Replica technique in the theory of equilibrium polymer systems

S. V. Panyukov

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR

(Submitted 13 November 1984)
Zh. Eksp. Teor. Fiz. **88**, 1795–1808 (May 1985)

The replica technique is used to calculate the correlation functions for individual molecules in a system with arbitrary bulk interactions which is in chemical equilibrium with respect to bond breakage and formation. Spontaneous breaking of replica symmetry is considered. For a system consisting of branched molecules, the condensate of the replica field describes the formation of an infinite molecular gel. The correlation functions for the gel have a singularity at the gel point and on the spinodal, and their small-scale behavior is unusual. A perturbation theory is developed for concentrated systems, and the expansion coefficient is determined both before and after the gel transition. The limits of validity of the percolation model are also discussed.

INTRODUCTION

The recent rapid advances in polymer physics have been made possible primarily through the use of field-theoretic methods. The analogy between polymers and magnets was exploited in Refs. 1–3 to develop a theory of linear polymer chains. In the present paper we develop a theory for systems of branched polymers which is based on the replica technique. Branched polymers can form, e.g., by polycondensation of monomeric structural RA^f units (cf. Fig. 1a). Each unit consists of a monomer R connected by flexible polymer chains to f functional groups A. When two of the A groups come into contact, they can react to form a chemical bond (Fig. 1a, b), with or without the formation of additional byproducts. In what follows, we will refer to the flexible polymer chain joining two monomers (Fig. 1b) as a bond. The topological structure of the molecules becomes more complicated as the number of bonds increases, and cyclic aggregates may form (Fig. 1c). We will henceforth assume that the chemical bonding is reversible and that the system is in equilibrium with respect to bond formation and breakage. In this case, the branched molecules form by an equilibrium polycondensation process.

The state of the system is uniquely determined by two parameters, which we may take to be the degree of conversion p and the monomer density ρ. The degree of conversion p is defined as the number of bonds divided by the theoretical maximum and can be varied experimentally (e.g., by changing the concentrations of the reaction by-products). For small degrees of conversion the system contains only molecules of finite dimensions (sol), whereas a gel (an infinite network of flexible chains) forms if p exceeds a critical value p_c called the gel point. Sol molecules continue to be present for $p > p_c$. The sol-gel transition can be observed experimentally by measuring the viscosity, which becomes infinite at the gel point. We will consider primarily concentrated systems for which $\rho a^3 \gtrsim 1$, where a is the persistence length, i.e., the length of the chain within which the orientations of the segments are mutually correlated. The density fluctuations will then be small and the Flory-Stockmayer theory[4–6] (which neglects cyclization) describes the system to first order. This mean-field theory predicts that $p_c = (f-1)^{-1}$ and yields an expression for the molecular mass distribution (MMD) of the sol molecules. However, the theory does not suffice to determine the mean diameter and inertial radius of the molecules; however, these geometric characteristics are completely determined by the correlation functions (CF) for the density of the individual molecules of the system.

The mean-field approximation breaks down near the gel point, where the critical density fluctuations become large. In particular, it fails to explain the experimentally observed dependence of p_c on the density ρ and on the flexibility of the polymer chains. Nor does it describe the interaction between units which are located far apart on a molecule but may approach one another as a result of thermodynamic fluctuations. These so-called "bulk" interactions are not negligible; they determine the three-dimensional shape of the molecules and imply, in particular, that no two monomers can occupy the same point in space (the excluded volume effect).

Even when the bulk interactions are neglected, it is a nontrivial task to describe the behavior of branched molecular systems which are in chemical equilibrium and have arbitrary topologies. However, there are indications that bulk effects should be even more important for branched molecules than for linear ones,[6] where they already play a decisive role. In particular, the bulk interactions are necessary in order for systems to be thermodynamically stable beyond the gel point. The gel-forming process in such systems is unusual in several respects. For one thing, the bulk interactions suppress the density fluctuations in the system, and neither the CFs for the total density nor the thermodynamic parameters themselves yield any information about the gel point p_c. We note that p_c is defined by the condition that the average molecular weight of the polymerized molecules becomes infinite; the latter is obtained by averaging the degree of polymerization (the number of monomers contained in the individual molecules) over the MMD. Any theory that aims to describe gel formation in chemically equilibrium systems must therefore provide an expression for the MMD and for the CFs for the individual molecules in the system (including the infinite gel molecules).

The analogy between polymers and magnets can be used to describe branched molecules only for a few model

0038-5646/85/051065-08$04.00

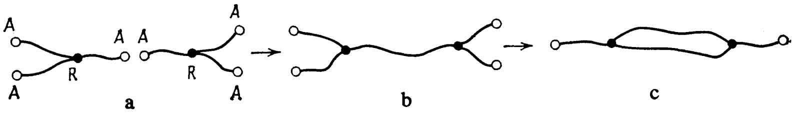

FIG. 1. Polycondensation of monomer units RA^f. a) before start of chemical reaction; b) during chemical bond formation; c) formation of a cycle.

systems.[8,9] Because of the complexity of these mathematical models, in which the order parameters appear as the elements of a tensor, it is not possible to describe the behavior beyond the gel point.

In this paper we use the replica technique[10–12] to calculate the CFs and MMD for individual molecules of a system in chemical equilibrium with respect to bond breakage and formation. We treat arbitrary bulk interactions V and determine the properties of the system both before and after the gel transition at $p = p_c$. In Sec. 2 we give the basic definitions and describe the model briefly (cf. Refs. 7 and 13 for more details). Section 3 is devoted to the derivation of the CFs as functional integrals over the replica fields φ_i. We examine the self-consistent field (SCF) approximation and estimate the size of the fluctuation region in Sec. 4. Spontaneous symmetry breaking between the replicas occurs at the gel point, and the ground state of the system is degenerate for $p > p_c$. We calculate the CFs for an infinite gel; they are singular both at the gel point and on the spinodal,[6] where the system becomes thermodynamically unstable. The cyclic aggregates in the gel suppress the density fluctuations over distances comparable to their dimensions and are responsible for the anomalous behavior of the density correlator for the monomeric units in the gel.

Section 5 is devoted to a precise formal calculation (in the context of the replica technique[10–12]) of the fundamental properties of polymer systems; the treatment, which allows for the fluctuations in the replica fields φ_i, sheds light on the unusual type of spontaneous symmetry breaking that occurs in these systems. Section 6 develops a perturbation theory for the MMD of concentrated systems, for which the density fluctuations are small. In Sec. 7 we examine the percolation model for the sol molecules both before and after the gel point; percolation can occur only if the bulk interactions are sufficiently strong. Finally, we close by discussing the choice of the order parameter for the sol-gel transition.

2. CHOICE OF THE MODEL. FUNDAMENTAL DEFINITIONS

We will consider the model in Ref. 13, in which a polymer system consists of N identical monomer units located at the points $\mathbf{x}_1, \ldots, \mathbf{x}_N$. The bulk interactions are described by the potential energy $\Sigma V(\mathbf{x}_i - \mathbf{x}_j)$, while the chemical bonding is described by the correlation function $\lambda(\mathbf{x} - \mathbf{x}')$ for the nearest neighbors in the chains. The function $\lambda(\mathbf{x})$ varies over a characteristic length a and is normalized by $\int\lambda(\mathbf{x})d\mathbf{x} = 1$. The maximum number of bonds that each particle (monomer unit) can form with the others is equal to f, the number of functional groups. An (l, m)-mer is defined as an aggregate of l monomer units joined only by m chemical bonds, where $m = l + r - 1$ and r is the number of independent cycles in the molecule. By definition, the spatial distribution function for a configuration G_N consisting of n_1 monomers, n_2 dimers, ..., n_l l-mers $(\Sigma n_l l = N)$ is

$$W\{G_N|\mathbf{x}_1,\ldots,\mathbf{x}_N\}=(f!\Lambda_T{}^3)^{-N}\exp\{[\Omega(\mu)-\Sigma V(\mathbf{x}_i-\mathbf{x}_j)]/T\}\Pi k\lambda(\mathbf{x}_i-\mathbf{x}_j), \tag{1}$$

where μ is the chemical potential of the monomer units, and each bond between units located at $\mathbf{x}_i$ and $\mathbf{x}_j$ corresponds to a factor $k\lambda(\mathbf{x}_i - \mathbf{x}_j)$; k is defined by $k = k_0 \exp(-\varepsilon/T)$, where k_0 and ε are the bond entropy and energy. The factor $\Lambda_T^{-3} = (MT/2\pi\hbar^2)^{3/2}$ in (1) results from the integration of the distribution function (DF) over momentum space; M is the mass of the particles. The factor $f!$ accounts for the fact that all of the f functional groups of each particle are identical. The thermodynamic potential Ω of the system is determined by the normalization condition

$$1=\sum_{N,G_N}\frac{z^N}{N!}\int d\mathbf{x}_1\ldots d\mathbf{x}_N W\{G_N|\mathbf{x}_1,\ldots,\mathbf{x}_N\},\quad z=e^{-\mu/T}, \tag{2}$$

where the sum is over all configurations G_N. Now consider a given configuration G_N and chose one molecule $C_{l,m}$ with l monomer units and m bonds. The microscopic density of the monomer units is given by $\rho_c(\mathbf{x}) = \Sigma\delta(\mathbf{x} - \mathbf{x}_i)$, where the sum is over the coordinates of all of the units in the molecule $C_{l,m}$. We define the correlation function for individual (l, m) — mers by the expression

$$g_{l,m}(\mathbf{x}_1,\ldots,\mathbf{x}_k)=\sum_{N,G_N}\frac{z^N}{N!}\int d\mathbf{x}_1\ldots d\mathbf{x}_N \times W\{G_N|\mathbf{x}_1,\ldots,\mathbf{x}_N\}\sum_{C_{l,m}}\rho_c(\mathbf{x}_1)\ldots\rho_c(\mathbf{x}_k), \tag{3}$$

where the second sum in (3) is over all (l, m)-mers in the configuration G_N. The definition (3) implies that the function $g_{l,m}$ is symmetric in the $\mathbf{x}_i$ and

$$\int d\mathbf{x}_0 g_{l,m}(\mathbf{x}_0,\mathbf{x}_1,\ldots,\mathbf{x}_k)=lg_{l,m}(\mathbf{x}_1,\ldots,\mathbf{x}_k). \tag{4}$$

In the special case $k = 0$, $g_{l,m} = \rho_{l,m}$ is equal to the average density of the (l, m)-mers and determines the molecular mass distribution (MMD). The extent of conversion p and the average polymerization N_w (by weight) are given by

$$p=2\rho_c/f\rho,\quad N_w=\rho^{-1}\Sigma\rho_{l,m}l^2,\qquad \rho=\Sigma\rho_{l,m}l,\quad \rho_c=\Sigma\rho_{l,m}m, \tag{5}$$

where ρ and ρ_c are the density of monomer units and bonds; the extent of conversion p $(0 \leqslant p \leqslant 1)$ is defined as the number of bonds divided by the theoretical maximum. For $k = 2$ the CFs (3) determine both the complete correlation function for the monomer density in individual molecules:

$$g(\mathbf{x}-\mathbf{x}')=\Sigma g_{l,m}(\mathbf{x},\mathbf{x}'), \tag{6}$$

and the correlation radius ξ and mean square radius of the

(l, m)-mer:

$$\xi^2 = \int d\mathbf{x}\, x^2 g(\mathbf{x}) \Big/ \int d\mathbf{x}\, g(\mathbf{x}),\ R^2_{l,m} = \int d\mathbf{x} x^2 g_{l,m}(\mathbf{x}, 0) \Big/ \int d\mathbf{x} g_{l,m}(\mathbf{x}, 0). \quad (7)$$

In general, the CFs give a detailed description of polymer molecules. The fundamental problem considered in this paper is to calculate the CFs (3) for systems with arbitrary bulk interactions V.

3. FIELD THEORY FOR THE CORRELATION FUNCTIONS OF INDIVIDUAL MOLECULES

If there are no bulk interactions ($V = 0$), the CFs (3) for the individual molecules are completely determined by the thermodynamic potential of the system (assumed to be in an external field):

$$\Omega(\mu(\mathbf{x}), \mu_c) = -T\pi^{(0)}\{s(\mathbf{x}), s_c\}, \quad \mu(\mathbf{x}) = \mu + T \ln s(\mathbf{x}), \quad \mu_c = T \ln s_c.$$

Here $\mu(\mathbf{x})$ and μ_c are the chemical potentials of the monomer units and bonds in the system. In particular, we can express the generating function

$$g(\mathbf{x}_1, \ldots, \mathbf{x}_k | s, s_c) \equiv \sum g_{l,m}(\mathbf{x}_1, \ldots, \mathbf{x}_k) s^l s_c^m \quad (8)$$

for the correlation functions (3) in terms of the functional $\pi^{(0)}$:

$$T^k g(\mathbf{x}_1, \ldots, \mathbf{x}_k | s, s_c) = \frac{\delta^k}{\delta\mu(x_1) \ldots \delta\mu(\mathbf{x}_k)} \pi^{(0)}\{s(x), s_c\} |_{s(\mathbf{x})=s}. \quad (9)$$

The representation

$$\exp(\pi^{(0)}\{s(\mathbf{x}), s_c\}) = \int \delta\varphi \exp\Big[-L_0 + \int d\mathbf{x} \frac{zs(\mathbf{x})}{\Lambda_T^3 f!}(1+\varphi(\mathbf{x}))^f\Big] \Big/ \int \delta\varphi \exp(-L_0),$$
$$L_0(\varphi) = \iint d\mathbf{x}\, d\mathbf{x}' \lambda^{-1}(\mathbf{x}-\mathbf{x}') \varphi(\mathbf{x}) \varphi(\mathbf{x}')/2ks_c \quad (10)$$

for the statistical sum as a functional integral was first derived in Ref. 13 for this model. We note that the irreducible correlators for the total density are found by differentiating Ω with respect to $\mu(\mathbf{x})$. The formulas (9) that relate the individual CFs to the CF for the entire system are simple in this case, because for $V = 0$ the DF (1) factorizes into a product of terms representing the contribution from each separate molecule. No such factorization is possible for $V \neq 0$; in this case we use the identity

$$\exp\Big(-\sum \frac{V(\mathbf{x}_i - \mathbf{x}_j)}{T}\Big) = \Big\langle \exp\Big[-\sum \frac{v(\mathbf{x}_i)}{T}\Big]\Big\rangle, \quad (11)$$

where the averaging is understood in the field-theoretic sense for the theory with the quadratic Lagrangian[14]

$$H_0(v) = -\iint d\mathbf{x}\, d\mathbf{x}' V^{-1}(\mathbf{x}-\mathbf{x}') v(\mathbf{x}) v(\mathbf{x}')/2T,$$
$$\int d\mathbf{x}_1 V(\mathbf{x}-\mathbf{x}_1) V^{-1}(\mathbf{x}_1 - \mathbf{x}') = \delta(\mathbf{x}-\mathbf{x}'). \quad (12)$$

In particular, (11) implies that for a system with no chemical bonds, the thermodynamic potential

$$\Omega_0(\mu(\mathbf{x})) = -T\pi_0\{z(\mathbf{x})\}, \quad z(\mathbf{x}) = \Lambda_T^{-3} \exp(\mu(\mathbf{x})/T)$$

can be written in the form[15]

$$\exp(\pi_0\{z(\mathbf{x})\}) = \Big\langle \exp\Big[\int d\mathbf{x} z(\mathbf{x}) \exp\Big(-\frac{v(\mathbf{x})}{T}\Big)\Big]\Big\rangle. \quad (13)$$

If we substitute (11) into (2) and sum over N before averaging, we find that

$$\exp(-\Omega/T) = \langle \exp[\pi^{(0)}\{\exp(-v/T), 1\}]\rangle. \quad (14)$$

After similar calculations for the CFs (3) for the individual molecules, we get

$$g_{l,m}(\mathbf{x}_1, \ldots, \mathbf{x}_k) = \langle g_{l,m}(\mathbf{x}_1, \ldots, \mathbf{x}_k | v) \exp[\pi^{(0)}\{\exp(-v/T), 1\}]\rangle / \langle \exp[\pi^{(0)}\{\exp(-v/T), 1\}]\rangle, \quad (15)$$

where $g_{l,m}(\mathbf{x}_1, \ldots, \mathbf{x}_k | v)$ is the CF calculated for $V = 0$ for a system in an external field $v(\mathbf{x})$. The equations (15) have a straightforward physical interpretation—they describe fluctuations in systems with a random bulk interaction field that is highly nongaussian. The integration over the field will be performed exactly. The simplest method is to integrate the statistical sum (14); substituting (10) into (4) and interchanging the order of integration over $\varphi(\mathbf{x})$ and $v(\mathbf{x})$, we find from (13) that

$$\exp\Big(-\frac{\Omega}{T}\Big) = \int \delta\varphi \exp\Big[-L_0 + \pi_0\Big\{\frac{z}{\Lambda_T^3 f!}(1+\varphi(\mathbf{x}))^f\Big\}\Big] \Big/ \int \delta\varphi \exp(-L_0); \quad (16)$$

this result was first derived in Ref. 13. In evaluating (15) it is helpful to work with the generating functional $\pi\{s(\mathbf{x}), s_c\}$ for the CFs [it is similar in form to expressions (8) and (9)]. According to (10), $\pi^{(0)}\{s(\mathbf{x}), s_c\}$ can be expressed as the logarithm of a functional integral, and we can use the replica technique[10] to take the average in (15) by setting

$$\pi^{(0)}\{s(\mathbf{x}), s_c\} = \lim \frac{1}{n}[\exp(n\pi^{(0)}\{s(\mathbf{x}), s_c\}) - 1]. \quad (17)$$

The number n is assumed to be an arbitrary integer in the calculations; the limit $n \to 0$ is taken only in the final results. The final expression for the functional is

$$\pi\{s(\mathbf{x}), s_c\} = \frac{1}{n}\Big[\int \delta\varphi_i \exp \Gamma_n\{\varphi_i | s, s_c\} \Big/ \int \delta\varphi_i \exp \Gamma_n\{\varphi_i | 0, s_c\} - 1\Big]$$
$$\Gamma_n\{\varphi_i | s, s_c\} = -L_0\{\varphi_i | s_c\} + \pi_0\Big\{\frac{z}{\Lambda_T^3 f!}\Big[(1+\varphi_0)^f + s(\mathbf{x}) \sum^n (1+\varphi_\alpha)^f\Big]\Big\}, \quad (18)$$

where the quadratic form L_0 is defined by

$$L_0\{\varphi_i | s_c\} = \frac{1}{2k} \iint d\mathbf{x}\, d\mathbf{x}' \lambda^{-1}(\mathbf{x}-\mathbf{x}') \times \Big[\varphi_0(\mathbf{x})\varphi_0(\mathbf{x}') + \frac{1}{s_c}\sum^n \varphi_\alpha(\mathbf{x})\varphi_\alpha(\mathbf{x}')\Big]. \quad (19)$$

The integration in (18) is over the $(1+n)$th component of the field $\varphi_i(\mathbf{x}) = [\varphi_0(\mathbf{x}), \varphi_\alpha(\mathbf{x})]$, $\alpha = 1, \ldots, n$. If a solvent is present, the functional $\pi_0\{z, z_s\}$ will also depend on the activity z_s of the solvent particles. The result (18) generalizes easily to multicomponent systems.

4. SELF-CONSISTENT FIELD APPROXIMATION

A. The molecular-mass distribution (MMD)

If the fluctuations in the fields $\varphi_i(\mathbf{x})$ are small, we can find the MMD by using the saddle point method to evaluate the functional integrals (18). For $p<p_c$, we set $\varphi_0 = p/(1-p)$ and $\varphi_\alpha = \varphi_\beta = pu/(1-p)$ at the saddle point. The equations for the latter then reduce to the formulas in the Flory-Stockmayer theory[6,16]:

$$u = ss_c(1-p+pu)^{f-1}, \tag{20}$$

where p, defined by

$$\rho = p/kf(1-p)^2, \tag{21}$$

is the conversion factor (5). The result (21) was derived by expressing the characteristics of the system in terms of the density ρ (5). The generating functional (18) for the MMD can be written in the form

$$\frac{\pi^{(s)}(s, s_c)}{\mathscr{V}} = \sum \rho_{l,m} s^l s_c{}^m = \rho\left[-\frac{pf}{2s_c}u^2 + s(1-p+pu)^f\right], \tag{22}$$

where $\mathscr{V}$ is the volume of the system; in this approximation, only molecular "trees" with $m = l - 1$ give a nonzero contribution. By definition, N_w in (5) becomes infinite at the gel point, so that $p_c = (f-1)^{-1}$ in this approximation.

We will now examine the behavior of a system beyond the gel point, i.e., for $p \geqslant p_c$. The sol-gel transition is described by the total CFs for the individual molecules (6), which are determined by the variational derivatives of (18) at the point $s = s_c = 1$. For $s = s_c = 1$ the Lagrangian in (18), (19) is symmetric under permutations of the fields φ_i in the extended replica space $(\varphi_0, \varphi_\alpha)$. However, this symmetry breaks spontaneously for $p \geqslant p_c$, and the ground state becomes $(1+n)$-fold degenerate:

$$\varphi_0^{(0)} \neq \varphi_\alpha^{(0)} = \varphi_\beta^{(0)}, \quad \varphi_\alpha^{(\alpha)} \neq \varphi_0^{(\alpha)} = \varphi_\beta^{(\alpha)}, \quad \beta \neq \alpha, \quad \alpha = 1, \ldots, n. \tag{23}$$

Here the superscripts label the type of the ground state. The generating functional (18) for $p \geqslant p_c$ is equal to the sum of the contributions from all of the saddle points (23):

$$\pi\{s, s_c\} = \lim_{n\to 0}\left\{\frac{1}{n}\left[\exp\left(\Gamma_n^{(0)}\{s, s_c\} - \Gamma_0^{(0)}\right) - 1\right] + \frac{1}{n}\sum_{\alpha=1}^{n} \exp\left(\Gamma_n^{(\alpha)}\{s, s_c\} - \Gamma_0^{0)}\right)\right\}, \tag{24}$$

$$\Gamma_n^{(j)}\{s, s_c\} \equiv \Gamma_n\{\varphi_i^{(j)} \mid s, s_c\}.$$

For $s, s_c \neq 1$ the Lagrangian in (18) is symmetric only under permutations of the replica fields φ_α, and the sum in the right-hand side of (24) reduces to a multiplication by n. Letting $n \to 0$, we find that

$$\pi\{s, s_c\} = \left.\frac{d\Gamma_n^{(0)}\{s, s_c\}}{dn}\right|_{n=0} + \exp\left(\Gamma_n^{(1)}\{s, s_c\} - \Gamma_0^{(0)}\right). \tag{25}$$

The CFs for the sol component are expressible in terms of the derivatives of (25) with respect to s and s_c at the point $s = s_c = 0$, and only the first term in (25) survives in the thermodynamic limit. The second term is nonzero only at the point $s = s_c = 1$; it determines the generating functional $\pi^{(g)}(s, s_c)$ for the gel. In particular, (25) and (23), (24) imply that $\pi^{(g)}(s, s_c) = 0$ except for $s = s_c = 1$, in which case $\pi^{(g)}(1, 1) = 1$, i.e., there is only a single gel molecule for $p \geqslant p_c$. For $s = s_c = 1$, the SCF approximation for $p > p_c$ gives

$$\varphi_i^{(i)} = p/(1-p), \quad \varphi_i^{(j)} = pu/(1-p), \quad j \neq i, \tag{26}$$

where u is defined as the smallest positive solution of Eq. (20). The density $\rho^{(s)}$ and the extent of conversion $p^{(s)}$ for the sol component are related by

$$\rho^{(s)} = p^{(s)}/kf(1-p^{(s)})^2. \tag{27}$$

After evaluating the derivatives of (25) with respect to s and s_c for $s = s_c = 1$, we can express $p^{(s)}$ and $\rho^{(s)}$ in terms of the total degree conversion and density p, ρ:

$$p^{(s)} = pu^{(f-2)/(f-1)}, \quad \rho^{(s)} = \rho(1-p+pu)^f \tag{28}$$

at $s = s_c = 1$. Here p and ρ are related by (21). Equations (26)–(28) coincide with the Flory-Stockmayer formulas[16] for $p \geqslant p_c$. However, Eq. (25) provides a more detailed description of the gel. The most fundamental property of the gel molecule is the number r of independent cycles it contains; in the SCF approximation we have the expression

$$r = 1 + N(1-u)[pf(1+u)/2 - 1 - pu]. \tag{29}$$

We define $\tau \equiv 1 - p/p_c$, so that $-\tau \ll 1$ near the transition point; here the gel has a tree-like structure and r increases very slowly with p,

$$r = 2f(f-1)N|\tau|^3/3(f-2)^2. \tag{30}$$

The gel contains many cyclic aggregates far from the transition point $(1-p \ll 1)$, and here r increases linearly with the conversion: $r = Np(f-2)/2$.

B. Correlation functions

Evaluation of the variational derivatives in (9), (25) leads to the expression

$$g^{(s)}(\mathbf{q} \mid s, s_c) \equiv \sum g_{l,m}^{(s)} s^l s_c{}^m = \frac{\rho p f s^2 s_c \xi^{2f-2}}{\lambda^{-1}(\mathbf{q}) - p(f-1) s s_c \xi^{f-2}}. \tag{31}$$

for the Fourier component of the generating function (8) for the two-point CFs for the sol molecules; here $\xi = 1 - p + pu$. The total CF for the sol molecule density (6) follows by setting $s = s_c = 1$ in (31). This CF is singular at the point $p = p_c$ and (for $V \neq 0$) differs from the correlator for the total density of the monomer units of the sol [cf. (36) below]. The weak cyclization of the gel (30) beyond the transition point (for $-\tau \ll 1$) gives rise to large fluctuations in the density of the sol phase—a single bond cleavage in a treelike gel molecule may suffice to liberate a sol molecule from the gel. Since

r increases with p, the density fluctuations of the sol component become smaller.

The second term in (25) determines the CF for the density of monomer units in the gel molecule:

$$\begin{gathered}\langle \delta\rho_{\mathbf{q}}^{(g)}\, \delta\rho_{-\mathbf{q}}^{(g)} \rangle = \hat{g}(\mathbf{q}) + \hat{g}^2(\mathbf{q})\hat{\chi}(\mathbf{q})/\rho, \\ \hat{g}(\mathbf{q}) = \rho^{(g)} + \frac{\rho p f}{\lambda^{-1}(\mathbf{q}) - p(f-1)} - g^{(s)}(\mathbf{q}\,|\,1,1);\end{gathered} \tag{32}$$

where $\rho^{(g)} = \rho - \rho^{(s)}$ and the function $\hat{\chi}(\mathbf{q})$ is defined by

$$\begin{gathered}[\hat{\chi}(\mathbf{q})]^{-1} = [\chi_2(\mathbf{q})]^{-1} - pf/\rho[\lambda^{-1}(\mathbf{q}) - p(f-1)], \\ \chi_2(\mathbf{q}) = \langle \delta\rho_{\mathbf{q}}\delta\rho_{-\mathbf{q}}\rangle_0 - \rho.\end{gathered} \tag{33}$$

Here $\chi_2(\mathbf{q})$ is the irreducible CF for the system of broken chemical bonds (of density ρ). The CF (32), which vanishes for $p < p_c$, is singular at the two points

$$p = p_c = (f-1)^{-1}, \qquad p = p_0 = (f\langle\delta\rho_0\delta\rho_0\rangle_0/\rho - 1)^{-1}.$$

The equation of state in the SCF approximation takes the form[13]

$$P(\rho) = P_0(\rho) - \rho f T p/2.$$

Using Eq. (21), we find that the system becomes thermodynamically unstable at $p = p_0$: $\partial P(\rho)/\partial\rho = 0$. Here we have assumed that $p_0 \ll 1$, since otherwise the gel persists even for $p = 1$. In the immediate vicinity of the transition point ($|\tau| \ll \tau_0 \equiv 1 - p/p_0$), the CF (32) is independent of the specific form of the bulk interaction V and is given by

$$\langle \delta\rho^{(g)}(\mathbf{x})\,\delta\rho^{(g)}(\mathbf{x}')\rangle = \frac{f}{4\pi(f-1)}\,\frac{\rho|\tau|^{1/2}}{a^3}\exp\left(-\frac{|\mathbf{x}-\mathbf{x}'|}{\xi}\right) \tag{34}$$

Note the anomalous small-scale behavior of the correlator (34) over distances $|\mathbf{x}-\mathbf{x}'| \ll \xi = a/|\tau|^{1/2}$—instead of the usual $|\mathbf{x}-\mathbf{x}'|^{-1}$ dependence (cf. Ref. 17), (34) tends to a constant as $p \to p_c$. This behavior occurs because the cycles (30) in the gel increase its rigidity, so that density fluctuations are suppressed over distances comparable to the cycle diameters. Setting $\mathbf{x} = \mathrm{x}'$ in (34), we find the condition

$$\varkappa(|\tau|) \equiv \frac{\langle(\delta\rho^{(g)})^2\rangle}{(\rho^{(g)})^2} = \frac{(f-2)^2}{16\pi f(f-1)\rho a^3|\tau|^{3/2}} \ll 1 \tag{35}$$

for the gel density fluctuations to be small. Away from the transition point ($1 - p \ll 1$) the CF (32) reduces to the correlator for the total density of the monomer units:

$$[\langle\delta\rho_{\mathbf{q}}\delta\rho_{-\mathbf{q}}\rangle]^{-1} = [\langle\delta\rho_{\mathbf{q}}\delta\rho_{-\mathbf{q}}\rangle_0]^{-1} - pf/\rho[\lambda^{-1}(\mathbf{q}) + p]. \tag{36}$$

We thus see that if (35) is satisfied, the SCF approximation provides detailed information on the properties of the system for both $p < p_c$ and $\mathrm{p} > p_c$. We note that Eq. (35) contains a small numerical factor (equal to 0.03 for $f = 3$), and the fluctuation region is very narrow if $\rho a^3 \gtrsim 1$.

5. FLUCTUATIONS ON THE REPLICA FIELDS

We start by making the change of variable $\varphi_\alpha(\mathbf{x}) \to s_c^{1/2}\varphi_\alpha(\mathbf{x})$ in the functional integral (18), where $\alpha = 1, \ldots, n$. We will use the effective action formalism[18] to treat the fluctuations in the fields $\varphi_i(\mathbf{x})$, according to which the functional $\Gamma_n^{(j)}\{s, s_c\}$ is given by

$$\Gamma_n^{(j)}\{s, s_c\} = -L_0\{\varphi_i^{(j)}(\mathbf{x})\,|\,1\} + F_n\{\varphi_i^{(j)}(\mathbf{x})\,|\,h_m(\mathbf{x}), h_f(\mathbf{x})\} \tag{37}$$

[recall that $\Gamma_n^{(j)}$ determines the generating functional (25) for the CFs of the individual molecules]. Here the functional F_n is the sum of the contributions from the irreducible diagrams of the $\tilde{\varphi}_i(\mathbf{x})$ field theory with the Lagrangian

$$\begin{gathered}L_0\{\tilde{\varphi}_i(\mathbf{x})\,|\,1\} - \pi_0\Bigg\{\frac{z}{\Lambda_T{}^3 f!}\Bigg[(1+\varphi_0(\mathbf{x})+\tilde{\varphi}_0(\mathbf{x}))^f \\ + h_m(\mathbf{x})\sum_{\alpha=1}^{n}(h_f(\mathbf{x})+\varphi_\alpha(\mathbf{x})+\tilde{\varphi}_\alpha(\mathbf{x}))^f\Bigg]\Bigg\}, \\ h_m(\mathbf{x}) = s(\mathbf{x})\,s_c^{-f/2}, \quad h_f(\mathbf{x}) = s_c^{-1/2}.\end{gathered} \tag{38}$$

The functions $\varphi_i^{(j)}(\mathbf{x})$ are determined by the requirement that they maximize the right-hand side of (37). For $p \geqslant p_c$ and $s = s_c = 1$ we use the rules (23) to select the solutions (j) for the $\varphi_i(\mathbf{x})$.

For $p < p_c$, the second term in (25) is not present, the φ_α ($\alpha = 1, \ldots, n$) are all equal, and φ_0 is independent of the "counters" s, s_c in the limit $n \to 0$. The density $\rho_f = \varphi_0/k$ of unreacted functional groups is obtained by differentiating (37) with respect to h_f and determines the conversion: $1 - p = \rho_f/\rho f$. The total density and the average polymerization N_w [cf. (5)] are given by the expressions

$$\begin{gathered}\rho = F'_{h_m}, \quad F' \equiv \frac{1}{\mathscr{V}}\frac{dF_n}{dn}\bigg|_{n=0}, \\ N_w = 1 + \frac{1}{\rho}\left[F'_{h_m^2} + \frac{(F'_{h_m h_f})^2}{k^{-1} - F'_{h_f^2}}\right].\end{gathered} \tag{39}$$

Here the subscripts denote partial derivatives with respect to the corresponding fields at the point $h_m = h_f = 1$, and $\varphi_\alpha = \varphi_0$. At the gel point, which is determined by the condition that N_w is infinite, we have $kF'_{h_f^2} = 1$.

Beyond the gel point ($p > p_c$), the ground state for $s = s_c = 1$ is $(1+n)$-fold degenerate (23) and $\varphi_i^{(i)} = k\rho_f$, while the remaining fields with $j \neq i$ are determined by the density of the unreacted functional groups in the sol molecules: $\varphi_i^{(j)} = k\rho_f(s)$. Spontaneous symmetry breaking thus occurs at $p = p_c$: $\rho_f^{(g)} = \rho_f - \rho_f^{(s)} > 0$. The thermodynamic potential is equal to

$$\Omega = -P(\rho)\mathscr{V} = -T\Gamma_0^{(0)}$$

and has no singularities at $p = p_c$. We find from (9) and (37) the expression

$$\begin{gathered}g^{(s)}(\mathbf{q}\,|\,s, s_c) \equiv \sum g_{l,m}^{(s)}(\mathbf{q})\,s^l s_c{}^m \\ = F_{mm}(\mathbf{q}) + [F_{mf}(\mathbf{q})]^2[\lambda^{-1}(\mathbf{q})/k - F_{ff}(\mathbf{q})]^{-1}, \\ F_{AB}(\mathbf{q}) \\ = \lim_{n\to 0}\frac{d}{dn}\left[\int d\mathrm{x}\,e^{i\mathbf{q}\mathbf{x}}\,\frac{\delta^2 F_n\{\varphi_i^{(0)}\,|\,h_m(\mathbf{x}),\, h_f(\mathbf{x})\}}{\delta h_A(0)\,\delta h_B(\mathbf{x})}\right]_{\substack{h_m = s s_c^{-f/2} \\ h_f = s_c^{-1/2}}}\end{gathered} \tag{40}$$

for the generating function for the density correlators of the sol molecules; (40) is valid both for $p < p_c$ and for $p > p_c$.

The second term in (25) determines the CFs for the gel, and Mayer's first theorem implies that for $s(\mathbf{x})$, $s_c \to 0$, $\Gamma_0^{(1)}\{s(\mathbf{x}), s_c\} - \Gamma_0^{(0)}$ is a generating functional for the irreducible correlators of the gel. One can show that $\langle \delta\rho_{\mathbf{q}}^{(g)}\, \delta\rho_{-\mathbf{q}}^{(g)} \rangle$ is singular at $p = p_c$ and p_0 (recall that $\partial P(\rho)/\partial\rho = 0$ at $p = p_0$).

All of the properties of the system can thus be expressed in terms of the functional F_n, which is given by the sum of the irreducible diagrams (38) for the field theory with the Lagrangian (38). This result is in fact an analog of Mayer's second theorem for polymer systems. Since the diagrams containing r loops involve an integration over r independent momenta, their contribution is small of order $(\rho a^3)^{-r}$. To lowest order ($r = 0$), we recover the results in the previous section. If p is not too close to p_c and the parameter $\varkappa$ in (35) is small, we can limit ourselves to the contribution from cycles with $r = 1$.

6. PERTURBATION THEORY

Let us examine the properties of a system in which the sol molecules contain only single-loop cycles. The corresponding contribution (37) is given by the sum of the single-loop diagrams for the field theory (38):

$$\frac{\pi^{(3)}\{s, s_c\}}{\mathscr{V}} \equiv \sum \rho_{l,m} s^l s_c{}^m = -\frac{\hat{\rho} f \alpha^2 u}{2\hat{p} s_c} + s\xi^f\Big[\hat{\rho} + \frac{1}{2}\sum_{\mathbf{q}} \frac{\hat{p}\psi(\mathbf{q})}{\lambda^{-1}(\mathbf{q}) - \hat{p}\eta(\mathbf{q})}\Big]$$
$$+\frac{1}{2}\sum_{\mathbf{q}}\Big\{\frac{\hat{\chi}(\mathbf{q})}{\hat{\rho}^2} g^{(3)}(\mathbf{q}|s, s_c) - \ln[1 - \lambda(\mathbf{q})\hat{p}(f-1) s s_c \xi^{f-2}]\Big\}, \tag{41}$$

where we have set $\varphi_0 = \alpha/(1-\alpha)$; the value of u ($\varphi_\alpha = \alpha u/(1-\alpha)$) is chosen so as to maximize (41). The distribution parameters α, $\hat{\rho}$, and $\hat{p}$ are related to z, z_s, and k by

$$\hat{\rho} \exp\frac{\mu^*(\hat{\rho})}{T} = \frac{z}{(1-\alpha)^f}, \quad \hat{p} = f k \hat{\rho}(1-\alpha)^2. \tag{42}$$

The relations (42) enable us to eliminate the activities z, z_s, and k from the equations, so that only a minimum of information regarding V is required. The functions $\hat{\chi}(\mathbf{q})$ and $g^{(s)}(\mathbf{q}|s, s_c)$ are defined by (33) and (31), with ρ, p replaced by $\hat{\rho}$ and $\hat{p}$; $\xi = 1 - \alpha + \alpha u$, and

$$\eta(\mathbf{q}) = f\langle \delta\hat{\rho}_{\mathbf{q}} \delta\hat{\rho}_{-\mathbf{q}}\rangle_0/\hat{\rho} - 1, \quad \mu^*(\hat{\rho}) = \mu_0 - T\ln\hat{\rho},$$
$$\psi(\mathbf{q}) = (f-1)\chi_2(0)/\hat{\rho} + f\chi_3(\mathbf{q}, 0)/\hat{\rho}, \quad \chi_2(\mathbf{q}) = \langle \delta\hat{\rho}_{\mathbf{q}} \delta\hat{\rho}_{-\mathbf{q}}\rangle_0 - \hat{\rho}. \tag{43}$$

Here $\chi_2(\mathbf{q})$ and $\chi_3(\mathbf{q}_1, \mathbf{q}_2)$ are the Fourier components of the irreducible CFs for the structural units (of density $\hat{\rho}$) in the system of broken bonds; μ_0 is the chemical potential of the broken bond system. In the coordinate representation

$$\chi_3(\mathbf{x}_2 - \mathbf{x}_1, \mathbf{x}_3 - \mathbf{x}_1) = \langle \delta\hat{\rho}(\mathbf{x}_1)\, \delta\hat{\rho}(\mathbf{x}_2)\, \delta\hat{\rho}(\mathbf{x}_3)\rangle, \quad \mathbf{x}_1 \neq \mathbf{x}_2 \neq \mathbf{x}_3.$$

The distribution parameters α, $\hat{\rho}$, and $\hat{p}$ can be expressed in terms of the total density ρ:

$$\hat{\rho} = \rho - \frac{1}{2}\sum_{\mathbf{q}} \frac{\hat{p}[\eta(\mathbf{q}) + \psi(\mathbf{q}) + f\chi_2(\mathbf{q})]}{\lambda^{-1}(\mathbf{q}) - \hat{p}\eta(\mathbf{q})},$$
$$\frac{\alpha}{\hat{p}}\hat{\rho} = \rho - \frac{1}{f}\sum_{\mathbf{q}} \frac{\hat{p}\eta(\mathbf{q})}{\lambda^{-1}(\mathbf{q}) - \hat{p}\eta(\mathbf{q})} \tag{44}$$

and in terms of the extent of conversion $\hat{p}$:

$$1 - p = \hat{\rho}\alpha(1-\alpha)/\rho\hat{p}. \tag{45}$$

Relation (45), which follows from $\rho_f = \rho f(1-p)$, remains valid to all orders in perturbation theory; by contrast, (44) is only valid to first order in $(\rho a^3)^{-1}$. For an incompressible fluid, we find that $\hat{\rho} = \rho$ to all orders. The equation of state to first order in $(\rho a^3)^{-1}$ is of the form

$$P(\rho) = P_0(\hat{\rho}) - \frac{\hat{\rho} f \alpha^2 T}{2\hat{p}} - \frac{T}{2}\sum_{\mathbf{q}} \ln[1 - \lambda(\mathbf{q})\hat{p}\eta(\mathbf{q})]. \tag{46}$$

Equations (41)–(45) completely describe the molecular mass distribution for a system with arbitrary V, provided the sol molecules contain only single-loop cycles. For $V = 0$, this problem was solved in Ref. 19 for $p < p_c$ by applying the theory of branching processes to the law of mass action. The MMD at any time t can be found by differentiating (41) with respect to s and s_c at the point $s = s_c = 1$; the corresponding derivatives at $s = s_c = 0$ give the density of the (l, m)-mers. The density of monomer units in the gel is given by

$$\rho^{(g)} = \rho - \sum \rho_{l,m} l$$

for $p \geqslant p_c$.

We will begin by analyzing the first moments of the DF (these determine the density of the monomer units and bonds). The first term in curly brackets in (41) treats the bulk interactions between the monomer units in all the molecules, while the second term accounts for cyclization in the sol molecules. Although both of these terms diverge at the point $p = p_c$, their sum remains finite. The fluctuations in the total density are thus suppressed for $p \approx p_c$ because the cyclization (which makes the sol molecules more compact) is offset by the bulk interactions (which tend to spread the molecules out). The series (44) for the distribution parameters [and (46) for the equation of state] are thus singular only on the spinodal $p = p_0$; the solution of Eqs. (44) becomes discontinuous at $p = p_0$, and all of its terms have the same order of magnitude. Far from the spinodal, we can expand the solution in the parameter $\varkappa(\tau_0)$, where the function $\varkappa(\tau)$ is defined by (35) with ρ replaced by $\hat{\rho}$ ($\tau_0 = 1 - p/p_0$).

For $s = s_c = 1$ and $p < p_c$, the right-hand side of (41) is a maximum for $u = 1$; beyond the gel point ($p \geqslant p_c$), the maximum occurs in the interval $0 \leqslant u \leqslant 1$. The cancellation is incomplete for the higher moments. For $p < p_c$ the series can be expanded in the parameter $\varkappa(\hat{\tau})$, where $\hat{\tau} = 1 - \hat{p}(f-1)$; moreover, $\varkappa(\hat{\tau}_c) \approx 1$ at the gel point itself, which enables us to estimate the correction to the value of p_c given by the Flory-Stockmayer theory. For $|\tau| \gg \tau_c$ (beyond the gel point), the expansion is carried out in powers of the parameter $\varkappa(|\tau|)$ in (35).

7. THE PERCOLATION MODEL

The fluctuations in the total density can be neglected if the parameter $\varkappa(\tau_0)$ is small near p_c ($|\tau|\ll 1$). If we make the change of variables

$$\varphi_0(\mathbf{x})\to\varphi(\mathbf{x})-\Sigma\varphi_\alpha(\mathbf{x}).$$

in the functional integral (18), it can be shown easily that the field $\varphi(\mathbf{x})$ fluctuates only slightly for $\varkappa(\tau_0)\ll 1$; we will therefore integrate $\varphi(\mathbf{x})$, as in the Wilson renormalization group method. Setting $\mathbf{x}=a\mathbf{r}$, $\tau=1-p(f-1)$, and $\varphi_\alpha=p/(1-p)+(k/a^3)^{1/2}\psi_\alpha$, we can then find the effective Lagrangian L for the replica fields φ_α under the assumption that $|\tau|\ll\tau_0$ and the fluctuations in $\phi(\mathbf{x})$ can be neglected. If we use the transformation

$$\psi_j=-\sum_\alpha e_\alpha^{(j)}A_\alpha$$

to diagonalize its quadratic part, L reduces to the Lagrangian for the zero-component in the Potts model:

$$L(A_\alpha)=\int d\mathbf{r}\left[\frac{1}{2}\sum(\nabla A_\alpha)^2+\frac{\tau}{2}\sum A_\alpha^2+\frac{\lambda}{6}\sum d_{\alpha\beta\gamma}A_\alpha A_\beta A_\gamma\right],$$

$$d_{\alpha\beta\gamma}=\sum_{j=0}^{n}e_\alpha^{(j)}e_\beta^{(j)}e_\gamma^{(j)},\qquad e_\alpha^{(0)}=1,\quad e_\alpha^{(\gamma)}=\frac{1}{2}-\delta_{\alpha\gamma},\tag{47}$$

$$\sum_j e_\alpha^{(j)}e_\beta^{(j)}=\delta_{\alpha\beta},\qquad\sum_j e_\alpha^{(j)}=0,\quad\lambda^2=\frac{(f-2)^2}{f(f-1)\rho a^3}.$$

We first examine the self-consistent field approximation. According to the general results in Sec. 4, $1+n$ types of spontaneous symmetry breaking can occur for $\tau<0$: $A_\alpha^{(j)}=e_\alpha^{(j)}A$, where $A=2\tau/\lambda$. The Fourier components of the irreducible correlator

$$G_{\alpha\beta}(\mathbf{x}-\mathbf{x}')=\langle\langle A_\alpha(\mathbf{x})A_\beta(\mathbf{x}')\rangle\rangle$$

are found to be

$$G_{\alpha\beta}^{(j)}(\mathbf{q})=\delta_{\alpha\beta}(|\tau|+\mathbf{q}^2)^{-1}+2|\tau|e_\alpha^{(j)}e_\beta^{(j)}(|\tau|+\mathbf{q}^2)^{-2}.\tag{48}$$

Equation (48) then determines the total CFs for the density of the functional groups in the sol ($j=0$) and gel ($j=\alpha$):

$$\begin{gathered}\sum g_{fl,m}^{(3)}(\mathbf{q})=k(|\tau|+a^2\mathbf{q}^2)^{-1},\\ \langle\delta\rho_{f\mathbf{q}}^{(\Gamma)}\delta\rho_{f-\mathbf{q}}^{(\Gamma)}\rangle=2k|\tau|(|\tau|+a^2\mathbf{q}^2)^{-2},\qquad\tau<0.\end{gathered}\tag{49}$$

The field theory (47) describes bond percolation for large fluctuations ($\varkappa(\tau)\sim 1$). This corresponds to the percolation in the model in Refs. 8 and 9, where a point interaction $V(\mathbf{x}-\mathbf{x}')=V\delta(\mathbf{x}-\mathbf{x}')$ was considered only for structural units with two reacting functional groups. Unfortunately, the limitations of the percolation approximation were not determined there. However, an estimate for the fluctuations in the field $\varphi(\mathbf{x})$ shows that the percolation model will be valid if $\varkappa(\tau_0)\ll 1$, where $\tau_0=1-p/p_0$ and $p_0^{-1}=fT/[\partial P_0(\rho)/\partial p]-1$. One can show by the renormalization group method that the percolation results (47) break down for large-amplitude fluctuations (however, this occurs at larger and larger amplitudes as $\varkappa(\tau_0)\to 0$). We note that the fluctuation region in the percolation regime is very small for $\varkappa(\tau_0)\ll 1$. Since $\varkappa(|\tau|)\ll 1$ almost up to the gel point itself, one can apply the perturbation theory developed in Secs. 5 and 6 in the limiting case of an incompressible fluid:

$$\chi_2(\mathbf{q})=-\rho,\qquad\chi_3(\mathbf{q},\mathbf{q}')=2\rho,\qquad\hat{\rho}=\rho$$

(we also set $\alpha=\hat{p}=p$). Expression (49) must be replaced by the scaling law

$$\langle\delta\rho_{f\mathbf{q}}^{(\Gamma)}\ \delta\rho_{f-\mathbf{q}}^{(\Gamma)}\rangle\approx k/|\tau|^\gamma[1+\mathbf{q}^2\xi^2]^2,\quad\xi\approx a|\tau|^{-\nu}\tag{50}$$

in the strong fluctuation region (here $q\xi\ll 1$, and γ and ν are the critical indices of the percolation theory).

CONCLUSIONS

We will now discuss how to choose the order parameter for the sol-gel transition. For $p<p_c$ we have $\langle\varphi_i\rangle=\langle\varphi_j\rangle$. The fluctuation correlator between different replicas

$$\langle\varphi_i(\mathbf{x})\varphi_j(\mathbf{x}')\rangle,\qquad i\neq j\tag{51}$$

diverges for a symmetric phase for $p\to p_c$ and $s=s_c=1$; however, the correlator $\langle\varphi_i(\mathbf{x})\varphi_i(\mathbf{x}')\rangle$ remains finite. The divergence of (51) at $p=p_c$ is responsible for the spontaneous symmetry breaking (23), and the order parameter is the zero-component field

$$A_\alpha(\mathbf{x})=\sum e_\alpha^{(j)}\varphi_j(\mathbf{x}).$$

Here $\langle A_\alpha\rangle^{(j)}=e_\alpha^{(j)}k\rho_f{}^{(g)}$ is nonzero only for $p\geqslant p_c$. The fluctuations in the total density are suppressed at $p=p_c$, and the thermodynamic variables are nonsingular. The sol–gel transition is thus not a true phase transition.

The phase diagram of the system was given schematically in Ref. 6. Depending on the parameters characterizing the bulk interaction V, the line of phase equilibrium (binodal) for a transition of the first kind may be located either before ($P<p_c$) or after ($p>p_c$) the gel point. However, if V is repulsive, the spinodal $p=p_0$ at which the system becomes thermodynamically unstable lies beyond the gel point: $p_0>p_c$. The fluctuations in the total density increase near the spinodal, and the correlator (51) with $i=j=(i)$ becomes infinite.

We may summarize our principal results as follows.

1. A field theory has been developed for finding the correlation function for individual molecules in a polymer system. In addition to providing a detailed description of the sol molecules, the theory can also be used to calculate the correlation functions for the gel molecule for branched polymers ($f\geqslant 3$).

2. The correlation functions of the gel and sol molecules were calculated for arbitrary bulk interactions V by neglecting the density fluctuations. The region of strong critical fluctuations for the sol-gel transition was found to be very small for concentrated systems. We also developed a perturbation theory which is valid for concentrated systems and involves expansion in a parameter inversely proportional to the monomer concentration.

3. The percolation model was found to be valid for concentrated systems everywhere except for a narrow region of large critical fluctuations. We have shown for the percolation transition that the infinite gel cluster and the finite sol molecules are described by different equivalent vacuum states of the theory.

We note in closing that the replica technique can be used to generalize the description of linear molecular systems proposed in Refs. 1–3 to systems with arbitrary bulk interactions.

I am deeply grateful to S. I. Kuchanov and S. V. Korolev for assistance in this work, and to I. Ya. Erukhimovich and the participants at a seminar at Moscow State University for a stimulating discussion of the above results.

[1] P. G. de Gennes, Phys. Lett. **38A**, 339 (1972).

[2] J. de Cloizeaux, J. de Phys. **36**, 281 (1975).

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

[4] W. Stockmayer, J. Chem. Phys. **11**, 45 (1943); **12**, 125 (1944); B. Zimm and W. Stockmayer, J. Chem. Phys. **17**, 1301 (1949).

[5] M. Gordon, Proc. R. Soc. (London) **268A**, 240 (1962).

[6] P. G. de Gennes, Scaling Concepts in Polymer Physics [Russian translation], Mir, Moscow (1982), p. 159.

[7] S. I. Kuchanov, S. V. Korolev, and M. G. Slin'ko, Dokl. Akad. Nauk SSSR **267**, 122 (1982).

[8] T. C. Lubensky and J. Isaacson, Phys. Rev. **A20**, 2130 (1979).

[9] T. C. Lubensky and J. Isaacson, J. de Phys. **42**, 175 (1981).

[10] S. F. Edwards and P. W. Anderson, J. de Phys. **5**, 1965 (1975).

[11] A. J. Bray and M. A. Moore, Phys. Rev. Lett. **41**, 1068 (1978); J. Phys. C **12**, 79 (1979).

[12] G. Parisi, J. Phys. A **13**, 1101 (1980).

[13] I. Ya. Erukhimovich, Candidate's Dissertation, Moscow (1979).

[14] V. N. Popov, Kontinual'nye Integraly v Kvantovoĭ Teorii Polya i Statisticheskoĭ Fizike (Path Integrals in Quantum Field Theory and Statistical Physics), Atomizdat, Moscow (1976), p. 21.

[15] A. N. Vasil'ev, Funktsional'nye Metody v Kvantovoĭ Teorii Polya i Statistike (Functional Methods in Quantum Field Theory and Statistics), Mir, Leningrad (1976), p. 173.

[16] S. I. Kuchanov, Metody Kineticheskikh Raschetov v Khimii Polimerov (Kinetic Computational Methods in Polymer Chemistry), Khimiya, Moscow (1978).

[17] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Fluktuatsionaya Teoriya Fazovykh Perekhodov (Fluctuation Theory of Phase Transitions), Nauka, Moscow (1975), p. 30.

[18] J. M. Cornwall, R. Jackiw, and E. Tomboulis, Phys. Rev. **D10**, 2428 (1974).

[19] S. I. Kuchanov, S. V. Korolev, and M. G. Slin'ko, Vysokomolek. Soed., No. 10, 2160 (1982).

Translated by A. Mason