Spontaneous symmetry breaking in polymer theory

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The replica method is used to construct a field theory for describing dilute solutions of polymer macromolecules in the presence of arbitrary bulk interactions. It is shown that a spontaneous breaking of the replica symmetry describes the formation of a giant gel macromolecule and the coil-globule transition of a linear chain with a fixed primary structure. The correlation functions for the density of the constituent units of the gel in a polymer system with an arbitrary frozen molecular-structural distribution are calculated, and the Ginzburg number, which determines the size of the region of strong critical fluctuations in a dilute solution of branched macromolecules, is found.

1. INTRODUCTION

Field-theory methods have been used in a number of papers[1–5] for the statistical description of polymers. One of the most fruitful ideas in field theory has been the concept of spontaneous symmetry breaking. Polymer theory, however, has yet to incorporate this concept in a practical manner. In this paper we show that the spontaneous breaking of the replica symmetry[5,6] describes the formation of giant polymer macromolecules, and we calculate their correlation functions.

Polymer molecules can be obtained, for example, by polycondensation of monomeric units (see Fig. 1a). Each polymer molecule consists of a monomer R and a number f of its functional groups. Two functional groups can form a chemical bond (see Fig. 1b), and in certain polycondensation processes the formation of the chemical bond can occur as a reversible reaction. In the presence of chemical equilibrium with respect to the formation and breaking of the bonds, the polymer macromolecules found in solution are statistical and have no definite primary (chemical) structure.

Equilibrium polycondensation is widely used for synthesizing polymers. In the majority of experiments, however, the chemical reaction is "frozen" at a certain level, and the solution obtained is subsequently diluted. In the dilute solution one can determine the molecular-structural distribution and the average dimensions of the molecules and their radius of inertia.[7] Geometric characteristics of this kind are described completely by the correlation functions for individual macromolecules that were determined in Ref. 5.

Thus, in a dilute solution the primary structure of the macromolecules can be regarded as fixed and its monomeric units as being in thermodynamic equilibrium. Thermodynamic fluctuations can bring together units which are widely separated along the molecule; the interactions between such units are called bulk interactions. These interactions determine the spatial configuration of the macromolecules, and they must be taken into account along with the chemical bonds which form the primary structure of the macromolecule. The correlation functions of individual macromolecules in the dilute solution can be very different from their values in the solution in which the reaction occurred, since in the dilute solution the excluded volume effects are weaker than in the initial solution.

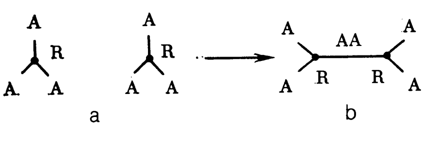

FIG. 1. Monomeric units RA^3 (a) and the formation of a chemical bond between their functional groups (b).

In this paper we consider polymer systems with arbitrary frozen molecular-structural distributions. An important particular case of such a system is that of dilute polymer solutions of polymer macromolecules, where one can neglect the bulk interaction of the units of different macromolecules and consider only the intramolecular interactions and the interaction of the units of the macromolecules with the solvent. The case of concentrated solutions of macromolecules in chemical equilibrium is treated by the replica method in Ref. 5.

In Sec. 2 we study the thermodynamic fluctuations of branched macromolecules with $f \geqslant 3$ obtained in the course of an equilibrium polycondensation of the monomeric units. The behavior of molecules of finite dimensions was considered in Refs. 3 and 8. The statistical properties of such macromolecules are determined by the conversion p, which is the ratio of the number of bonds in the system to the maximum possible number of bonds. For $p \geqslant p_c$ a macromolecule of infinite dimensions, i.e., a gel, arises. The correlation functions of such a giant macromolecule in the initial concentrated solution are calculated in Ref. 5.

In Sec. 3 we use the replica method to construct a field theory for the statistical description of the thermodynamic fluctuations of the gel macromolecule in a dilute solution. It is shown that beyond the gel point the replica symmetry is spontaneously broken. In the case $f = 2$ the molecules are in the form of chains or loops (Fig. 2). In Sec. 3 we also find an exact representation of the partition function of a chain with a fixed primary structure in the presence of arbitrary bulk interactions, in the form of a functional integral over the replica field. It is shown that the coil-globule transition[9] of such a chain is also described by the spontaneous breaking of the replica symmetry.

In Sec. 4 we find in the self-consistent field approxima-

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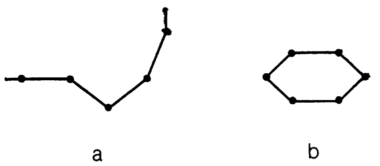

FIG. 2. Linear polymers: chain (a) and loop (b).

tion the correlation functions of the giant polymer network of the gel in a system of arbitrary chemical composition and in the presence of arbitrary bulk interactions between its units. In Sec. 5 we calculate the correlation functions of the gel in a dilute solution. We find the Ginzburg number, which determines the dimension of the region of strong critical fluctuations of the density of units of the gel.

2. GRAND CANONICAL ENSEMBLE

Let us consider a solution of N monomeric units with coordinates $x_1, \ldots, x_N$ each of which has f_α functional groups of type α, where $\alpha = 1, \ldots, w$. Two functional groups of units i, j can form a chemical bond, and we denote by $\lambda(x_i - x_j)$ the conditional probability of finding these units at a distance $|x_i - x_j|$ from each other. We use the term (l, m)-isomer macromolecule to describe l units linked only among themselves by $m = l + r - 1$ chemical bonds, and we let r be the number of independent loops of the macromolecule. Obviously, macromolecules having the same numbers (l, m) can have different topologies. Let us consider a configuration G containing a number $n_{l,m}$ of (l, m)-isomers, so that the total number of units, bonds, and macromolecules in this configuration are respectively

$$N = \sum n_{l,m} l, \quad N_b = \sum n_{l,m} m, \quad \Pi = \sum n_{l,m}. \tag{1}$$

We describe the bulk interactions by the interaction potential energy $V(x - x')$ of pairs of monomeric units. In the presence of chemical equilibrium with respect to the formation and breaking of chemical bonds, we assume that in configuration G the Gibbs distribution function for the coordinates of the particles in a d-dimensional space is equal by definition to

$$W_G\{\mathbf{x}_1, \ldots, \mathbf{x}_N\} = z^N z_b^{N_b} n^{\Pi} / N! \prod (f_\alpha!) \Lambda_T^{dN}$$
$$\times \exp\left\{\frac{1}{T}[\Omega - \Sigma V(\mathbf{x}_i - \mathbf{x}_j) - \Sigma h(\mathbf{x}_i)]\right\} \prod k_{\alpha b} \lambda(\mathbf{x}_i - \mathbf{x}_j). \tag{2}$$

Here h is the external field, T is the absolute temperature, and a factor $k_{\alpha\beta} \cdot \lambda(x_i - x_j)$, where $k_{\alpha\beta} = k_0 \exp(-\varepsilon_{\alpha\beta}/T)$, is associated with each bond between functional groups of types α and β (k_0 and $\varepsilon_{\alpha\beta}$ are the entropy characteristic and energy characteristic of the bond). The factors $N!$ and $f_\alpha!$ take into account the identical nature of the units and of the groups of each unit, $\Lambda_T = (MT/2\pi\hbar^2)^{-1/2}$ is the thermal wavelength,[3] M is the mass of the units, and z, z_b, and n are the activities (relative fugacities) of the units, bonds, and molecules. The thermodynamic potential Ω is determined by the normalization condition.

$$1 = \sum_G \int d\mathbf{x}_1 \ldots d\mathbf{x}_N W_G\{\mathbf{x}_1, \ldots, \mathbf{x}_N\}, \tag{3}$$

where the summation is over all possible configurations G. The correlators of the density of units of the system are found by differentiating Ω with respect to the field h.

We note that for $n \to 0$ sum (3) contains a contribution to first order in n from configurations G which contain only a single molecule and, in particular, a giant gel macromolecule. Such a macromolecule results from the "freezing" of the chemical reactions at fixed values of the total density of units (ρ) and of the conversion $p \geqslant p_c$ beyond the gel point and the subsequent "washing out" of the finite macromolecules of the sol.

3. FIELD THEORY FOR THE STATISTICAL DESCRIPTION OF GIANT MACROMOLECULES

To evaluate the thermodynamic potential Ω(3) we use the method of Ref. 5, according to which Ω in the presence of arbitrary volume interactions can be expressed in terms of the thermodynamic potential $\Omega^{(0)}$ of a system with $V = 0$ in a random field $v(x)$. In the present case formula (14) of Ref. 5 becomes

$$\exp\left[-\frac{\Omega(h)}{T}\right] = \int Dv \exp\left[-\frac{H_0(v) + n\Omega^{(0)}(h+v)}{T}\right] \Big/ \int Dv \exp\left[-\frac{H_0(v)}{T}\right],$$
$$H_0(v) = -\frac{1}{2} \iint d\mathbf{x}\, d\mathbf{x}'\, V^{-1}(\mathbf{x}-\mathbf{x}') v(\mathbf{x}) v(\mathbf{x}'), \tag{4}$$
$$\int d\mathbf{x}_1\, V(\mathbf{x}-\mathbf{x}_1) V^{-1}(\mathbf{x}_1-\mathbf{x}') = \delta(\mathbf{x}-\mathbf{x}').$$

A representation of $\Omega^{(0)}$ in the form of a functional integral is found in Ref. 4:

$$\exp\left[-\frac{\Omega^{(0)}(h)}{T}\right] = \int D\varphi_\alpha \exp\left[-L_0(\varphi_\alpha) + \int dx \frac{z \exp[-h(\mathbf{x})/T]}{\Lambda_T{}^d} \times \prod_{\alpha=1}^{w} \frac{(1+\varphi_\alpha(\mathbf{x}))^{f_\alpha}}{(f_\alpha)!}\right] \Big/ \int D\varphi_\alpha \exp[-L_0(\varphi_\alpha)], \tag{5}$$

where the integration is over the w-component field φ_α, and the quadratic form L_0 is given by the expression

$$L_0(\varphi_\alpha) = \frac{1}{2 z_{\text{CB}}} \iint dx\, dx'\, \lambda^{-1}(\mathbf{x}-\mathbf{x}') \sum_{\alpha=1}^{w} (k^{-1})_{\alpha\beta} \varphi_\alpha(\mathbf{x}) \varphi_\beta(\mathbf{x}'). \tag{6}$$

Performing exactly the integration in (4) over the field v of the volume interactions with the aid of the replica method, we find (see Ref. 5 for details)

$$\exp\left[-\frac{\Omega(h)}{T}\right] = \int D\varphi_{\alpha i} \exp(\Gamma_n\{\varphi_{\alpha i} | h\}) \Big/ \int D\varphi_{\alpha i} \exp\left[-\sum_{i=1}^{n} L_0(\varphi_{\alpha i})\right], \tag{7}$$
$$\Gamma_n\{\varphi_{\alpha i} | h\} = -\sum_{i=1}^{n} L_0(\varphi_{\alpha i})$$
$$+ \pi_0 \left\{\frac{z \exp[-h(\mathbf{x})/T]}{\Lambda_T{}^d} \sum_{i=1}^{n} \prod_{\alpha=1}^{w} \frac{[1+\varphi_{\alpha i}(\mathbf{x})]^{f_\alpha}}{(f_\alpha)!}\right\},$$

where the integration is over the nw-component replica field $\varphi_{\alpha i}$. The functional π_0 determines the thermodynamic potential Ω_0 of a system of broken-up units ($k_{\alpha\beta}=0$) in an external field $h(x)$ (Ref. 9):

$$\Omega_0(h)=-T\pi_0\{z\exp[-h(\mathbf{x})/T]/\Lambda_T{}^d\}. \tag{8}$$

The correlators of the density of units of such a system are found by differentiating π_0 with respect to the field h:

$$\rho(\mathbf{x})=-T\delta\pi_0/\delta h(\mathbf{x}),\quad \langle\delta\rho(\mathbf{x})\delta\rho(\mathbf{x}')\rangle_0 =T^2\delta^2\pi_0/\delta h(\mathbf{x})\delta h(\mathbf{x}'). \tag{9}$$

At a low density ρ of units and at $h=0$, the equation of state of a system of boken-up units is determined by the virial expansion

$$P_0(\rho)=-\Omega_0/\mathscr{V}=\rho T+\rho^2B(T)T+2\rho^3C(T)T+\dots. \tag{10}$$

Here $\mathscr{V}$ is the volume of the system, and the virial coefficients B and C are assumed to be renormalized on account of the solvent molecules (see below and also Ref. 9).

The Lagrangian Γ_n in (7) is symmetric with respect to permutation of the replica fields. Beyond the gel point this symmetry is spontaneously broken and the ground state is degenerate.[5] If fluctuations of the replica fields are neglected, the extremum of the functional Γ_n is reached for the solutions

$$\overset{(0)}{\varphi}_{\alpha i}=\overset{(0)}{\varphi}_{\alpha},\quad i=1,\dots,n, \tag{11}$$

$$\overset{(i)}{\varphi}_{\alpha i}=\bar{\varphi}_{\alpha},\quad \overset{(i)}{\varphi}_{\alpha j}=\varphi_{\alpha},\quad i\neq j,\quad \bar{\varphi}_{\alpha}\geqslant\varphi_{\alpha}.$$

Here the superscript indicates the type of solution (ground state). Evaluating the integral in (7) by the method of steepest descents and summing the contributions of the steepest-descent trajectories (11), we find

$$\exp\left[-\frac{\Omega(h)}{T}\right]=\exp(\Gamma_n\{\overset{(0)}{\varphi}_{\alpha i}|h\})+\sum_{i=1}^{n}\exp(\Gamma_n\{\overset{(i)}{\varphi}_{\alpha j}|h\}) \tag{12}$$

and to first order in n for $n\to0$ we have

$$\exp\left[-\frac{\Omega(h)}{T}\right] =1+n\left[\frac{d}{dn}\Gamma_n\{\overset{(0)}{\varphi}_{\alpha}|h\}|_{n=0}+\exp(\Gamma_0\{\overset{(1)}{\varphi}_{\alpha j}|h\})\right], \tag{13}$$

where the first term in the square brackets is the contribution from finite molecules of the sol. The second term exists only beyond the gel point, and it determines the thermodynamic potential of the gel macromolecule in a dilute solution:

$$\Omega^{\Gamma}(h)=-T\Gamma_0\{\overset{(1)}{\varphi}_{\alpha j}|h\}. \tag{14}$$

To incorporate fluctuations of the replica fields in (14), one should replace Γ_0 by the effective-action functional, which was determined for this system in Ref. 5.

A field theory capable of describing the thermodynamic fluctuations of a linear chain ($f=2$) with fixed primary structure in the self-consistent field approximation as proposed in Ref. 4. The replica method permits finding an exact representation of the partition function of such a chain in the form of a functional integral over the zero-component replica field $\varphi_i(x)$. The Lagrangian of the corresponding field theory is of the form

$$L\{\varphi_i\}=\frac{1}{2}\iint dx\,dx'\,\lambda^{-1}(\mathbf{x}-\mathbf{x}')\sum_{i=1}^{n}\varphi_i(\mathbf{x})\varphi_i(\mathbf{x}') -\pi_0\left\{\frac{z}{2}\sum_{i=1}^{n}\varphi_i{}^2(\mathbf{x})\right\}, \tag{15}$$

where for simplicity we have considered a homogeneous chain ($w=1$). For a bulk interaction of the excluded-volume type the macromolecule is found in the coiled state and the density of its units is low. Using the expansion (10), we find that the thermodynamic fluctuations of such a chain are described by a φ^4 theory of the zero-component replica field φ_i (Ref. 1). In the presence of attraction the chain can be found in a globular state.[9] The Lagrangian (15) is symmetric with respect to rotations in isotopic replica space. At the point of the coil-globule transition this symmetry is spontaneously broken:

$$\varphi_i(\mathbf{x})=\varphi(\mathbf{x})e_i,\quad \sum_{i=1}^{n}e_i{}^2=1,$$

where e_i is a unit vector. In neglect of fluctuations of the replica fields, the equations for the function $\varphi(x)$ are equivalent to the equations of Lifshitz[10] (see also Ref. 9) for the description of the globular state of the chain. The effective-action method[11,5] enables one to evaluate the fluctuation corrections to these equations and to find the correlation functions of such a chain.

4. SELF-CONSISTENT FIELD

Let us consider a gel molecule obtained by equilibrium polycondensation of monomeric units RA^f, for which $f_1=f$ and $f_\alpha=0$ for $\alpha\neq1$ (see Fig. 1). Neglecting fluctuations of the replica fields, $\varphi_{ij}=\varphi_j$, the maximum of the functional Γ_0 in the dilute solution at $h=0$ is reached for the solution

$$\bar{\varphi}=p/(1-p),\quad \varphi=pu/(1-p),\quad u=\xi^{f-1},\quad \xi=1-p+pu, \tag{16}$$

which exists only for $p>p_c=(f-1)^{-1}$, with $0<u<1$. Here the parameter p is related to k, z, and z_b by the expressions

$$\frac{p}{(1-p)^2}=fkz_b\rho,\qquad \rho\equiv\frac{z}{f!(1-p)^f}\pi_0'\left(\frac{z(1-\xi^f)}{\Lambda_T{}^d(1-p)^f}\right),$$
$$\pi_0'(z')=\frac{\delta\pi_0\{z'\}}{\delta z'}. \tag{17}$$

The density of units ρ^g and the density of bonds ρ_b^g of the gel macromolecule are found by differentiating the thermodynamic potential (14) with respect to the logarithm of the activities z and z_b. They determine the conversion p^g and the number r of independent loops per unit volume of the gel macromolecule:

$$p^g\equiv\frac{2\rho_b{}^g}{f\rho^g}=\frac{p(1+u)}{1+pu},\quad \rho^g=\rho(1-\xi^f),$$

$$r=\rho(1-u)\left[\frac{pf}{2}(1+u)-1-pu\right]. \tag{18}$$

We note that relations (16) and (18) agree with the relations found in Ref. 5 for a system in chemical equilibrium if p and ρ are identified with the conversion and density of units of such a system. By calculating the second variational derivative of (14) with respect to the field h, we find the Fourier component of the correlation function of the density of units of the gel:

$$[\langle \delta\rho_{\mathbf{q}}^{g}\delta\rho_{-\mathbf{q}}^{g}\rangle]^{-1}=[\langle \delta\rho_{\mathbf{q}}^{g}\delta\rho_{-\mathbf{q}}^{g}\rangle_0]^{-1}-(\rho^{g})^{-1}+[\hat{g}(\mathbf{q})]^{-1}. \quad (19)$$

Here $\langle ...\rangle_0$ is the correlation function of the density of broken-up units of the gel macromolecules (9). The function $\hat{g}(\mathbf{q})$ is determined by the topological structure of the polymer network of the gel and is given by (see also Ref. 5)

$$\hat{g}(\mathbf{q})=\rho^{g}+\frac{\rho p f}{\lambda^{-1}(\mathbf{q})-p(f-1)}-\frac{\rho p f \xi^{2f-2}}{\lambda^{-1}(\mathbf{q})-p(f-1)\xi^{f-2}}. \quad (20)$$

Relation (20) can be used to describe the change in the behavior of the infinite network of the gel resulting from a change in the physical conditions under which it is found. For a system with a given molecular-structural distribution the correlator $\langle ...\rangle_0$ is equal to the correlation function of test particles—monomers of density ρ^g—placed in the system under study. Since such a correlator is completely determined by the partition function of the system in an external field $h(\mathbf{x})$, it can be evaluated by the diagram methods developed in Ref. 4. Straightforward but awkward manipulations yield

$$\langle \delta\rho_{\mathbf{q}}^{g}\delta\rho_{-\mathbf{q}}^{g}\rangle=\hat{g}(\mathbf{q})+\hat{g}^{2}(\mathbf{q})\hat{\chi}(\mathbf{q})/\hat{\rho}^{2}. \quad (21)$$

Here and below we denote by $\hat{\rho}(\mathbf{x})$ the complete density of units of the gel and sol in a system with a frozen molecular-structural distribution. Expression (21) has the same form as in a system in chemical equilibrium with respect to the formation and breaking of chemical bonds.[5] The only thing that changes is the function $\hat{\chi}(\mathbf{q})$, which describes the bulk interaction of the gel units, screened by all the molecules of the system:

$$[\hat{\chi}(\mathbf{q})]^{-1}=[\chi_2(\mathbf{q})]^{-1}+\hat{\rho}^{-1}-[\hat{g}(\mathbf{q})+g^{(3)}(\mathbf{q})]/\hat{\rho}^{2},$$
$$\chi_2(\mathbf{q})\equiv\langle\delta\hat{\rho}_{\mathbf{q}}\delta\hat{\rho}_{-\mathbf{q}}\rangle_0-\hat{\rho}, \qquad g^{(3)}(\mathbf{q})=\sum_C n_C g_C(\mathbf{q}), \quad (22)$$

where n_C is the number of molecules of a given type C with l units and m bonds, $g^{(3)}$ is the structure function,[4] and g_C is the connectivity function of macromolecule C:

$$g_C(\mathbf{q})=\left\langle \sum_{i,j=1}^{l} \exp[i\mathbf{q}(\mathbf{x}_i-\mathbf{x}_j)]\right\rangle_C, \qquad g_C(0)=l^2. \quad (23)$$

The average in (23) is over all confirmations of the ideal macromolecule of type C. The average density of units of the system is

$$\hat{\rho}=\rho^{g}+\sum_C n_C l. \quad (24)$$

In many-component systems Eqs. (21)–(23) have a matrix structure.[4] The summation in (22) and (24) is over all molecule types C in the system, including monomers and solvent molecules. For the latter we have $l = 1$ and $g_C = 1$, so that the contribution of the solvent molecules reduces to just a renormalization of the density correlation function χ_2 (22) of a system of broken-up units. It was this renormalization that we had in mind in Eq. (10).

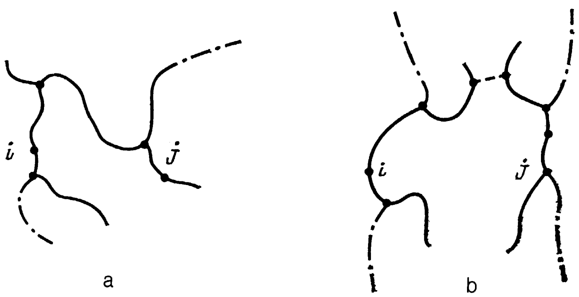

FIG. 3. Gel macromolecule configurations which contribute to the correlation function of the density of its units. The dashed lines represent the volume interaction of the units (see Ref. 4), and the dot-and-dash lines show the branches going out into the condensate.

To understand the physical meaning of (21), let us consider its diagrammatic interpretation. The most surprising feature of field theory (7) beyond the gel point is that even in the self-consistent field approximation it incorporates excluded-volume effects and the effects of loop formation in the gel macromolecule. The loops are constituents of the so-called condensate. As in the case of Bose condensation, the condensate is described completely by the macroscopic characteristics of the gel, such as the density of its units and bonds. Two arbitrary units i, j of the giant gel macromolecule can be linked together both directly (see Fig. 3a) and also only through the condensate (Fig. 3b). In addition, the correlations in the position of these units are due to the interaction between the monomeric units of the gel (see Fig. 3b). This interaction is screened both by the finite molecules of the sol (Fig. 4b) and by the infinite network of the gel (Fig. 4c). The resulting screened interaction is calculated in (22), and it can also be obtained by summing diagrams of the type in Fig. 4. Accordingly, the first term on the right-hand side of (21) takes into account the correlations shown in Fig. 3a, and the second term those in Fig. 3b. Allowance for fluctuations of the replica fields is equivalent to summing the loop diagrams that do not become part of the condensate.

We note that correlation function (21) has features both at the gel point and also on the spinodal. For a more detailed description of the system we must assign it a molecular-structural distribution $\{n_C\}$. For a system in which the molecular-structural distribution is determined by the condition of chemical equilibrium, result (21) goes over to the result of Ref. 5. We shall henceforth consider only a system consisting of a single gel macromolecule, for which $n_C = 0$.

5. DILUTE SOLUTION

For $1-p\ll 1$, correlator (21), (22) with $n_C=0$ goes over to the correlation function of the total density of units of a system in chemical equilibrium,[4,5] since for $p\to 1$ it consists of a single gel macromolecule. When $\tau = 1 - p/p_c$ is small, $|\tau|\ll 1$ the density of monomeric units of the gel is low: $\rho^g \ll \rho$. Since we will be interested in scales which are large compared to the bond dimension a, let us assume

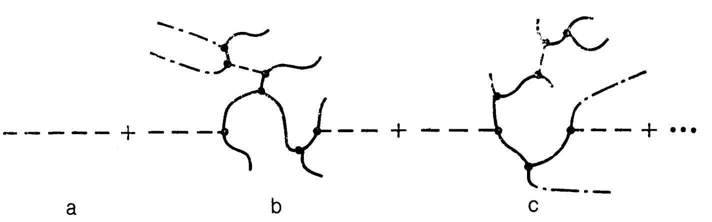

FIG. 4. Diagrams which determine the screening of the bulk interaction of the gel units in the self-consistent field approximation.

$$\lambda^{-1}(\mathbf{q})=1+a^2\mathbf{q}^2,\qquad \rho^g=2f\rho|\tau|(f-2)^{-1}. \tag{25}$$

Substituting (25) into (21) and (22), we find for $\mathbf{q}\neq 0$

$$\langle\delta\rho_{\mathbf{q}}{}^g\delta\rho_{-\mathbf{q}}{}^g\rangle=\frac{2f}{f-1}\frac{\rho}{\tau_0+a^4\mathbf{q}^4/|\tau|},\qquad \tau_0=\tau+\frac{4B(T)\rho f}{f-1}, \tag{26}$$

where we have also assumed that the characteristic radius r_0 of the bulk interaction is small compared to the correlation length of the system.

$$\xi_c=a/2^{1/2}(\tau_0|\tau|)^{1/4}. \tag{27}$$

The denominator of (26) does not contain a $\mathbf{q}^2$ term, unlike the correlation function of the individual sol molecules (see Ref. 5), which is found by differentiating the first term in the square brackets in (13) with respect to the field h. Accordingly, in contrast to the case of a system in chemical equilibrium,[5] the quantity ξ_c in (27), even for $|\tau|\to 0$, is determined by the parameter B of the volume interactions. Let us discuss this anomalous behavior of the correlation length ξ_c.

The chemical bonds give rise to an effective attaction of the monomeric units,[7] and in the absence of volume interactions the gel is thermodynamically unstable.[4] Excluded-volume effects keep the polymer network of the gel from collapsing. The correlation length ξ_c of such a network is determined by the condition of statistical equilibrium of the chemical attraction and mutual repulsion of the monomeric units of the gel, which gives rise to anomalous behavior of ξ_c (27) and of the correlation function of the gel (26).

Correlator (26) permits estimation of the dimensions of the fluctuation region

$$\varkappa_d\equiv\langle(\delta\rho^g)^2\rangle/(\rho^g)^2\approx(\rho a^d)^{-1}|\tau|^{-(8-d)/4}\tau_0^{-(4-d)/4}\ll 1. \tag{28}$$

The Ginzburg number $\tau=\tau_G$ is determined from the condition $\varkappa_d\approx 1$. It follows from (28) that the upper critical dimensionality for gelation in a dilute solution is $d_c=8$, in accordance with the fact that the critical behavior of the system in the fluctuation region $|\tau|\lesssim\tau_G$ is the same as for "lattice animals" (Ref. 12). For $\tau_0=0$ the system loses thermodynamic stability, and for this transition (if it exists) the upper critical dimensionality is $d_c=4$.

For space of $d=3$ dimensions we find from (26) for $|\tau|\ll 1$

$$\langle\delta\rho^g(\mathbf{r})\,\delta\rho^g(0)\rangle=\frac{\rho f}{f-1}\left(\frac{|\tau|}{\tau_0}\right)^{1/2}\frac{\exp(-r/\xi_c)}{4\pi a^2 r}\sin\frac{r}{\xi_c}. \tag{29}$$

The correlation length ξ_c is given in (27); it goes to infinity both at the gel point $\tau=0$ and on the spinodal $\tau_0=0$. The parameter $\varkappa_3$ (28),

$$\varkappa_3=\frac{(f-2)^2}{2^{7/2}\pi f(f-1)\rho a^3}|\tau|^{-5/4}\tau_0^{-1/4}, \tag{30}$$

contains a small numerical factor ($5\cdot 10^{-3}$ for $f=3$). Therefore, the dimension τ_G of the fluctuation region for the gel macromolecule obtained by equilibrium polycondensation of a concentrated solution of monomeric units ($\rho a^3\gtrsim 1$ and $\rho B(T)\sim 1$) is small. For $|\tau|\gg\tau_G$ the self-consistent field approximation can be used for the statistical description of such a macromolecule practically right up to the transition point.

The θ point is determined from the vanishing of the second virial coefficient $B(T)=0$. Simple calculations show that under θ conditions the upper critical dimensionality is reduced to six (see also Ref. 13). At the θ point one must take three-body interactions into account, and the gel is thermodynamically stable only for

$$C(T)>(f-1)(f-2)/24f^2\rho^2.$$

To understand the importance of cyclization of the gel molecule, let us consider a giant branched molecule obtained by the polycondensation of monomeric units RBA^{j-1} (see Fig. 5); here chemical bonds can form only between groups A and B. This macromolecule has the feature that it has only one loop. As is shown in Ref. 8, a system in chemical equilibrium contains only finite sol macromolecules, and a molecule of macroscopic dimensions can arise only in a dilute solution. For this case

$$f_{\mathrm{A}}=1,\quad f_{\mathrm{B}}=f-1,\quad k_{\mathrm{AA}}=k_{\mathrm{BB}}=0,\quad k_{\mathrm{AB}}=k_{\mathrm{BA}}=k$$

and beyond the transition point there is a spontaneous breaking of the replica symmetry for the field $\varphi_{\mathrm{A}j}$. In the self-consistent field approximation we find for $k\rho^g\ll 1$

$$\langle\delta\rho_{\mathbf{q}}{}^g\delta\rho_{-\mathbf{q}}{}^g\rangle=[2B(T)+fa^4\mathbf{q}^4/(f-1)\rho^g]^{-1}.$$

Thus the anomalous behavior of correlator (26) is not due to the breaking of loops in the gel macromolecule but is determined by the bulk interactions of the monomeric units of the condensate that keep the giant branched macromolecule from collapsing.

6. CONCLUSION

We have shown in this paper that the spontaneous breaking of the replica symmetry enables one to calculate the

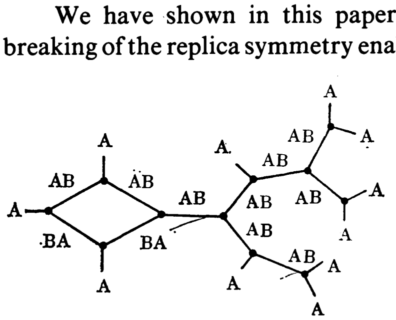

FIG. 5. Branched macromolecule obtained by polycondensation of monomeric units RBA^2.

correlation functions of giant polymer macromolecules found in a system with arbitrary molecular-structural distributions. Besides the problems considered in this paper, the concept of spontaneous symmetry breaking permits description of the statistical behavior of test macromolecules placed in the polymer network of a gel, the behavior of a gel near walls, etc.

Of course the possibilities of the replica method are not limited to the polymer model we have used (some of the models are reviewed in Refs. 9 and 14). The replica method permits one to "dress" the ideal macromolecules or ensembles of ideal macromolecules in each of the models in a "coat" of arbitrary bulk interactions.

The choice of order parameter for the sol-gel transition in a solution of branched polymers in chemical equilibrium is discussed in Ref. 5. In a dilute solution the correlators $\langle \varphi_i(\mathbf{x}) \varphi_j(\mathbf{x}') \rangle$ diverge on approach to the gel point for any $i,j = 1, \dots, n, n \neq 1$. Therefore, the order parameter is the n-component replica field $\varphi_i(\mathbf{x})$ for $n \to 0$. Beyond the gel point ($w = 1$), the quantity

$$\varphi = \lim_{n \to 0} \sum_{i=1}^{n} \varphi_i = k \rho_f{}^g$$

is determined by the density of unreacted functional groups ρ_f^g of the polymer network of the gel.

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