}}(\mathbf{R}^\perp)=h_\mathbf{q}(\mathbf{R}^\perp),\quad h_{2\mathbf{q}}(\mathbf{R}^\perp)=\Phi h_\mathbf{q}(\mathbf{R}^\perp)+v_\mathbf{q}(\mathbf{R}^\perp),\end{gathered} \tag{33}$$

where the "propagators" D_i are determined by the equations

$$\hat{D}_{i\mathbf{q}}^{-1}D_{i\mathbf{q}}(\mathbf{R}^{\perp},\ \mathbf{R}^{\perp\prime})=\delta(\mathbf{R}^{\perp}-\mathbf{R}^{\perp\prime}),$$
$$\hat{D}_{1\mathbf{q}}^{-1}=l^{-1}+\tau+a^2(\mathbf{p}^{(0)})^2-a^2\nabla_{\perp}^{2}-w\psi^2(z),$$
$$\hat{D}_{2\mathbf{q}}^{-1}=\tau+a^2(\mathbf{p}^{(0)})^2-a^2\nabla_{\perp}^{2}-3w\psi^2(z). \qquad (34)$$

Substituting the solution (33) into the Hamiltonian (19), we find

$$\Delta H=-\frac{1}{\lambda_x\lambda_y\lambda_z}\int\frac{d\mathbf{q}}{(2\pi)^3}\int d\mathbf{R}^{\perp}\int d\mathbf{R}^{\perp\prime},$$
$$\sum_{i=1}^{2}D_{i\mathbf{q}}(\mathbf{R}^{\perp},\mathbf{R}^{\perp\prime})h_{i\mathbf{q}}(\mathbf{R}^{\perp})h_{i-\mathbf{q}}(\mathbf{R}^{\perp\prime})\psi(z)\psi(z'). \qquad (35)$$

6. GOLDSTONE MODES OF EXCITATION

To describe the long-wavelength fluctuations we must substitute into (33) and (35) expansions of the functions $h_{\mathbf{q}}(\mathbf{R}^{\perp})$ and $v_{\mathbf{q}}(\mathbf{R}^{\perp})$ (32) in powers of the wave vector $\mathbf{q}$. However, the limit $\mathbf{q}\to 0$ should be taken very carefully. At first sight, for this it is sufficient to retain only terms of zeroth order in $\mathbf{q}$ in these expansions. However, terms linear in $\mathbf{q}$ also contribute to (35), even for $\mathbf{q}=0$. It is these terms that describe the effects of displacement deformations in polymer networks, and they owe their origin to the presence of soft modes in the spectrum of the elementary excitations of the system.

We shall consider first the spectrum of the operator $\hat{D}_2^{-1}$ (34), which describes fluctuations of the total density in the system. The eigenvalue $\lambda_{2\mathbf{q}}=a^2(\mathbf{p}^{(0)})^2$ of this operator is $3m$-fold degenerate, and corresponds to eigenfunctions of Goldstone soft modes:

$$\Phi_\mu(\mathbf{R}^{\perp})=J_2^{-1/2}\frac{\partial\psi}{\partial R_\mu^{\perp}},\qquad J_2=\frac{1}{3}\int d\mathbf{R}^{\perp}\left(\frac{\partial\psi}{\partial\mathbf{R}^{\perp}}\right)^2=\frac{\tau^2}{12a^2w}, \qquad (36)$$

that describe translational displacements in the directions $\mu=x, y, z$ in the replicas $k=1,\dots,m$. The presence of these modes is linked to the analysis of the ground state (26) of the system, with spontaneously broken symmetry (21). It is these translational modes that describe the loss of affine character upon deformation of the network, since they correspond to independent displacements $u_\mu^{(k)}$ in each of the replicas.

The smallest eigenvalue of the Hermitian operator $\hat{D}_2^{-1}$ is always nondegenerate. Therefore, it should be negative for small $\mathbf{q}$. The presence of this negative eigenvalue is connected with instability of the system under the conditions in which the network is prepared in the absence of interactions between its links. Allowance for interactions of the excluded-volume type eliminates this instability.

The spectrum of the remaining excitations of the operator $\hat{D}_2^{-1}$ has (besides the excitations discussed above) a gap, and the excitations describe density fluctuations that are not related to displacement and torsion effects.

We now consider the spectrum of the operator $\hat{D}_1^{-1}$ (34), which describes fluctuations of the density of individual deuterated chains. The smallest eigenvalue $\lambda_{1\mathbf{q}}=l^{-1}+a^2(\mathbf{p}^{(0)})^2$ of this operator is nondegenerate and corresponds to the soft-mode eigenfunction

$$\Phi_1(\mathbf{R}^{\perp})=J_1^{-1/2}\psi(z),\qquad J_1=\int d\mathbf{R}^{\perp}\psi^2(z)=\tau/w, \qquad (37)$$

which describes deuterated-chain density fluctuations that are frozen in the process of preparation of the network.

Separating the contributions of the soft modes considered above in the expressions (33), we find

$$\psi_{1\mathbf{q}}(\mathbf{R}^{\perp})=\psi(z)u_{\mathbf{q}}+\tilde{\psi}_{1\mathbf{q}}(\mathbf{R}^{\perp}),$$
$$\psi_{2\mathbf{q}}(\mathbf{R}^{\perp})=-\sum_{\mu}\frac{\partial\psi(z)}{\partial R_\mu^{\perp}}u_{\mathbf{q}\mu}+\tilde{\psi}_{2\mathbf{q}}(\mathbf{R}^{\perp}), \qquad (38)$$

where $u_{\mathbf{q}\mu}$ are the Fourier components of the displacement vector for macroscopic deformations of the medium:

$$u_{\mathbf{q}\mu}^{(k)}=J_2^{-1/2}\lambda_{2\mathbf{q}}^{-1}c_{2\mathbf{q}\mu}^{(k)},$$
$$c_{2\mathbf{q}\mu}=-ia(3w)^{-1/2}\left[p_{0\mu}^{\perp}\tilde{h}_{2\mathbf{q}}^{(0)}+c_{\mathbf{q}}\sum_{k=1}^{m}p_{k\mu}^{\perp}\tilde{h}_{2\mathbf{q}}^{(k)}\right],$$
$$c_{\mathbf{q}}=1+[(\lambda\mathbf{q})^2-\mathbf{q}^2](2a^2/\tau)\int_0^\infty dx\chi^2(x)+\dots, \qquad (39)$$

and $u_{\mathbf{q}}$ is the dimensionless amplitude of the statistical fluctuations of the density of the deuterated chains:

$$u_{\mathbf{q}}=-J_1^{-1/2}\lambda_{1\mathbf{q}}^{-1}c_{1\mathbf{q}},\qquad c_{1\mathbf{q}}=\tau w^{-1}\sum_{k=1}^{m}\tilde{h}_{\mathbf{q}}^{(k)}+\dots. \qquad (40)$$

7. FLUCTUATION MODES

We now consider density fluctuations that do not reduce to an elastic displacement, and also thermal excitations of the deuterated chains. These fluctuations are described by the terms $\tilde{\psi}_{1\mathbf{q}}$ and $\tilde{\psi}_{2\mathbf{q}}$, respectively, which are induced (in accordance with the fluctuation-dissipation theorem) by the fields $\tilde{h}_{1\mathbf{q}}$ and $\tilde{h}_{2\mathbf{q}}$:

$$[h_{1\mathbf{q}}(\mathbf{R}^{\perp})-\tilde{h}_{1\mathbf{q}}(\mathbf{R}^{\perp})]\psi(z)=c_{1\mathbf{q}}\Phi_1(\mathbf{R}^{\perp}),$$
$$[h_{2\mathbf{q}}(\mathbf{R}^{\perp})-\tilde{h}_{2\mathbf{q}}(\mathbf{R}^{\perp})]\psi(z)=\sum_{\mu}(c_{2\mathbf{q}\mu}\Phi_{2\mu}(\mathbf{R}^{\perp})). \qquad (41)$$

Substituting the expressions (38) into (35), we separate out the contribution of the Goldstone modes to the quantity ΔH:

$$\Delta H=\frac{1}{\lambda_x\lambda_y\lambda_z}\int\frac{d\mathbf{q}}{(2\pi)^3}(I_{1\mathbf{q}}+I_{2\mathbf{q}}),$$
$$I_{1\mathbf{q}}=c_{1\mathbf{q}}c_{1-\mathbf{q}}/\lambda_{1\mathbf{q}}-\int d\mathbf{R}^{\perp}\tilde{\psi}_{1\mathbf{q}}(\mathbf{R}^{\perp})\tilde{h}_{1-\mathbf{q}}(\mathbf{R}^{\perp})\psi(z),$$
$$I_{2\mathbf{q}}=\lambda_{2\mathbf{q}}^{-1}\sum_{\mu}c_{2\mathbf{q}\mu}c_{2-\mathbf{q}\mu}-\int d\mathbf{R}^{\perp}\tilde{\psi}_{2\mathbf{q}}(\mathbf{R}^{\perp})\tilde{h}_{2-\mathbf{q}}(\mathbf{R}^{\perp})\psi(z). \qquad (42)$$

The field $\tilde{h}_{1\mathbf{q}}$ makes a contribution to $I_{1\mathbf{q}}$ that is small in the parameter $\mathbf{q}^2$ and will not be taken into account in what follows. To determine the contribution of the field $\tilde{h}_{2\mathbf{q}}$ to the quantity $I_{2\mathbf{q}}$ we expand this field in powers of the wave vector $\mathbf{q}$. The contribution of the zeroth-order terms of this expansion to $I_{2\mathbf{q}}$ is equal to

$$I_{2\mathbf{q}}{}^{0}=h_{2\mathbf{q}}(0)h_{2-\mathbf{q}}(0)\int d\mathbf{R}^{\perp}\,d\mathbf{R}^{\perp\prime}D_{2\mathbf{q}}(\mathbf{R}^{\perp},\mathbf{R}^{\perp\prime})$$

$$=h_{2\mathbf{q}}(0)h_{2-\mathbf{q}}(0)(-2\tau+\lambda_{2\mathbf{q}})^{-1}. \tag{43}$$

The expression (43) describes statistical fluctuations of the network-link density that are "frozen" in the process of preparation of the network, and these exhaust the contribution of the field $\tilde{h}_{2\mathbf{q}}$ for $\mathbf{q}=0$.

We now calculate the terms of second order in $\mathbf{q}$ in $I_{2\mathbf{q}}$. We note that the term $\sim\mathbf{q}^2$ in the expansion of the field $\tilde{h}_{2\mathbf{q}}$ (32) in powers of $\mathbf{q}$ does not make a contribution to (42): $I^{2}_{2\mathbf{q}}=0$. Therefore, it is sufficient to consider only the linear terms of this expansion, for which

$$\tilde{\Phi}_{2\mathbf{q}}(\mathbf{R}^{\perp})=i\sum_{\mu}\sum_{k=1}^{m}(\mathbf{p}_{k\mu}{}^{\perp}\mathbf{R}_{\mu}{}^{\perp})\tilde{h}_{2\mathbf{q}}^{(k)}\,\delta\Phi(z). \tag{44}$$

The function $\delta\Phi(z)$ can be represented in the form

$$\delta\Phi(z)=(w\tau)^{-1/2}f(\tau z/2a^{2}), \tag{45}$$

where $f(x)$ is a certain dimensionless function, an equation for which can be obtained by "pulling" the factor $\mathbf{R}_{\mu}^{\perp}$ through the operator $\hat{D}_{2}^{-1}$ (34). Actually, the only quantity we need is the constant c that appears after substitution of the expressions (44) and (45) into (42):

$$I_{2\mathbf{q}}{}^{1}=(2ca^{2}/3\tau w)\sum_{k,l=0}^{m}(\mathbf{p}_{k\mu}{}^{\perp}\mathbf{p}_{l\mu}{}^{\perp})\tilde{h}_{2\mathbf{q}}^{(k)}\,\tilde{h}_{2-\mathbf{q}}^{(l)},$$

$$c=\int_{0}^{\infty}dx(\chi(x)+\chi'(x))f(x). \tag{46}$$

In the next section we shall obtain the magnitude of this constant c by means of simple physical considerations.

8. THE CORRELATION FUNCTIONS

As a consequence of the symmetry of the functional Ω_m (14) under permutations of the replicas $k=1,\ldots,m$, its expansion in powers of the fields h_i should have the form

$$\frac{\Delta\Omega_m}{T}=\int\frac{d\mathbf{q}}{(2\pi)^3}\Big[{}^1/{}_2\alpha_{\mathbf{q}}'\sum_{k=1}^{m}h_{1\mathbf{q}}^{(k)}\,h_{1-\mathbf{q}}^{(k)}$$

$$-{}^1/{}_2\beta_{\mathbf{q}}'\sum_{k,l=1}^{m}h_{1\mathbf{q}}^{(k)}\,h_{1-\mathbf{q}}^{(l)}+{}^1/{}_2\alpha_{\mathbf{q}}\sum_{k=1}^{m}h_{2\mathbf{q}}^{(k)}\,h_{2-\mathbf{q}}^{(k)}+{}^1/{}_2\alpha_{\mathbf{q}}{}^{(0)}h_{2\mathbf{q}}^{(0)}\,h_{2-\mathbf{q}}^{(0)}$$

$$-\beta_{\mathbf{q}}^{(0)}\sum_{k=1}^{m}h_{2\mathbf{q}}^{(k)}\,h_{2-\lambda\mathbf{q}}^{(0)}-{}^1/{}_2\beta_{\mathbf{q}}\sum_{k,l=1}^{m}h_{2\mathbf{q}}^{(k)}\,h_{2-\mathbf{q}}^{(l)}\Big], \tag{47}$$

where the vector $\lambda\mathbf{q}$ has components $\{\lambda_{\mu}q_{\mu}\}$. We also expand the functionals Ω^* given by (8), which describe the interaction of the monomer links, in powers of the fields $v^{(k)}$:

$$\Delta\Omega^{*(k)}=-\frac{T^{(k)}}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}\frac{v_{\mathbf{q}}^{(k)}\,v_{-\mathbf{q}}^{(k)}}{B^{(k)}}, \tag{48}$$

where $B^{(k)}=B$ $(k=1,\ldots,m)$ and $B^{(0)}$ are the effective virial coefficients in the conditions of the experiment and the synthesis, respectively.

Substituting the expressions (47) and (48) into (13) and calculating the correlation function (10), we find an expression for its Fourier component:

$$\overline{\langle\rho_{\mathbf{q}}\rho_{-\mathbf{q}}\rangle}=\beta_{\mathbf{q}}'-\alpha_{\mathbf{q}}'+\Phi^{2}(G_{\mathbf{q}}+C_{\mathbf{q}}),$$

$$C_{\mathbf{q}}=G_{\mathbf{q}}{}^{2}[\theta_{\mathbf{q}}+(\theta_{\mathbf{q}}{}^{(0)})^{2}G_{\lambda\mathbf{q}}^{(0)}/\lambda_{x}\lambda_{y}\lambda_{z}],$$

$$G_{\mathbf{q}}=(\varkappa_{\mathbf{q}}+B)^{-1},\quad G_{\mathbf{q}}{}^{(0)}=(\varkappa_{\mathbf{q}}{}^{(0)}+B^{(0)})^{-1}, \tag{49}$$

where the parameters $\varkappa$ and θ are related to the coefficients α and β by

$$\varkappa_{\mathbf{q}}{}^{(0)}=1/\alpha_{\mathbf{q}}{}^{(0)},\quad \varkappa_{\mathbf{q}}=1/\alpha_{\mathbf{q}},\quad \theta_{\mathbf{q}}{}^{(0)}=\beta_{\mathbf{q}}{}^{(0)}/\alpha_{\mathbf{q}}{}^{(0)}\alpha_{\mathbf{q}},$$

$$\theta_{\mathbf{q}}=[\beta_{\mathbf{q}}-(\beta_{\mathbf{q}}^{(0)})^{2}/\lambda_{x}\lambda_{y}\lambda_{z}\alpha_{\lambda\mathbf{q}}^{(0)}]/\alpha_{\mathbf{q}}{}^{2}. \tag{50}$$

To find α and β we substitute the expressions (39), (43), and (46) into (42). As a result, for the coefficient α we find the expression

$$\alpha_{\mathbf{q}}=[3w\lambda_{x}\lambda_{y}\lambda_{z}(\lambda\mathbf{n})^{2}]^{-1}\Big\{1+4a^{2}\tau^{-1}[(\lambda\mathbf{q})^{2}$$

$$-\mathbf{q}^{2}]\int_{0}^{\infty}dx\chi^{2}(x)-2ca^{2}\tau^{-1}(\lambda\mathbf{q})^{2}\Big\}, \tag{51}$$

where $\mathbf{n}$ is the unit vector in the direction of the wave vector $\mathbf{q}$. This coefficient determines the amplitude of the thermodynamic fluctuations of the density of the monomer links in the absence of steric interactions. According to (28), in the phantom networks it does not depend on λ_{μ}. Therefore, the corresponding dependence of the Goldstone contribution to (51) should cancel with the contribution of ordinary fluctuations, giving

$$c=2\int_{0}^{\infty}dx\chi^{2}(x)=1{,}44. \tag{52}$$

Using the result (52), we find, in analogy with (51),

$$\alpha_{\mathbf{q}}{}^{(0)}=w^{-1}[-2+a^{2}\tau^{-1}\mathbf{q}^{2}]^{-1},$$

$$\alpha_{\mathbf{q}}=[3w\lambda_{x}\lambda_{y}\lambda_{z}(\lambda\mathbf{n})^{2}]^{-1}(1+2R^{2}\mathbf{q}^{2})^{-1},$$

$$\beta_{\mathbf{q}}^{(0)}=\alpha_{\lambda\mathbf{q}}^{(0)}-(3w)^{-1}[1+R^{2}(\lambda\mathbf{q})^{2}+R^{2}\mathbf{q}^{2}]^{-1},$$

$$\beta_{\mathbf{q}}=\{\alpha_{\lambda\mathbf{q}}^{(0)}-(3w)^{-1}(1+2R^{2}\mathbf{q}^{2})^{-1}\}/\lambda_{x}\lambda_{y}\lambda_{z}, \tag{53}$$

where the amplitude R of the thermodynamic fluctuations of the links is determined in (28). In the approximation under consideration we also find

$$\alpha_{\mathbf{q}}=0, \quad \beta_{\mathbf{q}}'=\Phi(1-\Phi)\tau w^{-1}[l^{-1}+a^2(\lambda\mathbf{q})^2]^{-1}. \tag{54}$$

9. CONCLUSION

In this paper we have calculated correlation functions of deuterated chains that appear with volume fraction Φ in the composition of a polymer network. According to the results (49), (50) and (53), (54), the form factors appearing in the expression (1) have the form

$$\begin{gathered}
S_{\mathbf{q}}=\rho/[l^{-1}+a^2(\lambda\mathbf{q})^2], \\
G_{\mathbf{q}}=\rho/[B\rho+{}^3/_2\tau(\lambda\mathbf{n})^2+6ca^2(\lambda\mathbf{q})^2], \quad \mathbf{n}=\mathbf{q}/|\mathbf{q}|, \\
C_{\mathbf{q}}=\left[\frac{{}^3/_2\tau(\lambda\mathbf{n})^2+6ca^2(\lambda\mathbf{q})^2}{B\rho+{}^3/_2\tau(\lambda\mathbf{n})^2+6ca^2(\lambda\mathbf{q})^2}\right]^2 \\
\times\left\{{}^2/_3\rho\tau^{-1}B_{\mathbf{q}}+\frac{2\rho A_{\mathbf{q}}^2}{2B^{(0)}\rho^{(0)}-2\tau+a^2(\lambda\mathbf{q})^2}\right\},
\end{gathered} \tag{55}$$

where $\rho=\rho^{(0)}/\lambda_x\lambda_y\lambda_z$ is the density of the links of the network, and we have set

$$\begin{gathered}
A_{\mathbf{q}}=1+\frac{2-a^2\tau^{-1}(\lambda\mathbf{q})^2}{3[1+R^2(\lambda\mathbf{q})^2+R^2\mathbf{q}^2]}, \quad B_{\mathbf{q}}=\frac{2}{1+R^2(\lambda\mathbf{q})^2+R^2\mathbf{q}^2} \\
-\frac{1}{1+2R^2\mathbf{q}^2}+\frac{2-a^2\tau^{-1}(\lambda\mathbf{q})^2}{3[1+R^2(\lambda\mathbf{q})^2+R^2\mathbf{q}^2]^2}.
\end{gathered} \tag{56}$$

According to their definitions, $\overline{N}=1/\tau$ is the average length of the chains in the network and the vector $\lambda\mathbf{q}$ has components $\{\lambda_\mu q_\mu\}$.

We note that the functions $G_{\mathbf{q}}$ and $C_{\mathbf{q}}$ depend on the direction of the wave vector $\mathbf{q}$ even in the limit $\mathbf{q}\to 0$. They determine the intensity of the static scattering by fluctuations of the density of the polymer network, corresponding to the case $\Phi=1$:

$$I_{\mathbf{q}}=G_{\mathbf{q}}+C_{\mathbf{q}}. \tag{57}$$

Here $G_{\mathbf{q}}$ is equal to the correlation function of the thermodynamic (temporal) density fluctuations, and $C_{\mathbf{q}}$ is equal to the correlation function of the statistical (spatial) fluctuations of the density of the monomer links of the network.[8] The function $G_{\mathbf{q}}$ determines the dynamic-scattering intensity, and, in agreement with the experiment of Ref. 12, decreases in the direction of the stretching of the network. The correlation length depends on the direction of the wave vector, and, in agreement with the experiment of Ref. 7, is greater in the direction of stretching. The correlation function $C_{\mathbf{q}}$ of the statistical fluctuations describes iso-intensity patterns of the butterfly type, with maxima in the direction of stretching of the network (see Fig. 1a).

According to Eqs. (49) and (55), the correlator $C_{\mathbf{q}}$ of the frozen density fluctuations is proportional to the correlation function

$$G_{\lambda\mathbf{q}}^{(0)}/\lambda_x\lambda_y\lambda_z \tag{58}$$

of the density fluctuations under the conditions in which the network is prepared with affine extension of the network by factors of λ_μ along the axes $\mu=x, y, x$. It is this factor that is predicted in the framework of the classical theory of high elasticity.[2,3]

In reality, in the preparation of a network it is not the density of the links that is frozen but the topological structure of the network. The conditions of the experiment differ, generally speaking, from the conditions under which the network is synthesized. In the new conditions, defects of the topological structure of the network, together with affine stretching of the network, give rise to displacement and torsional deformations. It is these which lead to contributions in addition to (58) to the function $C_{\mathbf{q}}$, and also to the anomalous dependence of the correlation functions $G_{\mathbf{q}}$ and $C_{\mathbf{q}}$ on the direction of the wave vector $\mathbf{q}$ in the limit $\mathbf{q}\to 0$. In our formalism, such deformations are described by Goldstone modes of excitation of the system.

The neutron experiments performed in Refs. 1, 7, and 13 have made it possible to make these excitations visible in the form of unusual figures for the iso-intensity lines—butterflies and diamonds. We note that in these experiments strongly deformed networks ($\lambda_x/\lambda_y=1.3$–5) have been investigated, for which the deformation tensor satisfies $u_{\mu\nu}\gtrsim 1$. Therefore, the classical approach of Landau, based on expansion of the free energy in powers of $u_{\mu\nu}$, is, in principle, not applicable for the description of the systems under consideration. Allowance for nonlinear effects takes the classical theory of elasticity on to a higher level of complexity.

The approach developed in our paper does not come up against these difficulties, since it is essentially a generalization of the density-functional method to the case of solids—polymer networks. Displacement and torsional deformations are described in the framework of this approach by Goldstone density-fluctuation modes that owe their origin to the spontaneous breaking of the translational symmetry of the system in the solid state. On the basis of this approach we have calculated for the first time, by using mean-field theory, the correlation functions of the density of topologically disordered networks and also of probe deuterated chains cross-linked with them. As shown in Refs. 9 and 10, the results obtained can be carried over directly to the scaling regime by the renormalization of the system parameters that is found in these papers.

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