Topological interactions in the statistical theory of polymers

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(Submitted 22 February 1988)
Zh. Eksp. Teor. Fiz. **94**, 174–193 (November 1988)

A mean-field theory describing the effects of the topological interactions that occur in polymers on account of the mutual impenetrability of their chains is constructed by means of the replica formalism. On the basis of this theory for the description of a polymer with strongly entangled chains a physical model of a quasinetwork of effective hookings is proposed, the parameters of which are determined by the number $N_s \gg 1$ of links along a chain between two quasi-cross-links. The free energies of a linear polymer and of a polymer gel network, subjected to a specified stretching and swelling, respectively, are calculated in the leading approximation in the small parameter $\varepsilon = 1/N_s$. It is shown that the deformation of such a network has both an affine component and a nonaffine component associated with the partial disentangling of the chains of the network as the network is stretched. The deformation dependence of a gel network with entangled chains, obtained by equilibrium linking of the chains via polyfunctional monomers both close to and far from the gel-formation point, is calculated. It is shown that this dependence is in agreement with the experimental data.

1. INTRODUCTION

The progress in the statistical description of polymer systems that are in equilibrium in respect of the chemical reactions of the formation and breaking of chemical bonds[1–4] is due primarily to the fact that in the process of thermodynamic fluctuations such a system can occupy all states in configuration space. Therefore, to describe such a system we employ the standard method of the grand canonical ensemble. The construction of a theory of polymers in which the molecules have a fixed topological structure is an incomparably more complicated problem. It incorporates the problems both of fixing the topological structure of the molecules and of taking account of the topological exclusion of the mutual intersection of macromolecular chains. The first of these problems was solved in Ref. 5. In this article we shall make use of the method of Ref. 5 for a statistical description of polymers with allowance for the topological constraints. Because polymer chains cannot pass through each other without breaking, the configuration space of the system separates into a set of regions. Thermodynamic fluctuations are not capable of taking the system out of the region in which it was situated at the time of preparation.

Because of the extreme complexity of a detailed description of the geometrical structure of such topological constraints, several models have been proposed that make it possible to mimic the narrowing of the set of conformations of real chains in comparison with the case of phantom chains that can pass freely through each other. Usually, topological interactions (which, in the theory of high elasticity, are usually called steric[6]) are modeled by placing each chain in a certain tube[6,7] or in a lattice of obstables.[8,9]

In this paper we use the replica formalism of Ref. 5 to construct a mean-field theory for the calculation of the thermodynamic characteristics of a polymer system with topological interactions. To interpret the main results of the theory we propose a physical model of a quasinetwork of effective hookings. Since this model is close to the ideas that have been developed in the description of the classical experiments of Refs. 10 and 11 on the mechanical perturbation of a polymer melt of linear chains, we shall first give an account of these ideas.[11]

For rather long times $t \gg \tau_t$ the chains of such a system remained hooked around each other, and the system behaves like an elastic network. The characteristics of this quasinetwork of hookings (see Fig. 1) are determined by the number $N_e \sim 100$–300 (Ref. 12) of links along a chain between two successive hookings. In contrast to ordinary networks with fixed cross linkages between the chains, upon stretching of the polymer under consideration its chains can slide relative to each other, and this leads to partial mutual disentanglement of the chains and to increase of the parameter N_e. For a large chain length $\overline{N}$ the maximum relaxation time $\tau_t \sim \overline{N}^{3.3}$ (Refs. 11, 13) is macroscopically large.

We now formulate the physical model that we have used for the topological interactions. Its mathematical formulation (the mean-field theory) is given in the second section of the article. One of the main achievements of this paper is the construction, on the basis of this model, of a theory of the high elasticity of polymer networks that takes exact account of their (phantom) topological structure.

Thus, we shall assume that each chain of the polymer belongs to a quasinetwork characterized by the number N_s of links between two effective hookings of this chain (N_s

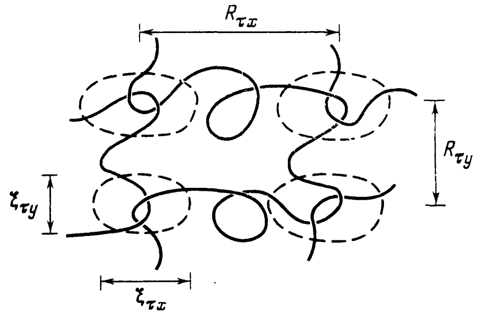

FIG. 1. Quasinetwork of effective hookings; $\xi_{\tau\mu}$ is the size of the fluctuations of its quasi-cross-links; $R_{\tau\mu}$ is the characteristic size of its unit cell in the direction of the axis $\mu = x,y,z$.

$=N_e$ for a melt of chains for $t \ll \tau_t$). The parameter $N_s^{(0)}$ determines the degree of entanglement of the chains under the conditions of synthesis. The case $N_s^{(0)} \ll \overline{N}$ corresponds to strongly entangled chains, while the case $N_s^{(0)} \gg \overline{N}$ corresponds to the absence of topological interactions of the chains. We shall show that when the polymer is stretched (swollen) by a factor of λ_μ along the axis $\mu = x,y,z$ the parameter $N_{s\mu} = N_s^{(0)}\lambda_\mu$ increases because of partial disentanglement of the chains. In the framework of the physical model that we are considering the entropy $\mathcal{S}$ of the polymer is equal to the entropy of the ideal network that has the same number N_μ^{eff} of elastically active chains as the quasinetwork:

$$\mathcal{S}(\lambda_\mu) = \text{const} - \frac{1}{2}\sum_\mu N_\mu^{\text{eff}}(\lambda_\mu^2 + 1), \quad N_\mu^{\text{eff}} = N/N_{s\mu}, \tag{1}$$

where N is the total number of links. We assume also that the characteristic size $R_{\tau\mu}$ of a cell of the quasinetwork and the magnitude $\xi_{\tau\mu}$ of the fluctuations of its quasi-cross-links (see Fig. 1) also coincide with the corresponding quantities of this ideal network:

$$R_{\tau\mu} \approx aN_{s\mu}^{1/2}\lambda_\mu, \quad \xi_{\tau\mu} \approx aN_{s\mu}^{1/2}, \tag{2}$$

where a is the bond length. The quantity ξ_τ determines only the mean-square size of the fluctuations, which is small in comparison with their maximum amplitude. This extremal conformation is realized for the case of a completely extended chain segment of length $aN_{s\mu}$ between two hookings, and its amplitude $r_{\tau\mu} \approx aN_{s\mu}$ is of the same order of magnitude. Thus, in the assumed physical model of the topological interactions there is a heirarchy of scales $a \ll \xi_\tau \ll r_\tau$, which owes its origin to the presence of the small parameter $\varepsilon = 1/N_s \ll 1$. The construction of a mean-field theory on the basis of this small parameter is the main result of this article.

All the estimates given above are a physical interpretation of the results obtained in this mathematical theory. From a more formal point of view, the role of the quasinetwork of effective hookings reduces entirely to the formation of a mean field v_τ that limits the fluctuations of each chain. The amplitude r_τ of an extremal fluctuation determines the characteristic interaction range of this field, and the inequality $\xi_\tau \ll r_\tau$ makes it possible, in the description of typical fluctuations, to confine ourselves to the quadratic terms of the expansion of the field v_τ in a Taylor series. Because of the attractive character of the field v_τ on scales large in comparison with ξ_τ, the chain is in a globularized state and its density fluctuations are small. We note that in the theory of the globular state the aforementioned hierarchy of scales follows directly from the results of Ref. 14, in which a quadratic attractive potential was considered (although this was not noted in Ref. 14). On scales small in comparison with ξ_τ the topological interactions are unimportant.

In Sec. 3 we calculate the free energy of a long entangled linear chain consisting of N links, under the assumption that its mean density at the time of synthesis is constant (see, e.g., Ref. 15). An analogous model of a polymer was considered in Ref. 16, in which it was shown that in the presence of hookings the free energy of this chain is an additive quantity $F \sim N$, but the coefficient of proportionality was not in fact obtained.

In Sec. 4 we study systems consisting of a large number of entangled chains. In particular, we consider a melt of II chains, investigated experimentally in Ref. 10. For the example of this very simple polymer we demonstrate the mathematical methods that we use later for the description of a polymer gel network obtained as a result of the linking of chains through their end groups. Besides the gel, in such a system there is a sol, consisting of molecules of finite size with a tree structure. Because of the absence of topological hookings between these molecules, after the freezing (fixing) of all the chemical bonds the sol fraction can be washed out of the polymer network. The topological structure of the resulting network is determined by the value of the conversion p of the initial equilibrium system, equal to the ratio of the number of bonds formed by the polyfunctional monomers to the maximum possible number of such bonds. Near the gel-formation threshold $p \to p_c$ a significant part of the gel consists of "freely dangling" chains, attached to the gel by only one end, while for $p = 1$ such chains are completely absent. These chains make a contribution to the total density of the gel, but do not affect its elastic properties. The order of the cross linkages uniquely fixes the topological structure of the networks, but their spatial structure depends strongly on the conditions of the experiment (which determine, in particular, the relative magnitudes of the parameters $N_{s\mu}$ and $\overline{N}$). For $N_{s\mu} \gtrsim \overline{N}$ the chains of the network are weakly entangled and the spatial structure of the network is shown in Fig. 2a. We shall show that such a gel can be described in the framework of the classical theory of high elasticity.[17,18] According to this theory, under uniaxial stretching of the network by a factor of λ the stress σ per unit area of the undeformed material (of volume $V^{(0)}$) is equal to

$$\sigma_{\text{cl}} = N^{\text{eff}} T\alpha_T^2(\lambda - \lambda^{-2})/V^{(0)}. \tag{3}$$

Here T is the experimental temperature, α_T is the coefficient of thermal expansion of the chains, and the effective number N^{eff} of elastically active chains is determined entirely by the

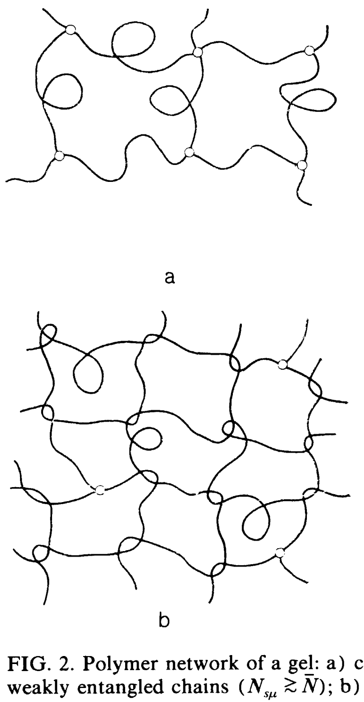

FIG. 2. Polymer network of a gel: a) characteristic form in the case of weakly entangled chains ($N_{s\mu} \gtrsim \overline{N}$); b) quasinetwork of effective hookings in the limit of strong entanglement of the chains ($N_{s\mu} \ll \overline{N}$).

topological structure of the polymer network. The theory presented makes it possible to calculate the quantity $N^{\rm eff}$ for any type of network synthesized in conditions of chemical equilibrium.

The relations (3), with an appropriate choice of $N^{\rm eff}$, gives a rather good description of the experimental data on the compression of a gel to $\lambda < 1$, despite the inapplicability of the classical theory to the description of gels with strongly entangled chains.[16] For $\lambda > 1$ the deviations from the results of the classical theory are usually described by the empirical Mooney-Rivlin formula[19,20]

$$\xi(\lambda^{-1}) \equiv \sigma/\sigma_{\rm cl} = c_1 + c_2\lambda^{-1}. \tag{4}$$

In theoretical papers these deviations have been ascribed to the presence of steric interactions of the chains of the polymer network. Their entanglement becomes strong for $N_{s\mu} \ll \overline{N}$, and the spatial structure of such a network is shown schematically in Fig. 2b. We shall demonstrate that the main contribution to the free energy of this gel is given by the elasticity of the quasinetwork of effective hookings shown in Fig. 1. In the framework of the theory presented, the deformation of a polymer network upon its stretching (swelling) has an affine and a nonaffine component. The first of these was taken into account in the classical theory, while the second is connected with the mutual disentanglement of the chains upon stretching of the network. This nonaffine character of the deformations has been observed experimentally,[21,22] and a crude phenomenological model of it has been given in Ref. 23.

In the Conclusion we compare the results obtained from our proposed model of a quasinetwork of effective hookings with results from the study of other models, some of which are also discussed in the main text of the article.

2. METHOD OF THE GRAND CANONICAL ENSEMBLE FOR THE DESCRIPTION OF POLYMERS WITH A FROZEN STRUCTURE AND TOPOLOGICAL INTERACTIONS. THE MEAN FIELD THEORY

The physical properties of a polymer with a fixed topological structure are determined by the characteristics of two systems—the initial system, in which the polymer was obtained and its chemical bonds frozen, and the final system, in which the sample is found at the time of the investigation. In the following we shall indicate parameters of the initial system by the superscript (0). In the mathematical description of the polymers we associate with each configuration a graph $G\{\mathbf{x}_i\}$, where $\mathbf{x}_i$ are the coordinates of the monomer links (sites of the graph).[24,25] We shall label topologically distinct regions of the configuration space $\{\mathbf{x}_i\}$ by the subscript τ. From the experimental point of view, the main interest is in the determination of the mean value of the free energy of the system in a given field h:

$$F\{h\} = -T\sum_{G_\tau} P_{G_\tau}^{(0)} \ln Z_{G_\tau}\{h\}. \tag{5}$$

Here T is the temperature of the final system, Z_{G_τ} is its partition function for a given configuration G_τ, and $P_{G_\tau}^{(0)}$ is the probability of this configuration, which is determined by the properties of the initial system. We shall assume that the initial system is in equilibrium, so that the probabilities are given by the Gibbs distribution

$$P_{G_\tau}^{(0)} = Z_{G_\tau}^{(0)}/Z^{(0)}, \qquad Z^{(0)} = \sum_{G_\tau} Z_{G_\tau}^{(0)}. \tag{6}$$

The partition function Z_{G_τ} is determined by an integral that is taken only over the region τ of the configuration space $\{\mathbf{x}_i\}$. We can represent it in the form of an integral over all space by introducing a δ-function:

$$\delta_\tau(G\{\mathbf{x}_i\}) = \begin{cases} 1, & G\{\mathbf{x}_i\} = G_\tau\{\mathbf{x}_i\} \\ 0, & G\{\mathbf{x}_i\} \neq G_\tau\{\mathbf{x}_i\} \end{cases}. \tag{7}$$

Summing (7) over all τ, for the given topology of the graph G we find the normalization condition

$$\sum_\tau \delta_\tau(G\{\mathbf{x}_i\}) = 1. \tag{8}$$

Since the polymer model that we are using has been described in detail in Refs. 5 and 24, here we give just a brief account of the definitions necessary for what follows. With the aid of (7), we can represent the partition function of the final system in the form

$$Z_{G_\tau}\{h\} = \prod_i \int d\mathbf{x}_i\, \delta_\tau(G\{\mathbf{x}_i\}) \times \exp\Big(-\sum_i h(\mathbf{x}_i) - U_0\{\mathbf{x}_i\}\Big) \prod_{\langle i,j\rangle} g(\mathbf{x}_i - \mathbf{x}_j). \tag{9}$$

Here U_0 is the potential energy of the interaction of the monomer links of the system (in units of T). With each bond with coordinates $\mathbf{x}$ and $\mathbf{x}'$ we associate in (9) a factor $g(\mathbf{x}-\mathbf{x}')$, which is usually chosen to be Gaussian[26]:

$$g(\mathbf{x}-\mathbf{x}') = g(2\pi a^2)^{-3/2} \exp[-(\mathbf{x}-\mathbf{x}')^2/2a^2], \tag{10}$$

where a is the characteristic length of a bond and g is the entropy and energy factor of the bond. Since each bond is characterized entirely by the coordinates $\mathbf{x}$ and $\mathbf{x}'$ of its beginning and end, the different, topologically inequivalent regions τ in the model under consideration are defined only to within $\sim a$. Since the characteristic scale of the topological interactions is $r_\tau \approx aN_s \gg a$ (see the introduction), this model makes it possible to describe the topological interactions to order $\varepsilon = 1/N_s \ll 1$.

In the calculation of the partition functions $Z_{G_\tau}^{(0)} \sim$ of the initial system we must replace T, U_0, and g in (9) by the corresponding characteristics of the initial system. For a system obtained in conditions of chemical equilibrium, $Z^{(0)}$ contains extra factors $z_l^{N_l}/\Lambda_l^{3N_l}N_l!$ for each type (l) of particle. Here N_l is the number of particles, z_l and Λ_l are their activity and thermal wavelength,[24] and the factor $N_l!$ takes into account that they are identical in the initial system. A mixture of several polymer systems (including a low-molecular-weight solvent) is also described by an expression of the type (9), in which now the potential $U_0^{(0)}$ is equal to the sum of the potentials of each of the initial systems (which have their own temperature, volume, etc.), while the potential U_0 takes account of the interaction of all these particles in the final system. Following Ref. 5, we represent the free energy (5) in the form

$$F\{h\} = -T\frac{d}{dm}\ln Z_m\Big|_{m=0}, \qquad Z_m \equiv \sum_{G_\tau} Z_{G_\tau}^{(0)} Z_{G_\tau}{}^m. \tag{11}$$

Using the normalization condition (8) it is not difficult to show tht for $m = 0$ the quantity $Z_0 = Z^{(0)}$ determines the complete partition function (6) of the initial system. For integer values of m the quantity Z_m takes the form

$$Z_m\{h\} = \sum_G \prod_l \frac{z_l^{N_l}}{\Lambda_l^{3N_l} N_l!} \prod_i \int d\mathbf{X}_i \times \exp\Big[-\sum_i \sum_{k=1}^{m} h(\mathbf{x}_i^{(k)}) - U(G\{\mathbf{X}_i\})\Big] \times \prod_{\langle i,j\rangle} Q(\mathbf{X}_i - \mathbf{X}_j), \tag{12}$$

where the summation runs only over the coordinate-free (phantom) graphs G, and the integration over the $3(1+m)$-dimensional space of the replicas with coordinates $\mathbf{X} = (\mathbf{x}^{(0)}, \mathbf{x}^{(1)},...,\mathbf{x}^{(m)})$. It is not difficult to show that Z_m in (12) has the meaning of the partition function of a chemically equilibrium system in a space of effective dimensionality $3(1+m)$ (Ref. 5). In such a system, in (12) we associate with each chemical bond with coordinates $\mathbf{X}$ and $\mathbf{X}'$ the factor

$$Q(\mathbf{X}-\mathbf{X}') = \prod_{k=0}^{m} g^{(k)}(\mathbf{x}^{(k)} - \mathbf{x}'^{(k)}), \tag{13}$$

and the potential of a given configuration $G\{\mathbf{X}_i\}$ is equal to

$$U(G\{\mathbf{X}_i\}) = \sum_{k=0}^{m} U_0^{(k)}\{\mathbf{x}_i^{(k)}\} + U_\tau(G\{\mathbf{X}_i\}). \tag{14}$$

Here U_τ is the potential of the topological interactions, by definition equal to

$$U_\tau(G\{\mathbf{X}_i\}) \equiv -\ln \sum_\tau \prod_{k=0}^{m} \delta_\tau(G\{\mathbf{x}_i^{(k)}\}). \tag{15}$$

We introduce the coordinates $r_\mu^{(k)} = x_\mu^{(k)}/\lambda_\mu$, $k = 1,...,m$; $r_\mu^{(0)} = x_\mu^{(0)}$, scaled to those of the initial system. It is not difficult to show that U_τ possesses exact symmetry under permutations of the aggregate $\{\mathbf{r}_i^{(k)}\}$ of these coordinates amongst any of the replicas $k = 0,...,m$.

A specific feature of the formalism used by us is the fact that the potential interactions $U_0^{(k)}$ act separately in each of the replicas $k = 0, 1,..., m$, whereas the topological interactions U_τ are manifested only as interactions between different replicas. The potential U_τ in (15) takes two values 0 and ∞, leaving only those configurations in which all the replicas are simultaneously in arbitrary but identical topologically inequivalent regions τ. An analogous potential was considered in the well known lattice model of polymers in Ref. 2. In this model the potential leaves only those configurations in which the particles are situated at arbitrary but different lattice sites. As shown in Ref. 2, in the description of a system with a singluar potential of this type, in the case when the fluctuations of the order parameter are small, the self-consistent field (SCF) approximation can be used. In the system that we are considering the order parameter is equal to the density $\rho(\mathbf{X})$ of links in the replica space. As will be shown below, an "attractive" topological interaction suppresses transverse fluctuations of $\rho(\mathbf{X})$, i.e., statistical density fluctuations from configuration to configuration. Therefore, if the longitudinal fluctuations of $\rho(\mathbf{X})$ (induced by the potential interactions $U_0^{(k)}$) in each of the replicas are small, the density is a self-averaging quantity and for the calculation of the partition function Z_m (12) of a chemically equilibrium system we can use the usual SCF approximation. As shown in Refs. 3 and 24–26, in this approximation Z_m factorizes into a product of factors:

$$Z_m\{h\} = Z_{m,\mathrm{cb}}\{h+v\} Z_{m,\mathrm{bl}}\{\rho\}/Z_{m,\mathrm{ig}}\{\rho\}. \tag{16}$$

Here $Z_{m,\mathrm{cb}}\{h+v\}$ is the partition function of the so-called system of chemical bonds, on the noninteracting particles of which ($U = 0$) acts a field $h + v$ that determines the density of links of this system in the replica space:

$$\rho(\mathbf{X}) = -\delta \ln Z_{m,\mathrm{x.c}}\{h+v\}/\delta h(\mathbf{X}), \quad \int d\mathbf{X}\, \rho(\mathbf{X}) = N, \tag{17}$$

where N is the total number of links. In the limit $m \to 0$ the function $\rho(\mathbf{X})$ gives the densities of links in the initial ($k = 0$) and final ($k = 1$) systems:

$$\rho^{(k)}(\mathbf{x}^{(k)}) = \prod_{l \neq k} \int d\mathbf{x}^{(l)} \rho(\mathbf{X}). \tag{18}$$

The condition (17) that the total numbers of links in the two systems be equal follows automatically from (18). The functional $Z_{m,\mathrm{bl}}\{\rho\}$ in (16) defines the partition function of the so-called system of broken links, which has the same density $\rho(\mathbf{X})$ (17). The particles of this system interact with each other with potential U (14), but do not form chemical bonds. Finally, the function $Z_{m,\mathrm{ig}}\{\rho\}$ in (16) is equal to the partition function of an ideal gas ($U = 0$) of the same density $\rho(\mathbf{X})$. In the system of broken links, owing to the absence of elasticity of the chemical bonds topological interactions are also essentially absent, and this, in the language of replicas, implies the absence of interaction of different replicas. As shown in Ref. 5, in the thermodynamic limit the partition function of such a system of broken links factorizes into the product of the partition functions of these replicas:

$$\ln(Z_{m,\mathrm{bl}}\{\rho\}/Z_{m,\mathrm{ig}}\{\rho\}) = \sum_{k=0}^{m} \int d\mathbf{x}^{(k)} P^{*(k)}(\rho^{(k)})/T^{(k)},$$

$$P^*(\rho) \equiv P_{\mathrm{bl}}(\rho) - \rho T, \tag{19}$$

where $P_{\mathrm{bl}}^{(k)}(\rho^{(k)})$ is the equation of state of the corresponding system of broken links, and, in the following, will be assumed to be known.[3,24]

Thus, in the SCF approximation the problem reduces to the determination of the partition function $Z_{m,\mathrm{cb}}$ of a chemically equilibrium system, situated in a $3(1+m)$-dimensional space, on each link i of which acts an external field

$$h(\mathbf{X}_i) + v(\mathbf{X}_i), \quad h(\mathbf{X}) = \sum_{k=0}^{m} h^{(k)}(\mathbf{x}^{(k)}). \tag{20}$$

According to (17), the one-particle field v is defined as the variable thermodynamically conjugate to the density $\rho(\mathbf{X})$, and is determined from the condition that this density distribution be reproduced. In the SCF approximation fluctuations of both the quantities $\rho(\mathbf{X})$ and $v(\mathbf{X})$ are neglected. Thus, unlike the potential (14), the field v is a continuous function of the coordinates and has a form analogous to (14):

$$v(\mathbf{X}) = \sum_{k=0}^{m} v_0^{(k)}(\mathbf{x}^{(k)}) + v_\tau(\mathbf{X}). \tag{21}$$

In a spatially uniform system the fields $v_0^{(k)}$ describing the potential (volume) interactions are constants; see (25) below. In accordance with the exact symmetry of the potential U_τ, the function v_τ should be symmetric under interchanges of the coordinates $r^{(k)}$ $(k) = 0, 1,..., m)$, and, in a spatially uniform system, depends only on their difference:

$$v_\tau(\mathbf{X}) \equiv v_\tau(\mathbf{r}^{(k)} - \mathbf{r}^{(k')}). \tag{22}$$

Expanding this in a Taylor series, we find

$$v_\tau(\mathbf{X}) = C_0 + \frac{C}{a^2} \sum_{k,k'} (\mathbf{r}^{(k)} - \mathbf{r}^{(k')})^2 + \dots, \tag{23}$$

where $a = a(T^{(0)})$. The constant term C_0 describes the renormalization of the field v_0 on account of collisions of links of the chains, and henceforth we shall assume it to be included in $v_0^{(k)}$ (21). To determine the functions $v_0^{(k)}$ $(\rho^{(k)})$ we equate the variational derivative of the functions $\ln Z_m$ (16) to zero. By making use of the relations (17)–(19) and $\delta P^* = \rho \delta \mu^*$, we obtain

$$\delta \ln Z_m = \sum_{k=0}^{m} \int d\mathbf{x}^{(k)} \rho^{(k)} (\mathbf{x}^{(k)}) (\delta \mu^{*(k)}/T^{(k)} - \delta v_0^{(k)}) = 0, \tag{24}$$

whence for the magnitude of the SCF volume interactions we find the expression

$$v_0{}^{(k)} = \mu^{*(k)}/T^{(k)}, \quad \mu^*(\rho) \equiv \mu_{\text{bl}}(\rho) - T \ln(\rho \Lambda_2{}^3), \tag{25}$$

where $\mu_{\text{bl}}^{(k)}(\rho^{(k)})$ is the chemical potential of the corresponding system of broken links of a given density $\rho^{(k)}$.

In the model under consideration the topological potential U_τ changes on a scale $\sim a$ when chains intersect each other. By analogy with the dynamical picture the entanglement of chains is usually simulated by placing them in a tube of diameter $\sim a N_s^{\frac{1}{2}}$ (Ref. 11). In reality, when thermodynamic fluctuations of the chains forming this tube are taken into account, the characterisitic range of the field v_τ limiting the fluctuations of this chain has a much greater scale: $r_\tau = a/C^{1/2} \approx a N_s \gg a$; see the Introduction. Repeated change of direction of a chain on this scale leads to effective averaging of the anisotropy of the field v_τ along and at right angles to the direction of the chains. Because of the weakness of the anisotropy the very idea of a tube loses its meaning in the thermodynamics. In the derivation of (24) we also neglected anharmonic terms in the expansion of the field v_τ. The possibility of such neglect is connected with the inequality $\xi_\tau \ll r_\tau$ already discussed in the Introduction. This inequality makes it possible to confine ourselves to the quadratic term in the expansion of (24) in the parameter $(\xi_\tau / r_\tau)^2 \approx 1/N_s \ll 1$. The more rigorous calculations performed in the following sections confirm these very simple estimates on the basis of the model of a quasinetwork of effective hookings. Thus, the derivation and applicability of the mean-field theory for the description of topological interactions are directly related to the existence of the small parameter $\varepsilon = 1/N_s \ll 1$. To calculate the parameter C of the topological interactions (23) it is necessary to describe in more detail the geometrical structure of the topological interactions. In the following we shall show that C is determined by the number $N_s^{(0)} \gg 1$ of links of the quasinetwork between two effective hookings (quasi-cross-links) in the initial system, and we shall assume it to be given by $C = (N_s^{(0)})^{-2}$.

When substituting the expressions (16) and (19) obtained into (11) one must take into account that the partition function $Z_{m,\text{cb}}$ depends on m both parametrically and through its argument:

$$\begin{gathered} F = -\int d\mathbf{x}\, P^*(\rho^{(1)}) - T \frac{\partial}{\partial m} \mathscr{S}_m |_{m=0}, \\ \mathscr{C}_m\{\rho(\mathbf{X})\} = \ln Z_{m,\text{cb}} - \int d\mathbf{X}\, v(\mathbf{X}) \rho(\mathbf{X}), \end{gathered} \tag{26}$$

where the derivative of the first term is taken at a fixed argument $h + v$, and that of the second term is taken at a fixed density (17). Thus, in the framework of the replica method, in the calculation of the derivative with respect to m the Legendre transformation (26) from the field $v(\mathbf{X})$ to the density $\rho(\mathbf{X})$ is performed automatically. The physical meaning of this procedure is obvious: The field v specifies external constraints imposed on the system, while the interactions of the particles are internal constraints. Therefore, to determine the entropy of such a system we must subtract from its free energy the energy of the interaction with the external field; see, e.g., Refs. 26 and 27. To bring the free energy (26) to the standard form we separate out from this energy term the contribution of the volume interactions $v_0^{(k)}$ (21), (25). Using the relation (18), we finally obtain

$$F(\lambda_\mu) = E\{\rho^{(1)}\} - T \mathscr{S}(\lambda_\mu), \tag{27}$$

$$E\{\rho^{(1)}\} = \int d\mathbf{x}\, f^*(\rho^{(1)}), \quad f^*(\rho^{(1)}) \equiv \rho^{(1)} \mu^*(\rho^{(1)}) - P^*(\rho^{(1)}).$$

The formula (27) for $f^*(\rho^{(1)})$ defines the Legendre transformation to the density $\rho^{(1)}$ in real space. The topological constraints do not make a contribution to the energy term f^* but determine the entropy of the system:

$$\mathscr{S}(\lambda_\mu) = \frac{d}{dm} \ln Z_{m,\text{cb}}\{v_\tau\}|_{m=0}. \tag{28}$$

The relations (27), (28), (23), and (12) with $U = 0$ completely determine, in the SCF approximation, the free energy of a polymer with a specified fixed topological structure and entangled chains.

3. TOPOLOGICAL INTERACTIONS IN LINEAR CHAINS

We shall consider a polymer consisting of a single long chain with N links. We shall assume that the density of this polymer is constant and that the density fluctuations are small. In the initial system such a situation can be realized, e.g., in the globular state of the chain,[26] in a system of limited volume (see the Appendix), or as a result of joining of the ends of a large number of chains having a spatially uniform density.[15] In the thermodynamic limit $N \to \infty$ the relaxation time τ_t of such a polymer tends to infinity, and the polymer can be described in the framework of the theory (27).

We denote the coordinates of the beginning and end of the chain in the k-th replica by $\mathbf{x}^{(k)}$ and $\mathbf{x}'^{(k)}$. Then for the partition function $Z_{m,\text{cb}}^N$ of such a chain with fixed ends, the links of which are in the external field (23), we obtain the recursion relation

$$Z^{N+1}_{m,\mathrm{cb}}(\mathbf{X},\mathbf{X}') = \int d\mathbf{Y} Q(\mathbf{X}-\mathbf{Y}) \exp\{-v_\tau(\mathbf{Y})\} Z^{N}_{m,\mathrm{cb}}(\mathbf{Y},\mathbf{X}') . \tag{29}$$

To determine the function $Z^{N}_{m,\mathrm{cb}}$ we expand it in the eigenfunctions of the following eigenvalue equation (with eigenvalues Λ_m):

$$\int d\mathbf{Y} Q(\mathbf{X}-\mathbf{Y}) \exp\{-v_\tau(\mathbf{Y})\} \psi_{\mathbf{q},n}(\mathbf{Y}) = \Lambda_m(\mathbf{q},n)\psi_{\mathbf{q},n}(\mathbf{X}). \tag{30}$$

Here $\mathbf{q}$ is the wave vector characterising the fluctuations in the initial spatially uniform system, and the subscript n labels the fluctuational modes of the chain with hookings. The desired expansion has the form[26]

$$Z^{N}_{m,\mathrm{cb}}(\mathbf{X},\mathbf{X}') = \sum_{\mathbf{q},n} \Lambda_m{}^N(\mathbf{q},n)\psi_{\mathbf{q},n}(\mathbf{X})\psi_{-\mathbf{q},n}(\mathbf{X}'). \tag{31}$$

Under the assumption that the largest eigenvalue $\Lambda_m(0,0)$ belongs to the discrete spectrum and is separated by a finite interval from the next eigenvalues in the sum (31), it is sufficient to confine ourselves to the single term with $\mathbf{q} = n = 0$. In the Appendix it is shown that these conditions are fulfilled for $N \gg N_{s\mu} = N_s^{(0)}\lambda_\mu$, $N_s^{(0)} = C^{-1/2} \gg 1$ (in the opposite case of a sufficiently short chain with $N \ll N_{s\mu}$, all the terms in the sum (31) are important and the sum factorizes into a product of contributions from each of the replicas). Thus, as already discussed in the Introduction, for $N \gg N_{s\mu}$ the chain is in the globular state. We shall seek the solution of Eq. (30) for a Gaussian chain (10) in the form

$$\psi_{00}(\mathbf{X}) = \exp \sum_{\mu} \Big[-\frac{A_\mu}{a^2} \sum_{k=1}^{m} (\mathbf{r}_\mu^{(0)} - \mathbf{r}_\mu^{(k)})^2 - \frac{B_\mu}{2a^2} \sum_{k,k'}^{m} (\mathbf{r}_\mu^{(k)} - \mathbf{r}_\mu^{(k')})^2 \Big]. \tag{32}$$

Substituting (32) and (27) into (30), we obtain

$$\begin{aligned} &A_\mu = Cf[C(\lambda_\mu^{-2}+m)], \quad f(x) = (1+x^{-1})^{1/2}-1, \\ &B_\mu = Cf[C\lambda_\mu^{-2}(1+m)](1+m)/m - Cf[C(\lambda_\mu^{-2}+m)]. \end{aligned} \tag{33}$$

For the quantity Λ_m (0,0), in first order in m, we find the expression

$$\begin{aligned} &\Lambda_m(0,0) = g^{(0)} g^m \exp\Big[-v_0^{(0)} - m v_0^{(0)} - \frac{m}{2} \sum_\mu \varkappa(\lambda_\mu) \Big], \\ &\varkappa(\lambda) = \frac{\lambda^2-1}{(1+\lambda^2/C)^{1/2}} - \ln \frac{(1+\lambda^2/C)^{1/2}+1}{(1+\lambda^2/C)^{1/2}-1}. \end{aligned} \tag{34}$$

The formulas (31) and (34), together with (21) and (29), completely determine, in the SCF approximation, the free energy of a chain with hookings. It is not difficult to convince oneself that under identical external conditions $T = T^{(0)}$, $V = V^{(0)}$, and $f^* = f^{*(0)}$, the pressures $\pi^{(k)} = -\partial F^{(k)}/\partial V^{(k)}$ also coincide in the initial and final systems.

We now discuss the role of statistical fluctuations of the order parameter. The average value of the density of the links of the system is determined by the variational derivative of the free energy with respect to the field $h^{(1)}$ (20):

$$\overline{\rho^{(1)}(\mathbf{x})} = -\frac{\delta \ln Z_{0,\mathrm{cb}}\{h+v_\tau\}}{\delta h^{(1)}(x)} = -N \frac{\delta \ln \Lambda_0}{\delta h^{(1)}(\mathbf{x})}.$$

The correlation function of the statistical density fluctuations in different configurations (replicas) is found analogously:

$$\frac{\overline{\rho^{(1)}(\mathbf{x})\rho^{(2)}(\mathbf{x}')}}{\overline{\rho^{(1)}(\mathbf{x})}\,\overline{\rho^{(2)}(\mathbf{x}')}} - 1 = \frac{1}{N} \frac{\delta^2 \ln \Lambda_0/\delta h^{(1)}(\mathbf{x})\,\delta h^{(2)}(\mathbf{x}')}{(\delta \ln \Lambda_0/\delta h^{(1)}(\mathbf{x}))(\delta \ln \Lambda_0/\delta h^{(2)}(\mathbf{x}'))} \sim \frac{1}{N}.$$

Thus, the density of the links of a strongly entangled chain is a self-averaging quantity, i.e., has a normal distribution with width $\sim N^{-1/2} \ll 1$. It is not difficult to show that the free-energy density is also a self-averaging quantity.

We now elucidate the physical meaning of the parameter C. According to (23), the maximum amplitude of fluctuations of the links of the chain is equal to $r_{\tau\mu} \approx a\lambda_\mu C^{-1/2}$. In the model of a quasinetwork of effective hookings (see the Introduction) it is of the order of the length of a segment between two hookings. Hence, for the parameter $N_{s\mu}$ for arbitrary anisotropic stretching of the network we obtain the expression $N_{s\mu} = N_s^{(0)}\lambda_\mu$, $N_s^{(0)} = C^{-1/2}$. Henceforth we shall confine ourselves to treating the most interesting case $N_s^{(0)} \gg 1$, to which corresponds $C \ll 1$. Using the solution (32), (33) obtained above, we obtain the mean-square extent of the fluctuations in the μth direction:

$$\xi_{\tau\mu} = \langle (\delta x_\mu^{(1)})^2 \rangle^{1/2} \approx a N_{s\mu}^{1/2},$$

which coincides with the formula (2). Thus, we have shown that for $\varepsilon_\mu = 1/N_{s\mu} \ll 1$ we have the hierarchy of scales $a \ll \xi_{\tau\mu} \ll r_{\tau\mu}$ that was discussed in the Introduction.

For the free energy of the chain under consideration of $\varepsilon_\mu \ll 1$ we find the expression ($\rho = \rho^{(0)}/\lambda_x\lambda_y\lambda_z$)

$$F(\lambda_\mu) = E\{\rho\} + \frac{NT}{2N_s^{(0)}}(\lambda_x+\lambda_y+\lambda_z+\lambda_x^{-1}+\lambda_y^{-1}+\lambda_z^{-1}). \tag{35}$$

It is not difficult to show that (35) is equivalent to the expression (1) obtained in the framework of the model of a quasinetwork of effective hookings. The swelling coefficient $\alpha = \lambda_\mu$ of the polymer in a given solvent is determined by minimizing the functional (35). As a rule, in the deformation of a polymer we can neglect the change of its volume. In this approximation, for the stress σ in the case of uniaxial stretching by a factor of λ ($\lambda_x = \alpha\lambda$, $\lambda_y = \lambda_z = \alpha\lambda^{-1/2}$) we find the expression

$$\sigma(\lambda) \equiv \frac{1}{V}\frac{\partial F}{\partial \lambda} = \frac{\rho T}{2N_s^{(0)}}\Big(\alpha + \frac{1}{\alpha\lambda^{1/2}}\Big)\Big(1 - \frac{1}{\lambda^{3/2}}\Big). \tag{36}$$

The modulus of elasticity of the polymer is equal to

$$E \equiv \frac{\partial\sigma(\lambda)}{\partial\lambda}\Big|_{\lambda=1} = \frac{3\rho T}{4N_s}(1+\alpha^2)$$

in agreement with the result $E \sim \rho T/N_e$ (Ref. 11) of classical theory.

The exact solution (32)–(34) that we have obtained makes it possible to convince oneself of the correctness of the assumptions made in its derivation. In determining the function $v_\tau(\mathbf{X})$ we confined ourselves to the quadratic terms in the expansion (23). We shall show that the discarded terms of higher order are indeed small. By making use of the expressions (32) and (33), we find the characteristic values of the coordinate difference $\mathbf{r}^{(k)} - \mathbf{r}^{(k')}$ in (23). In the case $C \ll \lambda_\mu^2$, for $k, k' \neq 0$, we have

$$\frac{C}{a^2}(r_\mu^{(0)} - r_\mu^{(k)})^2 \sim \frac{C^{1/2}}{\lambda_\mu}, \frac{C}{a^2}(r_\mu^{(k)} - r_\mu^{(k')})^2 \sim \frac{C^{1/2}}{\lambda_\mu(1+\lambda_\mu^2)} < \frac{C^{1/2}}{\lambda_\mu}. \tag{37}$$

Thus, for $N_{s\mu} \gg 1$ both the field (23) itself and the next terms of its expansion are small in the parameter $\varepsilon_\mu = 1/N_{s\mu}$.

We now write out the most general form of the field $v_\tau(\mathbf{X})$ with allowance for the anisotropy of the interaction along and at right angles to the chain:

$$v_\tau(\mathbf{X}_i) = \sum_{k,k'}^{1+m} \left\{ \frac{C'}{a^2} \sum_\mu (r_{i\mu}^{(k)} - r_{i\mu}^{(k')})^2 - \frac{C''}{a^2} \left[\sum_\mu (r_{i\mu}^{(k)} - r_{i\mu}^{(k')}) n_{i\mu}^{(k)} \right]^2 \right\}. \tag{38}$$

Here the unit vector $n_{i\mu}^{(k)}$ characterizes the direction of the bond between the links i and $i+1$ in the kth replica for $C'' = C'$ the field (38) depends only on the components transverse to $\mathbf{n}^{(k)}$). When (38) is substituted into (30) we must take account of the explicit form of this vector:

$$n_\mu^{(k)} = (x_\mu^{(k)} - y_\mu^{(k)}) / |\mathbf{x}^{(k)} - \mathbf{y}^{(k)}|.$$

It is not difficult to verify that for $N_{s\mu} \gg 1$, to within corrections of order ε_μ, the solution of Eq. (30) has the form (32), (33) with $C = C' - C''/3$. In the following we shall disregard these small corrections, assuming the field v_τ to be isotropic.

4. TOPOLOGICAL INTERACTIONS IN POLYMER SOLUTIONS AND GELS. FIELD THEORY

We now study the properties of a polymer consisting of a large number of sufficiently long chains, with $\overline{N} \gg 1$. Under this condition we can neglect the change of the field v in (25) near the ends of these chains. In such a system, we must not only take into account the mutual impenetrability of the chains but also fix their length distribution and the order of the cross links to be the same as at the time of preparation in the initial system.

We shall consider two systems, the first being a melt of chains. Their hookings are described by the parameter $C_e = (N_e^{(0)})^{-2}$ in (23); see the Introduction. The second system is a polymer network obtained by joining chains through their end groups. The free energy of such a gel network is equal to

$$F_\Gamma\{h\} = -T \sum_{\Gamma_\tau} P_{\Gamma_\tau}^{(0)} \ln Z_{\Gamma_\tau}\{h\}, \tag{39}$$

where Γ_τ are topologically inequivalent configuration of the gel. Their probabilities $P_{\Gamma_\tau}^{(0)}$ are determined by the expressions (6) and (9), in which we must take $\Gamma\{\mathbf{x}_i\}$ as the argument of the δ_τ-function (7). To calculate (39) it is convenient to introduce the generating functional of the free energies F_C of all the $n_C^{(0)}$ molecules C washed out (see the Introduction and Ref. 5), including the gel, for which $n_\Gamma^{(0)} = 1$:

$$F\{s|h\} \equiv \sum_C n_C^{(0)} s^l F_C\{h\} = -T \frac{d\Psi_m}{dm}\bigg|_{m=0},$$

$$\Psi_m\{s|h\} \equiv [Z^{(0)}]^{-1} \sum_{C_\tau} n_{C_\tau}^{(0)} s^l Z_{C_\tau}^{(0)} Z_{C_\tau}{}^m\{h\}, \tag{40}$$

where 1 is the number of links of the molecule C. Neglecting the effects of the hookings in the washed-out molecules of the gel, we must set for these molecules $C_\tau = C$ and $Z_{G_\tau}^{(0)} = Z^{(0)}$. In the thermodynamic limit the free energy (39) of the gel is obtained from (40) by taking the limit

$$F_\Gamma\{h\} = F\{1|h\} - \lim_{s\to 1,\, s<1} F\{s|h\}. \tag{41}$$

The subsequent transformations of the expression (40) are carried out in the same way as in Ref. 5, in which it is shown that the functional Ψ_m has the meaning of the generating functional of the correlation functions of individual molecules placed in a space of dimensionality $3(1+m)$. The only difference from Ref. 5 for $m \neq 0$ is the presence of the additional topological potential $U_\tau(G\{\mathbf{X}_i\})$ acting only on the coordinates $\mathbf{X}_i$ of the links of the polymer-network skeleton that is obtained by cutting out of the gel the chains that are attached to it by only one end. The change in the position of such chains over times long in comparison with τ_t does not change the topological invariants that parametrize the regions τ of the configuration space. Therefore, topological interaction of their links is absent. In the mean-field approximation the steric interaction of the links of the skeleton is described by the potential $v_\delta(\mathbf{X})$, the expansion of which in a Taylor series has the form (23) with $C = C_s = (N_s^{(0)})^{-2}$.

To calculate the partition function $Z_{m,\text{cb}}$ from (12) and (16), and the generating functional $\Psi_{m,\text{cb}}$ from (40) for the corresponding systems, we make use of their representation in the form of a functional integral over a field $\varphi(\mathbf{X})$. In the SCF approximation $\overline{\varphi}(\mathbf{X})$ should be found by minimizing the effective action $S_m\{\overline{\varphi}\}$. Since it is difficult to find an analytic solution of the equations that we have obtained for $\overline{\varphi}(\mathbf{X})$, we make use of the variational approach, assuming the coordinate dependence of $\overline{\varphi}(\mathbf{X})$ to be Gaussian, corresponding to the Gaussian character of the fluctuations of links of the chains. We note that in the limit of strong topological interactions (32) this approximation becomes exact.

A. Solution of linear chains

It is not difficult to show, in the same way as in Refs. 1–4, that the partition function $Z_{m,\text{cb}}$ of this system can be "packed" as a Gaussian functional integral with effective action

$$S_m\{\varphi\} = \int \frac{d\mathbf{X}}{g^{(0)} g^m} \left[\frac{\tau_m}{2} \varphi^2 + v_\tau(\mathbf{X}) \frac{\varphi^2}{2} + \frac{a^2}{2} (\nabla \varphi)^2 - H\varphi \right]. \tag{42}$$

In deriving (42) we have used the smallness of the field v_τ (37). The quantity H in (42) defines the activity of the ends of the chains, and we have set

$$\tau_m = 1 - \frac{g^{(0)} g^m}{\Lambda_2{}^3} \exp\left[- \frac{\mu^{*(0)}}{T^{(0)}} \right] \ll 1. \tag{43}$$

In the SCF approximation the partition function $Z_{m,\text{cb}}$ in

(16) and the density $\rho(\mathbf{X})$ (17) in the replica space are given by the expressions

$$\ln Z_{m,\mathrm{cb}} = -S_m\{\overline{\varphi}\}, \quad \rho(\mathbf{X}) = \overline{\varphi}^2(\mathbf{X})/2g^{(0)}g^m, \tag{44}$$

where $\overline{\varphi}(\mathbf{X})$ is found by minimizing the action (42). In the Gaussian approximation, $\overline{\varphi}(\mathbf{X}) = \overline{\varphi}\psi_{00}(\mathbf{X})$, where the function ψ_{00} is defined in (32), and the parameters $\overline{\varphi}$, A_μ, and B_μ are found by minimizing the action (42):

$$\overline{\varphi} = H\overline{N} = H/\tau_0, \quad A_\mu = C_e^{1/2}\lambda_\mu[(1+z_\mu^2)^{1/2} - z_\mu], \quad z_\mu \equiv \lambda_\mu/2\overline{N}C_e^{1/2},$$

$$B_\mu = \frac{A_\mu}{2}[1+\lambda_\mu^2 + (1-\lambda_\mu^2)z_\mu/(1+z_\mu^2)^{1/2}]. \tag{45}$$

From (44) and (18), for the density of links we find the expression $\rho = \rho^{(0)}/\lambda_x\lambda_y\lambda_z$ with $\rho^{(0)} = \overline{\varphi}^2/2g^{(0)}$, while from (44) and (21), (23) we obtain for the free energy of the system

$$F(\lambda_\mu) = E\{\rho\} + \frac{N}{2}\sum_\mu \left[A_\mu(1+\lambda_\mu^{-2}) + \frac{1}{\overline{N}}\ln(A_\mu\lambda_\mu^2) \right]. \tag{46}$$

For $N_e \ll \overline{N}(z_\mu \ll 1)$ the expression (46) obtained goes over into (35), since such a polymer can be regarded as one gigantic chain of total length $N = \Pi\overline{N}$. In the opposite case $\overline{N} \lesssim N_e$ ($z_\mu \gg 1$) the equation of state that follows from (46) is the same as in the absence of hookings. Thus, the Gaussian approximation makes it possible to give a correct description of hooked chains over times short in comparison with τ_t, for arbitrary relative magnitudes of the parameters $\overline{N}$ and N_e.

B. Polymer network of a gel

We shall make use of the concept, obtained in Refs. 4 and 5, of the generating functional (40) for a system of chemical bonds (see (16) in the form of a functional integral over fields $\varphi_0(\mathbf{x}^{(0)})$, $\varphi_i(\mathbf{X})$ ($i = 1, ..., n$) with effective action

$$S_{nm}\{s|\varphi_i\} = S_0\{1|\varphi_0\} + \sum_{i=1}^{n} S_m\{s|\varphi_i\} + S_\tau\{\varphi_i\},$$

$$S_m\{s|\varphi\} = \int \frac{d\mathbf{X}}{g^{(0)}g^m}\left\{\frac{\tau_m}{2}\varphi^2 + \frac{a^2}{2}\left[(\nabla^{(0)}\varphi)^2 + \frac{1}{\alpha_T^2}\sum_{k=1}^{m}(\nabla^{(k)}\varphi)^2\right] - \frac{sw}{f!}(1+\varphi)^f\right\}, \quad w = \frac{z_f g^{(0)}g^m}{\Lambda_f^3}. \tag{47}$$

Here $\alpha_T = a(T^{(0)})/a(T)$ is a factor describing the thermal expansion of the chains and z_f is the activity of the f-functional links through which the joining occurs. The functional S_τ describes the contribution of the topological interactions:

$$S_\tau\{\varphi_i\} = \int d\mathbf{X}[v_e(\mathbf{X})\rho(\mathbf{X}) + v_s(\mathbf{X})\rho_s(\mathbf{X})],$$

$$\rho(\mathbf{X}) = \sum_{i=1}^{n}\varphi_i^2(\mathbf{X})/2g^{(0)}g^m, \tag{48}$$

$$\rho_s(\mathbf{X}) = \left(\sum_{i=1}^{n}\varphi_i(\mathbf{X})\right)^2 \Big/ 2g^{(0)}g^m.$$

The fields v_e and v_s describing, respectively, the hookings of all the chains and the effective hookings of the chains of the gel skeleton have been determined earlier. The function $\rho(\mathbf{X})$ is equal to the density of links of the gel network in the replica space, while $\rho_s(\mathbf{X})$ is the density of links of the skeleton of this network. These functions are related to the corresponding densities in the initial and final systems by the relation (18). It is not difficult to show that the interaction v_e makes a contribution both to the gel fraction and to the sol fraction, describing the effects of hookings of their chains. Henceforth we shall neglect such effects ($C_e = 0$), confining ourselves to times that are long in comparison with the maximum relaxation time: $t \gg \tau_t$. The field $v_s(\mathbf{X})$ makes a contribution only to the gel fraction, and describes the effect of the steric interaction of the chains of the gel skeleton. The assertions advanced above are a consequence of the following formulas, obtained in Refs. 4 and 5:

$$\Psi_m^{5}\{s|h\} = -\left.\frac{dS_{nm}\{s|\varphi_i^{(1)}\}}{dn}\right|_{n=0}$$

$$\Psi_m^{g}\{s|h\} = \exp[-S_{0m}\{s|\varphi_i^{(1)}\} + S_{0m}\{s|\varphi_i^{(0)}\}], \tag{49}$$

which determine in the SCF approximation the contributions of the sol fraction and gel fraction to the functional Ψ_m (40). The fields $\varphi_i^{(j)}$ in (49) are found by minimizing the action S_{nm} (47). The index $j = 0$ corresponds to a symmetric (with respect to the replicas) extremal value $\varphi_i^{(j)}$, while the indices $j = 1, ..., n$ correspond to a nonsymmetric extremal value. In the Gaussian approximation for $i \neq 0$,

$$\varphi_0^{(j)}(\mathbf{x}^{(0)}) = \overline{\varphi}_0^{(j)}, \quad \varphi_i^{(j)}(\mathbf{X}) = \overline{\varphi}_i^{(j)}\psi_{00}(\mathbf{X}),$$

where ψ_{00} is defined in (32). Minimizing (47) with respect to $\overline{\varphi}_i^{(j)}$ in the limit $n = m = 0$ gives

$$\overline{\varphi}_j^{(j)} = p/(1-p), \quad \overline{\varphi}_{i\neq j}^{(j)} = pu/(1-p), \quad u = (1-p+pu)^{f-1}, \tag{50}$$

where $0 < u < 1$ for $p > p_c = (f-1)^{-1}$. The parameters A_μ and B_μ are determined by the expressions (45), in which we must set

$$C = (1-u)C_s/(1+u), \quad C_s = (N_s^{(0)})^{-2},$$
$$z_\mu = -\lambda_\mu R_g/2N_g C^{1/2}. \tag{51}$$

The main difference between (51) and (45) is the change of sign of z_μ, which strongly alters the result in the limit of weak entanglement of the chains. Whereas for $z_\mu \to \infty$ the relations (45) describe a system of noninteracting chains, in gels for $z_\mu \to -\infty$ the expression (51) leads to the classical theory of high elasticity. In (51) the quantities N_g and R_g are the numbers of links and independent rings in the gel, and are related to the total number N of links in the initial system by the relations

$$N_g = N(1-u)(1+pu),$$

$$R_g = N(1-u)[pf(1+u)/2-1-pu]/\overline{N}.$$

Near the gel-formation threshold, at $\tau = p/p_c - 1 \ll 1$, we find $\rho \sim \tau$, $\rho_s \sim \tau^2$, and $R_g \sim \tau^3$.

In the limit of strong entanglement of the chains the gradient terms $(\nabla\varphi)^2$ and field terms $v_s\varphi^2$ in (47) are of the same order of magnitude $\sim\varepsilon \ll 1$. From this condition it is not difficult to obtain the estimate (37) for the applicability of the expansion (23) of v_s. The anisotropy of the field v_s (38) along and at right angles to the direction of the chain makes a contribution only to small cross terms of the form $v_s(\nabla\varphi)^2 \sim \varepsilon(\nabla\varphi)^2$, which we did not even begin to write out in (47). With decrease of the entanglement of the chains the contribution of both effects is reduced still further. For the free energy of the network for $\varepsilon \ll 1$ there follows from (49), (40), (41), and (21) the expression

$$F(\lambda_\mu) = E\{\rho\} + \frac{R_g T}{2}\,\Phi(\alpha_T\lambda_x) + \Phi(\alpha_T\lambda_y) + \Phi(\alpha_T\lambda_z)\,].$$

$$\Phi(\lambda) = \frac{1+\lambda^2}{2}\left\{1+\left[1+\left(\frac{2\lambda_s}{\lambda}\right)^2\right]^{1/2}\right\}$$
$$-\ln\left\{1+\left[1+\left(\frac{2\lambda_s}{\lambda}\right)^2\right]^{1/2}\right\}. \qquad (52)$$

Here the parameter $\lambda_s = N_g C^{1/2}/R_g \gtrsim 1$ characterizes the magnitude of the steric interactions. It depends essentially on the conditions of preparation of the polymer network, and increases with increase of the entanglement of its chains in the initial system. In the case $\lambda_s \gtrsim \lambda_\mu$, from (52) we find

$$\Phi(\lambda_\mu) = \lambda_s(\lambda_\mu + \lambda_\mu^{-1}) + \frac{\lambda_\mu^2+1}{2} + \ln\frac{\lambda_\mu}{\lambda_s}. \qquad (53)$$

According to (53), the deformation of the network is composed of an affine and a nonaffine component. The affine deformation is described by the last two terms in (53). The first of these ($\sim\lambda_\mu^2$) describes the elastic response of the network under affine stretching of the points at which its chains are joined. The logarithmic term in (53) determines the entropy of the entanglement of the chains: For a given position of the joining points the chains can be interwoven in different ways. For $\lambda_s \gg \lambda_\mu$ both these terms are small in comparison with the first term, which describes the nonaffine deformation of the lattice. This term, analogous to that obtained in (35), arises from the partial disentanglement of the chains of the network as it is stretched. Complete disentanglement in a given direction $\mu = x, y, z$ occurs when $\lambda_\mu \sim \lambda_s$, after which the chains remain entangled only as a result of true topological hookings. For $\lambda_s \lesssim \lambda_\mu$, from (52) we find

$$\Phi(\lambda_\mu) = \lambda_\mu^2 + 1 + 2\lambda_s^2, \qquad (54)$$

and the free energy of the gel is determined by the classical-theory expression with $N^{\text{eff}} = R_g$; see (3).

We shall compare the result (53) with the phenomenological formulas that describe the experimental data with great accuracy. As shown in the work of Bartenev and Khazanovich,[29] uniaxial and biaxial stretchings of polymer networks are well described by formulas that can be obtained from (52) with the choice

$$\Phi(\lambda_\mu) = E_1\lambda_\mu + E_2\lambda_\mu^2. \qquad (55)$$

When this is compared with (53) we must take into account that the constant terms in (53) are unimportant and the logarithmic term does not make a contribution to the stress σ when the deformation of the gel is not accompanied by change of its volume. When this is taken into account for $\alpha^2\lambda \gg 1$ (53) goes over into (55) (α is the swelling coefficient of the gel, characterizing the change of its dimensions in comparison with the dimensions in the initial system). Priss[28] proposed a formula that follows from (52) with

$$\Phi(\lambda_\mu) = C''\lambda_\mu^{-1} + C'\lambda_\mu^2. \qquad (56)$$

It gives a correct description of a compressed gel and a sufficiently good description of the experimental data on the stretching of a compressed gel. It is not difficult to see that our result (53) is also in excellent agreement with the formula (56). Thus, the expression (52) essentially takes into account both the elasticity mechanisms considered in Refs. 28 and 29 and gives a correct description of highly elastic polymer-network deformations that are small in comparison with the maximum values (500–1000%).

The equilibrium swelling coefficient $\alpha = \lambda_\mu$ of a gel is determined by minimizing its free energy (52). In uniaxial stretching (compression) of such a gel, not accompanied by change of volume, the quantities $\lambda_x = \alpha\lambda$ and $\lambda_y = \lambda_z = \alpha\lambda^{-1/2}$. Differentiating (52) with respect to λ, we find

$$\sigma = \frac{R_\Gamma T\alpha_T}{2V^{(0)}\alpha^2}\left[\Phi'(\alpha_T\alpha\lambda) - \frac{1}{\lambda^{3/2}}\Phi'\left(\frac{\alpha_T\alpha}{\lambda^{1/2}}\right)\right]. \qquad (57)$$

For $\lambda_s \ll \alpha$ this expression goes over into the classical-theory result (3), with $N^{\text{eff}} = R_g$. In the case $\lambda \gtrsim \lambda_s/\alpha$ the chains of the gel are completely disentangled in the direction of the axis of stretching, but remain entangled in the perpendicular directions. Disentanglement in these directions occurs only under strong compression ($\lambda \lesssim \alpha^2/\lambda_s$).

The characteristic form of the dependence (57) is shown in Fig. 3 in the Mooney-Rivlin coordinates (4). For small $\lambda^{-1} < 1$, in accordance with the formula (4) the function $\xi(\lambda^{-1})$ is linear and decreases slowly with increase of $\lambda^{-1} \gtrsim 1$. With increase of α the steepness of the linear part at $\lambda^{-1} < 1$ decreases, and for sufficiently strong swelling α the classical theory (3) becomes applicable. The region of applicability of the classical theory increases with decrease of λ_s. For sufficiently small $\lambda_s \lesssim 5$ the function $\xi(\lambda^{-1})$ does not decrease with increase of $\lambda^{-1} > 1$, but remains constant or increases slowly. The distinctive features of the behavior of $\xi(\lambda^{-1})$ that are considered here are in agreement with the

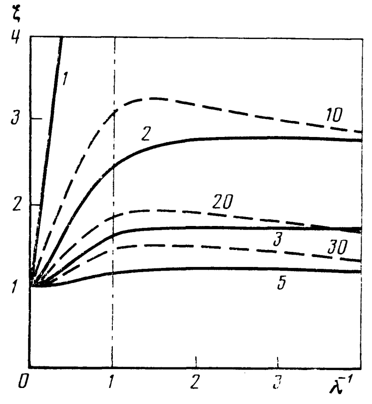

FIG. 3. The theoretical deformation dependence (57) of a polymer network in the Mooney-Rivlin rectifying coordinates $\xi(\lambda^{-1}) = \sigma/\sigma_{\text{cl}}$ for the parameter values $\alpha_T = 1$ and $\lambda_s = 10$ (the solid curves) and $\lambda_s = 100$ (the dashed curves). The numbers denote the corresponding values of the parameter α.

experimental data of Ref. 6. We emphasize that the quantity α is the swelling coefficient relative to the situation in the conditions of synthesis, and not the the dry state of the network, as is usually assumed in experiments.

5. CONCLUSION

Thus, we have shown that in the framework of the mean-field theory (16) the free energy of a polymer with a fixed topological structure and entangled nonintersecting chains has the form (21), (29), and we have calculated the entropy term (23) in the leading approximation in the small parameter $\varepsilon = 1/N_s \ll 1$. In the case of weakly entangled chains (see Fig. 2a), the results obtained reproduce the results of the classical theory of high elasticity.[17,18] In the limit of strongly entangled chains (see Fig. 2b) we have shown that the entropy of the gel is determined by the elasticity of the quasinetwork of effective hookings (Figs. 1 and 2b).

The method of replicas in the formalism of functional integration over paths (rather than over fields[5]) was first used for the description of polymer networks in Refs. 30 and 31. In these papers the network that is obtained as a result of the joining of a phantom chain at the points of its self-intersection was considered. In Ref. 31, in fact, a model of a quasinetwork was proposed for the description of topological interactions. This quasinetwork consisted of mobile cross links that could fluctuate along the chain, within certain limits, about their stationary average positions. In the calculations, both the fixed cross links of the initial network and the mobile cross links of the quasinetwork were simulated by a quadratic external field acting in the replica space on the links of the phantom chain. Unfortunately, in this model no account was taken of the nonaffine character of the stretching of the quasinetwork, which arises on account of the partial disentanglement of the polymer chains (see the Introduction). But since it is precisely this effect that distinguishes a quasinetwork from an ordinary network, the authors of Ref. 31 did not succeed in obtaining even the Mooney-Rivlin dependence (4) for values of λ not too close to unity.

The method of introducing an external field to describe the topological interactions has been used in a large number of papers. First we shall consider those in which the topological constraints are modeled by impenetrable walls or by rods placed in the polymer. In such models the fluctuation length ξ_τ coincides with the range r_τ of the field, and there is no small parameter: $\varepsilon \approx (\xi_\tau / r_\tau) \sim 1$. In reality, the fluctuating chain under consideration is in no way different from the chains (simulated by obstacles) that surround it, and their fluctuations wash out the θ-functions interaction. Therefore, the modeling of topological interactions by sharp constraints is too crude to display the presence of the small parameter $\varepsilon = 1/N_s \ll 1$.

We shall discuss these models in more detail. As shown in Ref. 32, in the model of a "chain in a lattice of obstacles" a closed chain of given length N has, on a scale large in comparison with ξ_τ, a fractal dimensionality $D = 4$ greater than the dimensionality of the space in which it is situated, and its free energy is not additive in N. In the opinion of the author, this model, which predicts such a superglobular state, exaggerates the compressive effect of the topological interactions. The neighboring chains, which in the model are understood as obstacles, are in reality not "nailed down," but adjust themselves in such a way as to form an effective field (26) that globularizes the chain on a scale larger than ξ_τ (so that $F \sim N$ and $D = 3$).

In the "chain in a tube" model[11] one assumes the presence of strong anisotropy singling out the direction of the tube. We have shown (see (38)) that, as a result of the "smearing out" of the walls of the tube by thermodynamic fluctuations of the chains composing it, such anisotropy makes a contribution that is small in the parameter $\varepsilon \ll 1$, so that the idea of a tube loses its meaning. We note that over short times, when such fluctuations can be neglected, both models give a good description of the dynamics of the chain.[33,11,13]

Example of continuous analogs of the "chain in a tube" model are the various modifications of the "channel" model of Refs. 6 and 7, in which the topological interactions are modeled by a harmonic potential binding a chain to a channel. We note that in such models, in fact, one calculates not the entropy of the system but the free energy F of the system in a given external field. To calculate the entropy of the system with internal constraints we must subject from F the energy of the interaction with this field (see the discussion after (28)), which is of the same order of magnitude as the entropy itself. This subtraction can change not only the magnitude of the entropy but also its functional dependence on λ_μ.

In conclusion we shall consider possible generalizations of the theory proposed. To take account of the finite extensibility of the chains we must replace the Gaussian bond function $g(\mathbf{x})$ (10) by a more realistic function, e.g., one with free articulation: $g(\mathbf{x}) = g\delta(|\mathbf{x}| - a)$. The results that are then obtained for strong stretchings $\lambda_\mu \sim \lambda_{\max} \sim \overline{N}^{-1/2}$ in the case $\lambda_s \lesssim \lambda_{\max}/\alpha$ are in agreement with the theory of Isihara *et al.*[34]

We now discuss the role of fluctuation effects. The mean-field theory (16) developed in this paper is based on the assumption that the fluctuations of the density $\rho(\mathbf{X})$ in the replica space are small. The longitudinal fluctuations of $\rho(\mathbf{X})$ in each of the replicas are due to the potential interactions (the excluded-volume effect). The principal distinguishing feature of the topological interactions is the fact that they tend to suppress transverse fluctuations of the density $\rho(\mathbf{X})$, thereby carrying the chain into a statistically certain[26] globular state. This is why the mean-field theory gives an adequate description of the system in the case of weak excluded-volume effects. As is well-known,[11] the potential interaction of the links of the chains of a network (quasinetwork) is also well described in the framework of the Flory (SCF) approximation that we have used. In the swollen state of networks in the scaling region topological interactions are unimportant. The replica formalism proposed by us makes it possible to take exact account not only of excluded-volume effects but also of the topological structure of networks. As shown in Refs. 11 and 5, such a gel can be described in the framework of the concept of blobs, the internal structure of which depends in an essential way on the magnitude of the conversion p of the polymer network.[35,5]

The author expresses his gratitude to A. R. Khokhlov, F. F. Ternovskiĭ, and also the participants in the seminar on the theory of polymers at Moscow State University for useful discussions on the results of this work.

APPENDIX

Calculation of the eigenvalues of Eq. (30)

For a nonzero wave vector ($\mathbf{q}\neq 0$) a replica-symmetric solution of (30) is easily found:

$$\psi_{\mathbf{q},0}(\mathbf{X})=\psi_{0,0}(\mathbf{X})\exp\left[i\sum_{\mu}q_{\mu}\left(x_{\mu}^{(0)}+\lambda_{\mu}\sum_{k=1}^{m}x_{\mu}^{(k)}\right)\right]. \quad (\text{A.1})$$

Here ψ_{00} is defined in (32) and the corresponding eigenvalue is equal to

$$\Lambda_m(\mathbf{q},0)=\Lambda_m(0,0)\exp\left[-\frac{a^2q^2}{2}\left(1+m\sum_{\mu}\lambda_{\mu}^2\right)\right]. \quad (\text{A.2})$$

It is also not difficult to find the following eigenvalues:

$$\Lambda_m(\mathbf{q},\mathbf{n})=\Lambda_m(\mathbf{q},0)\Big/\prod_{\mu}[\Delta(\lambda_{\mu})]^{n_{\mu}}, \qquad n_{\mu}=0,1,2,\ldots,$$
$$\Delta(\lambda)=1+1/f[C\lambda^{-2}(1+m)], \quad (\text{A.3})$$

to which correspond degenerate replica-aymmetric eigenfunctions. According to (A.3), the eigenvalues with $n_{\mu}=1$ closest to the largest eigenvalue ($n=0$) are separated from it by a finite interval and, for sufficiently long chains ($N\gg 1/\ln\Delta(\lambda_{\mu})\simeq N_{s\mu}$), may be disregarded. If in the initial system the polymer had dimensions $L_{\mu}^{(0)}$, the wave vector $\mathbf{q}$ in (A.1) takes a discrete series of values:

$$q_{\mu}=\pi k_{\mu}/L_{\mu}^{(0)},\quad k_{\mu}=0,\ \pm 1,\ \pm 2,\ldots. \quad (\text{A.4})$$

According to (A.2), for $N\gg(L^{(0)}/a)^{1/2}$ the eigenvalues with $\mathbf{q}\neq 0$ are unimportant. Thus, when both inequalities on N are fulfilled, the free energy of the chain is completely determined by the expression (35). We note that the inequality $N\gg(L^{(0)}/a)^{1/2}$ implies that the size of the polymer in the initial system is small in comparison with the radius $\sim aN^{1/2}$ of a Gaussian coil. The density fluctuations are correspondingly small, and this ensures that the mean-field theory is applicable for the description of the initial system.

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Translated by P. J. Shepherd