Theory of elasticity and relaxational dynamics of "soft" solids

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A density-functional method for describing soft solids is developed. The method is based on the introduction of the Edwards–Anderson order parameter for these amorphous substances. A thermodynamic description of irregular polymer networks, formed both near and far from the gel-formation threshold by cross-linking of linear chains, is obtained with the help of the method. It is shown that in the abbreviated description of soft bodies on the basis of the theory of elasticity Landau's free-energy functional must be regarded as a random quantity. The distribution functions of the parameters of this functional were calculated with the help of the density functional method. A theory of relaxation processes in strongly deformed polymer networks is constructed and it is shown that it agrees with the experimentally observed dynamics of the butterfly effect.

1. INTRODUCTION

Interest in so-called "soft" solids—materials which can deform significantly without rupturing—has increased significantly in the last few years. Rubbers, gels, and polymer melts (studied over finite times) are examples of such materials. Soft solids are interesting not only because of their important practical applications but also because of the unusual results obtained in experiments on low-angle neutron scattering by them. The isointensity scattering curves reflect in an extremely illustrative form the elastic properties of these amorphous materials.

Classically,[1–3] the isointensity curves for materials subjected to uniaxial tension should be ellipses. Such curves have indeed been observed at short times (or, equivalently, at low temperatures) after instantaneous stretching of polymer networks and melts.[4,5] At longer times (or at high temperatures), however, the isointensity curves became butterfly-shaped, peaking in the direction of stretching of the network (so-called anomalous butterfly effect; see Fig. 1).[5–7]

The spectrum of theoretical explanations of these unusual results is extremely wide. It has been shown[8–11] that butterfly figures are obtained even when thermodynamic fluctuations of the density are taken into account, but in this case the peaking occurs in a direction perpendicular to the direction of stretching of the material (normal butterfly effect). To explain the experimentally observed patterns for the anomalous butterfly effect it was hypothesized that statistical fluctuations of the moduli of elasticity are due to networks of point defects which become frozen-in during the preparation process.[12] Such networks of point defects evidently do not occur in polymer melts, so that this hypothesis is obviously insufficient to explain the effects under discussion. In Ref. 11 it was suggested for this purpose that thermodynamic fluctutations of the density be taken into account as strain-tensor-independent variables.

Thus the basic question of the theory of soft solids—the relation between their microstructure and the macroscopic elastic characteristics which determine the scattering intensity—remains open. In the present paper, in order to clarify the physical situation, we study a clearly defined model of a network that is prepared under conditions of equilibrium with respect to the formation and breaking of chemical cross-links between chains in the network. Unfortunately, the method of replicas,[13,14] which permits a rigorous analysis of such a model, is itself a "black box." By means of simple analytical calculations it makes it possible to obtain the experimentally observed butterfly-type isointensity patterns,[15,16] but it says nothing about the physical meaning of these patterns. Another significant shortcoming of this method is that it cannot describe dynamical processes. For this reason, we first translate the results obtained by the replica method into the standard language of the theory of elasticity, which we then employ to describe relaxation processes in polymer materials.

One of the most important and often discussed questions in the theory of soft solids is the spatial size of frozen-in nonuniformities. According to most modern theories of high elasticity, spatial correlations over scales larger than the unit-cell size of the network (or quasinetwork in melts) do not exist. At the same time, experiments[7,8] indicate that gels exhibit significant heterogeneity over significantly larger scales.

We show below that there exist two types of spatial nonuniformities in gels. The first type corresponds to nonuniformities of finite size, formed at the time the network is prepared and deformed in an affine manner together with the network. These are the nonuniformities that in Ref. 12 are modeled by point defects and which, according to a valid remark made in Ref. 11, do not occur in the case of a melt consisting of finite-size molecules. It is significant that when networks are formed, it is not the density of their monomeric units that is fixed but rather the chemical (topological) structure of the networks, which is uniquely determined by their density. Nonuniformities of the second type are related with this ambiguity. In amorphous solids such nonuniformities, being the static analog of the standard Brownian thermal motion, do not have a maximum characteristic scale and they are virtually independent of

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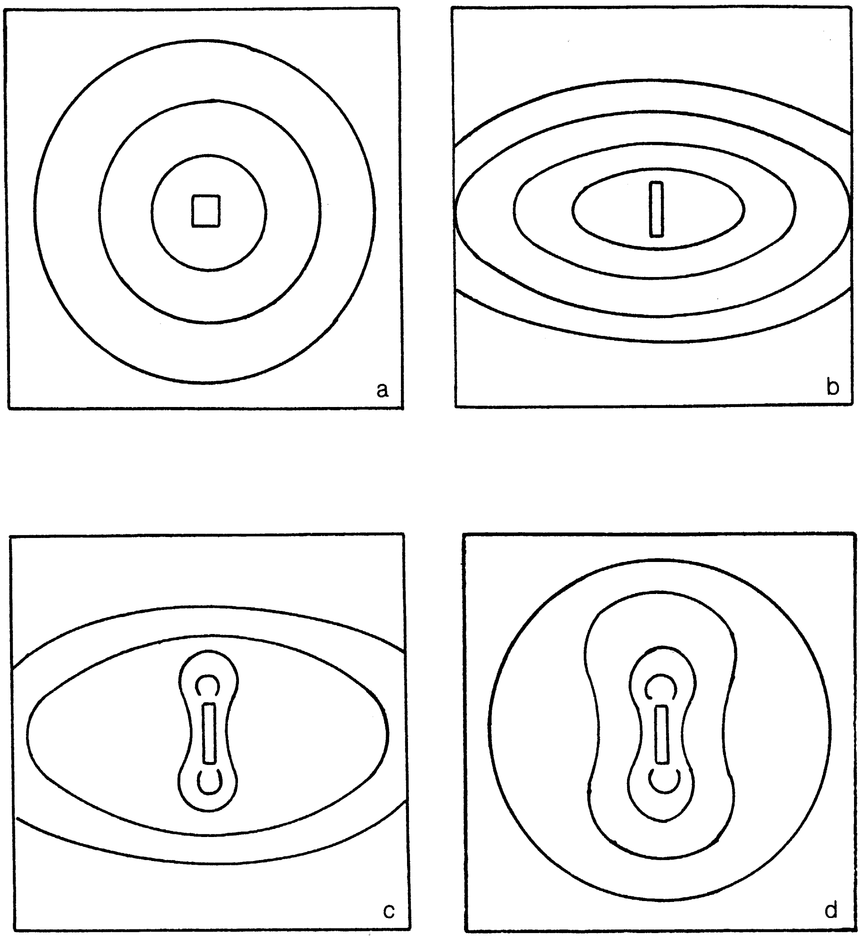

FIG. 1. Experimentally observed dynamics of the butterfly effect in statistically cross-linked polymer networks:[4,5] a) before the sample is stretched; b) immediately after the sample is stretched uniaxially; c) appearance of butterfly wings at small wave vectors q (the characteristic time and temperature are $t=10$ min and $T=140\,^\circ\mathrm{C}$); d) stabilized butterfly effect at long times (high temperatures).

the conditions under which the network is prepared. It is this type of statistical fluctuation that remains in deformed melts of polymer molecules and is responsible for the scattering anisotropy observed in such melts.

From the standpoint of the standard Landau approach[17] nonuniformities of the first type are described by a single-component density of monomeric links, while the multicomponent nature of the order parameter—the strain tensor

$$u_{\mu\nu}(x)=\frac{1}{2}\left[\frac{\partial u_\mu(\mathbf{x})}{\partial x_\nu}+\frac{\partial u_\nu(\mathbf{x})}{\partial x_\mu}\right] \qquad (1)$$

is important for the existence of long-range correlations of the second type. A characteristic feature of the theoretical description of amorphous bodies is the ambiguity of the displacement vector $u_\mu(\mathbf{x})$, where $\mu=x, y, z$. This ambiguity is associated with the impossibility of introducing an undeformed spatially uniform state. Such an undeformed state in amorphous materials is characterized by a spatially nonuniform density distribution $\{n(\mathbf{x})\}$. This ambiguity does not occur when the system is described in terms of the density distribution $\{\rho(\mathbf{x})\}$, connected with the strain tensor (1) by the relation

$$\rho(\mathbf{x})=n(\mathbf{x})-\rho\sum_\mu u_{\mu\mu}(\mathbf{x}), \qquad (2)$$

where ρ is the volume-averaged density. The condition $|u_{\mu\nu}|\ll 1$, which is not significant for ordinary solids, is not suitable for describing soft solids, which in the experiments of Refs. 3–7 undergo a strong anisotropic deformation, with respect to the conditions under which they are prepared, by a factor $\lambda_\mu>1$ along the corresponding coordinate axes $\mu=x, y, z$. This limitation strongly restricts the applicability of Landau's classical approach to the description of such substances.

In the present paper we take as the undisturbed state the strongly nonuniform state of an affinely stretched network. The density $n(\mathbf{x})$ in such a state is related to the density $\rho^{(0)}(\mathbf{x})$ by the following obvious relation under the condition that the network is ready at the moment its chemical structure is fixed:

$$n(\mathbf{x})=\rho^{(0)}(\lambda^{-1}\mathbf{x})/\lambda_x\lambda_y\lambda_z. \qquad (3)$$

Here and below the notation $\lambda^{-1}\cdot x$ is employed for the vector with the components $\lambda_\mu^{-1}x_\mu$ (tensor contraction). Since on large scales the stretching of a network is always affine, with the choice of (3) the long-wavelength components of the strain tensor (1) are small and can be correctly described even in the Gaussian approximation.

The Ginzburg–Landau microscopic approach, a brief exposition of which is given in Ref. 15, is developed in Sec. 2 for describing polymer networks. In Sec. 3 it is shown that a polymer network is described by the solution of the Ginsburg–Landau equations with spontaneously broken translational symmetry and the free energy of the undisturbed state of the network synthesized both near and far from the gel-formation threshold is found. In Sec. 4 it is shown that the elastic properties of networks are described by the Goldstone modes and the coefficients Λ and $\tilde{\sigma}$ in the expansion of the Landau free energy in powers of the strain tensor (1) are found:

$$\frac{F\{u,\tilde{\sigma}\}}{T}=\int d\mathbf{x}\left[\frac{1}{2}\sum_{\mu,\nu,\alpha,\beta}\Lambda_{\mu\nu\alpha\beta}\,u_{\mu\nu}u_{\alpha\beta}+\sum_{\mu,\nu}\tilde{\sigma}_{\mu\nu}\,u_{\mu\nu}\right], \tag{4}$$

where T is the temperature.

From the standpoint of Landau's expansion (4) the random stress tensor $\tilde{\sigma}$ is the source of the spatial nonuniformities. In accordance with the results of the general theory of disordered media[18] the fluctuations of the elastic moduli Λ, as studied in Ref. 12, are negligibly small compared with the effect of fluctuations of $\tilde{\sigma}$. In Refs. 9–12 an alternative choice of displacement vectors u was employed: They were chosen from the condition that there be no linear terms in the expansion (3). In so doing the frozen-in nonuniformities are taken into account by finding the density distribution $n(\mathbf{x})$ in the undisturbed state. Unfortunately, this problem was not considered at all in Refs. 9–12, which, with $n(\mathbf{x})=\text{const}$, are restricted to much weaker fluctuations of the modulus of elastic Λ.

Detailed information about the microscopic structure of networks can be obtained by introducing into the networks quite short polymer chains. In the experiments of Refs. 4 and 5, the dynamics of the intensity of scattering by such deuterated chains after the network is stretched instantaneously was studied. The theory of the corresponding relaxation processes is constructed in Sec. 5.

2. DENSITY-FUNCTIONAL METHOD FOR DESCRIBING POLYMER NETWORKS

Collective variables

The basic concepts of a rigorous thermodynamic description of a system of linear chains were developed in Refs. 19 and 20 with the help of the path-integration method. In this approach the state of a polymer system is characterized by a set of microscopic coordinates $\mathbf{x}_i(s)$ of the sth monomeric unit $(0<s<l)$ in the ith chain. Significant progress in the theory of polymer liquids was achieved by transferring from the coordinates $\{\mathbf{x}_i(s)\}$ to the densities of the monomeric units as collective macroscopic variables

$$\rho^s(\mathbf{x})=\sum_i^{N^s}\int_0^l ds\langle\delta(\mathbf{x}-\mathbf{x}_i(s))\rangle. \tag{5}$$

Here the summation extends over all N^s chains in the system and the angle brackets indicate a thermodynamic average. In addition to solutions consisting of linear chains, the transformation (5) to the collective variables also makes it possible to describe a sol—a system of finite-size branching macromolecules.

In this section we show how the method of collective variables can be extended so as to describe gigantic branching macromolecules—polymer networks, which are obtained by random cross-linking of linear chains with one another during the process of formation of cross-links. The topological structure of the network obtained in this manner is characterized by the collection of numbers $\mathbf{s}=\{s_i^j\}$, which determine the number s_i^j of the monomeric unit of the jth cross-link on the ith chain.[14,21] The coordinates of such a linkage of chains i and j are

$$\mathbf{x}_i(s_i^j)=\mathbf{x}_j(s_j^i). \tag{6}$$

We confine ourselves below to the case of instantaneous (irradiation) cross-linkage of chains under equilibrium conditions, when the probability distribution of s is determined by the expression[21]

$$P(\mathbf{s})=Z^{(0)}(\mathbf{s})\Big/\int d\mathbf{s}'Z^{(0)}(\mathbf{s}'), \tag{7}$$

where $Z^{(0)}$ is the partition function of the initial system in which the network was formed. In such a system macromolecules of a sol are synthesized together with a gel. For this reason their contribution must also be included in $Z^{(0)}(\mathbf{s})$.

Our aim is to describe a network with a fixed chemical structure s in a finite system, where the network can be subjected to swelling or stretching. We denote the partition function of the network in this system by $Z(\mathbf{s})$. In the experiments the sol is first flushed out of the polymer network. For this reason $Z(\mathbf{s})$, in contrast to $Z^{(0)}(\mathbf{s})$, is determined only by the contribution of the gel. The main problem here is the mathematical description of the procedure of eliminating the sol from a finite system. In the case of the networks studied by Edwards,[14,21] which were obtained far from the gel-formation threshold, there is no sol and such problems do not arise at all. Similarly to Edwards' derivation,[21] the free energy of the network which we studied

$$F\equiv -T\int d\mathbf{s}P(\mathbf{s})\ln Z(\mathbf{s})=\left.\frac{dF_m}{dm}\right|_{m=0} \tag{8}$$

can be expressed in terms of the free energy

$$F_m=-T\ln\int d\mathbf{s}Z_m(\mathbf{s}),\quad Z_m(\mathbf{s})=Z^{(0)}(\mathbf{s})Z^m(\mathbf{s}) \tag{9}$$

of a replica system, in which the sol occupies three-dimensional space and the gel occupies a space of dimension $3(1+m)$. The coordinates $(\mathbf{x}^{(0)},\mathbf{x}^{(1)},\ldots,\mathbf{x}^{(m)})$ of the point $\mathbf{X}$ in such a replica space comprise a collection of coordinates $\mathbf{x}^{(k)}$ of the replicas $k=0,1,\ldots,m$, each of which is determined in the usual three-dimensional space.

By analogy with the formula (5), we introduce as the collective variables the density of monomeric units of the gel in replica space

$$\rho^g(\mathbf{X})=\sum_i^{N^g}\int_0^l ds\langle\delta(\mathbf{X}-\mathbf{X}_i(s))\rangle=\sum_i^{N^g}\int_0^l ds\prod_{k=0}^m\langle\delta(\mathbf{x}^{(k)}-\mathbf{x}_i^{(k)}(s))\rangle, \tag{10}$$

where the summation extends only over N^g chains of the gel. In accordance with the second equality in Eq. (10), the density $\rho^g(\mathbf{X})$ is the generalized Edwards–Anderson order parameter, which is well known in the theory of disordered systems.[22] It describes the overlapping of the replica $k=0$ of the initial system, in which the network was prepared, and the replicas $k=1,...,m$ of the final system under the conditions of an experiment. According to the definition (10), the density of monomeric units of the gel in the kth replica is connected with the order parameter by the relation

$$\rho^{g(k)}(\mathbf{x})=\int d\mathbf{X}\rho^g(\mathbf{X})\delta(\mathbf{x}-\mathbf{x}^{(k)}). \qquad (11)$$

In the case of uniform networks the densities $\rho^{g(k)}$ do not depend on $\mathbf{x}$. For this reason, $\rho^g(\mathbf{X})$ can depend on the coordinates of the replicas only through their linear combinations

$$y_\mu^{(y)}=x_\mu^{(k)}-\lambda_\mu x_\mu^{(0)}; \quad k=1,...,m, \quad \mu=x,y,z. \qquad (12)$$

A glassy state is described by an order parameter with broken symmetry between replicas.[23] In what follows, we confine our attention to temperatures T above the glass-transition temperature of the polymer, when the order parameter is symmetric with respect to permutations of its arguments (12).

Density functional

As in ordinary thermodynamics, the succeeding analysis is most conveniently done within the grand canonical ensemble, whose potential Ω is related to the free energy (9) of the replica system by the standard relation

$$\Omega_m(z,\mu)=F_m(N,N_c)-NT\ln z_a-N_cT\ln\mu, \qquad (13)$$

$$Nl=-\frac{1}{T}\frac{\partial\Omega_m}{\partial\ln z_a}, \quad N_c=-\frac{1}{T}\frac{\partial\Omega_m}{\partial\ln\mu}. \qquad (14)$$

Here z_a and μ are the activities of the monomeric units and cross-links, and N_c is the number of cross-links. Substituting the relation (13) into Eq. (8) and using the conditions (14) we express the free energy of the network in terms of the potential Ω as follows:

$$F=\left.\frac{d\Omega_m}{dm}\right|_{m=0}. \qquad (15)$$

To obtain an explicit expression for Ω_m we note that the collective macrovariables introduced above can fluctuate around their average values. For this reason, the partition function of the grand canonical ensemble is represented in the form of a functional integral over the fluctuating densities of the sol (5) and gel (10) (see, for example, Ref. 24):

$$\begin{aligned}\exp\left(-\frac{\Omega_m}{T}\right)&=\int D\rho^s(\mathbf{x})\int D\rho^g(\mathbf{X})\exp\Biggl\{-\frac{\Omega^s_{0\ \mathrm{CB}}\{\rho^s\}}{T}\\&-\frac{\Omega^g_{m\ \mathrm{CB}}\{\rho^g\}}{T}-\frac{1}{2}\sum_{k=1}^{m}\int d\mathbf{x}d\mathbf{x}'w(\mathbf{x}-\mathbf{x}')\rho^{g(k)}\\&\times(\mathbf{x})\rho^{g(k)}(\mathbf{x}')-\frac{1}{2}\int d\mathbf{x}d\mathbf{x}'w^{(0)}(\mathbf{x}-\mathbf{x}')[\rho^s(\mathbf{x})\\&+\rho^{g(0)}(\mathbf{x})][\rho^s(\mathbf{x}')+\rho^{g(0)}(\mathbf{x}')]\Biggr\}. \end{aligned} \qquad (16)$$

Here the functions $w^{(0)}$ and w describe the interaction of monomeric units in the initial and final systems, and the fact that the total density of the monomeric units in the initial system is $\rho^s+\rho^{g(0)}$ has been taken into account. The thermodynamic potential of the so-called system of chemical bonds,[25] whose monomeric units do not interact with one another and occupy the $3(1+m)$-dimensional replica space, is denoted by $\Omega_{m\ \mathrm{CB}}$. Since in this system different macromolecules do not interact with one another, the thermodynamic potential of the system splits into the separate contributions of the gel (g) and the sol (s):

$$\exp\left(-\frac{\Omega_{m\ \mathrm{CB}}\{\rho\}}{T}\right)=\int D\rho^g\exp\left(-\frac{\Omega^g_{m\ \mathrm{CB}}\{\rho^g\}+\Omega^s_{m\ \mathrm{CB}}\{\rho-\rho^g\}}{T}\right). \qquad (17)$$

The integration in Eq. (17) extends over the densities ρ^g and $\rho^s=\rho-\rho^g$ of monomeric units in the gel and sol, respectively.

The sol thermodynamic potential $\Omega^s_{m\mathrm{CB}}$ differs from $\Omega_{m\mathrm{CB}}$ only by an infinitely small negative correction to the activity $z_a\rightarrow z_a-0$, which in the thermodynamic limit $N^g\rightarrow\infty$ eliminates the contribution of the gel macromolecules. The equation (17) can be regarded as an equation for the thermodynamic potential $\Omega^g_{m\mathrm{CB}}$ of the gel. Below the gel formation point it has only the trivial solution

$$\Omega^g_{m\ \mathrm{CB}}\{\rho^g\}=-T\ln\delta\{\rho^g\}, \quad \Omega^s_{m\ \mathrm{CB}}\{\rho\}=\Omega_{m\ \mathrm{CB}}\{\rho\}, \qquad (18)$$

which corresponds to no gel ($\rho^g=0$). Networks obtained far from the gel point are another trivial particular case. For these networks

$$\Omega^s_{m\ \mathrm{CB}}\{\rho^s\}=-T\ln\delta\{\rho^s\}, \quad \Omega^g_{m\ \mathrm{CB}}\{\rho\}=\Omega_{m\ \mathrm{CB}}\{\rho\}, \qquad (19)$$

in accordance with the absence of a sol ($\rho^s=0$) in such a system.

For our model the functional $\Omega_{m\ cb}$ can be represented in the form

$$\frac{\Omega_{m\ \mathrm{CB}}\{\rho\}}{T}=\int d\mathbf{X}\left[\frac{a^2}{6}(\nabla\rho^{1/2})^2+\frac{\rho}{l}\ln\frac{\rho}{ezl}-\frac{\mu}{2}\rho^2\right]. \qquad (20)$$

The quantity a in Eq. (17) determines the size of a monomeric unit. The gradient term was first obtained by Lifshitz;[24] it originates from the Jacobian of the transformation from integration over the microvariables $\{\mathbf{x}_i(s)\}$ to functional integration over the collective macrovariables $\rho(\mathbf{X})$. The logarithmic term in Eq. (19) is equal to the translational entropy of chains of the network (the replica system is a liquid), and the term $-\mu\rho^2/2$, which can be rewritten in the form[21]

$$-\mu \sum_{i>j} \int_0^l ds_i^j \int_0^l ds_j^i \prod_{k=0}^m \delta[\mathbf{x}_i^{(k)}(s_i^j)-\mathbf{x}_j^{(k)}(s_j^i)], \tag{21}$$

determines the contribution of chemical cross-linkages (6) to the Ginzburg–Landau functional (20).

Thus we have developed in this section a density-functional method for describing polymer networks, obtained with the help of chemical cross-linkages of polymer chains. In melts their role is played by "physical" cross-linkages—topological linkages of chains and the ratio $Nl/N_c \approx N_e = 100$–300.[26] In this case, the state of the network before instantaneous stretching should be taken as the initial system, and the density functional describes the elastic properties of a quasinetwork of cross-linkages over times that are much shorter compared than the maximum relaxation time $\tau_e \propto l^3$.[26]

3. SPONTANEOUS BREAKING OF TRANSLATIONAL SYMMETRY

Neglecting density fluctuations, the functional integrals (16) and (17) over ρ^s and ρ^g can be calculated by the saddle-point method. We consider first the initial system, setting in the saddle-point equations $m=0$. Expressing with the help of the relations (14) the activities z_a and μ in terms of the density of monomeric units $\rho^{(0)}=Nl/V^{(0)}$ and the density of cross-linkages $\rho_c^{(0)}=N_c/V^{(0)}$ of such a system with volume $V^{(0)}$, we find

$$z=\rho^{(0)}l^{-1}\exp(w_0^{(0)}\rho^{(0)}l-2pl), \quad \mu=2p/\rho^{(0)},$$

where $p=\rho_c^{(0)}/\rho^{(0)}$ is the conversion ratio of the initial system. Here and below $w_\mathbf{q}$ designates the Fourier components of the corresponding function $w(\mathbf{x})$. The nontrivial solution $\rho^{g(0)}=\rho^{(0)}\Phi>0$ of the saddle-point equations

$$\Phi=1-\exp(-2pl\Phi)$$

exists only for $p>p_c=1/2l$.

We now return to the general case $m\neq 0$, when it is convenient to introduce instead of the densities ρ and ρ^s the order parameters for linear chains:[26]

$$\begin{aligned} &\rho(\mathbf{X})=\rho^{(0)}[\psi(\mathbf{X})]^2, \quad \rho^s(\mathbf{X})=\rho^{(0)}[\psi^s(\mathbf{X})]^2,\\ &\rho^b(\mathbf{X})=\rho^{(0)}[\psi^g(\mathbf{X})]^2, \quad \rho^d(\mathbf{X})=2\rho^{(0)}\psi^g(\mathbf{X})\psi^s(\mathbf{X}),\\ &\psi^g(\mathbf{X})=\psi(\mathbf{X})-\psi^s(\mathbf{X}), \quad \rho^g(\mathbf{X})=\rho(\mathbf{X})-\rho^s(\mathbf{X})\\ &\qquad =\rho^b(\mathbf{X})+\rho^d(\mathbf{X}). \end{aligned} \tag{22}$$

The functions ρ^b and ρ^d are the densities of monomeric units in the backbone of the network and the density of dangling ends of the network, which are connected to the backbone at only a single point. These quantities play an important role in the modern theory of nonideal networks.[27]

The multidimensional equations, determining the saddle-point trajectory, can be solved only because such a solution has extremely high symmetry, which also enables explicit analytical continuation to $m=0$. The Ginzburg–Landau functional (20) is isotropic in replica space. In the solid phase this symmetry is broken spontaneously, since the condition (12) separates three directions along the unit vectors

$$\begin{aligned} &\mathbf{E}_x=(\mathbf{e}_x,0,0), \quad \mathbf{E}_y=(0,\mathbf{e}_y,0), \quad \mathbf{E}_z=(0,0,\mathbf{e}_z);\\ &\mathbf{e}_\mu=(1,\lambda_\mu,\ldots,\lambda_\mu)/(1+m\lambda_\mu^2)^{1/2}. \end{aligned} \tag{23}$$

Our solution (12) can depend only on the components

$$\mathbf{R}^\perp=\mathbf{X}-\sum_\mu \mathbf{E}_\mu(\mathbf{X}\mathbf{E}_\mu) \tag{24}$$

of the vector $\mathbf{X}$ which are perpendicular to the vectors $\mathbf{E}_\mu$ (23). Moreover, owing to the rotational symmetry of the functional Ω_m (20) the solution depends only on the quantity[15,16]

$$z\equiv\frac{1}{2}(\mathbf{R}^\perp)^2=\frac{1}{2}\Big[\mathbf{X}^2-\sum_\mu(\mathbf{E}_\mu\mathbf{X})^2\Big].$$

For $p>p_c$ the desired solution has the form

$$\psi^s(\mathbf{X})=\psi^s, \quad (\psi^s)^2=1-\Phi; \quad \psi(\mathbf{X})=\psi_{cl}(z), \tag{25}$$

where the function ψ_{cl} is determined in the limit $m\to 0$ by the equation

$$\Big[-\frac{a^2}{3}z\frac{d^2}{dz^2}+\frac{1}{l}\ln\psi_{cl}+p(1-\psi_{cl}^2)\Big]\psi_{cl}=0$$

with the boundary conditions

$$\psi_{cl}(0)=1, \quad \psi_{cl}(\infty)=\psi^s.$$

Substituting this solution into the relations (15)–(17) we find with logarithmic accuracy the following expression for the free energy of the network:

$$F=rT\Big(\tfrac{1}{2}\sum_\mu \lambda_\mu^2+\ln R^3\Big)+\tfrac{1}{2}VTw_0\rho^2. \tag{26}$$

The cyclic rank r of the network and its conversion ratio p^g are, respectively,

$$r=N\Phi(p^g l-1), \quad p^g=p(2-\Phi). \tag{27}$$

According to Eq. (26) the quantity r determines the number of elastically effective chains which are constituents of the backbone of the network. The logarithmic term in Eq. (26) describes the decrease in the entropy of these chains due to their localization on a scale $R\approx a(p-p_c)^{-1}$ in the network. In Flory's theory[28] this effect is neglected and the term $\ln V$ appears in the free energy.

The form of the expression (26) corresponds to the theory of James and Guth,[29] which is based on the assumption that the stretching of the network is affine. The affine property is manifested explicitly in the symmetry of our solution (25) with respect to simultaneous displacement of the coordinates $\mathbf{x}^{(k)}$ of all replicas by the vectors $\mathbf{u}^{(k)}=\lambda\cdot\mathbf{u}^{(0)}$ with the components

$$u_\mu^{(k)}=\lambda_\mu u_\mu^{(0)}, \quad k=1,...,m, \quad \mu=x,y,z. \tag{28}$$

Thus the widely discussed[26–29] affine nature of network stretching is the result of neglecting fluctuation effects. In what follows Landau's approach will be employed to study fluctuation effects theoretically.

4. THEORY OF ELASTICITY OF STRUCTURALLY DISORDERED NETWORKS

In the classical theory of elasticity[17] an abbreviated description, in which the displacement vectors $\mathbf{u}(\bar{\mathbf{x}})$ referred to the coordinates $\bar{\mathbf{x}}$ of the undeformed body are chosen as the order parameter, is employed. As shown above, for disordered solids the order parameter is the density $\rho^g(\mathbf{X})$ of monomeric units in replica space. These two order parameters are related by the collective coordinates $\mathbf{u}^{(k)}(\mathbf{x})$ of the Goldstone modes, which appear in the density-functional method as a result of spontaneous breaking of translational symmetry in replica system.

The central concept in the derivation of Landau's functional (4) is transforming in the formula (16) from integration over $\rho^g(\mathbf{X})$ to an integral over the collective coordinates $\mathbf{u}^{(k)}(\bar{\mathbf{x}})$. We show below that in these variables the partition function of the replica system can be represented in the form

$$\exp\left(-\frac{\Omega_m}{T}\right)=\int DnW^{(0)}\{n\}\int D\tilde{\sigma}W\{\tilde{\sigma}\}\prod_{k=1}^{m}\int D\mathbf{u}^{(k)} \times\exp\left(-\frac{F\{\mathbf{u}^{(k)},n,\tilde{\sigma}\}}{T}\right). \tag{29}$$

Substituting the formula (29) into Eq. (15) for the free energy of the system we find the expression

$$F=-T\int DnP^{(0)}\{n\}\int D\tilde{\sigma}P\{\tilde{\sigma}\}\ln\int Du \times\exp\left(-\frac{F\{\mathbf{u},n,\tilde{\sigma}\}}{T}\right),$$

which makes it possible to regard the functionals

$$P^{(0)}\{n\}=\frac{W^{(0)}\{n\}}{\int DnW^{(0)}\{n\}}, \quad P\{\tilde{\sigma}\}=\frac{W\{\tilde{\sigma}\}}{\int D\tilde{\sigma}W\{\tilde{\sigma}\}}$$

as probability distributions of the density $n(\mathbf{x})$ of the undisturbed state (2) and the stress tensor $\tilde{\sigma}$ as well as to identify F with the desired Landau free-energy functional (4). Thus the transformation to collective variables $\mathbf{u}^{(k)}$ makes it possible to find not only Landau's functional but also the distribution function of the random parameters appearing in it.

Goldstone modes, together with thermal excitations (acoustic phonons), also describe static nonuniformities which are present in networks and which cause network stretching to lose its affine nature (28). These soft modes correspond to a displacement of the replica coordinates

$$\mathbf{x}^{(k)}\to\mathbf{x}^{(k)}+\mathbf{u}^{(k)}(\bar{\mathbf{x}}), \quad k=1,...,m \tag{30}$$

by independent displacement vectors $\mathbf{u}^{(k)}(\bar{\mathbf{x}})$. By analogy to the classical theory of elasticity, we assume that the coordinates $\bar{x}_\mu=\lambda_\mu x_\mu^{(0)}$ of the vector $\bar{\mathbf{x}}=\lambda\cdot\mathbf{x}$ are equal to the coordinates of the undisturbed state (3), obtained by affine stretching of the initial system. We emphasize that our choice of the undisturbed state not only is not unique (see the Introduction), but also differs from the standard definition of the collective coordinates[30] for the soliton solution $\varphi_{cl}(z)$ (25). According to Ref. 30, one should set $\bar{x}_\mu=\lambda_\mu R_\mu^{\|}$ (where $R_\mu^{\|}=\mathbf{E}_\mu\mathbf{X}$ are the longitudinal coordinates (24)), which differs from our choice by terms which are linear in the coordinates $\mathbf{x}^{(k)}$ of the replicas $k=1,...,m$ of the final system. Our choice was based on considerations of physical clarity, which is not always synonymous with mathematical simplicity.

Together with the Goldstone modes, it is also necessary to take into consideration excitations which do not reduce to elastic shear deformations (30). These are the excitations that describe density fluctuations in the initial system (which is a liquid) and fluctuations of the density of monomeric units of dangling ends in the final system. Let $v^{(k)}(\mathbf{x}^{(k)})$ designate fields which induce such density fluctuations in the kth replica. In the long-wavelength limit such fields give the corresponding correction to the chemical potential of the monomeric units of the replica system:

$$\ln z_a\to\ln z_a+\sum_k v^{(k)}(\mathbf{x}^{(k)}). \tag{31}$$

With Eqs. (30) and (31) the expressions for the order parameters ψ^s and ψ assume the following form to first order in the functions u and v:

$$\delta\psi^s(\mathbf{X})\equiv\psi^s(\mathbf{X})-\psi^s=\frac{\partial\psi^s}{\partial\ln z_a}\sum_{k=1}^{m}v^{s(k)}(\mathbf{x}^{(k)}),$$

$$\delta\psi(\mathbf{X})\equiv\psi(\mathbf{X})-\psi_{cl}(z) =\frac{\partial\psi_{cl}(z)}{\partial\ln z_a}\sum_{k=0}^{m}v^{(k)}(\mathbf{x}^{(k)})-\sum_{k=1}^{m}\sum_{\mu}\frac{\partial\psi_{cl}(z)}{\partial x_\mu^{(k)}}u_\mu^{(k)}(\bar{\mathbf{x}}). \tag{32}$$

We substitute the expansions (32) into the argument of the exponential function in Eq. (16), in which only the terms quadratic in $\delta\psi$ (32) should be retained. Switching in Eq. (16) to integration over the collective variables $\mathbf{u}^{(k)}$ and $v^{(k)}$ and calculating the Gaussian integrals over the fields $v^{(k)}$ by the saddle-point method, we find

$$\exp\left(-\frac{\Omega_m}{T}\right)$$

$$=\prod_{k=1}^{m}\int D\mathbf{u}^{(k)}\exp\left\{-\sum_{k=1}^{m}\frac{\widetilde{\Omega}\{\mathbf{u}^{(k)},h^{(k)}\}}{T}\right.$$

$$\left.+\frac{1}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}\left[\frac{\theta^{g(0)}_{\lambda\cdot\mathbf{q}}}{\lambda_x\lambda_y\lambda_z}\xi_{\mathbf{q}}\xi_{-\mathbf{q}}+\sum_{\mu,\nu}f_{\mu\nu,\lambda\cdot\mathbf{q}}\eta_{\mu\mathbf{q}}\eta_{\nu-\mathbf{q}}\right]\right\},$$

$$\xi_{\mathbf{q}}\equiv\sum_{k=1}^{m}\left[h^{(k)}_{\mathbf{q}}-\sum_{\mu}\left(w_{\mathbf{q}}\rho^{g}+\frac{\lambda_\mu^2\Phi}{g^g}\right)iq_\mu u^{(k)}_{\mu\mathbf{q}}\right],$$

$$\eta_{\mu\mathbf{q}}\equiv\sum_{k=1}^{m}u^{(k)}_{\mu\mathbf{q}},\qquad(33)$$

where, for subsequent identification of the densities $\rho^{g(k)}$, $(k=1,...,m)$, we introduced the fields $h^{(k)}(\mathbf{x}^{(k)})$ associated with them. The functional $\bar{\Omega}$ diagonal in the replicas is

$$\frac{\widetilde{\Omega}\{\mathbf{u},h\}}{T}=\int\frac{d\mathbf{q}}{(2\pi)^3}\left[\frac{(\lambda\cdot\mathbf{q})^2}{4}\rho^g\left(p^g-\frac{1}{l}\right)\sum_{\mu}u_{\mu\mathbf{q}}u_{\mu-\mathbf{q}}\right.$$

$$\left.+\frac{w_{\mathbf{q}}}{2}(\rho^g)^2\sum_{\mu,\nu}q_\mu q_\nu u_{\mu\mathbf{q}}u_{\nu-\mathbf{q}}+h_q i\rho^g\sum_{\mu}q_\mu u_{\mu-\mathbf{q}}\right].\qquad(34)$$

The first term in brackets in Eq. (34) corresponds to the elastic contribution ($\propto r$) to the free energy (26) of the network; the second term corresponds to the contribution of interactions ($\propto w_0$) in Eq. (26); the term proportional to h gives the energy of the external field.

We now consider terms in the expression (33) which are off-diagonal with respect to the replicas:

$$g^g=g-g^s,\quad g=\frac{2}{l^{-1}-2p},\quad g^s=\frac{2(1-\Phi)}{l^{-1}-2p(1-\Phi)},\qquad(35)$$

where g^g is the dimensionless structure factor of the network. The function $\theta^{g(0)}$ is the Fourier component of the fluctuations of the density of monomeric units of the gel in the initial system:[31,32]

$$\theta^{g(0)}_{\mathbf{q}}\equiv\overline{\rho^{g(0)}_{\mathbf{q}}\rho^{g(0)}_{-\mathbf{q}}}=\rho^{(0)}g^g-\frac{(\rho^{(0)}g^g)^2w^{(0)}_{\mathbf{q}}}{1+\rho^{(0)g}w^{(0)}_{\mathbf{q}}}.\qquad(36)$$

The tensor function

$$f_{\mu\nu,\mathbf{q}}=\lambda_\mu\lambda_\nu\rho^g\left[\delta_{\mu\nu}\frac{q^2}{2}\left(p^g-\frac{1}{l}\right)+q_\mu q_\nu\Phi\left(\frac{1}{g}-\frac{1}{g^g}\right)\right]\qquad(37)$$

depends only on the topological characteristics of the network.

In order to represent the expression (33) in the form (29) we introduce with the help of the Hubbard–Strattonovich transformation the Gaussian fields

$$n_{\mathbf{q}}=\rho^{g(0)}_{\lambda\cdot\mathbf{q}},\quad f^{\perp}_{\mu\mathbf{q}}=\sum_{\nu}iq_\nu\tilde{\sigma}_{\mu\nu,\mathbf{q}},\qquad(38)$$

adjoint to the variables $\xi_{\mathbf{q}}$ and $\eta_{\mu\mathbf{q}}$ in Eq. (33). In the coordinate representation the first equality in Eq. (38) has the form (3) with the obvious substitution $\rho\to\rho^g$, and the second term is the usual relation between the force $\mathbf{f}^{\perp}(\mathbf{x})$ and the random stress tensor $\tilde{\sigma}(\mathbf{x})$ generating it. The correlation function of the density field $\rho^{g(0)}$ is defined in Eq. (36), and the correlation function of the average force $\mathbf{f}^{\perp}$ has the form

$$\overline{f^{\perp}_{\mu\mathbf{q}}f^{\perp}_{\nu-\mathbf{q}}}=f_{\mu\nu,\lambda\cdot\mathbf{q}}.\qquad(39)$$

We note that the dependence of the correlation function (39) and (37) on the wave vector $\mathbf{q}$ corresponds to the fact that the spatial fluctuations of the tensor $\tilde{\sigma}(\mathbf{x})$ (38) at different points $\mathbf{x}'\neq\mathbf{x}$ are independent of each other; this is a consequence of the long-wavelength approximation.

The following expression is obtained from Eq. (33) for the Landau free-energy functional:

$$\frac{F\{\mathbf{u},n,\mathbf{f}\}}{T}=\int\frac{d\mathbf{q}}{(2\pi)^3}\left[\frac{(\lambda\cdot\mathbf{q})^2}{4}\rho^g\left(p^g-\frac{1}{l}\right)\sum_{\mu}u_{\mu\mathbf{q}}u_{\mu-\mathbf{q}}\right.$$

$$\left.+\frac{w_{\mathbf{q}}}{2}\rho^g_{\mathbf{q}}\rho^g_{-\mathbf{q}}-\sum_{\mu}f_{\mu\mathbf{q}}u_{\mu-\mathbf{q}}\right],$$

$$\rho^g_{\mathbf{q}}=n_{\mathbf{q}}-\rho^g\sum_{\mu}iq_\mu u_{\mu\mathbf{q}},\qquad(40)$$

where the coefficient in front of the external field $h_{-\mathbf{q}}$ is the density $\rho^g_{\mathbf{q}}$ of gel monomeric units. In the coordinate representation the expression for $\rho^g(\mathbf{x})$ assumes the form (2) with ρ^g replacing ρ. The Fourier components of the random force $\mathbf{f}$ are

$$f_{\mu\mathbf{q}}=f^{\parallel}_{\mu\mathbf{q}}+f^{\perp}_{\mu\mathbf{q}},\quad f^{\parallel}_{\mu\mathbf{q}}=-i\lambda_\mu^2q_\mu\Phi n_{\mathbf{q}}/g^g.\qquad(41)$$

As discussed in the Introduction, the components $\mathbf{f}^{\parallel}$ and $\mathbf{f}^{\perp}$ of the force $\mathbf{f}$ have different origins: $\mathbf{f}^{\parallel}$ is the gradient of the field $v(\mathbf{x})=\Phi(g^g)^{-1}\rho^{g(0)}(\mathbf{x})$ of density nonuniformities stretched affinely with the network, while $\mathbf{f}^{\perp}$ is generated by the statistical fluctuations of the topological structure of the networks.

In accordance with the form of the correlation function of the random force (37) $\mathbf{f}^{\perp}$ can be expanded into a sum

$$f^{\perp}_{\mu\mathbf{q}}=f^{b}_{\mu\mathbf{q}}-i\lambda_\mu^2q_\mu f^{d}_{\mathbf{q}},$$

of statistically independent contributions of the network backbone f^b whose correlation function

$$\overline{f^{b}_{\mu\mathbf{q}}f^{b}_{\nu-\mathbf{q}}}=\lambda_\mu^2\delta_{\mu\nu}\frac{(\lambda\cdot\mathbf{q})^2}{2}\rho^g\left(p^g-\frac{1}{l}\right)$$

is proportional to the number r (27) of elastically effective chains of the backbone and the contribution ($\propto f^d$) of frozen-in fluctuations of the density of dangling ends [corresponding to the definition in Eq. (22)].

The term linear in $\mathbf{u}$ and proportional to $\mathbf{f}$ can be removed from the Landau functional (40) by making an appropriate choice of the undisturbed state:

$$u_\mu(\mathbf{x})\to u_\mu(\mathbf{x})+\lambda_\mu u^{\parallel}_\mu(\lambda^{-1}\cdot\mathbf{x})+\lambda_\mu u^{\perp}_\mu(\lambda^{-1}\cdot\mathbf{x}).\qquad(42)$$

Here the functions $\mathbf{u}^{\parallel}$ and $\mathbf{u}^{\perp}$, generated by the corresponding components of the random force (41), do not depend on the degree λ_μ of the stretching of the network;

$\mathbf{u}^{\parallel}$ describes finite-size spatial nonuniformities of the network and $\mathbf{u}^{\perp}$ is the static analog of Brownian motion, in particular,

$$\overline{u_\mu^b(\mathbf{x})u_\nu^b(\mathbf{x}')}\sim\delta_{\mu\nu}|\mathbf{x}-\mathbf{x}'|^{-1}.$$

The expressions (35)–(41) obtained above determine completely the elastic properties of significantly irregular phantom polymer networks, obtained both near and far from the gel-formation threshold.

5. RELAXATION PROCESSES IN DEFORMED NETWORKS

General theory

The dynamics of relaxation processes in solids is described by the Langevin equations:[33,17,20]

$$\sum_\nu \frac{\partial}{\partial \mathbf{x}_\nu}(\sigma_{\mu\nu}+\sigma'_{\mu\nu})=\xi_\mu(\mathbf{x},t),\quad \sigma_{\mu\nu}=\frac{\delta F\{u\}}{\delta u_{\mu\nu}}. \tag{43}$$

According to Ref. 17, the dissipative stress tensor has the same tensor structure as the stress tensor $\sigma_{\mu\nu}$ (43):

$$\sigma'_{\mu\nu}=2\eta\left(\frac{\partial u_{\mu\nu}}{\partial t}-\frac{1}{3}\delta_{\mu\nu}\sum_\alpha\frac{\partial u_{\alpha\alpha}}{\partial t}\right)+\zeta\delta_{\mu\nu}\sum_\alpha\frac{\partial u_{\alpha\alpha}}{\partial t}, \tag{44}$$

where η and ζ are the effective coefficients of viscosity. The Fourier components of the correlation functions of the random Gaussian force ξ have the same form as the dissipative tensor (44):

$$\begin{aligned}&\langle\xi_{\mu\mathbf{q}}(t)\rangle=0,\quad \langle\xi_{\mu\mathbf{q}}(t)\xi_{\nu-\mathbf{q}}(t')\rangle\\&\quad=T[2\eta(q^2\delta_{\mu\nu}+\tfrac{1}{3}q_\mu q_\nu)+2\zeta q_\mu q_\nu]\delta(t-t').\end{aligned} \tag{45}$$

Operating with the operator $\partial/\partial x_\mu$ on both sides of Eq. (43) and summing over μ, we find an equation for only the density of monomeric units of the network:

$$\begin{aligned}&(\varkappa_\mathbf{q}+w_\mathbf{q})\rho_\mathbf{q}^g(t)+\left(\frac{4}{3}\eta+\zeta\right)\frac{1}{(\rho^g)^2T}\frac{\partial\rho_\mathbf{q}^g(t)}{\partial t}\\&\quad=\varkappa_\mathbf{q}n_\mathbf{q}-\frac{i}{q^2\rho^g}\sum_\mu q_\mu\left(f_{\mu\mathbf{q}}+\frac{\xi_{\mu\mathbf{q}}(t)}{T}\right),\\&\quad\varkappa_q\equiv\frac{(\lambda\cdot\mathbf{q})^2}{2q^2\rho^g}\left(p^g-\frac{1}{l}\right).\end{aligned} \tag{46}$$

In order to find the initial conditions to this equation we consider a network which is swelled by a factor of λ with respect to the conditions under which it was synthesized. In typical relaxation experiments, at the moment $t=0$ such a network is subjected to instantaneous stretching by a factor of $\alpha_\mu=\lambda_\mu/\lambda$ along the corresponding axes $\mu=x,y,z$. Owing to the affine nature of this stretching and our choice of the affinely deformed undisturbed state (3) we have

$$u_\mu(\mathbf{x},+0)=\alpha_\mu u_\mu(\alpha^{-1}\cdot\mathbf{x},-0). \tag{47}$$

This initial condition can be rewritten directly in terms of the density of monomeric units. Neglecting the change in the total volume of the network ($\alpha_x\alpha_y\alpha_z=1$) under stretching, we obtain from Eqs. (40) and (47)

$$\rho_\mathbf{q}^g(+0)=\rho_{\alpha\cdot\mathbf{q}}^g(-0). \tag{48}$$

The solution of the Langevin equation (46) for $t>0$ has the form

$$\begin{aligned}\rho_\mathbf{q}^g(t)&=\rho_\mathbf{q}^g(+0)\exp\left(-\frac{t}{\tau_\mathbf{q}}\right)+\frac{\varkappa_\mathbf{q}[1-\exp(-t/\tau_\mathbf{q})]}{\varkappa_\mathbf{q}+w_\mathbf{q}}n'_\mathbf{q}\\&\quad-\frac{i}{q^2(\zeta+4\eta/3)}\int_0^t d\tau\exp\left(\frac{\tau-t}{\tau_\mathbf{q}}\right)\sum_\mu q_\mu\xi_{\mu\mathbf{q}}(\tau),\end{aligned} \tag{49}$$

where

$$\frac{1}{\tau_\mathbf{q}}=T(\rho^g)^2\frac{\varkappa_\mathbf{q}+w_\mathbf{q}}{\zeta+4\eta/3},\quad n'_\mathbf{q}=\rho_{\lambda\cdot\mathbf{q}}^{g(0)}\frac{i}{\varkappa_q q^2\rho^g}\sum_\mu q_\mu f_{\mu\mathbf{q}}.$$

Here $n'_\mathbf{q}$ is the Fourier component, introduced in Refs. 15 and 34, of the density $n'(\mathbf{x})$ of monomeric units in the undisturbed state (42), i.e., the density maximizing the entropy functional of the network. The first two terms in the formula (49) describe density relaxation over times $\tau_\mathbf{q}$ from the value $\rho_\mathbf{q}^g(+0)$ for an affinely stretched network to its equilibrium value, minimizing the free-energy functional[15,34]

$$\begin{aligned}F\{\rho\}=\frac{1}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}&[\varkappa_\mathbf{q}(\rho_\mathbf{q}-n'_\mathbf{q})(\rho_{-\mathbf{q}}-n'_{-\mathbf{q}})\\&+w_\mathbf{q}\rho_\mathbf{q}\rho_{-\mathbf{q}}].\end{aligned}$$

The last term in Eq. (49) describes the contribution of thermal fluctuations. For the quantity $\rho_\mathbf{q}^g(+0)$ appearing in Eq. (49), we obtain from Eq. (46), with the help of the condition (48), the expression

$$\begin{aligned}\rho_q^g(+0)&=\frac{\varkappa n'_\mathbf{q}}{\varkappa+w_{\alpha\cdot\mathbf{q}}}-\frac{i}{(\alpha\cdot\mathbf{q})^2(\zeta+4\eta/3)}\int_{-\infty}^0 d\tau\\&\quad\times\exp\left(\frac{\tau}{\tau'_\mathbf{q}}\right)\sum_\mu\alpha_\mu q_\mu\xi_{\mu\alpha\cdot\mathbf{q}}(\tau),\end{aligned}$$

$$\varkappa=\frac{\lambda^2}{2\rho^g}\left(p^g-\frac{1}{l}\right),\quad 1/\tau'_\mathbf{q}=T(\rho^g)^2\frac{\varkappa+w_{\alpha\cdot\mathbf{q}}}{\zeta+4\eta/3}.$$

Averaging over random Gaussian forces ξ and $\mathbf{f}$ with the correlation functions (45) and (36)–(41), we represent the correlation function of the fluctuations of the density of monomeric units in the network

$$\overline{\langle\rho_\mathbf{q}^g(t)\rho_{-\mathbf{q}}^g(t)\rangle}=G_\mathbf{q}(t)+C_\mathbf{q}(t), \tag{50}$$

for $t>0$ as a sum of contributions of thermodynamic fluctuations

$$G_\mathbf{q}(t)=\frac{\exp(-2t/\tau_\mathbf{q})}{\varkappa+w_{\alpha\cdot\mathbf{q}}}+\frac{1-\exp(-2t/\tau_\mathbf{q})}{\varkappa_\mathbf{q}+w_\mathbf{q}}, \tag{51}$$

and statistical fluctuations

$$c_{\mathbf{q}}(t)=\left[\frac{\varkappa\exp(-t/\tau_{\mathbf{q}})}{\varkappa+w_{\alpha\cdot\mathbf{q}}}+\frac{\varkappa_{\mathbf{q}}[1-\exp(-t/\tau_{\mathbf{q}})]}{\varkappa_{\mathbf{q}}+w_{\mathbf{q}}}\right]^2 \times\left[A^2\frac{\theta^{g(0)}_{\lambda\cdot\mathbf{q}}}{\lambda_x\lambda_y\lambda_z}+2B\frac{\rho^g}{p^g-1/l}\right], \qquad (52)$$

where we have set

$$A=1-\frac{2\Phi}{g^g(p^g-1/l)}, \quad B=1+\frac{2\Phi(1/g-1/g^g)}{p^g-1/l}.$$

For networks obtained far from the gel-formation threshold ($p\gg 1/l$), the expressions (50)–(52) in the limit $t\to\infty$ were obtained previously on the basis of the thermodynamic theory.[15-34]

Comparison with experiment

Relaxation processes in a polymer network have been in greatest detail in experiments on neutron scattering by a polymer solvent, consisting of quite short chains, inserted in the network. The entropy contribution of such chains to the free energy of the system is

$$\frac{T}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}S_{\mathbf{q}}^{-1}c_{\mathbf{q}}c_{-\mathbf{q}}, \quad S_{\mathbf{q}}=\frac{c}{N^{-1}+\alpha^2q^2/12}, \qquad (53)$$

where N is the number of monomeric units in a single chain and c is the average density of monomeric units of the solvent. The local density $c(\mathbf{x})$ in the melt is related to the density $\rho(\mathbf{x})$ of monomeric units in the network by the incompressibility condition $c_{\mathbf{q}}=-\rho_{\mathbf{q}}$. For this reason, in accordance with the formula (53), a two-component system consisting of a network and a polymer solvent can be viewed as a single-component system with an effective interaction parameter $w_{\mathbf{q}}=S_{\mathbf{q}}^{-1}$ (53). Fifty-percent solutions of chains can also be described with the help of the above-obtained results, if the lengths and density of monomeric units of a chain are expressed in units of de Gennes blobs.[26] Thus the intensity of neutron scattering, which is proportional to the correlation function of the density fluctuations of the solvent,

$$I_{\mathbf{q}}(t)\equiv\langle c_{\mathbf{q}}(t)\overline{c_{-\mathbf{q}}(t)}\rangle=G_{\mathbf{q}}(t)+C_{\mathbf{q}}(t),$$

is determined completely by the expressions (51) and (52) with $w_{\mathbf{q}}=S_{\mathbf{q}}^{-1}$ (53).

In practice, it is more convenient to vary the temperature T instead of the time. In accordance with the expression (50), at low temperatures (in the limit $t\to 0$) the isointensity scattering curves are ellipses whose major axes are perpendicular to the direction of stretching of the network. Experimentally,[5] at short times $t\lesssim\tau_{\mathbf{q}}$ and small wave vectors q there also appear, against the background of the classical ellipses, butterfly wings which are oriented along the direction of stretching of the network. As the temperature and time increase further, this picture of the anomalous butterfly effect extends to increasingly higher values of q and at long times it assumes the form shown in Fig. 1d. We do not consider here the stabilized butterfly effect, since it was studied in detail in Ref. 34.

In the experiments of Ref. 5 the characteristic relaxation times $\tau_{\mathbf{q}}$ were of the order of the corresponding relaxation times of a mixture consisting of the same unlinked chains. For this reason, the effective coefficients of viscosity η and ζ in Eq. (59) are of the order of the coefficient of viscosity of the monomeric units of these chains.

6. BASIC RESULTS

In this paper a new theoretical approach was proposed for describing soft solids. The most important class of substances of this type are polymer networks. The density-functional method, which is well known in the theory of liquids, was extended, on the basis of Edwards generalized approach,[14] to the description of solids of this type. The topological structure of polymer networks is very irregular. For this reason, within the density-functional method their properties are described by the Edwards–Anderson order parameter (10), well-known from the theory of spin glasses.

The solid state corresponds to an order parameter with spontaneously broken translational symmetry. Goldstone modes corresponding to such symmetry breaking describe elastic deformations in solids. The obtained effective Hamiltonian (33), which depends on the collective coordinates of the Goldstone modes, made it possible to find Landau's free-energy functional (40). In contrast to the standard theory of elasticity, this functional is itself a random quantity, characterized by the distribution functions of the parameters of the functional.

It should be especially noted that in order to describe soft solids it is necessary to give, together with the field of the displacement vectors $\{u_\mu(\bar{\mathbf{x}})\}$ (or the strain tensor (1)), also the density distribution $\{n(\mathbf{x})\}$ (2), which is related uniquely to the choice of the argument $\bar{\mathbf{x}}$ of the function $u_\mu(\bar{\mathbf{x}})$. Unfortunately, the existence of this gauge field $n(\mathbf{x})$, which compensates the indefiniteness of the variable u_μ (see Introduction), was ignored in attempts to adapt the classical theory of elasticity to the description of the amorphous substances studied.[9-12] The physical variables, such as the density $\rho(\mathbf{x})$ of monomeric units (2), do not depend on the specific choice of gauge. In the present work we employed the simplest "affine" gauge $\bar{x}_\mu=\lambda_\mu x_\mu^{(0)}$, to which the function $n(\mathbf{x})$ in Eq. (3) corresponds.

We note that the existence of the above-considered gauge freedom falls outside the scope of the models studied here and is a specific feature of systems with frozen-in disorder, in which the variable $n(\mathbf{x})$ must be treated as an independent random field. Together with the random distribution $\{n(\mathbf{x})\}$ the most important stochastic parameter of the Landau functional is the random stress tensor $\{\tilde{\sigma}_{\mu\nu}(\mathbf{x})\}$, which describes irregular internal stresses in amorphous solids. Such stresses lead to the appearance of strong nonuniformities, distributed randomly in space, in the solids.

The effect of such static nonuniformities is most strikingly manifested in the appearance of the butterfly effect in deformed soft solids. We studied the dynamics of this effect and showed that our theory describes the basic experimentally observed features of the relaxation of density fluctuations.

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