Theory of polymers with a frozen structure

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A field theory describing polymers with a frozen topological structure is constructed. Branched polymers with a frozen molecular-structure distribution are studied in detail. It is shown that, because of the strong polydispersity, a semidilute solution of such polymers cannot be described by means of the concept of blobs. It is also shown that the swelling of a molecule with a tree-type structure in a good solvent occurs in a nonaffine manner, and the dependence of its swelling coefficient on the spatial scale is calculated. The dependence of the swelling coefficient of a cyclic molecule on the quality of the solvent is obtained. The swelling of an infinite polymer gel network with a fixed topological structure in a good solvent is considered separately. The thermodynamic and correlation functions of the gel network are calculated, and it is shown that in the scaling region such a network can be described in the framework of the concept of blobs, within which there exist correlations characteristic of isolated branched molecules. It is also shown that the equilibrium density of the swollen gel is determined by a condition on the threshold for overlap of such molecules. The results obtained make it possible to use the results of numerous papers devoted to the investigation of "ordinary" blobs. Other problems that can be considered in the framework of the proposed field theory are also mentioned.

1. INTRODUCTION

The use of field-theoretical methods[1-6] has made possible a complete theoretical description of polymer systems in equilibrium with respect to reactions involving the formation and breaking of chemical bonds. An important point is that the polymer systems used in practice can be equilibrium systems only during the process of their synthesis, and by the end of this process the chemical bonds "freeze." The conditions of exploitation of polymers usually differ appreciably from the conditions of their preparation. By varying the temperature and the type of solvent it is possible to change the equation of state and the correlation length of the system, but the molecular-structural distribution (MSD) $\{n_C\}$ remains unchanged, having been formed in the stage of synthesis (n_C is the number of molecules of a given topology C).

In the description of a system with a frozen MSD it is convenient to associate with each polymer configuration a graph G, each of the connected components of which corresponds to one of the molecules of the system (see Fig. 1a). The probability $P_G^{(0)}$ of configuration G is determined by the parameters of the initial system in which the polymers were obtained, while the free energy F_G of configuration G is determined by the parameters of the final system in the conditions of its exploitation. The thermodynamic characteristics of this final system with a frozen MSD are completely determined by the average value of the free energy of the system in a specified external field $h(\mathbf{x})$:

$$F\{h\}=\sum_G P_G{}^{(0)}F_G\{h\}. \tag{1}$$

For a more detailed study of the behavior of polymer molecules one usually uses a dilute solution in which the interaction of different isolated molecules can be neglected. The correlation functions of the molecules are found by differentiating the free energy $F_C\{h\}$ of macromolecule C with respect to the field h, and determine such characteristics as the size and radius of gyration of this molecule. To calculate these correlation functions it is convenient to introduce the generating functional

$$F\{s\,|\,h\}=\sum_C n_C s^l F_C\{h\}, \tag{2}$$

where l is the number of monomers of molecule C.

In the description of branched polymers the functional F (2) contains information both about the molecules of finite size (the sol) and about the infinite macromolecule (the gel). Such a giant polymer network is obtained by equilibrium polycondensation of monomers in the initial system. After the fixing of its topological structure and the subsequent wash-out of the sol molecules it is placed in a low-molecular-weight solvent, in which it swells. The topological structure of the network remains unchanged in this process, having been formed in the process of preparation of the network. In the thermodynamic limit the free energy of such a network is equal to

$$F^{(g)}\{h\}=F\{1\,|\,h\}-\lim_{s<1,\,s\to 1}F\{s\,|\,h\}. \tag{3}$$

The first term in the right-hand side of (3) is equal to the sum of the contributions of all the molecules, while the second is equal to the sum of the contributions of only the molecules of finite size.

In this paper we propose a method of calculating the functionals (1) and (2) that determine the characteristics of the finite molecules and the infinite molecule with a frozen topological structure. We shall consider a system consisting of the initial system and m replicas of the final system. Since all these subsystems have the same MSD, the configuration space of the system under consideration can be depicted by the graph **G**, which is obtained by "thickening" of the vertices and segments of the graph G (see Fig. 1b). With a thick vertex of this graph we associate the set of coordinates $\mathbf{X}_i=(\mathbf{x}_i^{(0)},\mathbf{x}_i^{(1)},\dots,\mathbf{x}_i^{(m)})$ of monomer i, while with a thick segment we associate the set of bonds between the monomers i and j in the initial system and each of the replicas.

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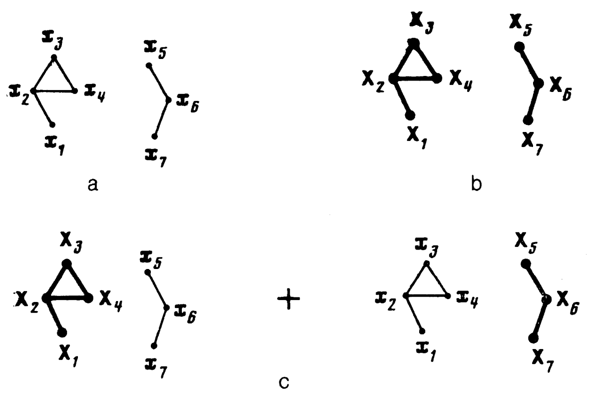

FIG. 1. Graphs associated with a configuration G containing two polymer molecules; their vertices correspond to monomers, and their segments correspond to chemical bonds. a) The graph G for the initial system; b) the graph G for the system consisting of the initial system and replicas of the final system with a frozen MSD; c) graphs G for a system consisting of the initial system and replicas of the final system of a dilute solution of polymers.

It is found that the thermodynamic potential Ω_m of this system in the presence of equilibrium with respect to the formation and breaking of thickened bonds determines the free energy (1) of the system with a frozen MSD:

$$F\{h\}=\partial\Omega_m\{h\}/\partial m|_{m=0}. \tag{4}$$

The functional (2) is calculated analogously. In the equilibrium system the generating functional Ψ_0 of the correlation functions of the individual molecules C is equal, by definition, to the sum of their contributions with the factor s^l (Refs. 5, 6). We shall show that to determine the functional (2) it is sufficient to thicken the connected subgraphs C corresponding to the molecules over which this summation is performed (see Fig. 1c):

$$F\{s|h\}=-T\partial\Psi_m\{s|h\}/\partial m|_{m=0}. \tag{5}$$

The relations (4) and (5) make it possible to reduce the problem of the description of a system with a frozen MSD to the analogous problem for the equilibrium system. Methods of solution of the latter were developed in Refs. 4–8, and we shall make use of them in this article. The results obtained for weakly fluctuating systems coincide with already-known results. For concentrated solutions (melts) they were found by perturbation-theory methods,[4,6] while for an infinite gel network they were found by field-theoretical methods.[9,6] In this article we shall concentrate attention on the description of strongly fluctuating systems, for which these methods are inapplicable.

A central feature of the description of such systems with molecules with a frozen topological structure is the swelling critical exponent ζ introduced below. Whereas in weakly fluctuating systems the swelling of polymers occurs by uniform (affine) dilation, in strongly fluctuating systems the swelling depends on the observation scale R. The exponent ζ determines the dependence on R of the degree of swelling of polymers:

$$\Lambda\equiv R/R^{(0)}\sim(R^{(0)})^{\zeta}\sim R^{\zeta'},\quad \zeta'=\zeta/(1+\zeta).$$

Here $R^{(0)}$ and R are the sizes of the regions occupied by the same particles in the initial and final systems.

The relations (4) and (5) make it possible to apply the field-theoretical renormalization-group (RG) method to the description of strongly fluctuating polymer systems. The solution of the RG equations, which are obtained in this article, determines the exponent ζ. In the one-loop approximation the latter coincides exactly with the result found by us in the framework of the Flory approximation.[10] Besides the characteristics of the sol molecules, the exponent ζ also determines the characteristics of the giant gel macromolecule in the fluctuation region.

We shall show that such a strongly fluctuating polymer network can be described by means of the blob concept originally introduced by de Gennes[1] to describe a semidilute solution of polymer chains. Inside each such blob of a size equal to the correlation length $\xi\sim l_B^{\nu}$ there exist correlations characteristic for a single branched molecule with $l_B\sim\rho^{-1/(d\nu-1)}$ monomers. Here ρ is the density of the monomers of the gel and d is the dimensionality of space. On scales large in comparison with ξ the polymer network is a melt of blobs. We note that the concept of blobs, together with ordinary scaling, presupposes a high degree of universality. In contrast to a gel in chemical equilibrium with sol molecules, the basic characteristics of the polymer network under consideration are described by a single exponent ν. It is equal to $\nu_t=(1+\zeta)/4$ for a gel obtained in a melt.

The material of the article can be divided into two parts. In the first of these (Sec. 2) we give a general derivation of field theories for the description of polymers with a frozen structure. In the Conclusion we discuss some of their generalizations. In the second part (Secs. 3–5) we use the example of very simple models of branched polymers to illustrate the basic physical ideas. The possibility of realization of these models is discussed in the Conclusion.

2. THE METHOD OF REPLICAS: A FIELD THEORY FOR POLYMERS WITH A FIXED TOPOLOGICAL STRUCTURE

The aim of this section is to prove the relations (4) and (5) discussed in the Introduction and to use them to derive field theories for the description of polymers with a fixed topological structure.

First we shall formulate a model of polymers, in the framework of which we shall establish the correspondence (discussed in the Introduction) between polymers and graphs. In this model the monomers are point particles with coordinates $\mathbf{x}_i$ and mass m, and have f functional groups, between each two of which a chemical bond can be formed. We shall denote by $\lambda(\mathbf{x}_i-\mathbf{x}_j)$ the conditional probability of finding the monomers of a bond at a distance $|\mathbf{x}_i-\mathbf{x}_j|$ from each other. The chemical bonds form the topological structure of the molecules, the different configurations of which can be represented in the form of graphs of the type in Fig. 1a (see also the review Ref. 6). For $f=2$, only linear chains are formed, while the case $f\geqslant 3$ corresponds to the formation of branched polymers, which can incorporate cyclic fragments. The spatial conformations of a molecule of a given topology are determined by the interaction of its monomers with each other. We shall describe these interactions by specifying the potential energy $U(\mathbf{x}_i-\mathbf{x}_j)$ of the interaction of an arbitrary pair of monomers (i,j).

Following Refs. 4–6, we write the distribution function for the configuration of polymers specified by the graph $G\{\mathbf{x}_i\}$ in the form

$$\mathscr{P}(G\{\mathbf{x}_i\})=\Lambda_T^{-dN}\exp\Big[-\frac{1}{T}\sum_{(i,j)}U(\mathbf{x}_i-\mathbf{x}_j)-\frac{1}{T}\sum_i h(\mathbf{x}_i)\Big]$$
$$\times\prod g(\mathbf{x}_i-\mathbf{x}_j),\quad \Lambda_T=(mT/2\pi\hbar^2)^{-1/2}. \tag{6}$$

Here N is the number of monomers in this configuration, T is the absolute temperature and Λ_T is the thermal wavelength.[5] With each segment of the graph G in (6) we associate a factor $g(\mathbf{x}\mathbf{z}_i-\mathbf{x}_j)=g\lambda(\mathbf{x}_i-\mathbf{x}_j)$ (g is the entropy characteristic of the bond). Integrating (6) over the coordinates of all the monomers, we find the free energy of the configuration G:

$$F_G\{h\}=-T\ln\Big[\prod_i\int dx_i\,\mathscr{P}(G\{\mathbf{x}_i\})\Big]. \tag{7}$$

In the following we shall indicate quantities pertaining to the initial system by a superscript $k=0$, and the index $k=1,\dots,m$ used for labeling the different replicas of the final system can be omitted (it is assumed that the values of the physical quantities coincide for all such $k\neq 0$).

In the initial system, in chemical equilibrium, the polymers are statistical and do not possess any definite topological structure. The probability of a given configuration G in the framework of the grand canonical ensemble (GCE) is equal to

$$P_G^{(0)}=z^N\exp\Big[\frac{\Omega^{(0)}-F_G^{(0)}}{T^{(0)}}\Big],$$

$$\exp\Big[-\frac{\Omega^{(0)}}{T^{(0)}}\Big]=\sum_G z^N\exp\Big[-\frac{F_G^{(0)}}{T^{(0)}}\Big], \tag{8}$$

where z is the activity of the monomers. The relations (1) and (6)–(8) determine the free energy of the system with a frozen MSD.

To calculate this free energy we shall consider the GCE for a chemically equilibrium system consisting of the initial system and m replicas of the final system (see the Introduction and Fig. 1b). Since such subsystems do not interact with each other, the distribution function for the configuration specified by the graph $\mathbf{G}\{X_i\}$ factorizes:

$$\mathscr{P}(\mathrm{G}\{\mathrm{X}_i\})=\prod_{k=0}^{m}\mathscr{P}^{(k)}(G\{\mathbf{x}_i^{(k)}\}) \tag{9}$$

and the partition function of this GCE takes the form

$$\exp\Big[-\frac{\Omega_m\{h^{(k)}\}}{T}\Big]$$
$$=\sum_{\mathrm{G}} z^N\exp\Big[-\frac{F_G^{(0)}\{h^{(0)}\}}{T^{(0)}}-m\frac{F_G\{h\}}{T}\Big]. \tag{10}$$

Differentiating (10) with respect to m, we find the identity (4) discussed in the Introduction which makes it possible to reduce the problem of the calculation of the free energy of a system with a frozen MSD to the problem of the equilibrium GCE of polymers in a space of effective dimensionality $d(1+m)$. According to (9) and (6), with each segment of the graph **G** in this problem we associate a chemical-bond factor:

$$Q(\mathbf{X}_i-\mathbf{X}_j)=\prod_{k=0}^{m}g^{(k)}(\mathbf{x}_i^{(k)}-\mathbf{x}_j^{(k)}). \tag{11}$$

A representation of the partition function (10) in the form of a path integral can be found analogously.[4,5] For this we note first that the distribution function (9) can be represented in the form

$$\mathscr{P}(\mathrm{G}\{\mathrm{X}_i\}\,|\,h^{(k)})=\langle\mathscr{P}_{\mathrm{cb}}(\mathrm{G}\{\mathrm{X}_i\}\,|\,h^{(k)}+v^{(k)})\rangle_{v^{(k)}}. \tag{12}$$

Here and below, the subscript *cb* means that only the presence of the chemical bonds is taken into account, and the interactions of the monomers are completely ignored ($U^{(k)}=0$). The averaging in (12) is to be understood in the sense of a field theory with a quadratic Lagrangian:

$$H_0\{v^{(k)}\}=-\frac{1}{2}\sum_{k=0}^{m}\frac{1}{T^{(k)}}\int\int d\mathbf{x}\,d\mathbf{x}'\,(U^{-1})^{(k)}$$
$$\times(\mathbf{x}-\mathbf{x}')\,v^{(k)}(\mathbf{x})\,v^{(k)}(\mathbf{x}'),$$

$$\int d\mathbf{x}''\,U^{(k)}(\mathbf{x}-\mathbf{x}'')\,(U^{-1})^{(k)}(\mathbf{x}''-\mathbf{x}')=\delta(\mathbf{x}-\mathbf{x}'). \tag{13}$$

According to (12), to calculate the partition function of the GCE it is sufficient to find it for $U^{(k)}=0$ and then average over the field $v^{(k)}$. The absence of interaction greatly simplifies the calculations. In particular, according to the first theorem of Mayer,[11] the thermodynamic potential in (10) is equal to a sum of contributions from the connected graphs **C**:

$$-\frac{\Omega_{m,\mathrm{cb}}\{h^{(k)}\}}{T}=\sum_{\mathrm{C}} z^l\exp\Big[-\frac{F_C^{(0)}\{h^{(0)}\}}{T^{(0)}}-\sum_{k=1}^{m}\frac{F_C\{h^{(k)}\}}{T}\Big]. \tag{14}$$

We shall make use of this relation below in an analysis of a dilute solution of polymers. Following Ref. 4, we shall find one further representation of the partition function of the system for $U^{(k)}=0$:

$$\exp\Big(-\frac{\Omega_{m,\mathrm{cb}}\{h^{(k)}\}}{T}\Big)=\int D\varphi\,\exp\Big[-L_m\{\varphi\}$$
$$+z^*\int d\mathbf{X}\exp\Big(-\sum_{k=0}^{m}h^{(k)}/T^{(k)}\Big)$$
$$\times(1+\varphi(\mathbf{X}))^f/f!\Big]\Big/\int D\varphi\,\exp(-L_m\{\varphi\}),$$

$$z^*=z/(\Lambda_T^{(0)})^d\Lambda_T^{dm},$$

$$L_m\{\varphi\}=\frac{1}{2}\int\int d\mathbf{X}\,d\mathbf{X}'\,(Q^{-1})(\mathbf{X}-\mathbf{X}')\,\varphi(\mathbf{X})\,\varphi(\mathbf{X}'). \tag{15}$$

Performing the averaging of (15) over the fields $v^{(k)}$ (13), we finally find

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

$$=\int D\varphi \exp(-S_m\{\varphi\}) \Big/ \int D\varphi \exp(-L_m\{\varphi\}),$$

$$S_m\{\varphi\}=L_m\{\varphi\}-\pi_m\Big\{0;\, z^* \exp\Big[-\sum_{k=0}^{m} h^{(k)}(\mathbf{x}^{(k)})/T^{(k)}\Big]$$

$$\times(1+\varphi)^f/f!\Big\}. \qquad (16)$$

The functional π_m is calculated in the Appendix. It contains information about the interaction of the particles both in the initial and in the final system, and is expressed in terms of thermodynamic functions of the corresponding systems of broken links (bl),[6,12] i.e., in the absence of chemical bonds. For $m = 0$,

$$\pi_0\{\bar{z}^*;z^*\}\equiv\pi_0\{\bar{z}^*+z^*\}=-\Omega_{\rm bl}^{(0)}\{\bar{z}^*+z^*\}/T^{(0)} \qquad (17)$$

and the expression (16) goes over into that found in Refs. 4–6.

We now consider a dilute solution of polymers. The relation (12) makes it possible to write the generating functional of the correlation functions of the individual "molecules" with thickened bonds (see the Introduction and Fig. 1c) in the form

$$\Psi_m\{s\,|\,h^{(k)}\}$$

$$=\left\langle \Psi_{m,\rm cb}\{s\,|\,h^{(k)}+v^{(k)}\}\exp\left[-\frac{\Omega_{\rm cb}^{(0)}\{h^{(0)}+v^{(0)}\}}{T^{(0)}}\right]\right\rangle_{v^{(k)}} \Big/$$

$$\left\langle \exp\left[-\frac{\Omega_{\rm cb}^{(0)}\{h^{(0)}+v^{(0)}\}}{T^{(0)}}\right]\right\rangle_{v^{(k)}}$$

$$(18)$$

For an equilibrium system the relation (18) for $m = 0$ was first obtained in Ref. 5, and its detailed derivation is given in Ref. 6. The functional $\Psi_{m,cb}$ is equal, by definition, to the sum of the contributions of the connected graphs **C** with weight s^l:

$$\Psi_{m,\rm cb}\{s\,|\,h^{(k)}\}=\sum_{\rm C}s^l z^l \exp\left[-\frac{F_C^{(0)}\{h^{(0)}\}}{T^{(0)}}-\sum_{k=1}^{m}\frac{F_C\{h^{(k)}\}}{T}\right\}. \qquad (19)$$

Substituting (19) into (18) and averaging over the fields $v^{(k)}$, we find the relation

$$\Psi_m\{s\,|\,h\}=\sum_C s^l n_C \exp(-mF_C\{h\}/T) \qquad (20)$$

Differentiating (20) with respect to m, we find the second important relation (5) discussed in the Introduction.

To find a field-theoretical representation of the functional Ψ_m, we note that, upon the replacement $z\to zs$ in (14),

$$-\Omega_{m,\rm cb}\{h^{(k)}\}/T=\Psi_{m,\rm cb}\{s\,|\,h^{(k)}\}. \qquad (21)$$

Following Ref. 5, we write the left-hand side of (21) in the form

$$-\frac{\Omega_{m,\rm cb}}{T}=\lim_{n\to 0}\frac{1}{n}\left[\exp\left(-\frac{n\Omega_{m,\rm cb}}{T}\right)-1\right]. \qquad (22)$$

The replica limit $n\to 0$ is taken at the end of the calculations. We substitute (22) and (21) into (18) and make use of the representation of the partition function (15) in the form of a path integral. Averaging (18) next over the fields $v^{(k)}$, we finally find

$$\Psi_m\{s\,|\,h\}=\lim_{n\to 0}\frac{1}{n}\Big[\int D\varphi_i \exp(-S_{nm}\{\varphi_i\,|\,s\}) \Big/$$

$$\int D\varphi_i \exp(-S_{nm}\{\varphi_i\,|\,0\})-1\Big], \qquad (23)$$

where $\varphi_0\equiv\varphi_0(\mathbf{x}^{(0)})$, $\varphi_i\equiv\varphi_i(\mathbf{X})$ $(i = 1,\dots,n)$ is the field of the replicas, and the action S_{nm} is given by the expression

$$S_{nm}\{\varphi_i\,|\,s\}$$

$$=L_0\{\varphi_0\}+\sum_{i=1}^{n}L_m\{\varphi_i\}-\pi_m\Big\{z^*\exp(-h^{(0)}/T^{(0)})\,(1+\varphi_0)^f/f!\,;$$

$$sz^*\exp\Big(-\sum_{k=0}^{m}h^{(k)}/T^{(k)}\Big)\sum_{i=1}^{n}(1+\varphi_i)^f/f!\Big\}. \qquad (24)$$

For $m = 0$ the expressions (24) and (23) go over into those found in Refs. 5 and 6 for the generating functional Ψ_0 of the individual molecules.

The expressions (16) and (23), together with our proof of the relations (4) and (5), are the main result of this section.

3. SYSTEM WITH A FROZEN MSD

In such a system different molecules can overlap strongly and interact with each other. Therefore, the main interest lies in the calculation of its overall characteristics, which is performed in this section on the basis of the relations (4) and (16).

In the self-consistent field (SCF) approximation the field $\bar{\varphi}$ is determined by minimizing the action S_m (16), and, in the absence of external fields, $\bar{\varphi} = p/(1-p)$ (p is the conversion, equal to the ratio of the number of bonds in the system to their maximum possible number $Nf/2$). For the equation of state of the system in this approximation we obtain the expression

$$P(\rho)=P_{\rm bl}(\rho)-\rho pfT/2, \quad P_{\rm bl}(\rho)=-\Omega_{\rm bl}/V,$$

which is in agreement with the results of the diagram technique of Refs. 4 and 6. In contrast to the latter papers, the field theory (16) makes it possible to go beyond the framework of perturbation theory.

The SCF approximation works well for the initial system if the polymers are obtained in the melt,[5] but may be violated for the final system when the latter is sufficiently dilute. Since in the following we shall be interested in scales that are large in comparison with the bond length a, we set

$$\lambda(\mathbf{x}-\mathbf{x}')=\delta(\mathbf{x}-\mathbf{x}')(1-a^2\nabla^2), \quad \mathbf{r}^{(k)}=\mathbf{x}^{(k)}[g^{(k)}]^{-1/d}.$$

In the new coordinates **r** the bond length is *equal to* $c = ag^{1/d}$. To investigate the fluctuation regime we expand the action (16) to terms of third order in $\psi = \varphi - \bar{\varphi}$:

$$S_m\{\psi\}=S_m\{0\}+\prod_{k=0}^{m}\int d\mathbf{r}^{(k)}\Big[-h\psi+\frac{\tau}{2}\psi^2+\frac{c^2}{2}(\nabla\psi)^2+\frac{w}{6}\psi^3\Big]+\sum_{k=0}^{m}\frac{\Delta^{(k)}}{2}\int d\mathbf{r}^{(k)}\Big[\prod_{j\neq k}\int d\mathbf{r}^{(j)}\psi\Big]^2 \tag{25}$$

In the case of a concentrated initial system we have $c^d \cong \rho^{(0)}a^d \gtrsim 1$, and the SCF approximation is applicable for its description. In this approximation, for $m=0$,

$$h=0,\quad w=2(f-2)/(f-1),\quad \tau=1-p/p_c\ll 1,\quad \Delta\approx 2B(T)/g.$$

Here $p_c=(f-1)^{-1}$ is the critical value of the conversion, at which an infinite gel molecule first appears, and $B(T)$ is the effective virial coefficient of the interaction of the monomers in the final system.

In the region of weak fluctuations, for the Fourier components of the correlators of the initial and final systems we find the expressions

$$\begin{gathered}\langle\delta\rho_{\mathbf{q}}^{(0)}\,\delta\rho_{-\mathbf{q}}^{(0)}\rangle\sim(\tau_s^{(0)}+c^2q^2)^{-1},\qquad \tau_s^{(0)}=\tau+\Delta^{(0)},\\ \langle\delta\rho_{\mathbf{q}}\delta\rho_{-\mathbf{q}}\rangle\sim(\tau_s+c^2q^2)^{-1},\quad \tau_s=\tau+\Delta V^{(0)}/V.\end{gathered} \tag{26}$$

Here $V^{(0)}$ and V are the volumes of the corresponding systems. The conditions $\tau_s^{(0)}=0$ and $\tau_s=0$ determine the position of the spinodal transition[1] in these systems. It is not difficult to show that when fluctuations in the initial system are neglected the perturbation-theory expansion is an expansion in the parameter $\varkappa$:

$$\varkappa\equiv\gamma/\tau_s^{4-d/2},\qquad \gamma\equiv K_d\Delta w^2/c^d,\quad K_d^{-1}=2^{d-1}\pi^{d/2}\Gamma(d/2). \tag{27}$$

Thus, the upper critical dimensionality[13] $d_c=8$.

We shall show that for $d<d_c$ in the region $\varkappa\gg 1$ the density fluctuations are described by the single index ζ defined in the Introduction. For this we write out the RG transformation $\mathbf{r}^{(k)}\to\mathbf{r}^{(k)}\exp l^{(k)}$ for the parameters of the action (25) in general form:

$$\begin{gathered}\tau(l)=\tau\exp 2l^{(0)},\quad w(l)=w\exp(3-d/2)l^{(0)},\\ \Delta(l)=\Delta\exp\Big\{(d+2)l^{(0)}-dl-\int_0^l dl\,f[\gamma(l)]\Big\},\\ l^{(0)}=l-\int_0^l dl\,\zeta'[\gamma(l)].\end{gathered} \tag{28}$$

Combining (28), we find the equation $8(1-\zeta')=d+f$ for the fixed point $\gamma=\gamma^*$ of the RG transformations. In the one-loop approximation the functions f and ζ' are easily calculated:

$$f(\gamma)=\gamma/2+O(\gamma^2),\quad \zeta'(\gamma)=\gamma/4+O(\gamma^2), \tag{29}$$

whence, for the swelling index, there follows the expression

$$\zeta=\zeta'(\gamma^*)/[1-\zeta'(\gamma^*)]=(8-d)/(d+2). \tag{30}$$

We shall assume that a solution of the equation for γ^* exists for all the dimensions $d<8$ of interest to us. Stopping the RG transformations at $\varkappa(l^*)=1$ (see (27)), we find an expression for the correlation length:

$$\xi=a\exp l^*[\tau_s(l^*)]^{-1/2}\approx a\gamma^{\zeta/(8-d)}\tau_s^{-(1+\zeta)/2}, \tag{31}$$

where the parameter $\tau_s=\exp[-2l^{(0)*}]$ that we have introduced is found from the solution of the equation

$$\tau_s=\tau+\Delta V^{(0)}/V\varkappa^{1-d\zeta/(8-d)},\quad \varkappa=\gamma/\tau_s^{4-d/2}. \tag{32}$$

The results (31) and (32) follow from the very fact of the existence of a fixed point of the RG transformations (28), but for the calculation of the index ζ in real space it is necessary to find the functions (29) in all orders in γ. The expression (30) corresponds to the approximation $f=2\zeta'$. As shown in Ref. 14, this one-loop approximation gives good accuracy for $d=3$, in contrast to the results of the usual ε-expansion.[13]

We now discuss the physical meaning of the results. With change of the quality of the solvent the correlation length varies nonmonotonically and reaches a maximum at $B=B_{\max}$, where

$$(B_{max}/a^d)^{-d\zeta/(8-d)}\approx\rho a^d\tau^{3-d(1+\zeta)/2},\quad \rho=\rho^{(0)}V^{(0)}/V.$$

In the case of weak repulsion of the monomers ($B\ll B_{\max}$) a dilute solution of polymers is realized (see the next section) and the characteristic size ξ of the polymer coils grows as the repulsion becomes stronger. The decrease of ξ with increase of the repulsion for $B\gg B_{\max}$ is connected with the screening of this interaction in a semidilute solution of polymers. In this limit the parameter τ determining the maximum degree of polymerization $l_m\cong\tau^{-2}$ of the sol molecules (which have size $R_m^{(0)}=\xi^{(0)}=a|\tau|^{-1/2}\cong a l_m^{1/4}$—the number of molecules with $l\gg l_m$ is exponentially small) drops out of the relation (32). Thus, in a semidilute solution the thermodynamic quantities are determined entirely by the local characteristics ρ and $B(T)$ of the system.

In the initial system the correlation length ξ (31) corresponds to the scale $R_\xi^{(0)}\cong a\tau_s^{-1/2}$. In the dilute limit $B\ll B_{\max}$ we find $R_\xi^{(0)}=R_m^{(0)}$, i.e., the quantity ξ (31) determines the size of the branched molecules with degree of polymerization $l=l_m$ in the dilute solution. For $B\gtrsim B_{\max}$ such molecules of the maximum size begin to come into contact with each other, and, because of the screening effect, $R_\xi^{(0)}\lesssim R_m^{(0)}$. In the semidilute limit $B\gg B_{\max}$ these molecules overlap strongly. For the average number $l_\xi=\rho\xi^d$ of monomers in a fluctuation cell we find from (31) the expression $l_\xi\cong\tau_s^{-3}$, to which corresponds $R_\xi^{(0)}\cong a l_\xi^{1/6}$. Since the size of isolated treelike molecules with degree of polymerization l is equal to $R_l^{(0)}\cong a l^{1/4}$, this dependence of $R_\xi^{(0)}$ suggests that the fluctuation cell is a more compact formation, incorporating a large number of molecules. Inside each large molecule in a semidilute solution is a set of smaller molecules. In fact, as is known for the Flory distribution,[15] the overwhelming number of molecules of the system have degree of polymerization $l\sim 1$, and these molecules determine the thermodynamic quantities of the system. Because of this strong polydispersity of the system under consideration a semidilute solution of branched polymers, in contrast to a semidilute solution of linear chains, cannot be described in the framework of the blob concept.[1]

The density-density correlation function is equal to

$$\langle\delta\rho_{\mathbf{q}}\delta\rho_{-\mathbf{q}}\rangle\sim(1+q^2\xi^2)^{-1},\quad q\xi\ll 1.$$

The important point is that it does not have singularities at the gel-formation point $p=p_c$. An exception is a dilute solution, considered in detail in the next section. The presence of a gel in such a system can be established only in "kinetic" experiments (e.g., on the passage of a ball of size exceeding the size of the gel cycles).

4. DILUTE SOLUTION OF POLYMERS

In this section we shall consider the characteristics of molecules of finite size only; i.e., in (2) we must set $s \neq 1$. The average value of the field φ_i in (24) is equal to

$$\bar{\varphi}_i^{(0)} = \bar{\varphi}_+ \delta_{i0} + \bar{\varphi}_- (1 - \delta_{i0}), \tag{33}$$

where in the case $s \to 1$ we have $\bar{\varphi}_+ = \bar{\varphi}_-$ for $p < p_c$ and $\bar{\varphi}_+ > \bar{\varphi}_-$ for $p > p_c$. In the limit $n \to 0$ we find from (23) the contribution of the sol molecules:

$$\Psi_m^{(s)} \{s|h\} = - \left. \frac{\partial S_{nm}^{\text{eff}} \{\bar{\varphi}_i^{(0)}\}}{\partial n} \right|_{n=0} \qquad \frac{\delta S_{0m}^{\text{eff}} \{\bar{\varphi}_i^{(0)}\}}{\delta \bar{\varphi}_i^{(0)}} = 0. \tag{34}$$

Here $S_{nm}^{\text{eff}} \{\bar{\varphi}_i\}$ is the effective-action functional[16,5] for the field theory (24), and takes into account the contribution of fluctuations of φ_i about the classical field $\bar{\varphi}_i$. The magnitude of this field is found by minimizing the functional S_{nm}^{eff}. The expression (34), together with (5), completely determines the characteristics of the sol molecules in a dilute solution.

As in the preceding section, we shall assume that the initial system is a melt; this makes it possible to neglect fluctuations of its density. In such a system, as shown in Refs. 4 and 5, the final molecules have, in the main, a treelike structure, and topological couplings with each other are absent. After the topological structure is fixed by rapid cooling, such molecules can be separated from each other by placing them in an appropriate solvent. The osmotic pressure of such noninteracting treelike molecules for $p < p_c$ is equal to

$$\pi/T = \sum_c n_c/V = \rho - \rho_b = \rho(1 - pf/2)$$

(ρ_b is the density of bonds), in agreement with the fact that the average degree of polymerization of the system is of order unity.

In the SCF approximation we have $S_{nm}^{\text{eff}} = S_{nm}$, where the action S_{nm} is defined in (24). From (34) and (5), for the correlation functions of the individual molecules there follow the same expressions as in the initial system.[5] More-interesting results are found in the scaling region.

We shall consider first the behavior of a "statistical-average" molecule with a fixed structure in a dilute solution by setting $s = 1$ in (23). When the density fluctuations in the initial system are neglected the average values of the fields φ_i are equal to $\bar{\varphi}_i = p/(1-p)$. We shall expand the action (24) in powers of $\psi_i = \varphi_i - \bar{\varphi}_i$. In analogy with Ref. 5 one can show that the fluctuations of the field

$$\psi(\mathbf{x}^{(0)}) = \psi_0(\mathbf{x}^{(0)}) + \sum_{i=1}^{n} \int dx\, \psi_i(X), \qquad \int dx \equiv \prod_{k=1}^{m} \int d\mathbf{x}^{(k)}$$

are small, since they are connected with the density fluctuations in the initial system. Integrating over the field ψ with neglect of these fluctuations, we find an effective action that depends only on the replica fields ψ_i ($i = 1,...,n$):

$$\begin{aligned} S_{nm}\{\psi_i\} = \int d\mathbf{r}^{(0)} \Big\{ & \frac{\tau}{2} \Big[\sum_{i=1}^{n} \int dr\, \psi_i^2 + \Big(\sum_{i=1}^{n} \int dr\, \psi_i \Big)^2 \Big] \\ & + \frac{c^2}{2} \Big[\sum_{i=1}^{n} \int dr\, (\nabla \psi_i)^2 + \Big(\sum_{i=1}^{n} \int dr\, (\nabla^{(0)} \psi_i)^2 \Big) \Big] \\ & + \frac{w}{6} \Big[\sum_{i=1}^{n} \int dr\, \psi_i^3 - \Big(\sum_{i=1}^{n} \int dr\, \psi_i \Big)^3 \Big] \Big\} \\ & + \frac{\Delta}{2} \sum_{k=1}^{m} \int d\mathbf{r}^{(k)} \Big(\sum_{i=1}^{n} \prod_{j \neq k} \int d\mathbf{r}^{(j)} \psi_i \Big)^2 \end{aligned} \tag{35}$$

For $m = 0$, after diagonalization of the quadratic part this action goes over into the action of the n-component Potts model, in the strong-fluctuation region $|\tau| \ll \tau_G \sim c^{-2/(6-d)}$ describing bond percolation.[17,18] We shall be interested in the opposite case $|\tau| \gg \tau_G$, when one can neglect the cyclization of a statistical-average molecule. For $m \to 0$ the RG equations have the same form as the RG equations (28) in a system with a frozen MSD. Stopping the RG transformations at $\tau(l^*) = 1$, we find the size of molecules with degree of polymerization $l = l_m \cong \tau^{-2}$:

$$R_l \approx a\gamma^{\zeta/(8-d)} l^{\nu_t}, \quad \nu_t = (1+\zeta)/4 \tag{36}$$

in complete agreement with the dilute limit (34). According to (36), the quantity $D_t = \nu_t^{-1}$ determines the fractal dimension[19] of a treelike molecule that has swollen in a good solvent. It differs substantially both from the quantity $D_t^{(0)} = 4$ for such a molecule in a melt (because of effects of the nonaffine character of the swelling) and from the value $D_a^{(0)} = \nu_a^{-1}$ for an isolated cyclic molecule. In the one-loop approximation, from (30) we find $D_t = 2(d+2)/5$, while for a cyclic molecule in this approximation one can obtain from Ref. 8 the value $D_a^{(0)} = 4(d+1)/9$. Thus, a cyclic molecule is a less compact formation ($D_a^{(0)} < D_t < D_t^{(0)}$), although its difference from a molecule with a treelike structure is rather small.

We now consider the characteristics of cyclic molecules with a fixed structure in a dilute solution. The number of such molecules in the initial system considered by us is exponentially small in l, whereas the sizes have only a power-law dependence on l. Therefore, one can neglect the intersection of such molecules with each other, and they too can be separated from the other molecules of the system as the system is diluted.

To describe molecules with a specified degree of polymerization l one must set $s = e^t > 1$ in (24); the case $l \gg 1$ corresponds to $t \ll 1$. The most important change in the action (35) for $t \neq 0$ is the appearance in it of an extra term (see also Ref. 7):

$$\frac{\Delta^{(0)}}{2} \int d\mathbf{r}^{(0)} \Big(\sum_{i=1}^{n} \int dr\, \psi_i \Big)^2, \qquad \Delta^{(0)} \approx t. \tag{37}$$

An action of this form for $m = 0$ has also been obtained in the problem of a dilute solution of polymers in a state of chemical equilibrium.[8] In this case the parameter $\Delta^{(0)}$ (37) is proportional to the virial coefficient $B^{(0)}(T^{(0)})$ of the interaction of the monomers of this system. Thus, for $m \to 0$, as well as the problem of the behavior of cyclic molecules obtained in the melt, the action (35), (37) describes the swelling of a branched molecule with a fixed structure, obtained in a dilute solution.

The change of symmetry of the action with $\Delta^{(0)} \neq 0$ leads to the appearance of a new fixed point of the RG transformation. Near this fixed point the relevant variables are $\gamma^{(k)} = K_d \Delta^{(k)} w^2/c^d$, and in the one-loop approximation for $m \to 0$ the renormalization-group equations can be written in the form

$$\delta\gamma^{(0)} = (8-d)\gamma^{(0)}\,\delta l^{(0)} - \frac{9}{2}(\gamma^{(0)})^2 \delta l^{(0)},$$
$$\delta\gamma = (8-d)\gamma\,\delta l - \left(4 - \frac{d}{4}\right)\gamma^{(0)}\gamma\,\delta l^{(0)} - \frac{d+2}{4}\gamma^2\,\delta l,$$
$$\delta l^{(0)}(1-\gamma^{(0)}/4) = \delta l(1-\gamma/4). \tag{38}$$

The equation for $\gamma^{(0)}$ is independent of the other equations, and this reflects the obvious fact that the conditions of preparation of the polymers are independent of the conditions of their exploitation. It was first obtained in Ref. 8. With the initial condition $\gamma^{(0)}(0) = 0$ we find also $\gamma^{(0)}(l^{(0)}) = 0$, and the system of the other equations in (38) is simply the differential form of the RG equations (28). We shall consider now the general case $\gamma^{(k)} \neq 0$. Equations (38) have the first integral

$$l - l^{(0)} = \frac{\zeta}{8-d} \ln\left[\frac{\gamma^{(0)}(l^{(0)})\gamma(0)}{\gamma(l)\gamma^{(0)}(0)}\right], \tag{39}$$

where the critical index ζ is calculated in (29). At large scales $\gamma^{(0)}$ and γ reach a universal asymptote

$$(\gamma^{(0)})^* = \gamma^* = 2\varepsilon/9, \quad \varepsilon = 8-d.$$

According to (39), this implies that the swelling of such molecules is affine. The correlation length ξ determines the size R_l of the molecule in dilute solution, and for the degree of swelling of the molecule we find from (39) the expression

$$\Lambda \equiv R_l/R_l^{(0)} = (\Delta/\Delta^{(0)})^{\zeta/(8-d)}, \quad R_l^{(0)} \sim l^{\nu_a}. \tag{40}$$

Thus, the swelling index ζ also characterizes the degree of swelling of a cyclic molecule upon dilution of the system. The relation (40) can be used to determine ζ experimentally. We shall make use of this relation to calculate ζ in the Flory approximation[10]:

$$R_l \sim B^{1/(d+2)} l^{5/2(d+2)}. \tag{41}$$

Comparing (40) and (41) we find $\zeta = (8-d)/(d+2)$, which coincides with the result (30) of the RG calculation. It is not difficult to verify that the dependence of (41) on l is the same as the dependence (36) for treelike molecules. Cyclic molecules have a sparser structure (see Fig. 2), and this leads to a change of the index ν_a in comparison with ν_t. This change is not picked up by the Flory approximation. In the one-loop approximation for $d = 3$ the difference $D_t - D_a = 2/9$, and can be detected experimentally (D_a has the exact value 2).

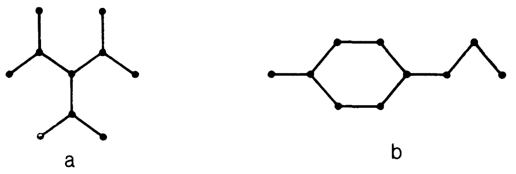

FIG. 2. Topological structure of branched molecules of degree of polymerization $l = 10$. The treelike molecule (a) consists of short chains of length $\bar{l} \sim 1$, while for the cyclic molecule (b) $\bar{l} \gg 1$.

By compression ($V \ll V^{(0)}$) of a system with a frozen MSD one can realize the interesting case in which molecules, obtained in dilute solution, begin to overlap each other. Since in the initial strongly fluctuating system they have largely the same degree of polymerization $l_m \cong t^{-1}$ ($t = \tau - \tau_{\rm cr}$),[8,20] the semidilute regime can be described in the framework of the blob concept. A tree structure of such molecules can be obtained by polycondensation of monomers AB_{f-1}, when chemical reactions are permitted only between groups A and B.[15,20] The main difficulty in the preparation of such a system arises from the long time of establishment of thermodynamic equilibrium in the system.

5. THE BLOB CONCEPT IN THE THEORY OF POLYMER NETWORKS

In this section we present a theory of the swelling of a polymer network with a fixed topological structure, obtained by equilibrium polycondensation in the melt. Since the molecules of the sol have a mainly treelike structure, they can be separated easily from the gel network. A method of describing a gel in a chemically equilibrium system was developed in Ref. 5, and we shall use this method here to calculate the characteristics of a swollen polymer network.

According to Refs. 5 and 6 for $s = 1$, beyond the gel-formation point ($p > p_c$), besides the replica-symmetric ground state (33) the field theory (24) has states $j = 1,\ldots,n$ for which this symmetry is spontaneously broken:

$$\bar{\varphi}_i^{(j)} = \bar{\varphi}_0\delta_{i0} + \bar{\varphi}_+\delta_{ij} + \bar{\varphi}_-(1-\delta_{i0}-\delta_{ij}). \tag{42}$$

Summing the quasiaverages[18] in each of these equivalent states, we find the contribution of the gel molecule to the functional Ψ_m (23):

$$\Psi_m^{(g)}\{1|h\} = \exp[-S_{0m}^{\rm eff}\{\bar{\varphi}_i^{(1)}\} + S_{0m}^{\rm eff}\{\bar{\varphi}_i^{(0)}\}]. \tag{43}$$

Substituting (43) into (5) and (3), we find the free energy of the gel molecule:

$$F^{(g)}\{h\} = -T\frac{\partial}{\partial m}[S_{0m}^{\rm eff}\{\bar{\varphi}_i^{(1)}\} - S_{0m}^{\rm eff}\{\bar{\varphi}_i^{(0)}\}]\big|_{m=0},$$

$$\frac{\delta S_{00}^{\rm eff}\{\bar{\varphi}_i^{(j)}\}}{\delta\bar{\varphi}_i^{(j)}} = 0. \tag{44}$$

The osmotic pressure of such a swollen gel is equal to

$$\pi \equiv -\Omega^{(g)}/V = -\partial F^{(g)}/\partial V. \tag{45}$$

In the SCF approximation, for the thermodynamic potential $\Omega^{(g)}$ of the gel we find an expression that coincides with the expression obtained in Ref. 9. This agreement is not surprising, since, essentially, in Ref. 9 the property of self-averaging of the gel free energy was used. This property has been well studied for the example of the condensed (globular) state of a random heteropolymer chain, and is connected with the fact that in the SCF approximation a spatially uniform self-consistent field μ^* acts on the particles (see the Appendix).

In the following we shall be interested primarily in the strong-fluctuation region, which cannot be considered in the framework of the approach of Ref. 9. To describe a network that has swollen in a good solvent, we make use of the action (35) obtained above. In the volume approximation the functions $\bar{\psi}_{\pm}$ are constant inside the volume occupied by the gel, and equal to each other outside it. Their values for $m = 0$ ($\bar{\psi}_{+} = 0$, $\bar{\psi}_{-} = 2|\tau|/w$) determine the density of the gel in the initial ($\rho^{(0)} = 2|\tau|/wg$) and final ($\rho = \rho^{(0)}V^{(0)}/V$) systems. Calculating the osmotic pressure with the aid of (45) in the SCF approximation, we find

$$\pi/T = B(T)\rho^2 - \rho(fp^{(g)}/2 - 1), \quad fp^{(g)}/2 - 1 = \tau^2/3w. \tag{46}$$

Here $p^{(g)}$ is the conversion of the gel macromolecule. For the Fourier components of the correlation functions of the gel in the respective systems we obtain the expression

$$\langle \delta\rho_{\mathbf{q}}^{(0)}\, \delta\rho_{-\mathbf{q}}^{(0)} \rangle = \frac{2|\tau|}{g(|\tau| + a^2q^2)^2},$$
$$\langle \delta\rho_{\mathbf{q}}\, \delta\rho_{-\mathbf{q}} \rangle = \frac{2V^{(0)}/V}{g(\tau_s + a^4q^4/|\tau|)}, \tag{47}$$

where the parameter $\tau_s = \tau + 2\Delta V^{(0)}/V$ characterizes the distance from the spinodal, on which the correlation length $\xi \cong a(|\tau|\tau_s)^{-1/4}$ diverges. The results (46) and (47) coincide with those obtained in Refs. 5, 6, and 9. We note that in the model under consideration collapse of the network ($\tau_s = 0$) occurs when $\pi > 0$ (see also the Conclusion). The region of applicability of the SCF approximation is determined by the condition $\varkappa \ll 1$, where

$$\varkappa = \langle (\delta\rho)^2 \rangle / \langle \rho \rangle^2 \approx \gamma / (\tau_s + |\tau|)\, |\tau|^{(8-d)/4} \tau_s^{(4-d)/4},$$

and we have made use of the expression (43).

In the region of strong fluctuations $\varkappa \gg 1$ the relations (46) and (47) are valid for the renormalized parameters of the action (35). By means of the RG transformations (28) we shall perform this renormalization up to the scale at which $\varkappa(l^*) = 1$. We shall show that in the case $\tau_s(l^*) \gg |\tau(l^*)|$ the gel network can be described in the framework of the blob concept.

Following Ref. 1, we shall call a fluctuation cell of a size equal to the correlation length ξ a blob. It is not difficult to convince oneself that the number of monomers per blob is $l_B = \rho\xi^d$, i.e., the network is a close-packed system of blobs that are not interacting with each other. For the correlation length we find the expression

$$\xi \approx a\gamma^{\zeta/(8-d)} l_B^{\nu_t}, \quad \nu_t = (1+\zeta)/4. \tag{48}$$

Comparing (48) with (36), we find that inside a blob there exist correlations typical of a branched single molecule. From scaling arguments at scales $x \lesssim \xi$, for the number $l(x)$ of monomers inside a sphere of radius x there follows an expression analogous to (48):

$$l(x) \approx \gamma^{-4\zeta'/(8-d)} (x/a)^{\nu_t^{-1}}, \quad \zeta' = \zeta/(1+\zeta).$$

The probability of finding two gel monomers at a specified distance $x \lesssim \xi$ from each other, equal to $P(x) = l(x)/x^d$, determines the density-density correlation function of the gel:

$$\langle \delta\rho(x)\delta\rho(0) \rangle = \rho P(x) \sim x^{-(d-\nu_t^{-1})}. \tag{49}$$

Using (49) and the renormalized relation (47), for the Fourier component of this correlator we obtain the expression

$$\frac{\langle \delta\rho_{\mathbf{q}}\, \delta\rho_{-\mathbf{q}} \rangle}{\rho^2\xi^d} \approx \begin{cases} (1+q^4\xi^4)^{-1}, & q\xi \ll 1 \\ (q\xi)^{-\nu_t^{-1}}, & q\xi \gg 1 \end{cases}. \tag{50}$$

Carrying out the renormalization of the action (35) for the determination of the effective-action functional (43), we find the osmotic pressure (45) of the swollen gel:

$$\pi \approx T\xi^{-d} \sim \rho^{d\nu_t/(d\nu_t - 1)}. \tag{51}$$

This formula is a consequence of the blob concept.[1] For $d = 8$ it goes over into the result (46) of the SCF theory. The characteristic size of the region that was occupied by the particles belonging to one blob in the initial system is equal to $R_{\xi}^{(0)} \cong a l_B^{1/4}$, in complete correspondence with the fact that, on scales small in comparison with $\xi^{(0)}$, the gel has a largely treelike structure. The condition for applicability of the blob concept to the description of polymer networks can be represented in the form $R_{\xi}^{(0)} \lesssim \xi^{(0)}$. In other words, the structure of the network should be self-similar on all scales up to the correlation length ξ. In studying such networks we can make use of the well-known results of the theory of semidilute solutions.[1] For example, the surface tension of a gel on a boundary with a repulsive wall is equal to $\sigma \sim T\xi^{1-d}$.

It is clear that the applicability of the concept of blobs to the description of a swollen gel is not restricted by the structure of the SCF. In the general case, for $R_{\xi}^{(0)} \lesssim \xi^{(0)}$, in (48)–(51) the index $\nu = \nu^{(0)}(1 + \zeta)$, where $\nu^{(0)}$ and ζ are critical exponents for the given structure (and solvent). The most interesting case is that of a percolation structure, which has fractal dimension $D_p^{(0)} = [\nu_p^{(0)}]^{-1} = (d + 2 - \eta_p)/2$ ($d < 6$), where η_p is the anomalous-dimension index. For $d < d_c^{(0)} = 6$ the swelling index ζ differs from that obtained in (30), but the RG calculation of it is made difficult by the difference in the upper critical dimensionalities $d_c = 8$ and $d_c^{(0)} = 6$. In the framework of the Flory method[10] the size R of the percolation cluster is found by minimizing its free energy:

$$F = R^2/a^2 l^{2\nu_0} + Bl^2/R^d, \quad \nu_0 = \nu_p^{(0)}(1 + \zeta_0).$$

The index ζ_0 describes the "swelling" of such a cluster when the interaction between its links is switched off. By making use of the analogy[1] with the calculation of the conductivity of a percolation network, we find $1 + \zeta_0 = \varphi_1 2\nu_p$, where φ_1 determines the conductivity critical index $t = (d - 2)\nu_p + \varphi_1$. Finally, for $d < 6$ we obtain

$$D_p = D_p^{(0)}/(1 + \zeta), \quad \zeta = (\varphi_1/\nu_p - \eta_p)/(d + 2).$$

In the case $R^{(0)} \gg \xi^{(0)}$ ($\tau_s(l^*) \ll |\tau(l^*)|$), for $d < 4$ we find

$$\pi \approx -\tau^2\rho T. \tag{52}$$

The fact that π is negative implies elastic expansion of the polymer network. We note that the asymptotic form (52) corresponds to the nonphysical region ($\partial\pi/\partial\rho < 0$) of the equation of state of the gel. It makes it possible to find the maximum (equilibrium) volume $V_{\max}$ occupied by the gel in the given solvent. This is determined by the condition $\partial F^{(g)}/\partial V = 0$, which, by means of (45), can be rewritten in the form $\pi = 0$. Comparing (51) and (52) we find that this condition implies that $R_{\xi}^{(0)} \cong \xi^{(0)}$. Thus, the equilibrium density of the swollen gel is determined by a condition on the threshold of overlap of single branched molecules with degree of polymerization $l_B = l_m \cong \tau^{-2}$:

$$\rho_{min} \approx \rho^* = a^{-d} \gamma^{-d\zeta/(3-d)} |\tau|^{2(d\nu_t - 1)}. \tag{53}$$

Equation (53) is analogous to the well-known Flory theorem on gels.[15,1] Increase of the repulsion of the monomers leads to a decrease of the quantity $\rho_{\min}$, i.e., to swelling of the network. We note that the structure of the blobs differs essentially from that considered in Ref. 15. The quantity $\tau(l^*) \lesssim 1$ determines the effective conversion of a gel consisting of such blobs, and, at the equilibrium density (53), $\tau(l^*) \sim 1$.

Because of lack of space we cannot dwell in detail on the description of the elastic properties of such a gel. We note only that the analogy indicated above makes it possible to carry over a considerable proportion of the results of Ref. 15, 1, and 21 to the polymer systems under consideration. Flory's approach[1] to the description of a swollen gel near the gel-formation threshold has been developed in Ref. 22.

To conclude this section we note the presence of the parametrization $(\mathbf{x}(\mathbf{x}^{(0)})$ of the monomers by their coordinates in the initial system. Specification of the function $\mathbf{x} = \mathbf{f}(\mathbf{x}^{(0)})$ for a certain fraction of the surface monomers makes it possible to describe the sticking of the surface of a gel to walls, and also to describe the case of partial adsorption of polymers on a surface.

6. CONCLUSION

We have given a brief description of a method that makes it possible to reduce the problem of the theory of polymers with a frozen structure to a certain field-theoretical problem. Besides the problems considered, it can be used to study the behavior of individual molecules of a system with a frozen MSD in the concentrated and semidilute regimes, and also the behavior of mixtures of polymers of various compositions.

The investigation of heteropolymers with molecules of a fixed topological structure is of special interest. In the presence of competition of the interactions of links of different types such polymers can form domain structures,[23] which can also be described in the framework of the method proposed in this paper.

In random heteropolymers with molecules of a fixed structure problems associated with the presence of disorder in the arrangement of monomers of different types over the molecule arise. Such topological disorder can lead to strong statistical fluctuations of physical quantities from molecule to molecule; see, e.g., Ref. 24. To describe these, one must divide the replicas into two subgroups:

$$h^{(k)} = h_1, \quad k = 1, \ldots, m_1; \quad h^{(k)} = h_2, \quad k = m_1 + 1, \ldots, m_1 + m_2.$$

The statistical correlator of the average density of the particles is equal to

$$\overline{\langle \rho(\mathbf{x}) \rangle \langle \rho(\mathbf{x}') \rangle} = -\lim_{m_{1,2} \to 0} \frac{T}{m_1 m_2} \frac{\delta^2 F\{h^{(k)}\}}{\delta h_1(\mathbf{x}) \delta h_2(\mathbf{x}')} \bigg|_{h_{1,2}=h}.$$

In the condensed state of polymers such fluctuations are small in the parameter $N^{-1/2}$.

We now discuss the possibility of physical realization of the polymer models considered in the article. A small value of the Ginzburg number τ_G, such as is necessary for treelike sol molecules to be obtained, is realized most simply by the joining of linear chains by f-functional monomers. We shall discuss briefly the field theory for this model and the differences between the results obtained from consideration of this theory and the results obtained above. The function g (6) associated with each segment of the graph of Fig. 1a has the meaning of the correlation function of the ends of a chain. In a system of chemical bonds we associate with the thickened segments in Figs. 1b and 1c a function Q given by

$$Q^{-1}(\mathbf{X} - \mathbf{X}') = Q_0^{-1}(\mathbf{X} - \mathbf{X}') - z_2^* \delta(\mathbf{X} - \mathbf{X}') \exp\left[-\sum_{k=0}^{m} v^{(k)} / T^{(k)} \right], \tag{54}$$

where Q_0 is defined in (11) and z_2 is the activity of the links of the chains. We emphasize that (54) corresponds to a fixed number of links of the chains. After substitution of (54) into (15) the averaging over the fields $v^{(k)}$ is easily carried out.

In effect, the results of these calculations reduces to a renormalization of the parameters of the system considered in this paper. The physical meaning of this renormalization is obvious. In a melt of chains the quantity a is equal to the mean-square distance between their ends. In a semidilute solution each chain consists of ordinary[1] blobs. Taking these blobs as the structural units, we return to the melt situation. The result obtained from the above-discussed renormalizations in a swollen gel is the most important. The case when over a scale ξ there is only one blob corresponds to the usual Flory theory.[15,1] Such a situation obtains for gels far from the gel-formation threshold. We consider the opposite case $|\tau| \ll 1 (\tau = 1 - p/p_c)$, when the number of such blobs is large. For long chains in the SCF approximation it is not difficult to show that the condition $\pi = 0$ (see (46)) determining the equilibrium density of the gel is fulfilled up to the spinodal point. In the scaling region the renormalizations considered here are unimportant.

Thus, the method proposed in this paper makes it possible to give a complete theoretical description of polymer systems in which the molecules have a frozen topological structure.

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APPENDIX

Calculation of the functional π_m (16), (24)

We shall calculate the functional average

$$\exp \pi_m\{\bar{z}^*, z^*\} \equiv \langle \exp(-H\{v^{(k)}\}) \rangle_{v^{(k)}}, \tag{A.1}$$

where the averaging operation is defined in (12) and

$$H\{v^{(k)}\} = -\int d\mathbf{x}^{(0)} \bar{z}^*(\mathbf{x}^{(0)}) \exp[-v^{(0)}(\mathbf{x}^{(0)})/T^{(0)}] - \prod_{k=0}^{m} \int d\mathbf{x}^{(k)} z^*(\mathbf{X}) \exp\left[-\sum_{k=0}^{m} v^{(k)}(\mathbf{x}^{(k)})/T^{(k)} \right]. \tag{A.2}$$

For this we shall make use of the Feynman variational principle

$$\pi_m \geqslant \pi_m^{tr} + \langle H^{tr} - H \rangle_{tr}, \tag{A.3}$$

where the functional τ_m^{tr} and the average are calculated with a trial action $H_0 + H^{\mathrm{tr}}$, and we choose H^{tr} in the form

$$H^{tr}\{v^{(k)}\}=-\sum_{k=0}^{m}\int d\mathbf{x}^{(k)}z^{(k)}(\mathbf{x}^{(k)})\exp[-v^{(k)}(\mathbf{x}^{(k)})/T^{(k)}]. \tag{A.4}$$

The functions $z^{(k)}$ are found by maximizing the right-hand side of the inequality (A.3). After straightforward calculations we obtain

$$\begin{gathered}\pi_m\{\bar{z}^*, z^*\}=\sum_{k=0}^{m}\int d\mathbf{x}^{(k)}P^{*(k)}(\mathbf{x}^{(k)})/T^{(k)}-H\{\mu^{*(k)}\},\\ P^*\equiv P_{\rm bl}-\rho T,\quad \mu^*=\mu-T\ln(\rho\Lambda_T{}^d).\end{gathered} \tag{A.5}$$

Here $P_{\rm bl}^{(k)}(\rho^{(k)})$ and $\mu^{(k)}$ are the equation of state and chemical potential, respectively, of the corresponding system. In place of the functions $z^{(k)}$ we have introduced the densities $\rho^{(k)}$, which should be found by maximizing the right-hand side of (A.5). In the differentiation it is convenient to use the relation $\delta P^*=\rho\delta\mu^*$. According to (A.5), the function μ^* has the meaning of the self-consistent field acting on the monomers. Calculating explicitly the maximum with respect to $\rho^{(0)}$, we finally find

$$\begin{aligned}\pi_m\{\bar{z}^*, z^*\}=&\sum_{k=1}^{m}\int d\mathbf{x}^{(k)}P^*(\rho^{(k)}(\mathbf{x}^{(k)}))/T\\ &+\pi_0\left\{\bar{z}^*+\prod_{k=1}^{m}\int d\mathbf{x}^{(k)}e^{-\mu^*(\mathbf{x}^{(k)})/T}z^*\right\},\end{aligned} \tag{A.6}$$

where the functional π_0 is given in (17).

In the case of constant $\bar{z}^*$ and z^* the average (A.1) can be calculated exactly, and in the thermodynamic limit the result of these calculations goes over into (A.6). Thus, the variational approach neglects those fluctuations of the thermodynamic parameters of the system of broken links that are small in the parameter $N^{-1/2}$.

[1] P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca (1979) [Russ. transl., Mir, Moscow (1982)].

[2] J. des Cloiseaux, J. Phys. (Paris) **36**, 281 (1975).

[3] E. S. Nikomarov and S. P. Obukhov, Zh. Eksp. Teor. Fiz. **80**, 650 (1981) [Sov. Phys. JETP **53**, 328 (1981)].

[4] I. Ya. Erukhimovich, Candidate's Dissertation in Physical and Mathematical Sciences, Physicotechnical Institute of Low Temperatures, Academy of Sciences of the Ukrainian SSR, Kharkov (1979).

[5] S. V. Panyukov, Zh. Eksp. Teor. Fiz. **88**, 1795 (1985) [Sov. Phys. JETP **61**, 1065 (1985)].

[6] S. I. Kuchanov, S. V. Korolev, and S. V. Panyukov, Adv. Chem. Phys. **72**, 115 (1988).

[7] A. B. Harris and T. C. Lubensky, Phys. Rev. B **24**, 2656 (1981).

[8] T. C. Lubensky and J. Isaacson, Phys. Rev. A **20**, 2130 (1979).

[9] S. V. Panyukov, Zh. Eksp. Teor. Fiz. **90**, 169 (1986) [Sov. Phys. JETP **63**, 96 (1986)].

[10] T. C. Lubensky and A. J. McKane, J. Phys. (Paris) Lett. **42**, L331 (1981).

[11] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, New York (1940) [Russ. transl., IIL, Moscow (1958)].

[12] I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, Usp. Fiz. Nauk **127**, 353 (1979) [Sov. Phys. Usp. **22**, 123 (1979)].

[13] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, *Fluctuation Theory of Phase Transitions*, Pergamon Press, Oxford (1979) [Russ. original (2nd ed.), Nauka, Moscow (1982)].

[14] S. L. Ginzburg, Zh. Eksp. Teor. Fiz. **71**, 1145 (1976) [Sov. Phys. JETP **44**, 599 (1976)].

[15] P. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1971).

[16] J. M. Cornwall, R. Jackiw, and E. Tomboulis, Phys. Rev. D **10**, 2428 (1974).

[17] C. M. Fortuin and P. W. Kasteleyn, Physica **57**, 536 (1972).

[18] S. V. Panyukov, Zh. Eksp. Teor. Fiz. **93**, 1454 (1987) [Sov. Phys. JETP **66**, 829 (1987)].

[19] B. B. Mandelbrot, *The Fractal Geometry of Nature*, Freeman, San Francisco (1982).

[20] T. C. Lubensky, J. Isaacson, and S. P. Obukhov, J. Phys. (Paris) **42**, 1591 (1981).

[21] A. R. Khokhlov, Polymer **21**, 376 (1980).

[22] S. V. Panyukov, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 472 (1987) [JETP Lett. **46**, (1987)].

[23] I. Ya. Erukhimovich, Preprint, Scientific Centre of Biological Research, Pushchino (1985).

[24] S P. Obukhov, J. Phys. A **19**, 3655 (1986).

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