Statistical theory of the sol–gel transition in weak gels

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A microscopic theory of weak gels, i.e., systems of identical monomers capable of forming from 0 to $f>2$ reversible chemical bonds with other particles at thermodynamic equilibrium, is devised. A new primary approximation is proposed to describe an infinite network of bonds (a gel fraction), and it is used to show that the formation of a gel fraction (a sol–gel transition) in weak gels is a second-order phase transition. At the transition point both the geometric characteristics of the clusters of bonds (which are analogous to the structural characteristics of clusters of conducting bonds in the case of percolation) and the observable physical (thermodynamic) parameters are singular. In view of the fundamental importance of this result, it is obtained in three totally different ways: 1) in terms of formal derivatives of functions from the physically visualizable diagram technique, which makes it possible to analyze the decisive role of the cyclization effects accompanying a sol–gel transition; 2) by generalizing the approach developed by I. M. Lifshits in the theory of polymer globules on the basis of density-functional formalism; 3) by employing an approximation for the statistical sum of the grand canonical ensemble of the system under consideration by a certain two-field functional integral. The abrupt changes in the thermodynamic derivatives are calculated in that approximation, and the features of the density–density correlation function near the sol–gel transition point are found.

1. INTRODUCTION

We begin by introducing some definitions. Systems which are in a state of thermodynamic equilibrium with respect to the formation and cleavage of chemical bonds between the particles (monomers) in these systems are called equilibrium polymer systems. To describe the classical macroscopic properties of such systems, the chemical bonds are treated phenomenologically as a special type of interactions, which, unlike ordinary electrostatic interactions, have the property of saturation. Owing to the property of saturation of chemical bonds, the formation of macromolecules can be treated as the establishment of a natural sequence (topology) of particles which are indistinguishable before polymerization, in which proximity implies proximity of the particles in space. An important characteristic of a monomer is its functionality f, the maximum number of chemical bonds in which it can participate.

The interest in the behavior of equilibrium polymer systems stems from their primary importance for biophysics (water) and earth science (silicate melts), as well as from their diverse applications in technology.

The simplest example of an equilibrium polymer system is a system of identical f-functional monomers A_f (Refs. 1 and 2), i.e., particles which each have f identical chemical groups A, which are such that the formation of an A–A chemical bond is possible between any two of them. The character of the chemical equilibrium relative to the formation and cleavage of these bonds is determined by the values of the chemical equilibrium constant k for those reactions[3] and the functionality f of the monomer.

For $f=1$ such an equilibrium polymer system is a mixture of monatomic and diatomic molecules (Fig. 1a), and its treatment is a problem in the theory of low-molecular-weight systems. For $f=2$ the system is a mixture of linear (Fig. 1b) and similar cyclic (Fig. 1c) macromolecules A_2, A_3, ..., A_n, ..., in which a certain equilibrium distribution of those macromolecules among the degrees of polymerization n is established. This distribution depends on the density of the monomers $\rho=N/V$ (N is the total number of monomers, V is the volume of the system), the chemical equilibrium constant k, and the character of the bulk interaction of the monomers. As the fraction of functional groups which have reacted (the so-called extent of conversion) $\Gamma=2\nu/fN$ (ν is the equilibrium number of all the bonds) tends to unity, i.e., as the mean degree of polymerization of the macromolecules $L=(1-\Gamma)^{-1}$ increases, the behavior of a system of bifunctional monomers at chemical equilibrium becomes universal and is described by a model which is isomorphic to the model of an n-component magnet. This isomorphism was described by de Gennes[4] for $n=0$, which corresponds to a state of partial equilibrium, in which the formation of cyclic polymers is forbidden: as was first shown in Refs. 5 and 6, systems at partial equilibrium with an assigned chemical potential μ_c for the cycles, have $n=\exp(\mu_c/T)$, which can take any positive value (see also Refs. 7–9). In particular, at complete chemical equilibrium between the linear and cyclic chains, $\mu_c=0$ and $n=1$ hold, i.e., such an equilibrium polymer system is described by an ordinary Landau Hamiltonian with a scalar order parameter.[5–9]

Equilibrium polymer systems with $f>2$, which are capable of forming branched (Fig. 2a) and cyclized structures (Figs. 2b and 2c) are called weak gels.[2] One feature of weak gels is the so-called sol–gel transition, which occurs when the extent of conversion has a certain critical value $\Gamma=\Gamma_c^s<1$. For $\Gamma<\Gamma_c^s$ all the monomers appear in macromol-

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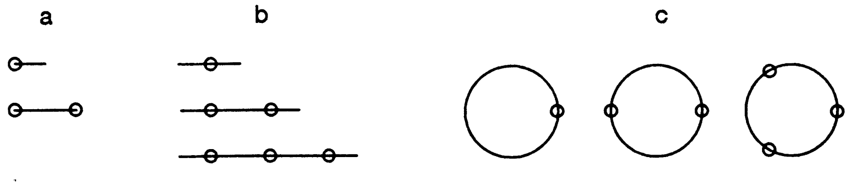

FIG. 1. Typical structural models appearing in equilibrium polymer systems: a) monomers and dimers for $f=1$; b, c) linear (b) and cyclic (c) 1-, 2-, and 3-mers for $f=2$.

ecules (clusters of chemical bonds) of finite size, which are collectively called the sol fraction, and for $\Gamma > \Gamma_c^s$ a finite fraction of the monomers is included in an infinite network of chemical bonds (the gel fraction).

The sol–gel transition just described clearly parallels the percolation formation of an infinite cluster, and many problems and concepts in the theory of weak gels can be translated into the language of percolation theory.[10–18] However, there is a fundamental physical difference between these theories, which stems from the following fact. The basic parameters of percolation theory are p and $1-p$, which are, respectively, the probabilities of percolation and nonpercolation between neighboring lattice sites, the sum of the probabilities of all the possible percolation structures being, of course, identically equal to unity. Accordingly, the main concerns of percolation theory are the structure of the infinite cluster and the size distribution of the finite clusters of bonds in the lattice. On the other hand, in the theory of weak gels, the extent of conversion Γ, which is analogous to p, is determined not only by the density of the monomers ρ and the chemical equilibrium constant $k(T)$, but also by all aspects of the size and structural distribution of the macromolecules. The sum of the weights (not the probabilities!) of all the structural realizations is the statistical sum of an equilibrium polymer system. Therefore, although the question of the structure of the clusters in the theory of equilibrium polymer systems is important, it is only of secondary importance. The main problem here is the calculation of the statistical sum and the free energy of such a system as functions of T and ρ and an analysis of the nature of the phase equilibria and transitions (including sol–gel transitions to weak gels).

An effective mathematical technique for such a calculation is to represent the statistical sum of the equilibrium polymeric system in the form of a certain functional integral with respect to a scalar field, which was obtained for the first time in Ref. 6 and served as a basis for Panyukov's work[19,20] and his replica–field formalism[21] (see also the reviews by Kuchanov *et al.*[17,18]). The calculation of this integral by the saddle-point method gives[19,20] expressions for observable physical (not geometric!) parameters, which do not contain singularities at the sol–gel transition point (the gel point). A similar conclusion regarding the nonsingular nature of the physical parameters at the gel point in a simple model of a weak gel had previously been drawn in Ref. 13.

However, a finer analysis based on explicit consideration of these nonsingular saddle-point expressions for asymptotic expansions in the small parameter $u=(f\rho a^3)^{-1}$ shows that they are applicable only for $\Gamma < \Gamma_c^s$ and that extending them into the $\Gamma > \Gamma_c^s$ region is incorrect. (A similar situation for contour integrals in the complex plane is well known in the theory of the WKB method and asymptotic expansions as the Stokes phenomenon.) The present work is devoted to performing such an analysis and to deriving expressions which are asymptotically correct in the postgelation region for the characteristics of equilibrium polymer systems.

The material is presented in following manner. In Sec. 2 we describe the original version of the functional integration technique and obtain the basic equations describing the behavior of an equilibrium polymer system in the mean-field approximation. Section 3 gives another derivation of these equations, which is based on a generalization of the density-functional formalism proposed by I. M. Lifshits in the theory of polymer globules[24] to equilibrium polymer systems. The results in Secs. 2 and 3 are valid only in the absence of a gel fraction, but the detailed presentation is necessary both for a comparison with Panyukov's work and for substantiating the fundamentally new "long-edge" approximation. This approximation, whose name will become clear when it is described in Sec. 4, is based on an analysis of the distribution of monomers among large cyclized macromolecules using the physically visualizable diagram technique. It makes it possible to describe the nontrivial structure of an equilibrium polymeric structure in the postgelation region and to show that the sol–gel transition in weak gels is a second-order phase transition in a certain primary approximation. The physical meaning of the order parameter associated with this transition is revealed in Sec. 5, where the equations of the long-edge approximation are derived, once again, on the basis of a modified density-functional formalism. In Sec. 6 we propose a representation of the statistical sum of an equilibrium polymer system in the form of a certain functional integral with respect to two scalar fields, one of which corresponds to monomers appearing in the composition of

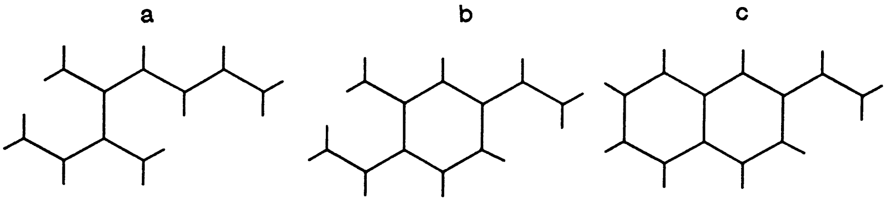

FIG. 2. Typical structures of molecules appearing in equilibrium polymer systems with $f=3$: a) branched; b, c) cyclized.

branched portions of macromolecules, while the other corresponds to monomers appearing in cyclized portions. Although this two-field representation, unlike the single-field analog considered in Sec. 2, is approximate, rather than exact, it makes it possible not only to give another derivation of the results in Secs. 4 and 5, but also to obtain an expression for the density–density correlation function for $\Gamma>\Gamma_c^s$ near the gel point. The logic and main results of this work are summarized in Conclusions.

2. FUNCTIONAL-INTEGRATION TECHNIQUE IN THE THEORY OF EQUILIBRIUM POLYMER SYSTEMS

Following I. M. Lifshits,[24] we redefine the problem of calculating the statistical sum of an equilibrium polymer system in the following manner. We assume that a theory of simple liquids has been devised and that we know everything about the thermodynamic and correlation characteristics of a so-called broken-link system, i.e., a model system of point particles interacting with a potential energy corresponding to the bulk interaction between the monomers.[1)] What are the effects of the including of thermally reversible (labile) chemical bonds between the monomers? Under such a formulation, it is natural to define the distribution function $f_N(\gamma)$, where $\gamma=(\mathbf{r}_1,\cdots,\mathbf{r}_N)$ is a point in the configuration space of an N-particle equilibrium polymer system ($\mathbf{r}_i$ is the radius vector of the ith monomer), as the product

$$f(\gamma)=f_{\mathrm{bls}}(\gamma)f_{\mathrm{str}}(\gamma). \tag{2.1}$$

The first factor in (2.1), which describes the contribution of the bulk interaction, is the Gibbs distribution function of a broken-link system:

$$f_{\mathrm{bls}}(\gamma)=\exp[-\Sigma_{ij}U(r_{ij})/T], \tag{2.2}$$

where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ is the distance between the ith and jth monomers, and $U(r)$ is the potential energy of their paired interaction. The second factor in (2.1) describes the variation of the energy and the restriction of the configuration space of the system due to the appearance of chemical bonds in it:

$$f_{\mathrm{str}}(\gamma)=\Sigma_G\prod_G g(|\mathbf{r}_i-\mathbf{r}_j|), \tag{2.3}$$

where the function $g(r)$ describes the additional correlation between the coordinates of the ith and jth monomers due to the appearance of an A–A chemical bond between them. It is related to the chemical equilibrium constant $k(T)$ for the formation and cleavage of A–A bonds by the expression

$$g_0=\int g(r)dV=k(T). \tag{2.4}$$

The product in (2.3), unlike that in (2.2) is taken only for the pairs of bonded particles or, stated differently, for the edges of a certain graph G, which characterizes the order in which the monomers are joined to one another, and then the summation is performed over all the possible topological structures (graphs) G of the system under consideration.

Let us consider the statistical sum of the grand canonical ensemble:

$$Z(V,T,\mu)=\sum_{N=0}^{\infty} Z_N(V,T)\ \exp(\mu N). \tag{2.5}$$

Here $Z_0(V,T)=1$ and

$$Z_N(V,T)=\frac{\int d\gamma f_N(\gamma)}{N!(\lambda^3 f!)^N}, \tag{2.6}$$

where λ is the thermal wavelength of the monomers, and the multiplier $[N!(\lambda^3 f!)^N]^{-1}$ takes into account the identical nature of the latter.

The following exact representation in the form of a functional integral with respect to the scalar fields ϕ is valid for the statistical sum (2.5) of an equilibrium polymer system:

$$Z(V,T,z)=\int\delta\phi\ \exp[S(\{\phi(\mathbf{r})\})]/\int\delta\phi \times\exp\left[-\int dV\phi\hat{g}^{-1}\phi/2\right], \tag{2.7}$$

$$S(\{\phi(\mathbf{r})\})=X(\tau\phi(\mathbf{r}))-\int dV\phi\hat{g}^{-1}\phi/2, \tag{2.8}$$

$$\tau(\phi(\mathbf{r}))=z(\phi(\mathbf{r})+Y)^f/f!, \tag{2.9}$$

where $z=\lambda^{-3}\exp\ (\mu/T)$, Y is an auxiliary multiplier, which is assigned to each free (unreacted) functional group A and is set equal to unity at the end of the calculations, and $\hat{g}^{-1}$ is the inverse of the integral operator $\hat{g}\phi=\int g(|\mathbf{r}-\mathbf{r}'|)\phi(\mathbf{r}')dV'$, whose kernel is the correlation function $g(r)$ defined above. Finally $X(\{\tau(\mathbf{r})\})$ is the generating functional of all the connected Mayer diagrams of the corresponding broken-link system, which is well known in the theory of simple liquids. Referring to Ref. 26 and 27 for the definition of the properties of this functional, here we present only the expressions used below for its first and second variational derivatives with respect to the local activities $\tau(\mathbf{r})$:

$$\tau(\mathbf{r})\delta X/\delta\tau(r)=\rho(\tau(r)), \tag{2.10}$$

$$\tau(\mathbf{r}_1)\tau(\mathbf{r}_2)\frac{\delta^2\chi_0}{\delta\tau(\mathbf{r}_1)\delta\tau(\mathbf{r}_2)}\bigg|_{\tau(\mathbf{r})=\tau}=G(\mathbf{r}_1-\mathbf{r}_2) -\rho(\tau)\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{2.11}$$

Here $\rho(\tau)$ and $G(\mathbf{r}_1-\mathbf{r}_2)=\langle\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\rangle-\langle\rho(\mathbf{r}_1)\rangle\langle\rho(\mathbf{r}_2)\rangle$ are, respectively, the density and the density–density correlator of the particles in the broken-link system as a function of their activity τ.

The representation (2.7), which was first obtained in Ref. 6 by comparing diagram expansions of the integral (2.7) and the statistical sum (2.5), realizes the basic idea of Lifshits's approach, viz., separation of the high-molecular-weight effects caused by the presence of bonds from the effects of the condensed state, which are determined by the bulk interaction. An alternative proof of this representation was given in Refs. 17–19. Both proofs were discussed in detail in Ref. 28.

The calculation of the integral (2.7) by the saddle-point method leads to the following equation for the saddle-point value of the order parameter $\bar{\phi}$:

$$\frac{\delta X}{\delta\tau(\mathbf{r})}\frac{\partial\tau}{\partial\phi}\bigg|_{\phi(\mathbf{r})=\bar{\phi}}=\frac{f\rho}{\bar{\phi}+1}=g_0^{-1}\phi(\mathbf{r})\bigg|_{\phi(\mathbf{r})=\bar{\phi}}, \tag{2.12}$$

where we used the definitions (2.8)–(2.10). Equation (2.12) makes it possible to relate the saddle-point value of the order parameter $\bar{\phi}$ and the monomer density ρ:

$$\bar{\phi}(\bar{\phi}+1)=g_0 f\rho=\tilde{\rho}. \tag{2.13}$$

On the other hand, the value of $\bar{\phi}$ is related to the value of the extent of conversion (the fraction of unreacted functional groups) Γ by the equation

$$1-\Gamma=\frac{Y\partial\chi}{\partial Y}\bigg/\frac{z\partial\chi}{\partial z}\bigg|_{Y=1}=\frac{1}{\bar{\phi}+1}. \tag{2.14}$$

The law of mass action[3] for the equilibrium reaction A + A $\rightleftarrows$ A_2 follows from (2.13) and (2.14):

$$\Gamma/(1-\Gamma)^2=\tilde{\rho}. \tag{2.15}$$

[The application of Eq. (2.15) and the second of equalities (2.13) to a monofunctional equilibrium polymer system also leads to the relation (2.4).] Next, the pressure P and the chemical potential μ of the equilibrium polymer system as a function of ρ and T are defined by the expressions

$$P(\rho,T)=-\frac{\partial\Omega}{\partial V}=\left\langle\chi_0(\tau,T)-\frac{T\phi^2}{2g_0}\right\rangle$$

$$=p_0(\rho,T)-\frac{Tf\rho\Gamma}{2}, \tag{2.16}$$

$$\tau=\frac{z(\bar{\phi}+1)^f}{f!}=\frac{\tau_0(\rho)}{f!}$$

whence we have

$$\mu=T\ln z=T\ln\frac{\tau_0(\rho(T))}{(\bar{\phi}+1)^f}$$

$$=\mu_0(\rho,T)+Tf\ln(1-\Gamma), \tag{2.17}$$

where p_0 is the pressure and μ_0 is the chemical potential of the broken-link system, whose dependences on ρ and T are assumed to be known from the theory of low-molecular-weight liquids or are determined on the basis of phenomenological arguments, and we have introduced the notation

$$\langle A(\{\phi(\mathbf{r})\})\rangle=\frac{\int\delta\phi A(\{\phi(\mathbf{r})\})\exp[\int dVS(\{\phi(\mathbf{r})\})]}{\int\delta\phi\exp[\int dVS(\{\phi(\mathbf{r})\})]}. \tag{2.18}$$

Finally, to calculate the density–density correlation function of an equilibrium polymer system, we use the standard relation

$$G(\mathbf{r}_1,\mathbf{r}_2)=T\frac{\delta^2}{\delta\varphi(\mathbf{r}_1)\delta\varphi(\mathbf{r}_2)}\ln Z(V,T,z\{\varphi(\mathbf{r})\}), \tag{2.19}$$

where $Z(V,T,z,\{\varphi(\mathbf{r})\})$ is the statistical sum of the system as a functional of the spatially nonuniform external field $\varphi(\mathbf{r})$, which is obtained by plugging the expression

$$\tau(\phi(\mathbf{r}))=\frac{z(\phi(\mathbf{r})+Y)^f}{f!}\exp\left[\frac{-\varphi(\mathbf{r})}{T}\right] \tag{2.9a}$$

into (2.7) and (2.8) instead of (2.9). A calculation of (2.19) using (2.10) and (2.11) gives

$$G(\mathbf{r}_1,\mathbf{r}_2)=\langle G(\{\tau(\phi)\},\ \mathbf{r}_1-\mathbf{r}_2)\rangle$$

$$+\langle\rho(\tau(\phi(\mathbf{r}_1)))\rho(\tau(\phi(\mathbf{r}_2)))\rangle-\langle\rho(\tau(\phi(\mathbf{r}_1)))\rangle$$

$$\times\langle\rho(\tau(\phi(\mathbf{r}_2)))\rangle. \tag{2.20}$$

For simplicity we shall henceforth assume that the characteristic scale r_0 of the correlation function $G_{\text{bls}}(\mathbf{r}_1-\mathbf{r}_2)$ of the broken-link system is always much smaller than the correlation radius R, which characterizes the correlation function (2.20) of the polymer system. (This assumption is, of course, subject to verification.) Under this approximation the correlation function $G_{\text{bls}}(\mathbf{r}_1-\mathbf{r}_2)$ can be written in the form

$$G_{\text{bls}}(\mathbf{r}_1-\mathbf{r}_2)=G_0\delta(\mathbf{r}_1-\mathbf{r}_2), \tag{2.21}$$

where G_0 satisfies the following rigorous thermodynamic equality (Ref. 3):

$$G_0=\rho T(\partial\rho/\partial p)_T. \tag{2.22}$$

A major role in the ensuing presentation is also played by the correlator

$$J(\mathbf{r}_1-\mathbf{r}_2)=\langle\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\rangle-\langle\phi(\mathbf{r}_1)\rangle\langle\phi(\mathbf{r}_2)\rangle, \tag{2.23}$$

for which an expression is easily obtained by restricting ourselves to only the quadratic terms in the expansion of the Lagrangian $S(\phi)$ appearing in integrals like (2.18) in the deviations $\delta\phi(\mathbf{r})=\phi(\mathbf{r})-\bar{\phi}$:

$$S(\{\phi(\mathbf{r})\})=S(\bar{\phi})+\int\delta\phi(\mathbf{r}_1)\frac{\delta^2 S}{\delta\phi(\mathbf{r}_1)\delta\phi(\mathbf{r}_2)}\frac{\delta\phi(\mathbf{r}_2)}{2}$$

$$=S(\bar{\phi})-\int\frac{d^3q}{(2\pi)^3}\frac{|\delta\phi_{\mathbf{q}}|^2}{2}J^{-1}(\mathbf{q}), \tag{2.24}$$

where

$$J^{-1}(\mathbf{q})=\int\frac{\delta^2 S\,d\mathbf{r}_2}{\delta\phi(\mathbf{r}_1)\delta\phi(\mathbf{r}_2)}\exp[-\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)],$$

$$\times\int dV\delta\phi(\mathbf{r})\exp(-i\mathbf{q}\cdot\mathbf{r})=\delta\phi_{\mathbf{q}}$$

are the corresponding Fourier transforms. A direct calculation of the second variational derivative of the functional S, which is explicitly defined by Eq. (2.8), gives

$$J^{-1}(\mathbf{q})=g_{\mathbf{q}}^{-1}-\left\{f(f-1)+f^2\left[T\left(\frac{\partial\rho}{\partial p}\right)_T-1\right]\right\}\frac{\rho}{(\bar{\phi}+1)^2}$$

$$=g_0^{-1}[\tilde{g}_{\mathbf{q}}^{-1}-(f-1)\Gamma-f\,\Gamma\beta(\rho,T)], \tag{2.25}$$

where we have used the equalities (2.8) and (2.9) and introduced the quantity

$$\beta(\rho,T)=(G_0-\rho)/\rho=T(\partial\rho/\partial p)_T-1, \tag{2.26}$$

which is identically equal to zero only for an ideal gas, as well as the normalized correlation function

$$\tilde{g}_{\mathbf{q}}=\int dV\,\frac{g(r)}{g_0}\,\exp(i\mathbf{q}\cdot\mathbf{r}).$$

The condition for stability of the resulting saddle-point solution $\phi(\mathbf{r})=\bar{\phi}$ is positiveness of the quantity $J^{-1}(\mathbf{q})$, i.e.,

$$\tilde{g}_{\mathbf{q}}^{-1}-(f-1)\Gamma-f\ \Gamma\beta(\rho,T)>0. \tag{2.27}$$

In the range of scales which are large compared with the root-mean-square bond $a^2=\int r^2g(r)dV/\int g(r)dV$, the Fourier transform $\tilde{g}_{\mathbf{q}}$ of the isotropic function $g(\mathbf{r})$ appearing in (2.25) can be expanded in powers of q^2a^2 to obtain the expression for the correlator $J(\mathbf{q})$

$$J(\mathbf{q})=g_0\left[1-(f-1)\Gamma-f\ \Gamma\beta(\rho,T)+\frac{q^2a^2}{6}+...\right]^{-1}. \tag{2.25a}$$

Calculating the averages of the form (2.18) appearing in the expression (2.20) for the correlation function of an equilibrium polymer system, we can easily show that the latter has the form

$$G(\mathbf{q})=G_0+\left(\frac{\partial\rho}{\partial\tau}\frac{\partial\tau}{\partial\phi}\right)^2J(\mathbf{q})+\{...\}$$
$$=G_0+\frac{G_0^2f\ \Gamma/\rho}{\tilde{g}_{\mathbf{q}}^{-1}-(f-1)\Gamma-f\ \Gamma\beta(\rho,T)}+\{\cdots\}, \tag{2.28}$$

where we used the symbol $\{\cdots\}$ to denote the sum of all the terms representing integrals of the form $\langle\phi^2(\mathbf{r})\rangle$, which diverge on small scales. As was shown in Refs. 7, 29, and 30, these integrals produce only some renormalization of the characteristics of the broken-link system (a broken-link system normalized in this manner is generally called a quasimonomer system[31]) and can be omitted provided $X(\tau)$ is understood to be a phenomenological functional which specifically characterizes the properties of the "quasimonomers." Then (2.28) can be rewritten in the following form (see Refs. 6, 17, and 32):

$$\frac{G(q)}{G_0}=\frac{\tilde{g}^{-1}(q)+\Gamma}{\tilde{g}_{\mathbf{q}}^{-1}-(f-1)\Gamma-f\ \Gamma\beta(\rho,T)}. \tag{2.29}$$

As is seen from (2.29), in the absence of a bulk interaction ($\beta=0$) the values of the correlation function $G(q)$ at $q=0$ and the correlation radius in the approximation under consideration become infinite at the critical value of the extent of conversion

$$\Gamma_c^s=(f-1)^{-1}. \tag{2.30}$$

The point defined by the condition (2.30) is called the gel point. It is known in the theory of polymers[1,2] that the so-called weight-average degree of polymerization of branched (with $f>2$) macromolecules diverges at just this point:

$$M_w=\sum_{l=1}^{\infty}l^2n(l)/\sum_{l=1}^{\infty}l\ n(l)\xrightarrow[\Gamma\to\Gamma_g^c-0]{}\infty \tag{2.31}$$

$[n(l)$ is the equilibrium number of l-mers per unit volume of the system], indicating the appearance of an infinite cluster of bonds, i.e., a gel fraction, in the system at $\Gamma>\Gamma_c^s$. The expressions (2.30) and (2.31), which define the gel point, also hold when there is a bulk interaction.[17,18] At the same time, the critical value Γ_c of the extent of conversion, at which the singularity of the correlation function (2.29) is achieved, has the form

$$\Gamma_c^{-1}=(\Gamma_c^s)^{-1}-f\beta(\rho,T), \tag{2.32}$$

and when there is a finite contribution from the bulk interaction ($\beta\neq 0$), it does not coincide with the value of Γ_c^s, which is characteristic of the gel point.

Thus, the foregoing fairly trivial calculation of the integral (2.4) by the saddle-point method followed by calculation of the correlation function of an equilibrium polymer system in the Gaussian approximation in accordance with Ref. 13–15,17–19 shows that the gel point $\Gamma=\Gamma_c^s$ is not associated with singularities of the thermodynamic behavior of weak gels in the general case. To understand how an error can be made in such a calculation at all, it is useful to present another derivation of Eqs. (2.12)–(2.17), which is based on a generalization of the explicit approach developed by I. M. Lifshits for the treatment of polymer globules. It makes it possible not only to better understand the physical meaning of these equations, but also to point out an important small parameter, which plays the role of the Ginzburg parameter in our problem.

3. DENSITY-FUNCTIONAL FORMALISM IN THE THEORY OF EQUILIBRIUM POLYMER SYSTEMS

As was first pointed out by I. M. Lifshits,[24] an expression for a statistical sum like (2.6) can be greatly simplified, if the characteristic scale a of the function $g(r)$ (the root-mean-square bond length) is large in comparison with both the mean distance between particles and the characteristic scale r_0 of the bulk interaction between them:

$$(\rho a^3)^{-1}\ll 1,\quad r_0/a\ll 1. \tag{3.1}$$

In this case the rapidly fluctuating quantity $\exp[-U(\gamma)/T]$ manages to be averaged and to become a functional of the smoothed density $\rho(\mathbf{r})$ during integration over small regions of configuration space in which the multiplier in front of it remains practically constant. Therefore, the integral in the configuration space (2.6) can be rewritten in the form of the following integral with respect to the smoothed densities:

$$Z(N,V,T)=\int\delta\rho(\mathbf{r})\exp-F(\{\rho(\mathbf{r})\},T)/T], \tag{3.2}$$

$$F(\{\rho(\mathbf{r})\},T)=F^*(\{\rho(\mathbf{r})\},T)+F_{\mathrm{str}}(\{\rho(\mathbf{r})\},T), \tag{3.3}$$

where the contribution of the bulk interaction $F^*(\{\rho(\mathbf{r})\},T)$ is equal to the free energy F_0 of the broken-link system minus the contribution of its configurational entropy:

$$F^*(\{\rho(\mathbf{r})\},T)=-T\ \ln\left\{\frac{[\int d\gamma\exp\{-U(\gamma)/T\}]_{\{\rho(\mathbf{r})\}}}{[\int d\gamma]_{\{\rho(\mathbf{r})\}}}\right\}$$
$$=F_0(\{\rho(\mathbf{r})\},T)-T\int dV\ \rho\ \ln\left(\frac{e}{\rho\lambda^3}\right), \tag{3.4}$$

and the contribution to the free energy determined by the structure of the system is

$$F_{\mathrm{str}}(\{\rho(\mathbf{r})\},T) = -T\ln\sum\left[\int d\gamma\prod g(|\mathbf{r}_{ij}|)\right]_{\{\rho(\mathbf{r})\}}\Big/[N!(\lambda^3 f!)^N]. \tag{3.5}$$

To calculate $F_{\mathrm{str}}(\{\rho(\mathbf{r})\},T)$ we note that, owing to the first of the inequalities (3.1), the quantity $\Sigma\Pi g(|\mathbf{r}_{ij}|)$ is itself a functional of the smoothed density $\rho_{\mathrm{A}}(\mathbf{r})$ of unreacted functional groups A, and the density $\rho(\mathbf{r})$ of monomers and can thus be moved outside the integral. Therefore,

$$F_{\mathrm{str}}(\{\rho(\mathbf{r})\},T)/T = -S_{\mathrm{id}}(\{\rho_f(\mathbf{r})\}) + \min\left\{\int f\rho[\Gamma\ln\Gamma+(1-\Gamma)\ln(1-\Gamma)]dV - \tilde{S}(\{\rho_{\mathrm{A}}(\mathbf{r})\})\right\}, \tag{3.6}$$

where $\Gamma(\mathbf{r})=\rho_{\mathrm{A}}(\mathbf{r})/f\rho(\mathbf{r})$ is the local extent of conversion.

Here the first term

$$S_{\mathrm{id}}(\{\rho_f(\mathbf{r})\}) = \int dV\,\rho_f(\mathbf{r})\ln\left(\frac{e}{f!\rho_f(\mathbf{r})\lambda^3}\right) \tag{3.7}$$

corresponds to the entropy of accommodation of the monomers A_f in space, and the minimum of the second term, in which the first component corresponds to the entropy of selection of the reacted groups and the second component corresponds to the entropy of accommodation of the bonds in the system of completely reacted groups selected, is sought in the space of all possible density distributions $\rho_{\mathrm{A}}(\mathbf{r})$ of the latter. The remaining calculation of the functional $\tilde{S}(\{\rho_{\mathrm{A}}(\mathbf{r})\})$ is carried out in the simplest way by applying Eq. (3.6) to a system of "completely linked" monofunctional units (i.e., monofunctional units which have reacted with one another):

$$\tilde{S}(\{\rho_{\mathrm{A}}(\mathbf{r})\}) = S_2(\{\rho_{\mathrm{A}}(\mathbf{r})\}) - S_{\mathrm{id}}(\{\rho_f(\mathbf{r})\}), \tag{3.8}$$

where $S_2(\{\rho_{\mathrm{A}}(\mathbf{r})\})$ is the exactly calculated entropy of a system of ideal particles bonded in pairs:

$$TS_2(\{\rho_{\mathrm{A}}(\mathbf{r})\}) = E(\{\varphi(\mathbf{r})\}) - F_2(\{\varphi(\mathbf{r})\}). \tag{3.9}$$

Here $\varphi(\mathbf{r})$ is the external field whose application to the system renders $\rho_{\mathrm{A}}(\mathbf{r})$ an equilibrium distribution, and $E(\{\varphi(\mathbf{r})\})$ and $F_2(\{\varphi(\mathbf{r})\})$ are, respectively, the energy and free energy of the system in that field and satisfy the following trivial expressions:

$$E(\{\varphi(\mathbf{r})\}) = \int \rho_{\mathrm{A}}(\mathbf{r})\varphi(\mathbf{r})dV, \tag{3.10}$$

$$F_2(\{\varphi(\mathbf{r})\}) = -T\ln\left[\left(\int \psi(\mathbf{r})(\hat{g}\psi)(\mathbf{r})dV\right)^N/(2^N N!)\right], \tag{3.11}$$

where

$$\psi(\mathbf{r}) = \exp[-\varphi(\mathbf{r})/T], \quad (\hat{g}\psi)(\mathbf{r}) = \int g(\mathbf{r}-\mathbf{r}')\times\psi(\mathbf{r}')dV', \tag{3.12}$$

$$\rho_A = \delta F_2/\delta\varphi(\mathbf{r}) = \mathcal{N}\psi(\mathbf{r})(\hat{g}\psi)(\mathbf{r}), \tag{3.13}$$

N is the number of pairs in the system, and we have introduced the normalized multiplier

$$T = \int \rho_{\mathrm{A}}(\mathbf{r})dV/\int \psi(\mathbf{r})(\hat{g}\psi)(\mathbf{r})dV. \tag{3.14}$$

Eliminating $\varphi(\mathbf{r})$ from (3.10) and substituting (3.9)–(3.14) into (3.8), we obtain

$$\tilde{S}(\{\rho_{\mathrm{A}}(\mathbf{r})\}) = \int dV\,\frac{\rho_{\mathrm{A}}(\mathbf{r})}{2}\ln\frac{\rho_{\mathrm{A}}(\mathbf{r})g\psi}{e\psi}, \tag{3.15}$$

where the functions ψ and ρ_{A} are related by Eq. (3.13), which, after evaluation of the integral (3.15), is equivalent to the Lifshits equation

$$\psi(\mathbf{r})\hat{g}\psi = \rho_{\mathrm{A}}(\mathbf{r}). \tag{3.16}$$

The application of Eq. (3.6) with consideration of (3.7), (3.8), and (3.15) to an equilibrium system of bifunctional units with $\Gamma(\mathbf{r})\equiv 1$ leads to the expression

$$F = -T\int \rho_2\ln\frac{(\hat{g}\psi)(\mathbf{r})}{\psi(\mathbf{r})}dV, \tag{3.17}$$

which was first derived by I. M. Lifshits[24] for the entropy of the condensed state of one macroscopic polymer chain. This would be expected, since an equilibrium system of bifunctional units with $\Gamma(\mathbf{r})\equiv 1$ is distinguished from one macroscopic polymer chain only by the presence of small rings, which are totally disregarded in the mean-field approximation under consideration.

Minimization of the second term in (3.6) for $\rho(\mathbf{r})=$ const again leads to Eq. (2.15) for the extent of conversion, and then the free energy of the equilibrium polymer system can ultimately be written in the form

$$F(\rho,T) = F_{\mathrm{bls}}(\rho,T) + NT\,f_1^0, \quad f_1^0 = f(\Gamma/2+\ln(1-\Gamma)), \tag{3.18}$$

where Γ as a function of $\tilde{\rho}=fg\rho$ is defined by Eq. (2.15).

It is easy to see that Eqs. (2.16) and (2.17) again follow from the expression (3.18) for the free energy. Their physical meaning is now understood: owing to the presence of the small parameters (3.1), all the thermodynamic parameters are composed of three additive contributions, viz., the energetic contribution of the bulk interaction, the entropic contribution associated with the combinatoric accommodation of the monomers in space [the first term in (3.6)], and the entropic–energetic contribution associated with accommodation of the bonds. This is manifested especially clearly in the expression for the pressure (2.16), which states that each bond makes an identical negative contribution to the pressure corresponding to the elimination of one translational degree of freedom of the system.

One weak point in the derivation presented is the approximation of both the total free energy, which is equal to the logarithm of the integral in (3.2), and the structural contribution to it $F_{\mathrm{str}}(\{\rho(\mathbf{r})\},T)$, which is defined in (3.6), by their extremum values (i.e., by the mean-field approximation). Nevertheless, the occurrence of the strongest fluctuations of the structural free energy near the gel point is indicated by the divergence of the correlation function (1.23), which determines the position of the gel point in an ideal weak gel, at that point. Therefore, the treatment performed must be refined particularly in the part which relates to the calculation of the structural contribution F_{str}.

4. DIAGRAM TECHNIQUE AND THE LONG-EDGE APPROXIMATION

4.1. Diagram technique and expansions in the cyclization parameter

Let us consider the diagram expansion of the functional integral (2.7) in the absence of a bulk interaction, i.e., when $\chi_0(\tau)=\tau$ holds:

$$Z(V,T,z)=\frac{\int \delta\phi \exp\left\{\int dV z(\phi(\mathbf{r})+Y)^f/f!-\int dV(\phi\hat{g}^{-1}\phi/2)\right\}}{\int \delta\phi \exp\left\{-\int dV\phi\hat{g}^{-1}\phi/2\right\}}. \tag{4.1}$$

Although such an expansion is only asymptotic for $f>2$, since the integral in (4.1) diverges in that case, when certain conditions[22] are satisfied, it can be treated as a convergent expansion. An important advantage of such an expansion is that it is exceptionally visualizable. In fact, the integral in (4.1), which is regarded as the formal generating function of all (connected and disconnected) the corresponding diagrams (Fig. 2), can be represented on the basis of Mayer's first theorem[26,27] in the form

$$Z(z,V,T)=\exp[V\chi(z,Y)], \tag{4.2}$$

where $\chi(z,Y)$ is the formal generating function of all the connected diagrams:

$$\chi(z,Y)=\sum \frac{W(G_{s,l})z^sY^l}{r(G_{s,l})}. \tag{4.3}$$

Here $r(G_{S,l})$ is the symmetry index of the diagram $G_{s,l}$, which has s vertices, l entering lines, and $fs-l$ internal lines, and its contribution $W(G_{s,l})$ is given by the integral

$$W(G_{s,l})=\int\left(\prod_G g(|\mathbf{r}_i-\mathbf{r}_j|)\right)\prod_{i=1}^{s} d\mathbf{r}_i, \tag{4.4}$$

where the product is taken over all the edges of the graph G. On the other hand, since there is no bulk interaction in the system under consideration, its pressure should be proportional to the density of all the molecules in the system (their number per unit volume):

$$\frac{P}{T}=\sum n(G). \tag{4.5}$$

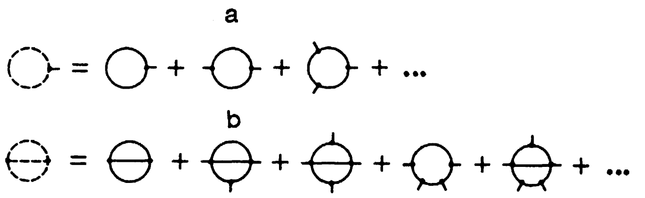

FIG. 3. Definition of the generating function $\sigma(z,t)$. A dashed line depicts the function G^{tree} defined by (4.17), and the solid line depicts the correlation function $g(r)$, a vertex depicts the multiplier z (the activity of the monomers), and the free "tails" depict the multiplier t (the generating function of all "appendages"). a) Sum of the contributions of the simple cyclic blocks of all sizes (the contribution of the structure depicted in Fig. 2b appears in this sum). b) Sum of the contributions of the simplest nontrivial cyclic blocks which are topologically equivalent to the structure depicted in Fig. 2c.

The physical meaning of the quantities on the left-hand sides of Eqs. (4.3) and (4.5) is identical, and so their right-hand sides are equal term-by-term, i.e., the contribution of each diagram is equal to the partial density of the macromolecules whose structural formula is described by that diagram. A more general statement is also valid: the density of any macromolecular fragment at chemical equilibrium is equal to the generating function of all the connected diagrams on which a part corresponding to the fragment under consideration can be identified. (This can easily be seen by considering the set of these fragments as a certain subsystem characterized by their chemical potential, which is assumed to be equal to zero after the concentration sought is calculated.)

Further progress requires the introduction of a topological classification. A graph is called a composite (1-reducible) graph, if it contains at least one edge (bridge), whose removal divides it into two unconnected parts. A graph in which all the edges are bridges is called a tree, and a graph which does not have bridges is called 1-irreducible (strongly connected). When all the bridges are broken, a graph is divided into blocks, which may be vertices with f tails ("seed f-tails"), simple cycles, and irreducible graphs with tails attached to their edges. The tails (or islands, according to Popov's terminology[33]) correspond to functional groups. The ones which were used to form edges appearing in blocks are called internal, and all the others (which did not react and were not used to form bridges) are called external. The structure of a block will be described here by the topology of the corresponding irreducible graph S, i.e., by the graph obtained from S when all of its external functional groups (tails) are removed, as shown in Fig. 3, and by assigning the number l_i of tails on the ith edge for all the edges of the graph S. The structure of a composite graph is described by the equivalent tree obtained after the replacement of each block by an l-functional vertex ("l-tail," where $l=\Sigma l_i$ is the total size of the block) and by indicating the structure of all the blocks.[34,35]

A fundamental role is played by the generating function of all the blocks

$$\sigma(z,t)=\sum \sigma(S_{m,l})=\sum_{m=1}^{\infty}\sum_{l=1}^{\infty}\sum_{S_{m},l}\frac{W(S_{m,l})z^mt^l}{r(S_{m,l})}, \tag{4.6}$$

where the summation is carried out first over all the topologically different graphs $S_{m,l}$ with assigned values of m and l and then over all the possible values of the latter. The function $\sigma(z,t)$ is used to express such fundamental characteristics of the system as the total concentration of monomers

$$\rho=\sum m\sigma(S_{m,l})=z\frac{\partial\sigma(z,t)}{\partial z}, \tag{4.7}$$

the total concentration of all external functional groups

$$\rho_f=\sum l\sigma(S_{m,l})=t\frac{\partial\sigma(z,t)}{\partial t}, \tag{4.8}$$

and the concentration of unreacted groups

$$n=Y\frac{\partial\chi(z,Y)}{\partial Y}=Y\frac{\partial\sigma(z,t)}{\partial t}, \tag{4.9}$$

where t (the generating function of all the "appendages" on an external functional group of a block) is related to the activities z and Y by the equation

$$t=Y+g_0\partial\sigma(z,t)/\partial t. \tag{4.10}$$

Equations (4.8)–(4.10) give expressions for the concentration of external bonds

$$\nu=\frac{\rho_f-n}{2}=\frac{t-1}{2}\frac{\partial\sigma}{\partial t} \tag{4.11}$$

and the pressure, i.e., the generating function $\chi(z,l)$,

$$\chi(z,l)=\int_0^l dY\frac{\partial\chi}{\partial Y}=\sigma(z,t)-\frac{g}{2}\left(\frac{\partial\sigma}{\partial t}\right)^2=\sigma-\nu$$
$$=\sigma(z,t)-\frac{t-1}{2}\frac{\partial\sigma}{\partial t}, \tag{4.12}$$

as well as the external extent of conversion

$$\Gamma_e=2\nu/\rho_f=1-t^{-1}. \tag{4.13}$$

In writing Eqs. (4.11)–(4.13) and below we utilize the fact that the auxiliary multiplier Y is equal to unity in a state of complete thermodynamic equilibrium with respect to the formation and cleavage of A–A chemical bonds. Equations (4.10) and (4.12) are simply somewhat unusual forms of the Legendre transformation corresponding to the transition from the thermodynamic potential characterizing the system in an assigned external field, whose role is played by the multiplier Y for the free ends of the diagrams, to the thermodynamic potential characterizing the system at an assigned value of the order parameter. The replacement of variables $\varphi+Y\rightarrow\varphi$ in the functional integral (4.1) would make it possible to bring these equations into a standard form, but it would worsen the interpretation of the transformed quantities in physically visualizable models and is therefore not advisable.

It is also useful to present the expressions for the total extent of conversion Γ and the internal extent of conversion Γ_i, which characterizes the degree of cyclization:

$$1-\Gamma=\frac{n}{f\rho}=\frac{t-1}{fg_0\rho}, \tag{4.14}$$

$$1-\Gamma_i=\frac{\rho_f}{3\rho}=\frac{t(t-1)}{fg_0\rho}. \tag{4.15}$$

We now move on to the calculation of $\sigma(z,t)$, restricting ourselves to the case of $f=3$ for simplicity. To this end we regroup the infinite sum in (4.6), first summing the contributions of the infinite subset of blocks with the assigned topology G over the lengths of all their edges and then summing the contributions thus obtained over all the topologies:

$$\sigma(z,t)=\frac{zt^3}{6}+\int_0^{zt}\frac{dx}{2(2\pi)^3}\int\frac{d^3q}{g_{\mathbf{q}}^{-1}-x}$$
$$+\sum_{l=1}^{\infty}\sum_{S_l}\frac{W(S_l)z^{2l}}{r(S_l)}. \tag{4.16}$$

Here the first term corresponds to the seed tritails and describes the contribution of the monomers appearing in the composition of the tree-like macromolecular fragments. The second term describes the contribution of the simple cycles (Fig. 3a). In the third term the summation is performed over all the irreducible graphs, whose contribution is calculated from Eq. (4.4) with the one difference that each edge is represented not by a seed correlation function $g(r)$, but by a function $G_{\text{tree}}(r)$, whose Fourier transform is defined by the expression

$$G_{\mathbf{q}}^{\text{tree}}=\int G_{\text{tree}}(r)\exp(i\mathbf{q}\cdot\mathbf{r})dV=(g_{\mathbf{q}}^{-1}-zt)^{-1}. \tag{4.17}$$

This term, the first of whose components is represented in Fig. 3b, describes the contribution of all the cyclized fragments of complex topology.

In the zeroth approximation, in which we leave only the first term in (4.16) when we substitute it into Eqs. (4.7)–(4.15), we have

$$\rho=zt^3/6,\quad t=1+zg_0t^2/2,\quad \Gamma_i=0, \tag{4.18}$$

whence it is easy to obtain

$$\Gamma=\Gamma_e=1-t^{-1},\quad zg_0=2\Gamma(1-\Gamma),\quad \tilde{\rho}=3g_0\rho$$
$$=\Gamma/(1-\Gamma)^2. \tag{4.19}$$

The second equality in (4.19) defines the dependence of the extent of conversion Γ on the activity z, and the last equality is equivalent to the law of mass action (2.15). The latter is thus a direct consequence of the zeroth approximation (the tree approximation), which completely ignores the effect of cyclization in the macromolecules.

We now evaluate the parameter κ in the expansion (4.16), which is naturally called the cyclization parameter, since an increase in it signifies an increase in the contribution of cycles. It is easy to see that κ has the form

$$\kappa\sim z^2\int\frac{G_{\mathbf{q}}^3d^3q}{(2\pi)^3}\sim\frac{z^2g_0^3/a^3}{(1-zg_0t)^{3/2}}. \tag{4.20}$$

Using the equations of the zeroth approximation (4.18) to go over to the physical variables ρ and Γ, we can easily see that the expression for the cyclization parameter has the form[6,35]

$$\kappa=(\rho a^3)^{-1}(\Gamma/\Gamma_c^s)^3/(\Gamma-\Gamma_c^s)^{3/2}, \tag{4.21}$$

where $\Gamma_c^s=1/2$ is the classical value of the critical extent of conversion following from the condition that the Green's function (4.17) calculated in the tree approximation goes to infinity. Thus, the role of the Ginzburg parameter, which ensures the possibility of employing the classical description almost up to the gel point, is played by $u=(\rho a^3)^{-1}$.

4.2. Long-edge approximation: what is the length of an edge and why is it large near the gel point?

To understand what happens in the immediate vicinity of the gel point and in the postgelation region, we elucidate the meaning of the quantity $\bar{l}^{-1}=l-zg_0t$. For this purpose we consider a block with a fairly large number of edges. Using the standard rules of the diagram technique, we obtain the total concentration of such blocks of all possible sizes[35]

$$\sigma_s=A(1-zg_0t)^{3/2}\left[\frac{z^2g_0^3}{a^3(1-zg_0t)^{3/2}}\right]^s, \tag{4.22}$$

as well as the size of these blocks

$$l_s=\frac{t}{3s}\frac{\partial\ln\sigma_s}{\partial t}=\left(1-\frac{1}{3s}\right)\frac{zg_0t}{2(1-zg_0t)}, \tag{4.23}$$

where $3s$ is the number of edges in the cyclized block under consideration.

Thus, $\bar{l}$ is simply the doubled length of an edge in an infinitely large block and can, therefore, be only positive. Just this circumstance permits application of the equations obtained above by expansion in the cyclization parameter to the analysis of the behavior of the system in the postgelation region. In fact, in the classical region the inverse length satisfies $\bar{l}^{-1}=1-2\Gamma$ and decreases as the extent of conversion increases until the cyclization parameter is of order unity. Then we have

$$\bar{l}^{-1}=1-\Gamma/\Gamma_c^s\cong u^{2/3}\ll 1. \tag{4.24}$$

As the extent of conversion increases further, this quantity can obviously only decrease, while remaining positive (it cannot increase, since the cyclization parameter would then become small again, and the system would return to the classical region). Therefore, to lowest order in u, we can set

$$1-zg_0t=0 \tag{4.25}$$

in the postgelation region.

The expansion in the cyclization parameter then becomes meaningless. This can be interpreted in the following manner: in calculating the characteristics of a cyclized material, we cannot restrict ourselves to consideration of only the few simplest cycles, and the entire set must be taken into account at once. For the constructive realization of this requirement we introduce the function δ, which is defined as the ratio of the concentration of all the external functional groups belonging to cycles (which is equal to the concentration ρ_2 of all monomers belonging to "long edges"), to the concentration $3\rho_3$ of all functional groups belonging to the simple tritails, which made the main contribution in the classical pregelation region:

$$\delta=\rho_2/3\rho_3,\quad \rho_3=zt^3/6. \tag{4.26}$$

Then Eq. (4.11) can be rewritten using the condition $Y=1$ and the definitions (4.26) in the form

$$t=1+g_0(\rho_2+3\rho_3)/t=1+(1+\delta)t/2, \tag{4.27}$$

where we used the condition (4.25) to pass to the latter equality. This condition allows us to assume that the number of all the monomers belonging to the set of all cycles (the "cyclizate") is simply equal to the number of their edge monomers (when the length of the edges is infinite or even simply very large, the number of monomers fastening them, without which, of course, there would be no cyclizate, can be neglected), i.e., the number of external functional groups in the cyclizate. Therefore, the total density of the monomers is given by the equation

$$\rho=\rho_3+\rho_2=t^2(1+3\delta)/6g_0, \tag{4.28}$$

which, together with Eq. (4.27), uniquely specifies t and δ as functions of $\tilde{\rho}=3g_0\rho$, which has the meaning of a reduced density:

$$\rho_2=3\delta\rho/(1+3\delta),\quad \rho_3=\rho/(1+3\delta), \tag{4.29a}$$

$$t=2/(1-\delta), \tag{4.29b}$$

$$\tilde{\rho}=2(1+3\delta)/(1-\delta)^2, \tag{4.29c}$$

$$zg_0=(1-\delta)/2. \tag{4.29d}$$

Equation (4.29d) is especially important for determining the properties of the set of all the finite (tree-like in our approximation) macromolecules (the sol fraction). In fact, since the sol fraction is a subsystem in thermodynamic equilibrium with the gel fraction, the activity of the monomers belonging to it is also specified by this equation. Therefore, in the postgelation region the extent of conversion and the total density of the monomers belonging to the sol fraction are determined by substituting this equation into (4.19):

$$1-\delta=4\Gamma_s(1-\Gamma_s)\rightarrow\Gamma_s=\frac{1-\sqrt{\delta}}{2},\quad \tilde{\rho}_s=2\frac{1-\sqrt{\delta}}{(1+\sqrt{\delta})^2}. \tag{4.30}$$

From (4.29) and (4.14) we obtain an equation for the total extent of conversion

$$\Gamma=1+6\delta+\delta^2/2(1+3\delta)$$

and equations for the density and the extent of conversion of the monomers belonging to the gel fraction

$$\tilde{\rho}_g=\tilde{\rho}-\tilde{\rho}_s=2\sqrt{\delta}(\delta+3)/(1-\delta)^2, \tag{4.31a}$$

$$\Gamma_g=(\Gamma\tilde{\rho}-\Gamma_s\tilde{\rho}_s)/\tilde{\rho}_g=2(1+\delta)/(3+\delta). \tag{4.31b}$$

It is also useful to present the expression for the fraction of intramolecular chemical bonds in the gel:

$$r=\lim_{N^0\rightarrow\infty}(N_g-N_g^0)/[\tfrac{3}{2}(N_g^0+1)]. \tag{4.32a}$$

The numerator in (4.32a) is the number of independent cycles (the cyclic rank) in a macromolecule formed from N_g^0+1 monomers.[15,18,19] It represents the excess of the number N_g of chemical bonds actually forming the macromolecule under consideration over the minimal number N_g^0 of chemical bonds needed to combine the same monomers in a single macromolecule. In the thermodynamic limit $N_g = 3N_g^0\Gamma_g/2$, the 1 can be neglected, and we obtain

$$r = \Gamma_g - \frac{2}{3} = \frac{4\delta}{3(3+\delta)}\,. \tag{4.32b}$$

Equations (4.29)–(4.32) parametrically specify the structural functions $\Gamma(\tilde{\rho})$, $\Gamma_s(\Gamma)$, $\Gamma_g(\Gamma)$, $\rho_s(\Gamma)$, $\rho_g(\Gamma)$, and $r(\Gamma)$ in the postgelation region, which differ from the classical description dating back to Flory[1] (see also Refs. 18 and 19), which is defined by Eqs. (4.18) and (4.19) of the tree approximation. For comparison, in parallel we present asymptotes of the main characteristics of the system in the postgelation vicinity of the gel point, writing the results of the classical "zero cyclization" approximation (4.18) in the upper row and the result of our long-edge (infinite-edge) approximation in the lower row (in the pregelation region the approximations are equivalent):

$$\Gamma - \Gamma_c^s \approx \begin{cases} \tau/12, \\ 3\tau/20, \end{cases} \tag{4.33}$$

$$\Gamma_c^s - \Gamma_s \approx \begin{cases} \tau/12, \\ \sqrt{10}\tau/20, \end{cases} \tag{4.34}$$

$$\tilde{\rho}_g = \begin{cases} 2\tau, \\ 3\sqrt{2\tau/5}, \end{cases} \tag{4.35}$$

$$1 - 2zg_0 = \begin{cases} (\tau/6)^2, \\ \tau/10, \end{cases} \tag{4.36}$$

where $\tau = \tilde{\rho} - 2$. As is seen from (4.33)–(4.36), the classical approximation leads to incorrect values not only of the amplitudes, but also of the exponents in the power-function asymptotes indicated.

Finally, for the structural contribution to the pressure we obtain

$$\frac{P}{T} = \int \frac{\rho}{z}\,dz = \begin{cases} \Gamma(2-3\Gamma)/6g_0(1-\Gamma)^2, \\ (1-6\delta-\delta^2)/6g_0(1-\delta)^2, \end{cases} \tag{4.37}$$

where Γ and δ are defined as functions of $\tilde{\rho}$ by equations (2.15) and (4.29), respectively.

The most striking difference between the two approximations under consideration is that upon passage through the gel point, such thermodynamic derivatives as the compressibility and the specific heat, as well as the derivative of the extent of conversion $(\partial\Gamma/\partial\rho)_T$, are continuous in the zero-cyclization approximation, as was already noted in the introduction, while in the long-edge approximation they have a discontinuity corresponding to a second-order phase transition. For example,

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial P_{\text{bls}}}{\partial \rho}\right)_T - \begin{cases} 3\Gamma/(1+\Gamma), \\ (6+3\delta)/(5+3\delta). \end{cases} \tag{4.38}$$

Therefore, our proposed approximation, which was obtained in a very permissive treatment with formal generating functions, requires additional substantiation.

5. PHYSICAL MEANING OF THE LONG-EDGE APPROXIMATION AND MODIFIED DENSITY-FUNCTIONAL FORMALISM

In order to clearly grasp the physical meaning of the "long-edge approximation," we consider the structure of an infinite cluster appearing after the sol–gel transition using the following procedure. We select a certain finite volume in this system (a "window") and color all the functional groups A located within this window in the following manner. If they form a bond belonging to at least one closed loop of bonds located completely within the window selected, we color them green; otherwise, we color them red (the unreacted groups will also be red). Increasing the size of the window selected step-by-step, we see that some of the originally red groups and bonds should be recolored green in the second or subsequent steps. Thus, as the size of the window L increases, the fraction of all the green bonds increases and tends to a certain limiting value when $L \to \infty$. As was shown above, in the pregelation region ($\Gamma < \Gamma_c^s$) this value is of the order of $u = (\rho a^3)^{-1}$, where ρ and a are the density of the functional groups A and the length of an A–A bond, respectively, and tends to zero when $u \to 0$.

However, as follows from the definition (4.21) of the cyclization parameter κ and the entire treatment performed in the preceding section, a finite fraction of long edges, which must consist of green bonds, appears in the infinite cluster. Also, the mean number of joints between green and red bonds per long edge is of the order of the mean degree of polymerization $\bar{l}$ in such an edge, and the number of joints between green bonds is of the order of the number of edge ends, i.e. ~ 1. Therefore, for $\bar{l} \gg 1$ the contribution of the latter for describing the effect of the difference between the green and red bonds is naturally neglected in the principal approximation, and our system is treated as a set of only AB_2 monomers with two green groups and one red group and A_3 monomers with three red groups, which have the densities ρ_2 and ρ_3, respectively. Then the free energy of the system under consideration can be written in the following form:

$$F_{\text{str}}(\{\rho(\mathbf{r})\},T)/T = \min\ F(\{\rho_3(\mathbf{r})\},\{\rho_2(\mathbf{r})\},\Gamma) \tag{5.1}$$

$$\begin{aligned} \frac{F(\{\rho_3(\mathbf{r})\},\{\rho_2(\mathbf{r})\},\Gamma_f)}{T} &= -\int dV \rho_2(\mathbf{r}) \ln\left[\frac{e}{2!\rho_2(\mathbf{r})\lambda^3}\right] \\ &\quad - \int dV \rho_3(\mathbf{r}) \ln\left[\frac{e}{3!\rho_3(\mathbf{r})\lambda^3}\right] - \tilde{S}(\{2\rho_2(\mathbf{r})\}) \\ &\quad - \tilde{S}(\{\rho_e(\mathbf{r})\Gamma_e(\mathbf{r})\}) + \\ &\quad + \int \rho_e[\Gamma_e \ln\Gamma_e + (1-\Gamma_e)\ \ln(1-\Gamma_e)]\,dV. \end{aligned} \tag{5.2}$$

The first two terms of the virtual free energy (5.2) correspond to the entropy of distribution in the space of AB_2 monomers belonging to long edges with a density $\rho_2(\mathbf{r})$ and A_3 monomers belonging to ordinary tails with a density $\rho_3(\mathbf{r})$ (with consideration of the different symmetry indices of these monomers), while the third and fourth terms, in which the functional $\tilde{S}$ is defined by (3.15), correspond to the free energies of formation of the bonds at chemical equilibrium between the "internal" B functional groups, which form long edges, and formations of "bridges" at chemical equilibrium between cycles and tritails of reacted "external" A functional groups having a density $\rho_e(\mathbf{r})\Gamma_e(\mathbf{r})$. Finally, the first term is the free energy of selection of the latter from all the external functional groups, which have a density $\rho_e(\mathbf{r})$. The densities appearing in (5.2) satisfy the relations

$$\rho_3(\mathbf{r})+\rho_2(\mathbf{r})=\rho(\mathbf{r}), \quad \rho_e(\mathbf{r})=\rho_2(\mathbf{r})+3\rho_3(\mathbf{r}), \tag{5.3}$$

and the equilibrium values $\Gamma_e(\mathbf{r})$ and $\rho_2(\mathbf{r})$ are given by the equations

$$\frac{\delta F}{\delta\Gamma_e(\mathbf{r})}=\frac{\rho_e}{2}\ln\frac{\Gamma_e}{(1-\Gamma_e)^2 g_0\rho_e}=0, \tag{5.4}$$

$$\frac{\delta F}{\delta\rho_2(\mathbf{r})}=-\ln\left[6g_0\rho_3(1-\Gamma_e)^2\right]=0. \tag{5.5}$$

Below the gel point (when $\tilde{\rho}=3g_0\rho>2$) the solution of Eqs. (5.3)–(5.5) leads to the same dependences of Γ_e and ρ_2 on $\tilde{\rho}$ as those obtained above in the long-edge approximation and presented in (4.26) and (4.29), whereas above the gel point ($\tilde{\rho}<2$) the derivative $\delta F/\delta\rho_2(\mathbf{r})$ is always positive and the free-energy minimum is achieved, as would be expected, when $\rho_2=0$.

Substituting the extremum values of ρ_2, ρ_3, ρ_e, and Γ_e into (5.2), we ultimately obtain the following expression for the free energy of the homogeneous equilibrium polymer systems below the gel point

$$F(\rho,T)=F_{\mathrm{bls}}(\rho,T)+NTf_1, \tag{5.6}$$

$$\begin{aligned} f_1&=-\frac{\rho_2}{\rho}\ln\frac{6g_0\rho_3}{e}+\ln\frac{\rho_3}{\rho}+\frac{\rho_e}{\rho}+\left[\frac{\Gamma_e}{2}+\ln(1-\Gamma_e)\right]\\ &=3\ln\frac{1-\delta}{2}-\ln(1+3\delta)+\frac{3}{4}\,\frac{1+6\delta+\delta^2}{1+3\delta}, \end{aligned} \tag{5.7}$$

where Eqs. (4.26) and (4.29) were used during the transition to the second line in (5.7). Taking the derivatives of (3.18) and (5.6), which define the free energies of the pre- and postgelation regions in our approximation, we can easily see that the entropy of the system at the gel point is continuous and that when the gel fraction forms the specific heat increases abruptly by a quantity which equals

$$\Delta C_V=\frac{N}{5}\left(\frac{d\ln k(T)}{d\ln T}\right)^2, \tag{5.8}$$

where $k(T)\equiv g_0$ is the chemical equilibrium constant, when $f=3$.

Thus, the long-edge approximation corresponds to taking into account the contribution of the green bonds to the thermodynamics of the system under consideration, and in this approximation we take into account the actual appearance of long edges (green bonds), due to the effective changes in the symmetry of the monomers forming them ($A_3 \rightleftarrows AB_2$), and we correctly describe the correlation of most of the green bonds, which are separated from one another (along the long edges) by a distance much smaller than the mean edge length $\bar{l}$. The picture of the gel fraction corresponding to this approximation can be represented as a solution of branched fragments, some of whose terminal monomers are "linked to" the condensate. The bonds by which they are "linked" are the same intramolecular bonds whose fraction is specified by Eqs. (4.32). All the bonds belonging to such branched fragments are red, and when $\Gamma=1$ holds, all the red bonds are intramolecular. The condensate can be represented as an infinite linear chain consisting of green bonds and filling the entire volume of the system with a finite density.

It should be stressed that such a picture of a condensate is exaggerated, since, as was shown above, it is possible to distinguish between red and green bonds because the free bonds, unlike the red bonds, "know" that they belong to a finite cycle (with a size $\geqslant \bar{l}$ monomers). However, our approximation assumes $\bar{l}=\infty$, so that on a finite scale as large as one desires, the only difference between the red and green bonds is the symmetry of the monomers forming these bonds (A_3 and AB_2), and just this difference is described with an accuracy $O(1/\bar{l})$ by the exaggerated picture of the condensate presented. The weak spot in this approximation is the extrapolation of the correlation thus obtained to distances much larger than $\bar{l}$. Therefore, the long-edge approximation can be regarded as a specific (postgelation!) mean-field approximation, which, however, clearly surpasses the older mean-field approximation (the tree approximation), which totally neglects the presence and correlation of the green bonds.

6. APPROXIMATION OF THE STATISTICAL SUM OF AN EQUILIBRIUM POLYMER SYSTEM BY A TWO-FIELD FUNCTIONAL INTEGRAL AND CORRELATION PROPERTIES OF THE GEL PHASE

The picture developed above of a sol–gel transition as a second-order phase transition associated with a change in the symmetry of a finite fraction of the monomers in the system also makes it possible to properly modify the field-theoretical description of an equilibrium polymer system developed in Sec. 2. To this end we note that the proposed picture of a weak gel as a set of branched "red" fragments and a linear "green" condensate in an approximation which does not take into account the contribution of large cycles of finite dimensions and the bulk interaction corresponds to the following generalization of the representation (4.1):

$$\begin{aligned} &Z(V,T,z)\\ &=\frac{\int\delta\phi\delta\psi\,\exp\{S_0(\{\phi(\mathbf{r}),\psi(\mathbf{r})\})-L_0(\{\phi(\mathbf{r}),\psi(\mathbf{r})\})\}}{\int\delta\phi\delta\psi\,\exp\{-L_0(\{\phi(\mathbf{r}),\psi(\mathbf{r})\})\}}, \end{aligned} \tag{6.1}$$

$$\begin{aligned} S_0(\{\phi(\mathbf{r}),\psi(\mathbf{r})\})=z\int dV\bigg[&\frac{(\phi(\mathbf{r})+Y)^f}{f!}\\ &+\frac{\psi^2(\mathbf{r})}{2}\,\frac{(\phi(\mathbf{r})+Y)^{f-2}}{(f-2)!}\bigg], \end{aligned} \tag{6.1a}$$

$$L_0(\{\phi(\mathbf{r}),\psi(\mathbf{r})\})=\frac{1}{2}\int dV(\phi\hat{g}^{-1}\phi+\psi\hat{g}^{-1}\psi), \qquad (6.1b)$$

where the field ϕ corresponds to red functional groups, and ψ corresponds to green functional groups. It is important to stress that, unlike the representation (4.1), whose diagram expansion coincides exactly with the expansion of the statistical sum (2.5), the representation (6.1) is only an approximation corresponding to the picture of red trees linked by a linear green condensate, which is valid in our approximation. This approximation, however, makes it possible to find the correct asymptotic expression for the functional integral (2.7) and the correlation functions of weak gels in the postgelation region.

Direct generalization of the arguments which led from (4.1) to (2.7) (see Refs. 6, 17–19, and 28) makes it possible to pass from (6.1) to the following functional-integral representation of the statistical sum of an equilibrium polymer system:

$$Z(z,V,T)=\frac{\int\delta\phi\delta\psi\ \exp\ S(\{\phi(\mathbf{r}),\psi(\mathbf{r})\})}{\int\delta\phi\delta\psi\ \exp[-L_0(\{\phi(\mathbf{r}),\psi(\mathbf{r})\})]}, \qquad (6.2)$$

$$S(\{\phi(\mathbf{r}),\psi(\mathbf{r})\})=X[\tau(\mathbf{r})]-L_0[\{\phi(\mathbf{r}),\psi(\mathbf{r})\}], \qquad (6.3a)$$

$$\tau = z\left[\frac{(\phi+y)^f}{f!}\exp\left[-\frac{\varphi_R(\mathbf{r})}{T}\right]+\frac{\psi^2}{2}\frac{(\phi+y)^{f-2}}{(f-2)!}\right.$$
$$\left.\times\exp\left(-\frac{\varphi_G(\mathbf{r})}{T}\right)\right]. \qquad (6.3b)$$

The multiplier $y(\mathbf{r})$, which corresponds to the unreacted functional groups, and the external fields $\varphi_R(\mathbf{r})$ and $\varphi_G(\mathbf{r})$ were introduced for convenience in certain intermediate calculations and are set equal to unity and zero, respectively, after those calculations.

Let us now consider the results produced by the new representation (6.2) for the statistical sum, restricting ourselves to the case of $f=3$ for simplicity. We start out from the mean-field equations specifying the values of the fields $\phi(\mathbf{r})$ and $\psi(\mathbf{r})$ which give the extremum value of the function (6.3a):

$$\frac{\delta S}{\delta\phi(\mathbf{r})}=\frac{1+\delta}{1+3\delta}\,\frac{3\rho_0(\tau)}{\bar{\phi}(\mathbf{r})+1}-\hat{g}^{-1}\bar{\phi}=0, \qquad (6.4a)$$

$$\frac{\delta S}{\delta\psi(\mathbf{r})}=\frac{2\psi(\mathbf{r})}{1+3\delta}\,\frac{3p_0(\tau)}{(\bar{\phi}(\mathbf{r})+1)^2}-\hat{g}^{-1}\psi=0, \qquad (6.4b)$$

where we have introduced the quantity

$$\delta(\mathbf{r})=\psi^2(\mathbf{r})/(\bar{\phi}(\mathbf{r})+1)^2\geq 0. \qquad (6.5)$$

Differentiation with respect to the auxiliary function $y(\mathbf{r})$ gives the mean value of the local density of unreacted functional groups, and differentiation with respect to $\varphi_R(\mathbf{r})$ and $\varphi_G(\mathbf{r})$ gives the mean values of the local densities of the red and red–green monomers, respectively:

$$n(\mathbf{r})=-y(\mathbf{r})\frac{\delta\Omega}{y(\mathbf{r})}\bigg|_{y(\mathbf{r})=1}=3\ \frac{\rho_0(\tau(\mathbf{r}))}{\bar{\phi}(\mathbf{r})+1}\ \frac{1+\delta}{1+3\delta}, \qquad (6.6a)$$

$$\bar{\rho}_3(\mathbf{r})=\frac{\delta\Omega}{\delta\varphi_R(\mathbf{r})}\bigg|_{\varphi_R(\mathbf{r})=0}=\frac{\rho_0(\tau(\mathbf{r}))}{1+3\delta}, \qquad (6.6b)$$

$$\bar{\rho}_2(\mathbf{r})=\frac{\delta\Omega}{\delta\varphi_G(\mathbf{r})}\bigg|_{\varphi_G(\mathbf{r})=0}=3\delta\frac{\rho_0(\tau(\mathbf{r}))}{1+3\delta}, \qquad (6.6c)$$

whence for the total density of the monomers $\bar{\rho}$ and the extent of conversion Γ we obtain

$$\bar{\rho}(\mathbf{r})=\bar{\rho}_2(\mathbf{r})+\bar{\rho}_3(\mathbf{r})=\rho_0(\tau(\mathbf{r})), \qquad (6.7)$$

$$\Gamma=1-\frac{n}{3\bar{\rho}}=\frac{1}{\bar{\phi}+1}+\frac{2\delta}{(\bar{\phi}+1)(1+3\delta)}. \qquad (6.8)$$

It is easy to see that Eqs. (6.4)–(6.7) have two sets of solutions, one of which coincides with the solution obtained in Sec. 2:

$$\psi(\mathbf{r})=0, \quad \phi(\phi+1)=\tilde{\rho}=3g_0\bar{\rho}. \qquad (6.9)$$

The other set satisfies a system of equations following from (6.4)

$$\bar{\phi}(\bar{\phi}+1)=\tilde{\rho}(1+\delta)/(1+3\delta), \qquad (6.10a)$$

$$(\phi+1)^2=2\tilde{\rho}/(1+3\delta), \qquad (6.10b)$$

which leads to the same parametric dependence of $\Gamma(\tilde{\rho})$ that was obtained in the preceding section in the long-edge approximation:

$$\frac{\bar{\phi}}{\bar{\phi}+1}=\frac{1+\delta}{2}\rightarrow\bar{\phi}=\frac{1+\delta}{1-\delta} \qquad (6.11a)$$

$$\tilde{\rho}=2(1+3\delta)/(1-\delta)^2, \qquad (6.11b)$$

$$\Gamma=\frac{1}{2}\,\frac{1+6\delta+\delta^2}{1+3\delta}. \qquad (6.11c)$$

Since, according to the definition (6.5), δ can only be positive, this new set of solutions exists only when $\Gamma>\Gamma_c^s=1/2$. To test the stability of these solutions, we find a matrix of second variational derivatives from the Lagrangian S defined by (6.2) and (6.3) with respect to its functional arguments $\phi_1(\mathbf{r})=\phi(\mathbf{r})$ and $\phi_2(\mathbf{r})=\psi(\mathbf{r})$:

$$\frac{\delta^2 S}{\delta\phi_i(\mathbf{r}_1)\delta\phi_j(\mathbf{r}_2)}=\frac{(\rho/\tau)\delta^2\tau}{\delta\phi_i(\mathbf{r}_1)\delta\phi_j(\mathbf{r}_2)}-g^{-1}(\mathbf{r}_1-\mathbf{r}_2)\delta_{ij}$$
$$+\rho\beta\,\frac{\delta\tau}{\delta\phi_i(\mathbf{r}_1)}\,\frac{\delta\tau}{\delta\phi_j(\mathbf{r}_2)}, \qquad (6.12)$$

where $g^{-1}(\mathbf{r}_1-\mathbf{r}_2)$ is the kernel of the operator $\hat{g}^{-1}$, and β is defined by (2.26). Performing the differentiations prescribed in (6.12) and finding the Fourier transforms of the functions appearing here, for the matrix

$$K_{ij}(q)=-\int d\mathbf{r}_2(\delta^2 S/\delta\phi_i(\mathbf{r}_1)\delta\phi_j(\mathbf{r}_2))\exp[i\mathbf{q}\cdot(\mathbf{r}_2-\mathbf{r}_1)]$$

we obtain

$$K_{ij}(q)=g_0^{-1}((L^{-1})_{ij}-g_0\rho\beta u_i u_k), \qquad (6.13)$$

where we have introduced the new notations

$$(L^{-1})_{ij}=\left(\tilde{g}_{\mathbf{q}}^{-1}-\frac{2\tilde{\rho}}{(1+3\delta)(\phi+1)^2}\right)\delta_{ij}+(\delta_{ij}-1)$$

$$\times\frac{2\tilde{\rho}\sqrt{\delta}}{(1+3\delta)(\phi+1)^2}, \tag{6.14}$$

$$u_1=\tau^{-1}\frac{\partial\tau}{\partial\phi_1}=\frac{3(1+\delta)}{(1+3\delta)(\phi+1)}, \tag{6.15a}$$

$$u_2=\tau^{-1}\frac{\partial\tau}{\partial\phi_2}=\frac{6\sqrt{\delta}}{(1+3\delta)(\phi+1)}. \tag{6.15b}$$

It is easy to see that the classical solution (6.9), for which the off-diagonal elements of K_{ij} are identically equal to zero, is stable when the condition (1.20a) and the inequality $\Gamma<\Gamma_c^s$, which ensure the positive signs of K_{11} and K_{22}, respectively, are satisfied. Therefore, when the inequality $\Gamma<\Gamma_c^s$ is violated, i.e., in the gel fraction, this solution must become unstable. With respect to the solution (6.10), the matrix L^{-1} for it at $\Gamma>\Gamma_c^s$ is written using (6.11) in the form

$$(L^{-1})_{ij}=x(q)\delta_{ij}+(\delta_{ij}-1)\sqrt{\delta}, \tag{6.16}$$

$$x(q)=\tilde{g}_{\mathbf{q}}^{-1}-1\cong q^2a^2/6. \tag{6.17}$$

We see that in the range of values of the total monomer density ρ for which β is positive (which corresponds to effective attraction of particles of the broken-link system), the solution (6.10) also exhibits instability, which corresponds to the impossibility of the existence of spatially uniform weak gels in this region. For $\beta<0$ the solution (6.10) is stable if the following inequality holds:

$$\beta<-[6(1+\delta)(1+3\delta)]^{-1}. \tag{6.18}$$

This means that the effective repulsion of the particles of the broken-link system needed to compensate the gel fraction against collapse due to the presence of intramolecular bonds must exceed a certain finite critical value.

Equation (2.29) is reproduced in analogy to the derivation of (1.13) and (1.23) for the density–density correlation function of all the monomers in an equilibrium polymer system for $\Gamma<\Gamma_c^s$, and for $\Gamma>\Gamma_c^s$ we obtain

$$\begin{aligned}G(q)&=G_0+G_0^2u_iu_j\langle\phi_i\phi_j\rangle(q)\\&=G_0+\frac{3(G_0^2/\rho)}{x_c-x_g}\left(\frac{2\Gamma_i\Gamma_e-\Gamma x_g}{x+x_g}+\frac{\Gamma x_c-2\Gamma_i\Gamma_e}{x+x_c}\right).\end{aligned} \tag{6.19}$$

One remarkable property of (6.19), which can be measured directly in experiments on the scattering of light by weak gels, is the fact that it can be separated into a sum of two contributions with different characteristic scales:

$$x_c=-\frac{1}{2}(3\beta\Gamma-\sqrt{9\beta^2\Gamma^2+\delta+6\beta\Gamma_i\Gamma_e}), \tag{6.20a}$$

$$x_g=-(3\beta\Gamma+\sqrt{9\beta^2\Gamma^2+\delta+6\beta\Gamma_i\Gamma_e}). \tag{6.20b}$$

The limiting value of the first of these contributions at the gel point (i.e., when $\delta\rightarrow0$) coincides with the limiting value of the correlation function in the limit $\Gamma\rightarrow\Gamma_c^s-0$, while the second contribution behaves in a very unusual manner: its limit as $\delta\rightarrow0$ is equal to zero at any finite value of the scattering vector q, but remains finite at $q=0$. The presence of this contribution can produce the observed effects and is another specific feature of our long-edge approximation.

7. CONCLUSIONS

Thus, in the present work we have shown that the classical description of chemical equilibrium in a system of branched and cyclized macromolecules using the law of mass action (2.15) is fundamentally incorrect when an infinite cluster of (even labile) chemical bonds appears in the system. The formation of such a cluster, i.e., the sol–gel transition, exhibits all the features of a second-order phase transition, i.e., it is manifested in singularities not only of the geometric probabilities of the distribution of the structures of the clusters of bonds, as is generally assumed, but also of the physical (thermodynamic) characteristics of the system. Here the specific singularity (6.19) of the density–density correlation function of the monomers is especially unusual. In view of the unconventional nature of the system under consideration (weak gels) and the combination of methods used to treat it, it would be useful to enumerate the main steps in the derivation of the results obtained once again.

1. The asymptotic expansion of the statistical sum (4.1) of a grand canonical ensemble of an ideal weak gel has the accuracy $O(\kappa)$, where κ is the cyclization parameter defined by (4.21). Therefore, as the gel point, at which $\kappa\rightarrow\infty$, is approached, the fraction of monomers belonging to cyclized macromolecules and blocks of such macromolecules ceases to be small.

2. When the small parameter $u=1/(f\rho a^3)$ is present, the main [with an accuracy $o(u)$] part of the monomers belonging to the cyclized blocks appear in the composition of the long edges of these blocks. Such monomers, which initially consist of identical functional groups, exhibit a natural symmetry difference between the functional groups which participate and which do not participate in the formation of the edge of a cycle. In particular, when $f=3$ holds, such monomers may be regarded as new monomers of the AB_2 type, which have a symmetry index equal to 2, while the original A_3 monomers had a symmetry index equal to 3!.

3. The cyclization effect can be described with an accuracy $O(u)$ by including the fraction δ of AB_2 monomers in the treatment as the parameter for minimization of the free energy, which can be calculated using the smoothed-density-functional formalism. Such a calculation (which is somewhat similar to the calculation of the asymptotic forms of high-order diagrams in Ref. 36) shows that $\delta=0$ holds for $\Gamma<\Gamma_c^s$ and $\delta>0$ holds for $\Gamma>\Gamma_c^s$. Thus, the classical treatment, which starts out from the assumption that all the bonds are identical or the equivalent assumption that the reactivities of all the functional groups are equal, regardless of the type of bond formed by them (in terms of our work this is equivalent to an assumption that δ is equal to zero both above and below the gel point), leads to an avoidably overestimated value of the free energy of weak gels in the postgelation region. We note that just such an assumption also implicitly

underlies the derivation of the assertion that the sol–gel transition is nonsingular in Ref. 13.

4. The single-field representation (2.7) of the statistical sum is a complicated analytical function of the activity z, which allows an expansion with terms of both signs in the parameters $\kappa>0$ and $\beta<0$ with a zero radius of convergence. Therefore, the fact that its calculation by the saddle-point method reproduces the results of the classical description signifies only that such a calculation is equivalent to a method for summing that series which ignores the $A_3 \rightarrow AB_2$ lowering of the symmetry of the monomers described above.

5. The correct procedure for summing this series (which takes into account the symmetry effect just cited) is realized by the two-field representation (6.2) of the statistical sum. The calculation of the corresponding functional integral by the saddle-point method shows that the classical solution $\psi=0$ in the postgelation region is not only less advantageous, but is also totally unstable. The density–density correlation function calculated for the stable solution $\psi\neq0$ in the vicinity of the gel point has a very specific singular contribution with an infinitely small amplitude, an infinitely large correlation radius, and a finite integral over the volume.

In conclusion we offer two more remarks. The results obtained for the postgelation region in this work in the long-edge approximation and the results obtained by Panyukov using his replica generalization[17–20] of our first one-field technique for describing weak gels, which was presented in Ref. 6 and in Sec. 2 of this paper [representation (2.7)] differ significantly. In our opinion, this is because the implicit representation of the structure of the cyclized material in the original version of the field formalism and its replica generalization do not permit correct summation of the contributions of all the diagrams corresponding to the description of an infinite cluster. However, the replica methods developed in Refs. 17–20 can be effectively employed to generalize our two-field representation (6.2) instead of the one-field representation (2.7). Such a generalization would be very useful, in particular, for describing "frozen" polymer networks.[21]

Our second remark is associated with the possibility of observing real systems characterized by the small parameter $u=1/(f\rho a^3)$. From a rigorous point of view, for real systems of point monomers A_f we have $u \geqslant 1$, so that their choice for consideration in this work was dictated mainly by methodical interests. The parameter u, however, is small for another completely realistic system, in which the role of the monomers is played by long chains of N monomers containing $f \ll N$ side-chain functional groups A (which are capable, for example, of forming hydrogen bonds[37]). Physically, such a system of "extended" monomers is totally analogous to the system of point monomers considered above, but its quantitative analysis requires some modification of the methods developed here. However, consideration of both of the generalizations cited is beyond the scope of the present work.

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[1)] The energy of the electrostatic interactions of monomers which belong to different macromolecules or monomers which belong to the same macromolecule, but are separated from one another by a large number of bonds and approach one another as a result of fluctuations of the orientation of the bonds relative to one another is generally included in the bulk interaction.[25]

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