Topology fluctuations in polymer networks

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The correlation function of polymer-network chain-density fluctuations induced by fluctuations of the network topology (i.e., of defects of the network structure and topological restrictions) is calculated by the replica method. It is shown that such statistical (spatial) density fluctuations can be considerably greater than the thermodynamic (temporal) fluctuations usually taken into account. The characteristic size and amplitude of the spatial nonuniformities of the network are calculated. It is shown that, as the quality of the solvent decreases, fluctuations of the topology of swollen networks give rise to microsyneresis effects even before the spinodal is reached. The entropy and the correlation functions of the thermodynamic fluctuations of the network density are also calculated in mean-field theory with allowance for the effects of topological restrictions. Exact solutions are obtained for a model of a calibrated gel in which each chain has a fixed length and for a model of critically branched networks synthesized near the gel-formation threshold.

1. INTRODUCTION

Fluctuations of the density $\rho(\mathbf{x})$ of polymer networks are commonly described by the correlation function[1]

$$g(\mathbf{x}, \mathbf{x}')=\langle\delta\rho(\mathbf{x})\delta\rho(\mathbf{x}')\rangle, \quad \delta\rho(\mathbf{x})=\rho(\mathbf{x})-\langle\rho(\mathbf{x})\rangle, \quad (1)$$

where the angular brackets denote the thermodynamic average (time average). In reality, the correlation function (1) permits one to describe only ideal networks, topologically equivalent to a regular lattice. In real systems there are always defects in the topological structure of the networks—elastically inactive rings, short rings, dangling ends,[1,2] etc. Regions of enhanced concentration of chains can arise even in the synthesis of defect-free networks. Because the chains are mutually impenetrable, the knots and topological entanglements that are formed remain unchanged during exploitation, and this also leads to irregularity of the topology of the networks.

Thus, real polymer networks are systems with frozen topological disorder. In this article we shall show that the density fluctuations $d\rho(\mathbf{x})$ associated with fluctuations of the network topology can be considerably greater than the usual thermodynamic fluctuations (1). When these statistical fluctuations are taken into account, the density-density correlation function of the network is equal to

$$\overline{\langle\Delta\rho(\mathbf{x})\Delta\rho(\mathbf{x}')\rangle}=\overline{g(\mathbf{x}, \mathbf{x}')}+G(\mathbf{x}-\mathbf{x}'), \qquad \Delta\rho(\mathbf{x})=\delta\rho(\mathbf{x})+d\rho(\mathbf{x}). \quad (2)$$

The bar denotes the statistical average (spatial average). Henceforth we shall assume that the network was synthesized in conditions of equilibrium with respect to reactions involving the formation and breaking of chemical bonds. The parameters of this "initial" system determine the topological structure (or graph—see Ref. 3) Γ of the network. After this has been fixed by rapid cooling the network can be placed in some low-molecular-weight solvent, in which it swells. We shall call this system the "final" system. Because of the presence of topological restrictions (impenetrability of the chains), the phase space of the system is broken down into a set of mutually nonintersecting regions τ, in one of which the network is "trapped" at the moment of freezing.[4,5] Thus, the topology of the network in the final system is determined by the configuration $\Gamma_\tau\{\mathbf{x}_n\}$, where the $\mathbf{x}_n$ are the coordinates of the monomer chains of the network.

Characteristics of the initial system will be labeled below by the superscript 0. The indices $k = 1, \ldots, m$ assigned to characteristics of the final system can be omitted. The volumes $V^{(k)}$ and temperatures $T^{(k)}$ of these systems, generally speaking, do not coincide. We shall denote by $\alpha = (V/V^0)^{1/3}$ the extension coefficient of the network, and by $\alpha_T = a(T^{(0)})/a(T)$ the coefficient of thermal expansion of its chains in the non-cross-linked state, where a is their persistent length.

The correlation function G of the statistical density fluctuations that appears in (2) is defined by the expression

$$G(\mathbf{x}-\mathbf{x}')=\overline{d\rho(\mathbf{x})\,d\rho(\mathbf{x}')}, \quad d\rho(\mathbf{x})=\langle\rho(\mathbf{x})\rangle-\overline{\langle\rho(\mathbf{x})\rangle} \quad (3)$$

and owes its origin to the fluctuations of the topology Γ_τ of the network. It has no analogs among the well-studied chemical-equilibrium systems,[3] for which $G\equiv 0$. In this article we shall calculate it in mean-field theory. As is well known from this theory,[3] the Fourier components of the correlation functions of thermodynamic density fluctuations can be represented in the form

$$g_{\mathbf{q}}^{(0)}=(\varkappa_{\mathbf{q}}^{(0)}+C_{\mathbf{q}}^{(0)})^{-1}, \quad \bar{g}_{\mathbf{q}}=(\varkappa_{\mathbf{q}}+C_{\mathbf{q}})^{-1}, \quad (4)$$

where the functions $\varkappa^{(k)}$ determine the purely entropic contribution and the $C^{(k)}$ are expressed in terms of the density–density correlation functions of the so-called broken-links (bl) system,[3,6] in which chemical bonds are absent:

$$C_{\mathbf{q}}^{(k)}=\langle\delta\rho_{\mathbf{q}}^{(k)}\,\delta\rho_{-\mathbf{q}}^{(k)}\rangle_{\mathrm{bl}}^{-1}-\langle\rho^{(k)}\rangle_{\mathrm{bl}}^{-1}. \quad (5)$$

Since the characteristic length scale for particle interactions is small in comparison with the corresponding correlation lengths $\xi^{(k)}$, it is possible to neglect the dependence of the right-hand side of (5) on $\mathbf{q}$. The dependence of the parameters $C^{(k)}$ on the form of the volume interactions has been well studied.[3]

As shown in the Appendix, fluctuations of the topology of polymer networks give rise to random spatial fluctuations of the pressure:

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$$dP^{(k)}(\mathbf{x}) = \langle \overline{\rho^{(k)}} \rangle T^{(k)} d\pi^{(k)}, \quad \overline{d\pi^{(k)}} = 0, \tag{6}$$

where the quantity π gives the pressure in dimensionless units. The corresponding density fluctuations in the network are equal to

$$d\rho(\mathbf{x}) = \int d\mathbf{x}' g(\mathbf{x}, \mathbf{x}') d\pi(\mathbf{x}') \approx \int d\mathbf{x}' \bar{g}(\mathbf{x}-\mathbf{x}') d\pi(\mathbf{x}'). \tag{7}$$

Using (7) to calculate the Fourier component of the function $G(3)$, we find

$$G_{\mathbf{q}} \equiv \overline{d\rho_{\mathbf{q}} d\rho_{-\mathbf{q}}} = \overline{d\pi_{\mathbf{q}} d\pi_{-\mathbf{q}}} \bar{g}_{\mathbf{q}}^2. \tag{8}$$

In deriving (7) we neglected the statistical fluctuations of the function $g(1)$ in comparison with the pressure fluctuations (6). The latter are substantially determined by the conditions of the preparation of the network.

We denote the corresponding correlation functions of the statistical fluctuations of the pressure for the network obtained in the uncompressed initial system by

$$\begin{aligned} \theta(\mathbf{x}-\mathbf{x}') &= \overline{d\pi(\mathbf{x}) d\pi(\mathbf{x}')}|_{\text{uncom}}, \\ \bar{\theta}(\mathbf{x}-\alpha\mathbf{x}') &= \overline{d\pi(\mathbf{x}) d\pi^{(0)}(\mathbf{x}')}|_{\text{uncom}}. \end{aligned} \tag{9}$$

In the Appendix it is shown that the correlation function of the statistical fluctuations of the pressure for a network synthesized in arbitrary initial conditions can be expressed in terms of the correlation functions (9):

$$\overline{d\pi_{\mathbf{q}} d\pi_{-\mathbf{q}}} = \theta_{\mathbf{q}} + g_{\alpha\mathbf{q}}^{(0)} \bar{\theta}_{\mathbf{q}}^2 \alpha^3. \tag{10}$$

The second term, proportional to $g^{(0)}$, in (10) gives the contribution of the fluctuations of the network topology that arise from fluctuations of the network density in the initial system. In regions with an enhanced density of links the chains are more strongly entangled and the probability that they will form cross links increases. As a result of the freezing, the fluctuations of the topology and structure of the networks give rise to a corresponding enhancement of the pressure fluctuations (10).

Thus, the problem reduces to calculating the correlation functions (9) and the functions $\varkappa$ and $\varkappa^{(0)}(4)$. As shown in the Appendix, for $\alpha = \alpha_T = 1$ the following universal relation exists between these quantities:

$$\theta_{\mathbf{q}} = \bar{\theta}_{\mathbf{q}} = \varkappa_{\mathbf{q}} - \varkappa_{\mathbf{q}}^{(0)} = g_{\mathbf{q}}^{-1} - (g_{\mathbf{q}}^{(0)})^{-1} + C_{\mathbf{q}}^{(0)} - C_{\mathbf{q}}, \tag{11}$$

which permits us to restrict ourselves to finding the correlation functions (4) of the thermodynamic fluctuations. For $\alpha, \alpha_T \neq 1$ there is a relation analogous to (11) only for phantom networks in which the effects of topological restrictions can be neglected. As shown in Sec. 3, in this case the correlation functions (9) of interest to us are equal to

$$\begin{aligned} \theta_{\mathbf{q}}(\alpha, \alpha_T) &= \alpha^7 \alpha_T^4 \theta_{\mathbf{q}}(1, 1), \quad \bar{\theta}_{\mathbf{q}}(\alpha, \alpha_T) = \alpha^2 \alpha_T^2 \theta_{\mathbf{q}}(1, 1), \\ \varkappa_{\mathbf{q}}(\alpha, \alpha_T) &= \alpha^5 \alpha_T^2 \varkappa_{\mathbf{q}}(1, 1). \end{aligned} \tag{12}$$

Their values for $\alpha = \alpha_T = 1$ are related to each other by (11). The theory developed in Sec. 3 makes it possible to calculate these functions for a phantom network of arbitrary topological structure.

The most difficult problem is to describe topological restrictions in networks, and we do this in Secs. 2, 4, and 5 using the mean-field theory developed in Ref. 7. We shall discuss first some of its physical aspects, using the very simple example of a structureless closed chain in which the number of links $N \to \infty$. In a concentrated initial system $[\rho^{(0)} a^3 \gtrsim 1]$ we can neglect the interaction of different segments of this rather rigid chain. We denote the probability of formation of a knot in such a chain of length n by $p(n)$. Then the average number $N_e^{(0)}$ of links between two effective entanglements (knots) along the chain will be determined by the obvious condition $p(N_e^{(0)}) \approx \frac{1}{2}$. Making use of numerical calculations[8] of the function $p(n)$ for a random noninteracting chain we obtain $N_e^{(0)} \approx 200$, which is in good agreement with experiment. In a dilute initial system a chain can be regarded as a noninteracting string of droplets (blobs), the number n/g of which is proportional to the number n of links in the initial chain; $g \approx (\rho^{(0)} a^3)^{-5/4}$ is the number of links in a blob.[1] From this we find the following concentration dependence of the parameter $N_e^{(0)}$, which agrees well with experiment: $N_e^{(0)} \approx 200 g \sim (\rho^{(0)})^{-5/4}$.

Thus, in the initial system a chain appears as an aggregate of a large number $N/N_e^{(0)}$ of interpenetrating loops. As the chemical bonds freeze in the final system, because of the presence of topological restrictions long-range order associated with the elasticity of this quasinetwork of entanglements appears. The corresponding order parameter is nonlocal and is the analog of the well known Edwards–Anderson parameter[9] (see Sec. 6). To describe this ordering we shall make use of the standard procedure of introducing a nonlocal external field v_τ conjugate to the order parameter. This mean-field theory is applicable because large length scales (on the order of the size of a loop) $\xi_T \approx a N_e^{1/2} \gg a$ are present over which effective averaging of the thermodynamic fluctuations of a large number of neighboring chains occurs.

Upon deformation of the polymer there is a change in the phase volume of the region τ in which the system is trapped at the time of freezing, and this gives rise to a corresponding change of the amplitude ξ_τ of the fluctuations of the links of the chain. We shall describe this effect in the framework of mean-field theory in Sec. 2. Unfortunately, the physically intuitive approach of this section is not constructive for the description of the topological structure of polymer networks, and in Secs. 4 and 5 we shall use for this the more formal method of replicas.[10] In Sec. 4 we shall confine ourselves to calculating the zero Fourier components of the functions θ, $\bar{\theta}$, and $\varkappa$, since only they are reduced by the action of topological restrictions. The gradient terms of these functions also describe at the same time fluctuations on scales small in comparison with ξ_τ (but large in comparison with a), on which the topological restrictions are unimportant. Therefore, they are determined by expressions obtained for the phantom network (see, e.g., the estimate in Sec. 5).

In Sec. 6 we discuss the physical meaning of the order parameter for polymer networks and certain physical consequences of the theory presented.

2. FORMULATION OF THE PROBLEM: MEAN-FIELD THEORY

We shall define first the probability measure with which the thermodynamic and statistical averages in (1)–(3) are calculated. The probability distribution of the coordinates of the monomeric links of a system of given topology Γ_τ can be represented in the form

$$W_{\Gamma_\tau}\{\mathbf{x}_n\} = Z_{\Gamma_\tau}^{-1}\delta_\tau(\Gamma\{\mathbf{x}_n\})W_\Gamma\{\mathbf{x}_n\}, \sum_\tau \delta_\tau = 1, \qquad (13)$$

where $W_\Gamma\{\mathbf{x}_n\}$ is the contribution of the phantom network of the same topological structure and the topological restrictions are described by a factor δ_τ that is equal to unity for the region τ of the configuration space $\{\mathbf{x}_n\}$ of the system and equal to zero otherwise. The partition function Z_{Γ_τ}, as usual, is determined from the condition that the probability (13) be normalized.

Since a polymer network consists of macroscopic regions with all possible topologies Γ_τ, the complete probability distribution of the coordinates $\{\mathbf{x}_n\}$ is found by statistical averaging of (13) over all these topologies:

$$P_\Gamma^{(0)}\{\mathbf{x}_n\} = \sum_\tau P_{\Gamma_\tau}^{(0)} W_{\Gamma_\tau}\{\mathbf{x}_n\},$$
$$P_{\Gamma_\tau}^{(0)} = Z_{\Gamma_\tau}^{(0)}/Z^{(0)}, \quad Z^{(0)} = \sum_{\Gamma_\tau} Z_{\Gamma_\tau}^{(0)}, \qquad (14)$$

where the partition function $Z_{\Gamma_\tau}^{(0)}$ of the initial system is determined from the normalization condition for the probability $W_{\Gamma_\tau}^{(0)}$, which is defined by an expression analogous to (13).

In mean-field theory the topological restrictions in an undeformed spatially uniform system are described by an effective field $v_{\tau n}(\mathbf{r}_n - \mathbf{R}_n)$, which limits the fluctuations of the nth link about its position $\mathbf{R}_n$ at the time of freezing.[11] Correspondingly, in the relations (13) and (14) we must set

$$\delta_\tau(\Gamma\{\mathbf{r}_n\}) = \Delta^{-1}\exp\Big[-\sum_n v_{\tau n}(\mathbf{r}_n - \mathbf{R}_n)\Big], \qquad (15)$$

where the normalization factor Δ is determined from the condition that the integral of (15) over all the $\mathbf{R}_n$ be equal to unity [see the second equality (13)].

The field $v_{\tau n}$ is a macroscopic thermodynamic variable, conjugate to the order parameter (see Sec. 6). Therefore, it does not depend on microscopic variables such as the direction of the chain.[6] The characteristic length scale $\mathbf{r}_\tau$ of the variation of the field v_τ is large in comparison with the scale ξ_τ of the thermodynamic fluctuations.[6] Therefore, it is sufficient to confine ourselves to the quadratic term of the expansion:

$$v_{\tau n}(\mathbf{r}_n - \mathbf{R}_n) = C_n'(\mathbf{r}_n - \mathbf{R}_n)^2/a^2, \quad a \equiv a(T^{(0)}). \qquad (16)$$

Below, we shall show that on scales large in comparison with ξ_τ the network is deformed as a continuous medium (affinely): $\mathbf{x}^{(1)} = \mathbf{f}(\mathbf{x}^{(0)})$, where $\mathbf{f}$ is a specified deformation function. Within mean-field theory such a deformation of the phase volume of a region τ is described by the corresponding change of the vector $\mathbf{R}_n$ and of the scale $r_\tau \gg \xi_\tau$ of the field v_τ:

$$\mathbf{R}_n \to \mathbf{f}(\mathbf{R}_n), \quad \mathbf{r}_\tau \to \lambda\mathbf{r}_\tau, \quad \lambda = \partial\mathbf{f}(\mathbf{x}^{(0)})/\partial\mathbf{x}^{(0)}.$$

It is more convenient to rewrite these relations in another form, introducing particle coordinates $\mathbf{r}_n$ reduced to the undeformed initial system $[\mathbf{f}(\mathbf{r}_n) = \mathbf{x}_n^{(1)}]$:

$$\delta_\tau(\Gamma\{\mathbf{x}_n^{(1)}\}) = \delta_\tau(\Gamma\{\mathbf{r}_n\}). \qquad (17)$$

The right-hand side of (17) is defined in (15). The relation (17) can be regarded as stating that the topological restrictions do not change when a network region of macroscopic size is deformed.

We now calculate the entropy of the system. The total self-consistent field acting on the nth link is equal to the sum of the contributions of the topological interactions (16) and the volume interactions:

$$v_n(\mathbf{x}_n) = v_{\tau n}(\mathbf{r}_n - \mathbf{R}_n) + v_v(\mathbf{x}_n). \qquad (18)$$

We shall denote by $Z_\Gamma\{\mathbf{R}_n | v_n\}$ the partition function of a polymer system whose particles are in the external field (18) but do not interact with each other. Performing a Legendre transformation, we find the entropy of such a network with a specified mean density $\langle\rho_n(\mathbf{x})\rangle$ of the nth link:

$$S_\Gamma\{\mathbf{R}_n | \langle\rho_n\rangle\} = \ln Z_\Gamma\{\mathbf{R}_n | v_n\} + \sum_n \int d\mathbf{x}\, v_n(\mathbf{x})\langle\rho_n(\mathbf{x})\rangle,$$
$$\langle\rho_n(\mathbf{x})\rangle = -\delta \ln Z_\Gamma\{\mathbf{R}_n | v_n\}/\delta v_n(\mathbf{x}). \qquad (19)$$

It is not difficult to convince oneself that the density $\langle\rho_n(\mathbf{x})\rangle$ found from the second relation in (19) coincides with the expression obtained by direct averaging of $\delta(\mathbf{x} - \mathbf{x}_n)$ with the probability (13), (15). The free energy of the system under consideration with specified coordinates $\{\mathbf{R}_n\}$ is equal to

$$F_\Gamma\{\mathbf{R}_n | \langle\rho_n\rangle\} = E_v\{\langle\rho\rangle\} - TS_\Gamma\{\mathbf{R}_n | \langle\rho_n\rangle\}, \quad \langle\rho\rangle = \sum_n \langle\rho_n\rangle,$$

where $E_v\{\langle\rho\rangle\}$ is the energy of the volume interactions of the system of broken links. For a region of macroscopic (in comparison with ξ_τ) size, both the average link density $\langle\rho(\mathbf{x})\rangle = \overline{\langle\rho(\mathbf{x})\rangle}$ and the functional F are self-averaging quantities:

$$F\{\overline{\langle\rho\rangle}\} = E_v\{\overline{\langle\rho\rangle}\} - TS(\lambda_\mu), \quad S(\lambda_\mu) \equiv \overline{S_\Gamma\{R_n | \langle\rho_n\rangle\}}$$
$$= \Big(1 - \sum_n C_n' \frac{\partial}{\partial C_n'}\Big)\overline{\ln Z_\Gamma\{R_n | v_{\tau n} + v_v\}} + \int d\mathbf{x}\, v_v(\mathbf{x})\overline{\langle\rho(\mathbf{x})\rangle}, \qquad (20)$$

where the statistical average (14) includes averaging over all topologically inequivalent regions τ for a given graph Γ [i.e., integration over the coordinates $\mathbf{R}_n$ with weight (13)–(15)] with subsequent averaging over the different topological structures Γ. The functional dependence of $v_v(\mathbf{x})$ on $\overline{\langle\rho(\mathbf{x})\rangle}$ is found from the condition for the maximum of the expression in the right-hand side of (20) for the entropy S with respect to v_v [see the second relation in (19)]. Minimizing the functional $F\{\overline{\langle\rho\rangle}\}$ given by (20) with respect to $\overline{\langle\rho\rangle}$ gives the self-consistency equation for the mean field of the volume interactions $v_v(\mathbf{x})$ (18):

$$v_v(\mathbf{x}) = \frac{1}{T}\frac{\delta E_v\{\overline{\langle\rho\rangle}\}}{\delta\overline{\langle\rho(\mathbf{x})\rangle}} \equiv \frac{\mu^*\{\overline{\langle\rho\rangle}\}}{T}.$$

Henceforth in this section, in the discussion of effects involving topological restrictions we shall set $v_v = 0$. Introduction of this field into the corresponding formulas does not require special discussion in view of the absence of distinctive features in comparison with the case of the liquid phase of polymers.[6,12]

The effects of topological restrictions will be considered first for the simplest case of a linear chain with $N \to \infty$ links.

This model was considered earlier in Ref. 7 using the replica method. In the continuum model of the chain[4] the probability distribution (13) of the link coordinates $\mathbf{x}(n)\equiv\mathbf{x}_n$ of such a phantom noninteracting chain is equal to

$$W^{(k)}\{\mathbf{x}(n)\}=\text{const}\exp\Big[-\int_0^N ds\Big(\frac{\mathbf{x}'(s)}{a}\Big)^2\Big], \tag{21}$$

where, as usual, the prime denotes the derivative. It is obvious that the quantity C_n' (16) does not depend on n. The probability (14) of interest is found by calculating the integral over all paths $\mathbf{x}(n)$ of the expression (13), (21), (15):

$$P^{(0)}\{\mathbf{R}(n)\}\equiv Z^{(0)}\{\mathbf{R}(n)\,|\,v_\tau\}/Z^{(0)}=\text{const}$$
$$\times\exp\Big[-\int_0^N\int_0^N\frac{ds\,ds'}{2N_e^{(0)}}\frac{\mathbf{R}'(s)\,\mathbf{R}'(s')}{a^2}\exp\Big(-\frac{|s-s'|}{N_e^{(0)}}\Big)\Big],$$
$$N_e^{(0)}=(C')^{-1}. \tag{22}$$

According to (22), the topological restrictions become important only at large distances $|s-s'|\gtrsim N_e^{(0)}$ along the chain, and do not make a contribution for $|s-s'|\ll N_e^{(0)}$.

An analogous calculation of the partition function of the final system, subjected to specified extensions by factors of λ_μ along the axes $\mu=x,y,z$, gives

$$\ln Z\{\mathbf{R}(n)\,|\,v_\tau\}=\text{const}-\sum_\mu\Big[\frac{N}{2N_{e\mu}}$$
$$+\lambda_\mu^2\int_0^N\int_0^N\frac{ds\,ds'}{2N_{e\mu}}\frac{R_\mu'(s)R_\mu'(s')}{a^2}$$
$$\times\exp\Big(-\frac{|s-s'|}{N_{e\mu}}\Big)\Big],\quad N_{e\mu}=N_e^{(0)}\lambda_\mu. \tag{23}$$

As follows from (23), the quantity Z depends only on the large-scale fluctuations $\mathbf{R}(s)$ ($|s-s'|\gtrsim N_{e\mu}$) characterizing the topology τ of the entangled chain. For a more detailed description of the chain we shall calculate the mean density (19) of the nth link:

$$\langle\rho_n(\mathbf{x})\rangle=\Big(\frac{2}{\pi}\Big)^{3/2}\prod_\mu\xi_{\tau\mu}^{-1}\exp\Big[\frac{-2(x_\mu-\hat R_\mu(n))^2}{\xi_{\tau\mu}^2}\Big], \tag{24}$$

where the quantity $\xi_{\tau\mu}=aN_{e\mu}^{1/2}$ determines the amplitude of the thermodynamic fluctuations of the chain along the axis μ about its mean position:

$$\hat R_\mu(n)=\lambda_\mu\int_0^N\frac{ds}{2N_{e\mu}}R_\mu(s)\exp\Big(-\frac{|n-s|}{N_{e\mu}}\Big). \tag{25}$$

The statistical distribution of these coordinates is fully described by the Gaussian correlation function

$$\overline{(\hat R_\mu(n)-\hat R_\mu(n'))^2}={}^1/_2\xi_{\tau\mu}^2 f(\lambda_\mu^2,\,|n-n'|/N_{e\mu}),$$
$$f(\lambda^2,x)=\lambda^2(x-1+e^{-x})+{}^1/_2(\lambda^2-1)[(1+x)e^{-x}-1]. \tag{26}$$

Here the average has been obtained by calculating the Gaussian integral over the coordinates $\mathbf{R}(s)$ with weight (22).

The expression (26) is in complete agreement with the physical quasinetwork model introduced in Ref. 7, with $N_{e\mu}$ links between two quasi-cross-links of the quasinetwork. By setting $n-n'=N_{e\mu}$ in (26), we find for the mean distance between quasi-cross-links the usual expression for an extended phantom network: $R_{\tau\mu}\approx aN_{e\mu}^{1/2}\lambda_\mu$.

At large distances $|n-n'|\gg N_{e\mu}$ along the chain the correlation function (26) is approximately equal to $a^2\lambda_\mu^2|n-n'|$ and does not depend on the parameter N_e of the topological interactions. Thus, on large scales the polymer experiences affine deformation. Over small distances $|n-n'|\ll N_{e\mu}$ it follows from (26) that $|\hat{\mathbf{R}}(n)-\hat{\mathbf{R}}(n')|\sim|n-n'|$. Therefore, $\hat{\mathbf{R}}$ can be regarded as the coordinate of the primitive chain path obained by smoothing the thermodynamic fluctuations of the chain on the scale ξ_τ.

We note that the formula (26) ceases to be valid for large $|n-n'|$ on scales of the order of the system size. In reality, a chain returns repeatedly to the neighborhood of each point of the space that it occupies, and it is this which ensures the self-averaging of the total density $\langle\rho\rangle$.

Substituting (23)–(25) into (20) and averaging with the probability (22), we find the entropy of the chain under consideration:

$$S(\lambda_\mu)=\text{const}-\sum_\mu\frac{N}{8N_{e\mu}}(\lambda_\mu^2+1).$$

An analogous expression was obtained earlier in Ref. 7 by the replica method.

The concluding part of this section is devoted to "translating" the basic relations of the theory presented above into the replica-method "language" (Refs. 7, 10) necessary for the description of the topological structure of polymer networks.[12] Calculations using the formulas (13)–(20) come up against a problem that is standard for systems with frozen topological disorder, namely, the averaging of the factor $Z_\Gamma^{-1}\{\mathbf{R}_n\,|\,v_n\}$ with the Gibbs measure (13). To circumvent this difficulty, we shall write this factor in the form $Z_\Gamma^{m-1}(m\to0)$ and, in the intermediate calculations, assume m to be a positive integer. After substitution of the resulting formula (13) into (14) and integration over all the coordinates $\{\mathbf{R}_n\}$, the probability measure (14) of the final system ($k=1$) takes the form

$$P_\Gamma^{(k)}\{\mathbf{x}_n^{(k)}\}=\prod_n\prod_{l\neq k}^m\int d\mathbf{x}_n^{(l)}\,P_{m\Gamma}\{\mathbf{X}_n\}. \tag{27}$$

Here $P_{m\Gamma}\{\mathbf{X}_n\}$ is the probability measure of the distribution of the coordinates $\mathbf{X}_n=(\mathbf{x}_n^{(0)},\ldots,\mathbf{x}_n^{(m)})$ of the particles in the replica space of dimensionality $d=3(1+m)$ (the coordinates $\mathbf{x}_n^{(k)}$ of a particle in the k th replica are the projections of the vector $\mathbf{X}_n$ onto the unit vectors of this replica):

$$P_{m\Gamma}\{\mathbf{X}_n\}=Z_m^{-1}W_{m\Gamma}\{\mathbf{X}_n\}\exp\Big[-\sum_n v_{\tau n}(\mathbf{X}_n)\Big],$$
$$W_{m\Gamma}\{\mathbf{X}_n\}=\prod_{k=0}^m W_\Gamma^{(k)}\{\mathbf{x}_n^{(k)}\}, \tag{28}$$

where Z_m is the normalization factor for the probability (28). The field $v_{\tau n}$ in (28) is determined by the expression

$$\exp[-v_{\tau n}(\mathbf{X}_n)]=\text{const}\int d\mathbf{R}_n\exp\Big[-\sum_{k=0}^m v_{\tau n}(\mathbf{r}_n^{(k)}-\mathbf{R}_n)\Big]. \tag{29}$$

Evaluating this integral with the aid of (16), we find

$$v_{\tau n}(\mathbf{X}_n)=\frac{C_n}{2a^2}\sum_{k,k'}^{m}(\mathbf{r}_n^{(k)}-\mathbf{r}_n^{(k')})^2,\quad C_n=\frac{C_n'}{1+m}. \tag{30}$$

For $k=0$ the expression (27) determines the probability measure of the initial system, and for $k=1,\ldots,m$ it determines that of the k th replica of the final system. Thus, the distribution (28) contains complete statistical information about the polymer system.

To calculate the entropy (19) we represent the average of the logarithm of the partition function in the form

$$\overline{\ln Z_\Gamma\{\mathbf{R}_n|v_n\}}=\frac{d}{dm}\ln Z_m|_{m=0},\quad \frac{Z_m}{Z^{(0)}}=\overline{Z_\Gamma{}^m\{\mathbf{R}_n|v_n\}}. \tag{31}$$

By making use of (31) and the relation (30) between C_n and C_n', we write the following chain of equalities, the first of which follows from (20):

$$\begin{aligned}S(\lambda_\mu)&=\Big(1-\sum_n C_n'\frac{\partial}{\partial C_n'}\Big)\overline{\ln Z_\Gamma\{R_n|v_n\}}\\&=\frac{d}{dm}S_m(1,\lambda_\mu,\ldots,\lambda_\mu)|_{m=0},\end{aligned} \tag{32}$$

$$\begin{aligned}S_m(\lambda_\mu^{(k)})&=\Big(1-\sum_n C_n\frac{\partial}{\partial C_n}\Big)\ln Z_m\\&=\ln Z_m+\sum_n\int d\mathbf{X}\,v_{\tau n}(\mathbf{X})\langle\rho_n(\mathbf{X})\rangle,\end{aligned} \tag{33}$$

where $\langle\rho_n(\mathbf{X})\rangle$ is the average density of the nth particle in the replica space:

$$\langle\rho_n(\mathbf{X})\rangle\equiv\langle\delta(\mathbf{X}-\mathbf{X}_n)\rangle=-\delta\ln Z_m/\delta v_{\tau n}(\mathbf{X}) \tag{34}$$

and the $\lambda_\mu^{(k)}$ in (33) denote the extension coefficients of the k th replica in the direction of the μ axis [so that in (30) $r_\mu^{(k)}=x_\mu^{(k)}/\lambda_\mu^{(k)}$].

The average density of links in the k th replica is determined by the expression

$$\overline{\langle\rho^{(k)}(\mathbf{x}^{(k)})\rangle}=\prod_{l\neq k}\int d\mathbf{x}^{(l)}\langle\rho(\mathbf{X})\rangle, \tag{35a}$$

$$\langle\rho(\mathbf{X})\rangle\equiv\sum_n\langle\rho_n(\mathbf{X})\rangle=\sum_n\overline{\prod_{k=0}^{m}\langle\rho_n(\mathbf{x}^{(k)})\rangle}. \tag{35b}$$

The physical meaning of the order parameter (35b) is discussed in Sec. 6. We note that for $m=0$ the quantity $S^{(0)}(\langle\rho^{(0)}\rangle)=S_0(\lambda^{(0)})$ is equal to the entropy of the initial system. With neglect of end effects we shall assume below that $C_n=C$ is independent of n.

We now make use of the replica formalism (27)–(35) to describe polymer networks. We start from the simplest case.

3. THEORY OF PHANTOM NETWORKS

The Gibbs probability measure of a noninteracting phantom network is established from its graph Γ (Ref. 3):

$$W_\Gamma^{(k)}\{\mathbf{x}_n\}=\prod_{\langle i,j\rangle}\hat{g}^{(k)}(\mathbf{x}_i-\mathbf{x}_j),$$

$$\hat{g}^{(k)}(\mathbf{x})=[\pi(a^{(k)})^2]^{-3/2}\exp\Big[-\Big(\frac{\mathbf{x}^{(k)}}{a^{(k)}}\Big)^2\Big] \tag{36}$$

where we associate with each bond (edge of the graph Γ) between links i and j a factor $\hat{g}(\mathbf{x}_i-\mathbf{x}_j)$. The probability measure of the initial system contains an extra factor $z^N/N!$, where z is the activity of the particles that are forming cross links and N is their number in the configuration Γ. Substituting (36) into (28), after making the change of variables $\mathbf{x}^{(k)}\to\mathbf{x}^{(k)}/\alpha_T(k=1,\ldots,m)$ we find the following expression for the probability measure in the replica space:

$$\begin{aligned}W_{m\Gamma}\{\mathbf{X}_n\}&=\frac{z^N}{N!}\prod_{\langle i,j\rangle}Q(\mathbf{X}_i-\mathbf{X}_j),\\Q(\mathbf{X})&=\frac{\alpha_T^{3m}}{(\pi a^2)^{3(1+m)/2}}\exp\Big[-\frac{\mathbf{X}^2}{a^2}\Big].\end{aligned} \tag{37}$$

In the new variables the extension coefficients of the k th replica become equal to $\hat{\lambda}_\mu^{(0)}=\lambda_\mu^{(0)}$, $\hat{\lambda}_\mu^{(k)}=\alpha_\tau\lambda_\mu^{(k)}$, $(k=1,\ldots,m)$.

We note that the probability measure (37) of the phantom networks is isotropic in the replica space. In the solid phase, as in the case of a ferromagnet at $T<T_c$, the introduction of a bare field $v_\tau\to 0$ (16) gives rise to spontaneous breaking of this symmetry, i.e., to identification of a direction $\mathbf{n}$ in which the network extends in the replica space (see the discussion in Sec. 6). Following Ref. 13, we introduce coordinates that are longitudinal [indicated below by the superscript (0)] and transverse to this direction:

$$\begin{aligned}&R_\mu^{(0)}=\sum_{k=0}^{m}n_\mu^{(k)}x_\mu^{(k)},\quad n_\mu^{(k)}=\hat{\lambda}_\mu^{(k)}\Big/\Big[\sum_{l=0}^{m}(\hat{\lambda}_\mu^{(l)})^2\Big]^{1/2},\\&\mathbf{R}^2=\mathbf{X}^2,\end{aligned} \tag{38}$$

where we choose the directions of the unit vectors of the transverse coordinates in the $3m$-dimensional replica subspace using the condition that the quadratic form $v_\tau(\mathbf{X})$ be diagonalized:

$$v_\tau(\mathbf{X})=C\sum_{k=1}^{m}\sum_\mu\Lambda_\mu^{(k)}(R_\mu^{(k)}/a)^2, \tag{39}$$

where the eigenvalues $\Lambda_\mu^{(k)}$ are the roots of the algebraic equation

$$\sum_{k=0}^{m}\prod_{l\neq k}[\Lambda_\mu^{(k)}-(1+m)/(\hat{\lambda}_\mu^{(l)})^2]=0. \tag{40}$$

The field v_τ (39) and, consequently, the order parameter $\langle\rho(\mathbf{X})\rangle$ (35b) induced by it do not depend on the longitudinal coordinates $\mathbf{R}^{(0)}$. In addition, because of the normalization condition (35a), the function $\langle\rho(\mathbf{X})\rangle$ should fall off rapidly as the transverse coordinates $|R_\mu^{(k)}|(k=1,\ldots,m)$ increase [the long-range order localizes the particles near their mean positions (24)].

An analogous coordinates dependence is also possessed by the density functional

$$\ln Z_m\{v_n\}=-\int d\mathbf{X}\,f_m\{\mathbf{X}|v_n\}. \tag{41}$$

Going over in (41) to integration over the coordinates $R_\mu^{(k)}$

(38), we find the entropy S_m (33) of the phantom networks in the replica space:

$$S_m(\lambda_\mu^{(k)}) = -\bar{V}^{(0)} \prod_\mu \Big[\sum_{k=0}^{m} (\hat{\lambda}_\mu^{(k)})^2 \Big]^{1/2} \bar{f}_m(v) + vN, \qquad (42)$$

$$\bar{f}_m(v) = \alpha_T^{-3m} \prod_{k=1}^{m} \int d\mathbf{R}^{(k)} f_m\{\mathbf{R}|v\}, \quad N \equiv \bar{N} N_c. \qquad (43)$$

Here the bar indicates parameters of the undeformed network, N_c is the number of chains in the network, $\bar{N}$ is the average number of links in one chain, and v is found from the condition for the maximum of the right-hand side of (42), as follows from the relations (34) and (35). For $m = 0$, from (43) we obtain $\bar{f}_0(v) = f_0(0|v)$. Substituting (42) into (32), we find the entropy of the phantom network in the initial and the final system:

$$S^{(0)}(\langle \rho^{(0)} \rangle) = -V^{(0)}[\bar{f}(v) - \langle \rho^{(0)} \rangle v],$$
$$\langle \rho^{(0)} \rangle = N/V^{(0)} = \partial \bar{f}_0(v)/\partial v; \qquad (44)$$
$$S(\lambda_\mu) = \text{const} - \frac{\alpha_T^2 N^{\text{eff}}}{2} \sum_\mu \lambda_\mu^2, \qquad N^{\text{eff}} = \bar{V}^{(0)} \bar{f}_0(v).$$

The relations (44) express the number N^{eff} of effective chains in a phantom network of arbitrary structure in terms of its thermodynamic characteristics in the conditions of its preparation. For defect-free networks the quantity N^{eff} was found earlier in Ref. 5.

To calculate the correlation functions we rewrite (43) by setting

$$\lambda_\mu^{(k)} = (V^{(k)}/V^{(0)})^{1/3}, \quad \alpha = (\bar{V}/\bar{V}^{(0)})^{1/3}$$

and expand the functional S_m in the density fluctuations

$$\Delta\rho^{(k)}/\bar{\rho}^{(k)} \equiv -\Delta V^{(k)}/\bar{V}^{(k)}, \quad \Delta V^{(k)} = V^{(k)} - \bar{V}^{(k)} \qquad (45)$$

up to terms quadratic in $\Delta\rho^{(k)}$. The correlation functions of interest to us are found by inverting the corresponding matrix $G_{\mathbf{q}}^{-1}$ of the quadratic form $\Delta\Phi_m = \Sigma\Delta E^{(k)} - T\Delta S_m$ (see the Appendix). As a result, we obtain the expressions (8) and (12), where the correlation functions θ and $\bar{\theta}$ of the statistical pressure fluctuations for $q = 0$ are determined by the expressions (12). Their values for $\alpha = \alpha_T = 1$ can be expressed directly in terms of thermodynamic characteristics of the initial system:

$$\varkappa_0^{(0)} = -1/\bar{f}_0''(0), \; \varkappa_0(1,1) = -\bar{f}_0(0)/3[\bar{f}_0(0)]^2,$$
$$\theta_0(1,1) = \bar{\theta}_0(1,1) = \varkappa_0(1,1) - \varkappa_0^{(0)}. \qquad (46)$$

The spatial scale of the functions $\varkappa$ and θ is equal to the amplitude ξ_T of the fluctuations of the cross links of the network. Since for phantom networks the quantity $\xi_T \sim a\bar{N}^{1/2}$ does not depend on α (Refs. 14, 15), the relations (12) remain valid for nonzero wave vectors $\mathbf{q}$ as well. A method for calculating the function $\bar{f}_0(v)$ for networks of arbitrary topological structure is described in Ref. 3. Therefore, here we shall give only the results for networks obtained by equilibrium polycondensation of 2- and f-functional monomers in a melt:

$$\bar{f}_0(0) = \bar{\rho}^{(0)}(1 - 2/fp^{(g)})/\bar{N}, \quad \bar{f}'(0) = -\bar{\rho}^{(0)},$$
$$\bar{f}_0''(0) = \frac{2\bar{\rho}^{(0)}\bar{N}}{1-u^2}\left[\frac{1}{p(f-1)-1} + \frac{u^2}{1-p^{(s)}(f-1)}\right] \qquad (47)$$

where $\bar{N}$ is the average number of links in a chain of the network between two f-functional monomers, and p, $p^{(s)}$, and $p^{(g)}$ are the conversions (the probabilities of formation of bonds between these monomers) of the initial system, the washed-out sol molecules, and the gel network, respectively:

$$p^{(s)} = pu^{(f-2)/(f-1)}, \quad p^{(g)} = p(1+u)/(1+pu),$$
$$u = (1-p+pu)^{f-1}.$$

The number N^{eff} of effective chains in such a network is equal to the number of independent rings in the network.

We now discuss the physical meaning of our results (46) and (47). The pressure fluctuations (6) in the network are determined both by fluctuations of the topology of its graph Γ and by fluctuations of the chain lengths in the network, i.e., of the edges of this graph. With neglect of the latter, i.e., in the model of a calibrated gel in which every chain has a fixed length $\bar{N}$, for $p = 1$ it is not difficult to show that

$$\theta_0(1,1) = Q/6\bar{\rho}^{(0)}\bar{N}, \quad Q = 1 - 2/f. \qquad (48)$$

In the model (47) fluctuations of the lengths of the chains give rise to an extra term $\Delta\theta = fQ^2/12\rho^{(0)}\bar{N}$ in (48). We now consider networks obtained near the gel-formation threshold [$\tau \equiv p/p_c - 1, \ll 1$ $p_c = (f-1)^{-1}$]. Their elastically active chains consist of a large number $\sim \tau^{-1} \gg 1$ of series-linked shorter chains of average length $\bar{N}$. Therefore, the fluctuations of these lengths are effectively averaged [$\Delta\theta \sim \tau\theta$], and the correlation function θ_0 is determined entirely by the fluctuations of the topology of the network graph:

$$\theta_0(1,1) = 8(f-1)\tau^2/9(f-2)\bar{\rho}^{(0)}\bar{N}.$$

4. TOPOLOGICAL RESTRICTIONS IN NETWORKS

When topological restrictions are taken into account the functional Z_m (31) also depends on the field v_τ (40), acting only on the links of the network skeleton (see Ref. 1). Below, we attach a subscript b to parameters pertaining to the links of the skeleton. The network skeleton is obtained by cutting off the chains attached to it by only one ring. We determine the functional dependence of the entropy S_m (33) on the parameters $\Lambda_\mu^{(k)}$ and the external fields $v_v = \Sigma v_v^{(k)}$ and $v_b = \Sigma v_b^{(k)}$ acting, respectively, on all the links of the network and only on the links of its skeleton. According to (37) and (40), in the coordinates (38) the probability measure (28) factors and is a product of contributions with different values of $\mu = x, y, z$ and $k = 0, \ldots, m$. Therefore, the partition function of the canonical ensemble for an arbitrary graph Γ also factors. We represent it in the form

$$Z_{m\Gamma} = \prod_{k=0}^{m} \prod_\mu Z_\Gamma^{(k)} \exp\Big[-Nv_v - N_b\Big(v_b + \sum_{k=0}^{m}\sum_\mu \chi_{\Gamma_b}(\Lambda_\mu^{(k)})\Big)\Big], \qquad (49a)$$

where the $Z_\Gamma^{(k)}$ are calculated for $v_v = v_b = \Lambda_\mu^{(k)} = 0$, and the contribution of the topological restrictions is included in a function χ, equal to

$$\chi_{\Gamma_b}(\Lambda_\mu) \sim C\Lambda_\mu(\xi_{T\mu}/a)^2. \qquad (49b)$$

Summing (49) over all Γ, we find the partition function of the grand canonical ensemble:

$$Z_m = Z_m\Big\{v_v, v_b + \sum_{k=1}^{m}\sum_{\mu}\chi(\Lambda_\mu^{(k)})\Big\}, \tag{50}$$

where the function Z_m in the right-hand side is calculated for the phantom network and χ is determined by averaging χ_{Γ_b} over all Γ_b. Substituting (50) into the first of the equalities (33), we bring the functional S_m to the form (42), where

$$\bar{f}_m(v_0) = \tilde{f}_m(v_v, \Sigma\chi(\Lambda_\mu^{(k)})) - \sum_{k=1}^{m}\sum_{\mu}\Lambda_\mu^{(k)}\frac{\partial \tilde{f}_m(v_v, \Sigma\chi(\Lambda_\mu^{(k)}))}{\partial\Lambda_\mu^{(k)}},$$
$$\tilde{f}_m(v_v, v_b) = \alpha_\tau^{-3m}\prod_{k=1}^{m}\int d\mathbf{R}^{(k)} f_m\{\mathbf{R}\,|\,v_v, v_b\}. \tag{51}$$

First we find the entropy of the system, by setting in (51) $\hat{\lambda}_\mu^{(0)} = 1$ and $\hat{\lambda}_\mu^{(k)} = \alpha_T\lambda_\mu$ $(k = 1,...,m)$. For these $\hat{\lambda}_\mu^{(k)}$ the solution of Eq. (40) is easily found:

$$\Lambda_\mu^{(1)} = (\alpha_\tau\lambda_\mu)^{-2} + m, \quad \Lambda_\mu^{(k)} = (1+m)(\alpha_\tau\lambda_\mu)^{-2}, \quad k = 2, \ldots, m. \tag{52}$$

We now calculate, to terms of first order in m, the combination

$$\sum_{k=1}^{m}\chi(\Lambda_\mu^{(k)}) = m[\chi(\Lambda_\mu) + \chi'(\Lambda_\mu)(1-m)], \quad \Lambda_\mu = (\alpha_\tau\lambda_\mu)^{-2}. \tag{53}$$

Substituting (53) into (51), to the same accuracy we find

$$\bar{f}_m(v_v) = \tilde{f}_m(v_v, 0) + m\frac{\partial\tilde{f}_0}{\partial v_b}\Big|_{v_b=0}\sum_{\mu}[\tilde{\chi}(\Lambda_\mu) + \tilde{\chi}'(\Lambda_\mu)(1-\Lambda_\mu)], \tag{54}$$
$$\tilde{\chi}(\Lambda_\mu) = \chi(\Lambda_\mu) - \Lambda_\mu\chi'(\Lambda_\mu).$$

The derivative of $\tilde{f}_0$ with respect to v_b is equal to the mean density $\bar{\rho}_b = N_b/\bar{V}$ of the links of the network skeleton. Using (54) and (42) we find the final expression for the network entropy (32):

$$S(\lambda_\mu) = \text{const} - \frac{N^{\text{eff}}\alpha_\tau^2}{2}\sum_{\mu}\lambda_\mu^2 - N_b\sum_{\mu}[\tilde{\chi}(\Lambda_\mu) + \tilde{\chi}'(\Lambda_\mu)(1-\Lambda_\mu)]. \tag{55}$$

It is not difficult to verify that for $\alpha_\tau = \lambda_\mu = 1$ we have $\partial S/\partial\lambda_\mu = \partial S^{(0)}/\partial\lambda_\mu^{(0)}$, which, for equal interactions of the links in the initial and final systems, leads to equality of their pressures: $P = P^{(0)}$ (Ref. 4).

We now calculate the correlation functions (9) of the pressure fluctuations. The entropy $S_m(\lambda_\mu^{(k)})$ is symmetric under permutations of all the replicas, and this permits us, when determining the coefficients of its expansion in powers of (45), to confine ourselves to the case

$$\hat{\lambda}_\mu^{(0)} = \lambda_0, \quad \hat{\lambda}_\mu^{(1)} = \lambda_1, \quad \hat{\lambda}_\mu^{(k)} = \lambda, \quad k = 2, \ldots, m. \tag{56}$$

For $m = 0$ the solution of Eq. (40) with the quantities $\hat{\lambda}$ defined in (56) has the form

$$\Lambda_\mu^{(1)} = \lambda^{-2} + \varepsilon^{1/2}, \quad \Lambda_\mu^{(2)} = \lambda^{-2} - \varepsilon^{1/2},$$
$$\Lambda_\mu^{(k)} = \lambda^{-2}, \quad k = 3, \ldots, m;$$
$$\varepsilon = (\lambda^{-2} - \lambda_0^{-2})(\lambda^{-2} - \lambda_1^{-2}). \tag{57}$$

In this case, for the quantity (53) to terms quadratic in ε we find

$$\lim_{m\to 0}\sum_{k=1}^{m}\chi(\Lambda_\mu^{(k)}) = \chi''(\lambda^{-2})\varepsilon + \chi^{\text{IV}}(\lambda^{-2})\varepsilon^2/12. \tag{58}$$

Substituting (58) and (51) into (42), we find the coefficients of the expansion of the entropy in powers of $\Delta\rho^{(k)}$ (45), and it is these coefficients that determine the correlation functions of interest to us (see the Appendix):

$$\theta_0(\alpha, \alpha_\tau) = \alpha^3\theta_0(\Lambda), \quad \bar{\theta}_0(\alpha, \alpha_\tau) = \bar{\theta}_0(\Lambda), \quad \varkappa_0(\alpha, \alpha_\tau) = \alpha^3\varkappa_0(\Lambda), \tag{59}$$

where $\Lambda = (\alpha_T\alpha)^{-2}$ and the functions θ, $\bar{\theta}$, and $\varkappa$ have, for $\Lambda = 1$, the very simple form

$$\theta_0(1) = \bar{\theta}_0(1) = \varkappa_0(1) - \varkappa_0^{(0)} = -[\bar{f}_0(0) + 4\tilde{\bar{\theta}}_b\chi''(1)]/3[\bar{f}_0'(0)]^2 + 1/\bar{f}_0''(0). \tag{60}$$

It is not difficult to obtain the corresponding expressions for $\Lambda \neq 1$ as well. Because they are cumbersome, we shall not give them here.

Thus, both the elastic and the correlation characteristics of the network in the presence of topological restrictions are fully described by the function $\chi(\Lambda)$ (49), (50). We give a qualitative estimate of this function. In the case of weakly entangled chains the amplitude ξ_τ of the fluctuations of their links does not depend on λ_μ. Substituting (49b) into (55), in full agreement with the experiment described in Ref. 15 we find that topological restrictions do not contribute to the entropy of such a network. We consider the case of strongly entangled chains first for the example of the long chain considered in Sec. 2. On the scale $\xi_\tau \sim aN_e^{1/2}$ the average energy of the field v_τ should be of the order of the temperature. The condition $N_e v_\tau(\xi_\tau) \sim 1$ permits us to estimate the parameter N_e in the final system: $N_e \approx N_e^{(0)}\lambda$, $N_e^{(0)} = C^{-1/2}$. From this, with the aid of (49b), we find $\chi(\Lambda) \sim v_\tau(\xi_\tau) \approx 1/N_e$. In the case of an arbitrary fractal structure we have $\xi_\tau \sim aN_e^{1/D}$, where D is the fractal dimensionality of the network skeleton. In particular, for networks obtained near the gel-formation threshold ($p \to p_c$), the quantity $D = 4$ and $N_e \sim N_e^{(0)}\lambda^{4/3}$, $N_e^{(0)} \sim C^{-2/3}$, and also $\chi \approx 1/N_e$.

In the next section we calculate the function $\chi(\Lambda)$ in a wide range of parameters of the system, in models admitting an exact solution.

5. EXACTLY SOLVABLE MODELS OF POLYMER NETWORKS

We consider two models of polymer networks. The first describes calibrated gels[1] with a fixed number $\bar{N}$ of links between neighboring cross-links, synthesized far from the gel-formation threshold ($p = 1$). The second describes critically branched networks obtained by f-functional polycondensation of monomers near the gel-formation threshold ($\tau = p/p_c - 1 \ll 1$).

The partition function (28), (37) for the calibrated-gel model can be reproduced by expanding the functional integral

$$Z_m = \int D\varphi \exp\left[-L_m\{\varphi\} + z\int d\mathbf{X}\frac{\varphi^f(\mathbf{X})}{f!}\right] \Big/ \int D\varphi \exp[-L_m\{\varphi\}],$$

$$L_m\{\varphi\} = \frac{1}{2}\int\int d\mathbf{X}\, d\mathbf{X}'\, G^{(-N)}(\mathbf{X},\mathbf{X}')\varphi(\mathbf{X})\varphi(\mathbf{X}') \qquad (61)$$

in powers of the activity z of the f-functional units that are cross-linking. Here,

$$\int d\mathbf{X}''\, G^{(-\overline{N})}(\mathbf{X},\mathbf{X}'')G^{(\overline{N})}(\mathbf{X}'',\mathbf{X}') = \delta(\mathbf{X}-\mathbf{X}')$$

and $G^{(\overline{N})}(\mathbf{X},\mathbf{X}')$ is the correlation function of the ends of a chain of $\overline{N}$ links that is situated in a space of dimensionality $d = 3(1+m)$ in the self-consistent field (18). For a Gaussian field v_τ (30) with $v_v = \text{const}$ this function is easily found[4]:

$$G^{(N)}(\mathbf{X},\mathbf{X}') = \frac{\exp(-v_v\overline{N})}{(\pi a^2\overline{N})^{3/2}}\prod_{k=1}^{m}[\pi a^2 N_{e\mu}^{(k)}\operatorname{sh}(\overline{N}/N_{e\mu})]^{-3/2} \times\exp\left\{-\frac{(R^{(0)}-R'^{(0)})^2}{a^2\overline{N}} - \sum_{k=1}^{m}\frac{[(R_\mu^{(k)})^2+(R_\mu'^{(k)})^2]\operatorname{ch}(\overline{N}/N_{e\mu}) - 2R_\mu^{(k)}R_\mu'^{(k)}}{a^2 N_{e\mu}\operatorname{sh}(\overline{N}/N_{e\mu})}\right\}, \qquad (62)$$

where the parameter $N_{e\mu}^{(k)} = (C\Lambda_\mu)^{(k)-1/2}$ with $\Lambda_\mu = (\alpha\alpha_T)^{-2}$ determines the average number of links between two effective entanglements [see also (23)].

Calculating the integral (61) by the method of steepest descent, we find the self-consistency equation for the function $\varphi(X)$:

$$\int d\mathbf{X}'\, G^{(-\overline{N})}(\mathbf{X},\mathbf{X}')\varphi(\mathbf{X}') = z\varphi^{f-1}(\mathbf{X})/(f-1)!, \qquad (63)$$

the solution of which has the form

$$\varphi(\mathbf{R}) = \bar{\varphi}\exp\left[-\sum_{k=1}^{m}s_\mu^{(k)}(R_\mu^{(k)}/a)^2\right]. \qquad (64)$$

Substituting (64) into the exponential in the integrand of (61) and calculating its extremum with respect to $\overline{\varphi}$, we find the quantity $\tilde{f}_m$ defined in (51):

$$\tilde{f}_m = Q\frac{N_\Pi}{\overline{V}^{(0)}}\exp\left\{\frac{\overline{N}}{Q}\left[v_v + \sum_{k=1}^{m}\sum_{\mu}\chi(s_\mu^{(k)},\Lambda_\mu^{(k)})\right]\right\}, \qquad (65)$$

$$Q = 1-\frac{2}{f}, \quad \overline{N}\chi(s_\mu^{(k)},\Lambda_\mu^{(k)}) = \frac{2}{f}\ln(fs_\mu^{(k)}) - \ln\left\{2s_\mu^{(k)}\operatorname{ch}\frac{\overline{N}}{N_{e\mu}^{(k)}} - \left[(s_\mu^{(k)})^2 N_{e\mu}^{(k)} + \frac{1}{N_{e\mu}^{(k)}}\right]\operatorname{sh}\frac{\overline{N}}{N_{e\mu}^{(k)}}\right\}.$$

The parameters $s_\mu^{(k)}$ are found by minimizing the function $\chi(s_\mu^{(k)},\Lambda_\mu^{(k)})$ with respect to them:

$$s_\mu^{(k)} = \frac{f-2+[(f-2)^2+4(f-1)\operatorname{th}^2(\overline{N}/N_{e\mu}^{(k)})]^{1/2}}{2(f-1)N_{e\mu}^{(k)}\operatorname{th}(\overline{N}/N_{e\mu}^{(k)})}, \qquad (66)$$

and it is the value of this function at the point of the minimum of the expression (65) that determines the function $\chi(\lambda_\mu)$ (50). In particular, its derivative is equal to

$$\chi'(\Lambda_\mu) = \frac{1}{2\Lambda_\mu}\left[\frac{1}{N_{e\mu}}\left(1+\frac{Q^2}{\operatorname{sh}^2(\overline{N}/N_{e\mu})}\right)^{1/2} - \frac{Q}{\overline{N}}\right]. \qquad (67)$$

We note that the extremum (65) with respect to $\overline{\varphi}$ is the maximum of the exponential in Eq. (61), so that the partition function (61), calculated with allowance for the fluctuations of the field $\varphi(\mathbf{X})$, is purely imaginary. This result is a consequence of the use of the grand canonical ensemble and leads to a real value of the entropy $S_m(\lambda_\mu^{(k)})$. In the absence of topological restrictions ($b_\tau = 0$) the result (65) was obtained earlier in Ref. 5.

From Eq. (63) for the amplitude of the fluctuations of the quasi-cross-links there follows the expression

$$\xi_{\tau\mu} \approx a(s_\mu)^{-1/2} \approx a\min(\overline{N}^{1/2}, N_{e\mu}^{1/2}).$$

For $\lambda_\mu = \alpha\alpha_T$ it determines the characteristic scale of the function

$$\varkappa_q \approx \varkappa_0(1+\xi_\tau^2 q^2).$$

For the model considered above with $p = 1$ the network skeleton coincides with the network itself. A different situation is realized in critically branched networks ($\tau \ll 1$), consisting predominantly of chains that are attached to the skeleton by only one ring and make no contribution to the elasticity of the network.

A field theory [with field $\varphi_i(\mathbf{X})$, $i = 1,\ldots,n$] describing such networks in the limit $n\to 0$ was constructed in Refs. 7 and 12. For $\tau \ll 1$ it is sufficient to confine ourselves to the third-order terms in the expansion of the effective action in powers of $\psi_i = \varphi_i - p/(1-p)$ (see Ref. 7). For $\alpha_T = 1$ and $v_v = v_b = 0$ this expansion takes the form

$$\tilde{f}_m = \frac{1}{g^{(0)}}\prod_{k=1}^{m}\int d\mathbf{R}^{(k)}\left\{\sum_{i=1}^{n}\left[-\frac{\tau}{2}\psi_i^2 + \frac{a^2}{2}(\nabla\psi_i)^2 - \frac{w}{6}\psi_i^3\right] + \frac{v_\tau(\mathbf{X})}{2}\left(\sum_{i=1}^{n}\psi_i\right)^2\right\}, \qquad (68)$$

$$g^{(0)} = 2\tau(f-1)/\bar{\rho}^{(0)}(f-2)^3, \quad w = (f-2)^2/(f-1).$$

According to Ref. 7, the solutions $\psi_i^{(j)}$ of the equations found by minimizing (68) (the solutions describing the polymer network) are degenerate ($j = 1,\ldots,n$) and must be sought in the form

$$\psi_j^{(j)}(\mathbf{R}) = \varphi(\mathbf{R}) + \psi(\mathbf{R})/2, \quad \psi_i^{(j)}(\mathbf{R}) = \varphi(\mathbf{R}) - \psi(\mathbf{R})/2, \quad i\neq j. \qquad (69)$$

After substituting (69) into (68) and eliminating the function $\varphi(\mathbf{R})$ found by minimizing (68) with respect to φ, we obtain an effective action that depends only on the field ψ. For $n = 0$ it takes the form

$$\tilde{f}_m = \frac{1}{g^{(0)}}\prod_{k=1}^{m}\int d\mathbf{R}^{(k)}\left[\frac{\tau^2}{2w}\psi - \frac{w}{24}\psi^3 + \frac{a^4}{2w}\frac{(\nabla^2\psi)^2}{\psi} + v_\tau(\mathbf{X})\frac{\psi^2}{2}\right]. \qquad (70)$$

To find the function $\chi(\Lambda)$ (50) we shall consider the Λ val-

ues specified by (52). In the calculation of the functional (70) to terms of first order in m it is sufficient to find the function $\psi(\mathbf{R})$ that minimizes the functional (70), the parameters of which are found for $m=0$. In the limit $m\to 0$ the isotropy under rotations in the $3m$-dimensional replica subspace is restored, and so the function sought depends only on the quantities ξ_μ:

$$\psi(\mathbf{R})=\frac{2\tau}{w}\eta(\zeta_\mu),\qquad \zeta_\mu=\sum_{k=1}^{m}(R_\mu^{(k)})^2. \tag{71}$$

Substituting (71) into (70), in first order in m we find

$$\tilde{f}_m=\frac{\tau^2\bar{\rho}^{(0)}(f-1)}{3(f-2)}+m\bar{\rho}_b^{(0)}\sum_\mu[\chi(\Lambda_\mu)+\chi'(\Lambda_\mu)(1-\Lambda_\mu)],$$
$$\bar{\rho}_b^{(0)}=2\tau\bar{\rho}^{(0)}(f-1)/(f-2),$$
$$\chi(\Lambda_\mu)+\chi'(\Lambda_\mu)(1-\Lambda_\mu)=\int_0^\infty d\zeta\left[\frac{\tau}{4\zeta}\left(\eta_\mu-\frac{\eta_\mu^3}{3}-\frac{2}{3}\right)+\frac{a^4\zeta}{\tau\eta_\mu}\left(\frac{d^2\eta_\mu}{d\zeta^2}\right)^2+\frac{Cw^2}{2a^2}\eta_\mu^2\right], \tag{72}$$

where the functions $\eta_x(\zeta)=\eta(\zeta,0,0)$ etc. are determined by the equations

$$\frac{\tau}{4\zeta}(1-\eta_\mu^2)+\frac{a^4}{\tau}\left[2\frac{d^2}{d\zeta^2}\left(\frac{\zeta}{\eta_\mu}\frac{d^2\eta_\mu}{d\zeta^2}\right)-\frac{\zeta}{\eta_\mu^2}\left(\frac{d^2\eta_\mu}{d\zeta^2}\right)^2\right]+\frac{Cw^2}{a^2}\Lambda_\mu\eta_\mu=0 \tag{73}$$

with the boundary conditions $\eta_\mu(0)=1$ and $\eta_\mu(\zeta\to\infty)\to 0$.

Equation (73) is simplified in the limit of phantom networks ($C\to 0$), when the function $\eta_\mu(\zeta)$ does not depend on μ and is determined by the equation

$$\zeta\, d^2\eta_\mu/d\zeta^2=\eta_\mu(1-\eta_\mu)/2(\xi_\tau^{(0)})^2,\qquad \xi_\tau^{(0)}=a\tau^{-1/2}. \tag{74}$$

For $\zeta\to\infty$, from (74) we find

$$\eta_\mu(\zeta)\sim\zeta^{1/4}\exp[-(\zeta/2)^{1/2}/\xi_\tau^{(0)}],\qquad \zeta^{1/2}\gg\xi_\tau^{(0)}. \tag{75}$$

The same asymptotic form (75) is also valid for $C>0$. In the case of strongly entangled chains there is an intermediate interval of lengths $\xi_\tau\ll\zeta^{1/2}\ll\xi_{(\tau)}^0$ in which the function $\eta_\mu(\zeta)$ decreases only by a power law:

$$\eta_\mu(\zeta)=(\xi_{\tau\mu}^2/\zeta)^3,\quad \xi_{\tau\mu}=a(N_{e\mu}/\tau)^{1/4},\quad N_{e\mu}\ll 1/\tau. \tag{76}$$

The parameter $N_{e\mu}$ is equal to the average number of links between two effective entanglements along an elastically active chain:

$$N_{e\mu}=\tau^{1/3}(96/Cw^2\Lambda_\mu)^{2/3}. \tag{77}$$

From (72) and (76) we find $\chi(\Lambda_\mu)\approx N_{e\mu}^{-1}\sim\Lambda_\mu^{2/3}$.

We note that the gradient expansion in (70)–(73) starts from terms of fourth order, this being connected with the fractal structure of the network for $\tau\ll 1$. The quantity $\xi_\tau\approx al^{1/D}$, where $D=4$ is the fractal dimensionality and l is the number of links in a region of size ξ_τ: $l\approx\tau^{-2}$ *for* $N_e\gg\tau^{-1}$ and $l\approx N_e/\tau$ for $N_e\ll\tau^{-1}$. The quantity ξ_τ determines the characteristic scale of the function $\varkappa_{\mathbf{q}}\approx\varkappa_0(1+q^4\xi_\tau^4)$. Using (4), we find expressions for the correlation function of the thermodynamic fluctuations of the density and for the correlation length of the final system:

$$g_{\mathbf{q}}\approx\bar{\rho}^{(0)}/(\tau\tau_{st}+a^4q^4),\qquad \xi\approx a(\tau\tau_{st})^{-1/4},$$
$$\tau_{st}\approx C\bar{\rho}^{(0)}/\tau+\max(1/N_e,\tau). \tag{78}$$

With neglect of the elastic contribution of the quasinetwork of entanglements,[7] these expressions were obtained in Ref. 16.

6. DISCUSSION OF THE RESULTS

In this paper we have constructed a statistical theory of polymer networks with allowance for both the thermodynamic and the statistical fluctuations of their density and in the presence of topological restrictions. The order parameter for such systems with a frozen topological structure is the density $\langle\rho(\mathbf{X})\rangle$ (35b) in the replica space. It determines, in particular, the densities (35a) of the links in each of the replicas. Integrating $\langle\rho(\mathbf{X})\rangle$ (35b) over the coordinates of all the replicas except k and l, we determine the "overlap" between replicas k and l:

$$\rho^{(kl)}(\mathbf{x},\mathbf{x}')=\sum_n\overline{\langle\rho_n^{(k)}(\mathbf{x})\rangle\langle\rho_n^{(l)}(\mathbf{x}')\rangle}.$$

The liquid phase of polymers corresponds to a solution of molecules of finite size, which was studied in Ref. 2. Because of the absence of correlation between the positions $\mathbf{r}_n$ and $\mathbf{r}_n'$ of a particle over long times, the quantity $\rho^{(kl)}$ is a constant, and in the thermodynamic limit $\rho^{(kl)}=\overline{\langle\rho^{(k)}\rangle}/\overline{V}^{(l)}$ vanishes. In the solid phase the coordinates $\mathbf{r}_n$ and $\mathbf{r}_n'$ are correlated and the order parameter $\rho^{(kl)}$ is finite. The structure of this phase is determined by the symmetry of the order parameter.

In a phase of the spin-glass type there are more than one of the "pure" states of Ref. 9, separated from each other by high potential barriers. In this case the order parameter $\rho^{(kl)}$ describes the overlap of states k and l. An exotic phase of this type can be realized only in random heteropolymers, the number of components of which is of the order of the number of their links.[17] In polymer networks a phase of the ferromagnetic type with a single ground state, to which the affine-deformation vector $\mathbf{n}$ (38) corresponds, is realized.

In mean-field theory the order parameter is determined by the self-consistency equation (63), which, for phantom networks ($v_\tau\to 0$), is symmetric under rotations in the replica space and has infinitely many solutions. Which of these is the correct one is determined by the conditions on the sample surface that break this symmetry. Thus, in the presence of long-range order $\rho^{(kl)}\neq 0$ one must not take the thermodynamic limit until the properties of the surface have been taken into account (Ref. 4, p. 85). This anomalous influence of the surface is due to the presence of the topological restrictions, which divide the phase space into a set of topologically inequivalent regions τ. Local deformation of the surface causes a global change of the region τ in which the system is trapped at the time of preparation. For any finite $v_\tau\neq 0$ the solution of the self-consistency equations is unique.

The extent to which the topological structure of the lattice differs from the ideal topological structure is described

by the correlation function (8), (10) of the spatial density fluctuations. We note that for $\alpha = 1$ and $C_q = C_q^{(0)}$

$$\langle\overline{\Delta\rho(\mathbf{x})\Delta\rho(\mathbf{x}')}\rangle = \langle\Delta\rho^{(0)}(\mathbf{x})\Delta\rho^{(0)}(\mathbf{x}')\rangle \equiv g^{(0)}(\mathbf{x}-\mathbf{x}').$$

This result is exact and not restricted to the mean-field approximation. The important point is that in the networks the spatial density fluctuations (3) can significantly exceed the thermodynamic fluctuations (4). To estimate their relative contribution we introduce the parameters

$$\tau_{st}^{(0)} = C^{(0)}/C_{st}^{(0)} - 1, \qquad \tau_{st} = C/C_{st} - 1,$$

which characterize the proximity of the initial system to its spinodal transition (at which $C^{(0)} = C_{st}^{(0)}$) and of the final system to its spinodal transition (at which $C = C_{st}$). Using the expressions (8), (10), and (11), when the wave vector vanishes, we find

$$G_0/g_0 \approx \tau_{st}^{-1}(1 + k/\tau_{st}^{(0)}), \qquad k \equiv \varkappa_0/\varkappa_0^{(0)}. \tag{79}$$

We now use the relations (59) and (60) to estimate the quantity k. In phantom networks we have $k \sim 1$, and in the case when the chains of the network are strongly entangled with each other we have $k \sim \bar{N}/N_e \gg 1$.

According to (79), the spatial density fluctuations in networks obtained in an uncompressed initial system exceed the thermodynamic fluctuations only near the spinodal transition. In the region $\tau_{st} \gg 1$ the classical theory of polymer networks, which neglects such fluctuations entirely, is valid. However, if in the initial system the density fluctuations are not too small, i.e., $\tau_{st}^{(0)} \lesssim k \gtrsim 1$, in the final system the spatial density fluctuations can significantly exceed the thermodynamic fluctuations even far from the spinodal transition. The role of such statistical fluctuations increases near the spinodals of the initial and final systems. In particular, near the spinodal of the final system for $q = 0$ the correlation function (2) increases not as $g_0 \sim \tau_{st}^{-1}$, but much faster, as τ_{st}^{-2}. Since it is this correlation function which determines the intensity of light scattering, x-ray scattering, and neutron scattering by polymer networks, fluctuations of the topology of the networks can be studied experimentally.

The strong spatial fluctuations in reticular polymers make it possible to explain their experimentally observed nonuniformity. The characteristic length scale R of the nonuniformities is determined by the expression

$$R^2 \equiv \int d\mathbf{x}\, x^2 G(\mathbf{x}) \Big/ \int d\mathbf{x}\, G(\mathbf{x}) = -G_0^{-1}\partial^2 G_q/\partial \mathbf{q}^2|_{q=0}.$$

By making use of the expressions (8), (10) for G_q and neglecting the dependence of θ and $\bar{\theta}$ on the wave vector $\mathbf{q}$, we find

$$R^2 = 2\xi^2 + f(\alpha)(\xi^{(0)})^2, \quad f(\alpha) = \alpha^2/(1 + \theta_0(\alpha)/\bar{\theta}_0(\alpha) g_0^{(0)} \alpha^3),$$

where the correlation lengths of the initial and final systems are defined by the usual expressions

$$(\xi^{(k)})^2 = \int d\mathbf{x}\, x^2 g^{(k)}(\mathbf{x}) \Big/ \int d\mathbf{x}\, g^{(k)}(\mathbf{x}).$$

The result (80) is easy to understand in limiting cases. If the network was obtained in an uncompressed intitial system, then $f(\alpha) = 0$ and $R \approx \xi$. But if the network was synthesized near the spinodal of the initial system ($\tau_{st}^{(0)} \lesssim k$), then $f(\alpha) = \alpha^2$ and far from the spinodal of the final system the size of the nonuniformities is equal to $R = \alpha\xi^{(0)}$.

The properties of a network that has swollen in the final system in the presence of a solvent differ substantially from its properties in the dry state. As the quality of the solvent worsens one observes in swollen networks the phenomenon of "microsyneresis" (Ref. 1), which consists in the formation of regions with an enhanced concentration of solvent. It is customary to assume[1] that microsyneresis can arise only beyond the spinodal point. In this case, it is only because the observation time is finite that macroscopic phase separation of the solution does not occur.

Strong spatial pressure fluctuations (6) can give rise to the appearance of microsyneresis long before the spinodal point. In such systems, solvent is partially expelled from regions of enhanced pressure into regions in which the pressure and the concentration of chains of the network are lower.

To describe this effect, besides the interaction C^{mm} of the monomer links with each other we must also take into account the monomer–solvent interaction C^{ms} and the solvent–solvent interaction C^{ss}. It is not difficult to show that the correlation function of the solvent-density fluctuations is determined by the expression

$$\overline{d\rho_q^s d\rho_{-q}^s} = (C^{ms}/C^{ss})^2\, \overline{d\rho_q^m d\rho_{-q}^m},$$

where the density–density correlation function for the links is given by the expressions (8), (10), and (11) with the renormalized interaction $C = C^{mm} + C^{ms}/C^{ss}$. Complete expulsion of the solvent from regions of enhanced pressure sets in when the condition $\overline{(d\rho^s)^2} \approx \overline{\langle\rho^s\rangle^2}$ is fulfilled, after which the network becomes strongly heterogeneous on microscopic scales. We stress that the heterogeneity of such networks is already manifested in their thermodynamic-equilibrium properties.

I wish to express my deep gratitude to S. P. Obukhov for discussing the results of this paper.

APPENDIX

THE CORRELATION FUNCTIONS OF POLYMER NETWORKS

We obtain first an expression for the thermodynamic potential of a network with allowance for its density fluctuations. In the microscopic approach of Ref. 6, for the partition function of a network of topology Γ_τ, under a given external pressure P, one finds the following expression:

$$Z_{\Gamma_\tau} = \int D\rho \exp[-(E_0\{\rho\} + PV)/T + S_{\Gamma_\tau}\{\rho\}], \tag{A1}$$

where S_{Γ_τ} is the entropy of the network and $E_0\{\rho\}$ is the internal energy of the system of broken links.[3,6] Performing statistical averaging over all topologies Γ_τ we find the thermodynamic potential of the network:

$$\Phi = -T\overline{\ln Z_{\Gamma_\tau}} \equiv -T\sum_{\Gamma_\tau} P_{\Gamma_\tau}^{(0)} \ln Z_{\Gamma_\tau}, \tag{A2}$$

where the probabilities $P_{\Gamma_\tau}^{(0)}$ are given by the expression (14), in which the partition function of the initial system is equal to

$$Z_{\Gamma_\tau}^{(0)} = \int D\rho^{(0)} \exp[-(E_0^{(0)}\{\rho^{(0)}\} + P^{(0)}V^{(0)})/T^{(0)} + S_{\Gamma_\tau}\{\rho^{(0)}\}]. \tag{A3}$$

Using the replica method (31), from (A1)–(A3) we obtain

$$\Phi=-T\frac{d}{dm}\ln Z_m|_{m=0},\quad Z_m=\int D\rho^{(k)}\exp\left(-\frac{\Phi_m\{\rho^{(k)}\}}{T}\right\},\tag{A4}$$

$$\frac{\Phi_m\{\rho^{(k)}\}}{T}=\sum_{k=0}^{m}\left(\frac{E_0^{(k)}\{\rho^{(k)}\}+P^{(k)}V^{(k)}}{T^{(k)}}\right)-S_m\{\rho^{(k)}\},$$

where the integration is over the densities $\rho^{(k)}$ of the initial system ($k=0$) and of each of the m replicas of the final system ($k=1,...,m$). The parameters $T^{(k)}=T$, $P^{(k)}=P$,... have the same values for all these replicas. For $m=0$ the functional $Z_0=Z(0)$ (A4) determines the partition function (14) of the grand canonical ensemble of the initial system. The entropy functional S_m in the replica space has the form

$$S_m\{\rho^{(k)}\}\equiv\ln\sum_{\Gamma_\tau}\exp\sum_{k=0}^{m}S_{\Gamma_\tau}\{\rho^{(k)}\}\tag{A5}$$

and is symmetric under the group of permutations of all the replicas $k=0,...,m$.

In the mean-field approximation the functional integrals (A4) are calculated by the method of steepest descent. In this approximation the entropy S_{Γ_τ} is given by the expression (19), and the function S_m has the form (33). We now obtain expressions for the density-fluctuation correlation functions (1)–(3) of interest to us in the language of the replica method [(A4), (A5)].

We first find an expression for the correlation function (3) of the statistical fluctuations of the density of links:

$$G(\mathbf{x}-\mathbf{x}')=\overline{\langle\rho(\mathbf{x})\rangle\langle\rho(\mathbf{x}')\rangle}-\overline{\langle\rho\rangle}^2.\tag{A6}$$

The average link density $\langle\rho(\mathbf{x})\rangle$ in a network of given topology Γ can be obtained by introducing into the integrand of (A1) the factor

$$\exp\int d\mathbf{x}\,h(\mathbf{x})\rho(\mathbf{x})$$

and differentiating $\ln Z_{\Gamma_\tau}$ with respect to the field h at $h=0$. The correlation function (A6) of interest to us is equal to

$$\overline{\langle\rho(\mathbf{x})\rangle\langle\rho(\mathbf{x}')\rangle}=\frac{\delta^2}{\delta h_1(\mathbf{x})\delta h_2(\mathbf{x}')}\overline{\ln Z_{\Gamma_\tau}\{h_1\}\ln Z_{\Gamma_\tau}\{h_2\}}|_{h_{1,2}=0}.\tag{A7}$$

Using the replica method, we can rewrite the average (A7) in the form

$$[\overline{Z_{\Gamma_\tau}^{m_1}\{h_1\}Z_{\Gamma_\tau}^{m_2}\{h_2\}}-\overline{Z_{\Gamma_\tau}^{m_1}\{h_1\}}\cdot\overline{Z_{\Gamma_\tau}^{m_2}\{h_2\}}+1]/m_1m_2\tag{A8}$$

with $m_{1,2}\to 0$. A contribution to the correlation function (A7) is given only by the first term in the square brackets of (A8), which differs from Z_m (A4) for $m=m_1+m_2$ only by the presence of the extra factor

$$\exp\int d\mathbf{x}\left[h_1(\mathbf{x})\sum_{k=1}^{m_1}\rho^{(k)}(\mathbf{x})+h_2(\mathbf{x})\sum_{k=m_1+1}^{m_2}\rho^{(k)}(\mathbf{x})\right]$$

in the integrand.

Differentiating the resulting functional $Z_m\{h_1,h_2\}$ with respect to h_1 and h_2 [see (A7)] and taking into account the symmetry of the action Φ_m (A4) under permutations of the replicas $k=1,...,m$, we find for $m\to 0$

$$G(\mathbf{x}-\mathbf{x}')=\langle\Delta\rho^{(1)}(\mathbf{x})\Delta\rho^{(2)}(\mathbf{x}')\rangle.\tag{A9}$$

The correlation function (1) of the thermodynamic density fluctuations in the final system is determined by the expression

$$\bar g(\mathbf{x}-\mathbf{x}')=\frac{\delta^2}{\delta h(\mathbf{x})\delta h(\mathbf{x}')}\overline{\ln Z_{\Gamma_\tau}\{h\}}|_{h=0}.\tag{A10}$$

Using the replica method, we can rewrite the average in (A10) in the form

$$[Z_m\{h,h\}-1]/m\tag{A11}$$

with $m\to 0$. After differentiating (A11) with respect to h [see (A10)], we obtain

$$\bar g(\mathbf{x}-\mathbf{x}')=\lim_{m\to 0}[\langle\Delta\rho^{(1)}(\mathbf{x})\Delta\rho^{(1)}(\mathbf{x}')\rangle+(m-1)\langle\Delta\rho^{(1)}(\mathbf{x})\Delta\rho^{(2)}(\mathbf{x}')\rangle].\tag{A12}$$

The expression (A12) together with (A9) for $m\to 0$ gives

$$\overline{\langle\Delta\rho(\mathbf{x})\Delta\rho(\mathbf{x}')\rangle}=\langle\Delta\rho^{(1)}(\mathbf{x})\Delta\rho^{(1)}(\mathbf{x}')\rangle.\tag{A13}$$

Finally, the expression

$$g^{(0)}(\mathbf{x}-\mathbf{x}')=\langle\Delta\rho^{(0)}(\mathbf{x})\Delta\rho^{(0)}(\mathbf{x}')\rangle\tag{A14}$$

for the correlation function of the density fluctuations of the initial system is a consequence of the identity $Z_0\{h^{(0)}=Z^{(0)}\{h^{(0)}\}$.

In the expressions (A9) and (A12)–(A14) the functional averaging of the right-hand sides over the density fluctuations $\Delta\rho^{(k)}=\rho^{(k)}-\langle\rho^{(k)}\rangle$ of the replicas is performed with the action Φ_m/T (A4). We now calculate these correlation functions in the Gaussian approximation.

We consider first the case $\alpha=1$. Expanding the functional Φ_m (A4) to terms quadratic in $\Delta\rho^{(k)}$, we obtain

$$\frac{\Delta\Phi_m\{\rho^{(k)}\}}{T}=\frac{1}{2}\sum_{k,k'=0}^{m}\int\frac{d^3q}{(2\pi)^3}(G_q^{-1})_{k,k'}\Delta\rho_q^{(k)}\Delta\rho_{-q}^{(k')},\tag{A15}$$

$$(G_q^{-1})_{k,k'}=[\varkappa_q+C_q^{(0)}\delta_{k0}+C_q(1-\delta_{k0})]\delta_{kk'}-\theta_q,$$

where the functions $\varkappa$, θ, and $C_q^{(k)}$ are defined as follows:

$$\theta_q\equiv\varkappa_q-\varkappa_q^{(0)}=-\frac{\delta^2S_m}{\delta\rho_q^{(k)}\delta\rho_{-q}^{(k')}},\quad k'\neq k;\tag{A16}$$

$$\varkappa_q^{(0)}=-\frac{\delta^2S_m}{\delta\rho_q^{(k)}\delta\rho_{-q}^{(k)}};\quad C_q^{(k)}T^{(k)}=\frac{\delta^2E_0^{(k)}}{\delta\rho_q^{(k)}\delta\rho_{-q}^{(k)}}.$$

Inverting the matrix G^{-1} (A15), we find

$$(G_q)_{k,k'}=[g_q^{(0)}\delta_{k0}+g_q(1-\delta_{k0})]\delta_{kk'}-g_q(1-\delta_{k0})(1-\delta_{k'0})/m+\frac{[1-\delta_{k0}(1-mg_q^{(0)}\theta_q)][1-\delta_{k'0}(1-mg_q^{(0)}\theta_q)]}{m[g_q^{-1}-m(\theta_q+g_q^{(0)}\theta_q^2)]},\tag{A17}$$

where the functions g_q and $g_q^{(0)}$ are defined by the expressions (4). In the limit $m\to 0$ the matrix (A17) in the mean-field approximation determines for $\alpha=1$ the correlation functions (A9), (A13), and (A14) of the replica densities.

The expressions thus obtained are given in (4), (8), (10), and (11).

The general case $\alpha \neq 1$ is treated analogously. We give the resulting expressions for the statistical pressure fluctuations (6):

$$d\pi^{(k)}(\mathbf{x}) = \frac{\delta S_{\Gamma_\tau}\{\rho^{(k)}\}}{\delta\rho^{(k)}(\mathbf{x})} - \overline{\frac{\delta S_{\Gamma_\tau}\{\rho^{(k)}\}}{\delta\rho^{(k)}(\mathbf{x})}} \qquad \text{(A18)}$$

Since these fluctuations are due to fluctuations of the topology of the network, only the entropy, and not the energy term E_v, contributes to them. The statistical averaging in (A18) and (9) is performed with the probability $P_\Gamma^{(0)} \sim \exp S_{\Gamma_\tau}\{\rho^{(0)}\}$ that the network is synthesized with topology Γ_τ in the uncompressed initial system.

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