General statistical approach to the description of polymers with an arbitrary chemical structure

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A field-theory approach using a replica method is proposed for calculating the thermodynamic and correlation characteristics of polymer solutions and melts containing macromolecules of various chemical compositions and various structures. The distribution of components among phases and the conditions for thermodynamic equilibrium are derived for arbitrary sets of macromolecules by a mean-field theory. In the case of solutions of linear heteropolymers in which the alternation of monomer units in the macromolecules obeys Markovian statistics, a phase diagram is constructed, and the conditions for the appearance of periodic spatial superstructures are derived. Over a wide range of the composition of such heteropolymers, there can be a third-order phase transition to a superstructure with a rhombohedral symmetry and a period which depends strongly on the parameters of the bulk interactions. The possibilities of this new general approach are demonstrated in the particular case of a calculation of the correlation function for density fluctuations in solutions of branched statistical heteropolymers of fairly arbitrary chemical structure.

INTRODUCTION

Most theoretical papers on polymers in which the macromolecules have a given chemical structure (or configuration) take Flory's classic approach.[1] It starts from a mean-field expression for the free energy $F\{n(C)\}$ of the polymer which depends on the numbers $\{n(C)\}$ of macromolecules of a given configuration C. In this approach, the position of the spinodal temperature of a spatially homogeneous state is found from the vanishing of the determinant of a matrix with the elements

$$\partial\mu(C)/\partial n(C'),\quad \mu(C)=\partial F\{n(C)\}/\partial n(C),\qquad (1)$$

where $\mu(C)$ is the chemical potential of a macromolecule of configuration C. For a polyphase system the distribution of the numbers $n^{(s)}(C)$ of macromolecules among the various phases s is found in the usual way by equating their chemical potentials $\mu^{(s)}(C)$.

It is important to note that the condition for the applicability of Flory's approach, $n(C)\gg 1$, is satisfied only for linear homopolymers and mixtures thereof. In the case of branched polymers or heteropolymers, the number of different configurations $\{C\}$ of macromolecules in a specific sample increases exponentially with increasing degree of polymerization, l, of these molecules. For real systems of large but finite volume, the mean numbers of macromolecules of a given configuration are small, $\bar{n}(C)\ll 1$, since they cannot be chosen as independent components in a conventional thermodynamic description.

In Sec. 1 we propose a more general approach, which is capable of describing polymers with arbitrary values of $\bar{n}(C)$. This approach is essentially one of choosing monomer units M_i of various types i as independent components. A similar approach has been taken previously to describe polymer systems which are in chemical equilibrium with respect to the formation and rupture of bonds.[2,3] In contrast with the latter, in the case of systems with a fixed distribution $\{\bar{n}(C)\}$ one should switch from the usual d-dimensional Euclidean space to a dm-dimensional replica space, in which the position of a point is characterized by the set $\mathbf{X}=(\mathbf{x}^{(1)},...,\mathbf{x}^{(m)})$ of coordinates $\mathbf{x}^{(k)}$ of the units M_i in each of m identical "replicas" of the system of interest. To describe the system obtained as a result, one uses the standard methods of the molecular theory of polymer systems in chemical equilibrium.[3] An important point is that the approach which we are proposing below makes it possible in principle to go beyond the scope of the mean-field theory on which Flory's classic theory is based.

In Sec. 2 we take this new approach to calculate correlation functions. We find a condition on the spinodal temperature which generalizes (1) to the case of arbitrary $\bar{n}(C)$. We also describe a polyphase system of such polymers, and we find the distribution of numbers $n^{(s)}(C)$ and the condition for a phase equilibrium.

In Sec. 3 we take this approach to study periodic spatial structures which form in heteropolymer systems. Structures of this type have been studied previously, both theoretically and experimentally,[4–8] in the case of regular copolymers consisting of a small number (two or three) of blocks of units M_i of a common type and of a given length. As is shown below, the nature of these structures is different from that studied below.

We examine the effect of a configurational disorder on the conditions for phase separation and on the characteristics of the spatial structure which results for the case of Markovian heteropolymers, which are the most common in practice.[9] For them, the mean numbers of macromolecules of a given configuration C (which is set by the sequence of alternation of the l units along the chain) are given by

$$\bar{n}(C)=\bar{n}\bar{\eta}_{i_1}\prod_{n=1}^{l-1}\nu_{i_n i_{n+1}}\eta_{i_l},\qquad (2)$$

where $\bar{n}$ is the total number of polymer units in the system, and the transition matrix elements $\nu_{i_n i_{n+1}}$ determine the conditional probability that unit $n+1$ of the chain is of type i_{n+1} in the case in which unit n is of type i_n. The quantities $\bar{\eta}_{i1}$ and η_{il} are the probabilities for finding initial and final units of types i_1 and i_l, respectively. Their normalization conditions are

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$$\sum_i \bar{\eta}_i=1, \quad \eta_i+\sum_j{}' \nu_{ij}=1. \tag{3}$$

The quantities $\bar{\eta}_i$ and ν_{ij} are usually treated as independent parameters.[9] Below we assume that the chains $(i_1,...,i_l)$ and $(i_l,...,i_1)$ are identical. The condition that the numbers of macromolecules in (2) must be independent of the direction in which the units of these molecules are numbered leads to the reciprocity relations

$$\bar{\eta}_i \nu_{ij} \eta_j=\bar{\eta}_j \nu_{ji} \eta_i, \tag{4}$$

which make it possible to express the parameters $\bar{\eta}_i$ in terms of the elements of the matrix ν in the case of symmetric heteropolymers.[9] For two-component systems we find from (4) and (3)

$$\bar{\eta}_1=\pi_1\eta_1/(\pi_1\eta_1+\pi_2\eta_2), \quad \bar{\eta}_2=\pi_2\eta_2/(\pi_1\eta_1+\pi_2\eta_2), \tag{5}$$

where the fractions π_i of units of type i are

$$\pi_1=\nu_{21}/(\nu_{12}+\nu_{21}), \quad \pi_2=\nu_{12}/(\nu_{12}+\nu_{21}). \tag{6}$$

Expressions (2)–(6) describe chemically different classes of polymers, depending on the ratios of ν_{ij}. The case $\nu_{12}=\nu_{21}=0$ corresponds to a mixture of polydisperse homopolymers each of whose macromolecules consists of units of a common type. In this limit the parameters $\bar{\eta}_i$ are equal to the fraction of the units which are of type i, and the quantities η_i determine their mean length: $l_i=\eta_i^{-1}$. The case ν_{12}, $\nu_{21}\neq 0$ corresponds to heteropolymers (or copolymers[9]) for which the mean number of units in the macromolecules is $\bar{l}=(\pi_1\eta_1+\pi_2\eta_2)^{-1}$. The case $\nu_{11}=\nu_{22}=0$ describes copolymers with regularly alternating units, the case $\nu_{11}\nu_{22}=\nu_{12}\nu_{21}$ corresponds to completely random (Bernoulli) copolymers, and the case $\nu_{11}\nu_{22}\gg\nu_{12}\nu_{21}$ describes multiblock copolymers.

1. REPLICA METHOD FOR SYSTEMS WITH AN ARBITRARY MOLECULAR-STRUCTURE DISTRIBUTION

We use a known model[2,3] to describe the polymer systems. In this model, the interaction of units M_i and M_j is described by a potential V_{ij}, and the conditional probability for finding the units of a bond $\langle n,n'\rangle$ separated from each other by a given distance $|\mathbf{x}_n-\mathbf{x}_{n'}|$ is given by

$$\lambda_d(\mathbf{x}_n-\mathbf{x}_{n'})=(4\pi a^2)^{-d/2}\exp(-x^2/4a^2), \tag{7}$$

where a is the mean size of the bond.

As was shown in Ref. 3, the partition function of an ensemble of macromolecules with a given distribution $\{n(C)\}$ can be represented as the mean of the partition function of the same noninteracting (ideal) macromolecules whose units are in a random field $\mathbf{v}=\{v_i\}$:

$$Z\{n(C)\}=\left\langle \prod_C \frac{\Xi_d^{n(C)}(C,\{z_i^* e_i\})}{n(C)!} \right\rangle_{\mathbf{v}}. \tag{8}$$

Here $e_i=\exp(-h_i/T)$, where h_i is the external field acting on the M_i units; $z_i^*=\exp(-v_i/T)$; and the factor $n(C)!$ appears because macromolecules with an identical configuration C are themselves identical. The angle brackets in (8) denote the average over stochastic fields v with a probability

$$\mathscr{P}\{v\}=\left\{\int Dv\exp[-H_0/T]\right\}^{-1}\exp[-H_0/T],$$
$$H_0(v)=-\frac{1}{2}\sum_{ij}\int d\mathbf{x}\,d\mathbf{x}'\,V_{ij}^{-1}(\mathbf{x}-\mathbf{x}')v_i(\mathbf{x})v_j(\mathbf{x}'), \tag{9}$$

and the matrix V^{-1} is found from

$$\sum_l \int d\mathbf{x}''V_{il}(\mathbf{x}-\mathbf{x}'')V_{lj}^{-1}(\mathbf{x}''-\mathbf{x}')=\delta_{ij}\delta(\mathbf{x}-\mathbf{x}'). \tag{10}$$

The partition function Ξ_d of an ideal macromolecule with a configuration C is given in the model of Refs. 2 and 3 by the expression

$$\Xi_d(C,\{z_i^*\})=\prod_n \int d\mathbf{x}_n z_{i_n}^*(\mathbf{x}_n)\prod_{\langle n,n'\rangle}\lambda_d(\mathbf{x}_n-\mathbf{x}_{n'}), \tag{11}$$

where the first product is over all units M_{i_n} in a macromolecule with configuration C, and the second product is over all its bonds $\langle n, n'\rangle$.

Various sets of configurations $\{n(C)\}$ can be realized in the synthesis process. We assume below that the probability for each set $\{n(C)\}$ is given by a Poisson distribution

$$P\{n(C)\}=\prod_C \exp\{-\bar{n}(C)\}[\bar{n}(C)]^{n(C)}/n(C)!. \tag{12}$$

The mean value of the free energy of the system is found by taking the average of the logarithm of the partition function (11) over all the $\{n(C)\}$ with probability (12). To carry out this averaging procedure, we use the following equation, which holds in the asymptotic limit $m\to 0$:

$$\ln Z\{n(C)\}=\frac{1}{m}\left[\left\langle \prod_C \Xi_d^{n(C)}(C,\{z_i^* e_i\})\right\rangle_{\mathbf{v}}^m-1\right]$$
$$-\sum_C \ln n(C)!. \tag{13}$$

In the replica method,[10,11] the parameter m in (13) is assumed to be some arbitrary integer, and the limit $m\to 0$ is taken only at the end of the calculations. The product of m identical factors in (13) can be represented as an average over the fields $\bar{\mathbf{v}}=\{\mathbf{v}^{(k)}(\mathbf{x}^{(k)})\}$, $k=1,...,m$ with a measure equal to the product of the measures (9) of each of the replicas k:

$$\left\langle \prod_C \Xi_{dm}^{n(C)}(C,\{z_i^*(\mathbf{X})e_i(\mathbf{X})\})\right\rangle_{\bar{\mathbf{v}}},$$
$$z_i^*(\mathbf{X})=\prod_{k=1}^m z_i^*(\mathbf{x}^{(k)}), \quad e_i(\mathbf{X})=\prod_{k=1}^m e_i(\mathbf{x}^{(k)}). \tag{14}$$

Substituting (14) into (13), and taking the average of the resulting expression over the sets $\{n(C)\}$ with probability (12), we find the following expression for the free energy of the polymer:

$$F=\left.\frac{\partial\Omega_{dm}\{h_i\}}{\partial m}\right|_{m=0}+T\sum_C \exp[-\bar{n}(C)]\sum_{n=0}^{\infty}\frac{[\bar{n}(C)]^n}{n!}\ln n!, \tag{15}$$

where Ω_{dm} is the thermodynamic potential of the chemically equilibrium system whose units are in a dm-dimensional space

$$\exp\left(-\frac{\Omega_{dm}}{T}\right)=\left\langle \exp\left(-\frac{\Omega_{dm}^{xc}\{z_i^*(\mathbf{X})e_i(\mathbf{X})\}}{T}\right)\right\rangle_{\bar{\mathbf{v}}}, \tag{16}$$

and Ω_{dm}^{xc} is the thermodynamic potential of the dm-dimensional system of chemical bonds[3] which consists of ideal macromolecules:

$$\Omega_{dm}^{xc}\{z_i^{*}(\mathbf{X})\}/T=-\sum_{C}\bar{n}(C)\Xi_{dm}(C,\{z_i^{*}(\mathbf{X})\}). \tag{17}$$

According to (17), the quantities $\bar{n}(C)$ serve as the activities of the macromolecules in such a system.

The interaction V_{ij} of the monomer units of the macromolecules in expression (16) is described by a strongly fluctuating stochastic field $\bar{\mathbf{v}}$. Over length scales short in comparison with a, such fluctuations do not contain the "polymer specifics." Their contribution should thus be summed beforehand. In the field formalism, this purpose is served by transforming to an integral over the new variables $z_i^{*(k)}$ in (16):

$$\exp\left(-\frac{\Omega_{dm}}{T}\right)=\int\prod_{i,k}Dz_i^{*(k)}\exp\left[-\frac{1}{T}\Omega_{dm}^{xc}\{z_i^{*}(\mathbf{X})e_i(\mathbf{X})\}\right.$$
$$\left.-\sum_{k=1}^{m}\Omega^{*}\{z_i^{*(k)}\}/T\right]. \tag{18}$$

As is shown in Appendix A, the functional Ω^* can be expressed directly in terms of the pressure $P^{ru}(\rho_i)$ and the chemical potentials $\mu_i^{ru}(\rho_j)$ of the "system of ruptured units":[3] an equilibrium ensemble of monomer units which interact with each other with a potential V_{ij} but which do not form chemical bonds,

$$\Omega^{*}\{z_i^{*}(\mathbf{x})\}=-\int d\mathbf{x}\,P^{*}(\rho_i(\mathbf{x})),\qquad z_i^{*}(\mathbf{x})=\exp(\mu_i^{*}(\rho_j)/T),$$

$$P^{*}(\rho_i)=P^{\text{ру}}(\rho_i)-T\sum_{i}\rho_i,\qquad \mu_i^{*}(\rho_j)=\mu_i^{\text{ру}}(\rho_j)-T\ln\rho_i. \tag{19}$$

In the lattice model of Ref. 3, excluded-volume effects are described by a parameter v, and binary interactions of units M_i and M_j are described by dimensionless Flory parameters χ_{ij}:

$$P^{*}(\rho_i)/T=-\frac{1}{v}\ln(1-v\rho)-\rho+\frac{v}{2}\sum_{ij}\chi_{ij}\rho_i\rho_j,$$
$$\rho=\sum_{i}\rho_i,\qquad \mu_i^{*}(\rho_j)/T=-\ln(1-v\rho)+v\sum_{j}\chi_{ij}\rho_j. \tag{20}$$

Expressions (17)–(20) completely determine the energy of a polymer system with arbitrary given mean values $\bar{n}(C)$ of the numbers of macromolecules of the various configurations.

2. MEAN-FIELD THEORY

A. General theory. When density fluctuations are ignored, the functional integral in (18) can be evaluated by the method of steepest descent. The equation for the saddle-point function z_i^* determines the mean density of units in the case of a spatially homogeneous state in the limit $m\to 0$:

$$\rho_i^{(0)}=\frac{1}{V^{(0)}}\sum_{\mathbf{l}}\bar{n}(\mathbf{l})l_i. \tag{21}$$

Here $V^{(0)}$ is the volume of the system, and $\bar{n}(\mathbf{l})$ is the composition distribution, i.e., the number of macromolecules with a composition vector $\mathbf{l}$ which has a given value and whose components l_i are equal to the numbers of units M_i in the molecule. From (15) and (18) we find the following expression for the free energy of the system:

$$F\{\bar{n}(C)\}=T\sum_{C}\left\{\exp[-\bar{n}(C)]\right.$$
$$\left.\times\sum_{n=0}^{\infty}\frac{[\bar{n}(C)]^n}{n!}\ln\frac{n!}{V^{(0)}}-\bar{n}(C)\ln\Xi_d(C,\{1\})\right\}$$
$$+V^{(0)}f^{*}(\rho_i^{(0)}), \tag{22}$$

where we have set

$$f^{*}(\rho_i)=P^{*}(\rho_i)-\sum_{i}\rho_i\mu_i^{*}(\rho_j). \tag{23}$$

Expression (22) agrees with the results of Flory's theory[1] for the lattice model in (20) only in the limit $\bar{n}(C)\gg 1$, in which the sum over n in (22) reduces to an integral which we can evaluate by the method of steepest descent. In this case the position of the spinodal temperature can indeed be found through a calculation of the determinant of matrix (1) with the help of (22). In general, the spinodal temperature should be found from the condition for the divergence of the Fourier component of the density-density correlation function:

$$\theta_{ij}(\mathbf{x}-\mathbf{x}')\equiv\langle\delta\rho_i(\mathbf{x})\delta\rho_j(\mathbf{x}')\rangle=-T\frac{\delta^2F}{\delta h_i(\mathbf{x})\delta h_j(\mathbf{x}')}. \tag{24}$$

Here $\delta\rho_i(x)$ are the fluctuations in the density of the M_i units. An important point is that the Fourier component $g_{\mathbf{q}}$ of the correlation function (24) is discontinuous at the point $q=0$. Exactly at the point $q=0$, this Fourier component is identically zero because of the conservation of the total number of the M_i units, but it is nonzero in an arbitrarily small neighborhood of this point. Everywhere in the discussion below, we understand the case $q=0$ as meaning the limit $q\to 0$ from the right ($q>0$).

Two qualitatively different cases are possible, depending on the magnitude of the wave vector q_0, at which the following conditions first hold:

$$D(q_0^2)=0,\qquad D(q^2)\equiv\det\theta_{\mathbf{q}}^{-1}. \tag{25}$$

The first of them, $q_0=0$, corresponds in particular to the ordinary spinodal transition. In the second case, $q_0^2>0$, the critical value of the external parameter (of the temperature, the pressure, etc.), at which stability is lost, is found from the condition $\partial D(q_0^2)/\partial q_0^2=0$.

Evaluating the variational derivatives (24) in the mean-field approximation, we find the following expression for the Fourier components of the matrix of correlation functions:

$$\theta_{\mathbf{q}}=g_{\mathbf{q}}(1-g_{\mathbf{q}}C_{\mathbf{q}})^{-1}. \tag{26}$$

On the right side of this expression are Fourier components of the structure function g,

$$g_{ij}(\mathbf{x}-\mathbf{x}')=m^{-1}T^{-1}\delta^2\Omega_{dm}{}^{xc}\{z^{*}\}/\delta\ln z_i^{*}(\mathbf{x})\,\delta\ln z_j^{*}(\mathbf{x}')\,|_{m=0}, \tag{27}$$

and of the matrix of the direct correlation functions C,

$$C_{ij}(\{\rho\},\mathbf{x}-\mathbf{x}')=-\delta\mu_i^{*}(\{\rho\},\mathbf{x})/\delta\rho_j(\mathbf{x}')T. \tag{28}$$

Expression (26) is a generalization of the corresponding expression which was derived in Refs. 2 and 3 by a thermodynamic approach.

We now consider a polyphase system for arbitrary values of $\bar{n}(C)$. In finding the q values of the various phases, we partition the replica space of dimensionality dm into q^m regions, each of which has a volume

$$\prod_s (V^{(s)})^{n_s},$$

where n_s is the number of replicas in phase s. The number of regions with identical sets of numbers n_s $(\Sigma n_s = m)$ is equal to the number of combinations $\begin{bmatrix} m \\ \{n_s\} \end{bmatrix}$. It is then not difficult to verify that the total number of regions and their total volume are q^m and V^m, respectively, with $V = \Sigma V^{(s)}$.

To evaluate the free energy, we separate from expression (11) (for the partition function of a macromolecule with configuration C) the integration over the collective variable of its center of mass, $\mathbf{X}_c$:

$$\Xi_{dm}(C, \{z_i^*\}) = \int d\mathbf{X}_c \theta_{dm}(C, \{z_i^*\}, \mathbf{X}_c)$$
$$= \sum_{\{n_s\}} \binom{m}{\{n_s\}} \prod_s (V^{(s)})^{n_s} \prod_i (z_i^{*(s)})^{n_s l_i} \theta_{dm}(C, \{1\}), \qquad (29)$$

where $z_i^{*(s)}$ is the value of the function $z_i^*(x)$ in phase s. Carrying out the summation over n_s in (29), and using the resulting expression in (17) and (15), we find the difference between the energies of the q-phase system and that of a single-phase system, (22):

$$\Delta F_q = -T \sum_{\mathbf{l}} \bar{n}(\mathbf{l}) \ln \Big[\sum_{s=1}^{q} \frac{V^{(s)}}{V^{(0)}} \prod_i (z_i^{*(s)})^{l_i} \Big]$$
$$+ \sum_{s=1}^{q} V^{(s)} f^*(\rho^{(s)}) - V^{(0)} f^*(\rho^{(0)}). \qquad (30)$$

We are assuming here that the densities $\rho_i^{(s)}$ of units M_i in phase s are related to $z_i^{*(s)}$ by (19). Minimizing the right side of (30) with respect to $\rho_i^{(s)}$, we find the equilibrium values of these densities to be

$$\rho_i^{(s)} = (V^{(s)})^{-1} \sum_{\mathbf{l}} \bar{n}^{(s)}(\mathbf{l}) l_i, \qquad (31)$$

where $\bar{n}^{(s)}(\mathbf{l})$, the mean numbers of macromolecules in phase s with a given composition vector $\mathbf{l}$, is given by

$$\bar{n}^{(s)}(\mathbf{l}) = \frac{\bar{n}(\mathbf{l}) V^{(s)} \prod_i (z_i^{*(s)})^{l_i}}{\sum_\sigma V^{(\sigma)} \prod_i (z_i^{*(\sigma)})^{l_i}}. \qquad (32)$$

The equilibrium values of the volumes $V^{(s)}$ of each of the phases are found by minimizing the functional (30) with respect to $V^{(s)}$ at a fixed total volume V. The conditions for a minimum are equations stating that the pressures $P^{(s)}$ in all the q coexisting phases are equal:

$$P^{(s)} = T \sum_{\mathbf{l}} \bar{n}^{(s)}(\mathbf{l}) + P^*(\rho_i^{(s)}). \qquad (33)$$

Equations (30)–(33) give a complete description of this q-phase system. The correlation functions in (26) and the difference between free energies in (30) are described correctly by Flory's equations, although Flory's theory is not valid at small values $\bar{n}(C) \ll 1$.

B. Markovian heteropolymers. The direct use of relations (22), (26), and (30) of the general theory requires a summation of series over all configurations C. A distinctive feature of the new approach of the present paper is that in the basic cases of practical interest this approach leads to a closed expression for the functional Ω_{dm}^{xc} in (17), without the need to carry out tedious combinatorial calculations. The calculation for branched polymers is discussed in Appendix B. In the case of linear n-component Markovian heteropolymers, (2), this functional can be written in the comparatively simple form

$$\Omega_{dm}\{z_i^*\}/\bar{n}T$$

$$= \sum_{i,j=1}^{n} (\nu^{-1})_{ij} \int d\mathbf{X} d\mathbf{X}' (\lambda_{dm}^{-1})(\mathbf{X}-\mathbf{X}') \bar{\varphi}_i(\mathbf{X}) \varphi_j(\mathbf{X}')$$
$$- \sum_{i=1}^{n} \int d\mathbf{X}\, z_i^*(\mathbf{X}) (\bar{\varphi}_i(\mathbf{X}) + \bar{\eta}_i)(\varphi_i(\mathbf{X}) + \eta_i), \qquad (34)$$

where the functions $\bar{\varphi}$ and φ are found by minimizing the right side of (34). They are functionals of $z^*(\mathbf{X})$. It is not difficult to verify that the expansion (34) in a functional series in powers of $z^*(\mathbf{X})$ does indeed reproduce series (17).

Evaluating the variational derivatives in (27) and (34), we find the following expressions for the Fourier components of the matrix g of structure functions (27) and of the density of the M_i units:

$$g_{ij\mathbf{q}} = \rho_i \delta_{ij} + \rho_i \varkappa_{ij\mathbf{q}} + \rho_j \varkappa_{ji\mathbf{q}}, \qquad (35)$$
$$\rho_i = (\bar{n}/V^{(0)}) [\bar{\eta}(\mathbf{E}-\boldsymbol{\nu})^{-1}]_i, \quad \boldsymbol{\varkappa}_{\mathbf{q}} = (\boldsymbol{\nu}^{-1}\lambda_{\mathbf{q}}^{-1} - \mathbf{E})^{-1},$$

where $\lambda_{\mathbf{q}} = \exp(-a^2\mathbf{q}^2)$ is the Fourier component of the function λ_d in (7).

To determine the boundaries of the region of absolute instability of the solution of a binary heteropolymer with the help of (25) and (26), we find a function $D(q^2)$ for it, working from (35):

$$D = \frac{A - B\lambda_{\mathbf{q}} + C\lambda_{\mathbf{q}}^2}{\rho_1\rho_2[1 + (\nu_{11}+\nu_{22})\lambda_{\mathbf{q}} + (\nu_{11}\nu_{22} - \nu_{12}\nu_{21})\lambda_{\mathbf{q}}^2]},$$
$$A = (1-\rho_1 C_{11})(1-\rho_2 C_{22}) - \rho_1\rho_2 C_{12}^2,$$
$$B = \nu_{11}[(1+\rho_1 C_{11})(1-\rho_2 C_{22}) + \rho_1\rho_2 C_{12}^2] +$$
$$+ \nu_{22}[(1-\rho_1 C_{11})(1+\rho_2 C_{22}) + \rho_1\rho_2 C_{12}^2] + 2(\rho_1\nu_{12} + \rho_2\nu_{21}) C_{12},$$
$$C = (\nu_{11}\nu_{22} - \nu_{12}\nu_{21})[(1+\rho_1 C_{11})(1+\rho_2 C_{22}) - \rho_1\rho_2 C_{12}^2]. \qquad (36)$$

The sign of D is the same as the sign of the numerator of expression (36), since the denominator is always positive. The condition for an instability, (25), for fluctuations with (a) a zero value or (b) a nonzero value of the wave vector q_0 is, correspondingly,

$$B = A + C \ (a), \qquad B^2 = 4AC \ (b). \qquad (37)$$

Figure 1 shows a phase diagram of this heteropolymer solution for the case $A > 0$. In the opposite case $A < 0$, which corresponds to an absolute thermodynamic instability of the system of ruptured units, the polymer system is always unstable. It can be seen from this figure that a necessary condition for the loss of stability at the wave vector $q_0 > 0$ is that all three coefficients A, B, and C be positive. Since $\lambda_{q0} = B/2C = 2A/B$, only a small neighborhood of the point M in Fig. 1, in which the inequality $q_0 a \ll 1$ holds, is of

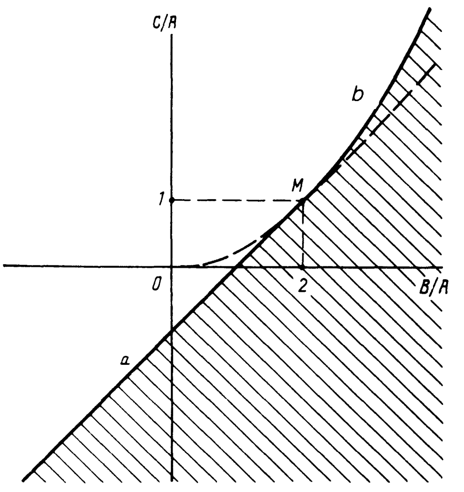

FIG. 1. Phase diagram of a solution of Markovian copolymers. The boundary of the hatched region, which is the region of thermodynamic instability, consists of a straight line a and a parabola b, both defined in (37).

practical interest for research on phase transitions of this sort.

Let us examine in more detail the most interesting case, $q_0R \gg 1$, where $R \approx a\bar{l}^{1/2}$ is a length scale of the macromolecules. Solving the second of equations (37) for $\nu_{12}+\nu_{21}$, and using (3) and (6), we find

$$\begin{gathered}\nu_{12}+\nu_{21}=2\beta^2/[((\beta^2+\alpha^2)(\beta^2+\gamma^2))^{1/2}+\beta^2+\alpha\gamma],\\ \beta^2=(\rho_1C_{11}-\rho_2C_{22})^2+4\rho_1\rho_2C_{12}^2, \qquad \alpha=1-\rho_1\rho_2(C_{11}C_{22}-C_{12}^2),\\ \gamma=\rho\Big[\sum_{i,j}C_{ij}\pi_i\pi_j+\pi_1\pi_2(2C_{12}-C_{11}-C_{22})\Big].\end{gathered} \tag{38}$$

From (38) we find $0<\nu_{12}+\nu_{21}<1$; this inequality should hold at the spinodal temperature in (37b). In the two important limiting cases of a mixture of homopolymers ($\nu_{12}+\nu_{21}=0$) and Bernoulli heteropolymers ($\nu_{12}+\nu_{21}=1$), this phase transition to a state with a nonzero wave vector $q_0>0$ is therefore not possible.

3. PERIODIC SPATIAL STRUCTURE IN MARKOVIAN HETEROPOLYMERS

We now consider a heteropolymer melt, which can be described quite accurately as incompressible. In this case we can use the lattice-gas model in (20). In the present section of the paper we assume for simplicity that the probability $\bar{\eta}_i$ for observing an initial unit of type i is equal to the mean fraction π_i of the units of this type [see (6)]. From (5) we then find $\eta_1=\eta_2\equiv\bar{l}^{-1}$.

According to results (36)–(38) of the preceding section of this paper, a spatially homogeneous state in the incompressible system under consideration here can become unstable only at $q_0=0$. The incompressibility condition corresponds to the limit $\rho\to v^{-1}$ in expression (20) for the function $\mu_i^*(\rho_j)$ of the lattice model. That function determines the parameters C_{ij} in (28). As a result we find that the region of absolute instability corresponds to the condition

$$\chi=\chi_{11}+\chi_{22}-2\chi_{12}>\chi_c,$$

where the parameter

$$\chi_c=\frac{\nu_{12}+\nu_{21}}{(1+\nu_{11})(1+\nu_{22})-\nu_{12}\nu_{21}}\times\Big[1+\nu_{12}+\nu_{21}+\frac{(1+\nu_{11})(1-\nu_{22})}{\nu_{12}}+\frac{(1-\nu_{11})(1+\nu_{22})}{\nu_{21}}\Big]$$

takes the following simple form in the heteropolymer limit $\bar{l}(\nu_{12}+\nu_{21})\gg 1$:

$$\chi_c=(\nu_{12}+\nu_{21})/\pi_1\pi_2(2-\nu_{12}-\nu_{21}). \tag{39}$$

Below we show that under the condition $\chi>\chi_c$, despite the condition $q_0=0$, there is a periodic structure with a period proportional to $(\chi-\chi_c)^{-1/2}$, which is much greater than the length scale of an individual block. Incommensurable structures of this sort are qualitatively different from those discussed previously,[4-6] for which these length scales are comparable.

To study the nature of the transition near the point $\chi=\chi_c$, we expand the functional Ω_{dm}^{xc} in (34) in powers of the functions

$$\begin{aligned}&u_1(\mathbf{X})\equiv\pi_1z_1^*(\mathbf{X})+\pi_2z_2^*(\mathbf{X})-1,\\ &\quad u_3(\mathbf{X})\equiv z_1^*(\mathbf{X})-z_2^*(\mathbf{X}),\\ &u_2(\mathbf{X})\equiv\pi_2z_1^*(\mathbf{X})+\pi_1z_1^*(\mathbf{X})-1,\end{aligned} \tag{40}$$

treating the latter as a small perturbation. With $u_i=0$, the quadratic form in (34) can be diagonalized by transforming to the new variables

$$\bar{\psi}(\mathbf{X})=\bar{\varphi}(\mathbf{X})S, \quad \psi(\mathbf{X})=S^{-1}\varphi(\mathbf{X}), \quad S=\begin{pmatrix}\pi_2 & 1\\ -\pi_1 & 1\end{pmatrix}. \tag{41}$$

In the momentum representation, the eigenvalues of the resulting quadratic form are proportional to the quantities

$$g_{i\mathrm{Q}}^{-1}=\lambda_i^{-1}\lambda_{\mathrm{Q}}^{-1}-1, \quad i=1,2, \quad \lambda_{\mathrm{Q}}=\exp(-a^2Q^2), \tag{42}$$

where λ_i are the eigenvalues of transition matrix ν, given by

$$\lambda_1=1-\bar{l}^{-1}, \quad \lambda_2=1-\bar{l}^{-1}-\nu_{12}-\nu_{21}.$$

Using (42), we can put the expansion of Ω_{dm}^{xc} in powers of the Fourier components of the functions in (40) in the form

$$\Omega_{dm}^{xc}/TV^m=\mathrm{const}-\rho V\Big[u_{00}+\sum_{\mathbf{Q}}u_{0\mathbf{Q}}g_{1\mathbf{Q}}u_{\mathbf{Q}0}+\ldots\Big], \tag{43}$$

$$\begin{aligned}u_{\mathbf{Q}\,-\mathbf{Q}'}=u_{1\mathbf{Q}}\Delta(\mathbf{Q}-\mathbf{Q}')&+\sum_{\mathbf{P}}u_{3\mathbf{Q}+\mathbf{P}}g_{2\mathbf{P}}u_{3-\mathbf{Q}'-\mathbf{P}}\\ &+\sum_{\mathbf{P},\mathbf{T}}u_{3\mathbf{Q}+\mathbf{P}}g_{2\mathbf{P}}u_{2\mathbf{T}-\mathbf{P}}g_{2\mathbf{T}}u_{3-\mathbf{Q}'-\mathbf{T}}+\ldots,\end{aligned} \tag{44}$$

where $\Delta(\mathbf{Q})$ is the Kronecker delta, and all the momenta **Q**, **P**, and **T** are defined in the dm-dimensional space.

The functional Ω^* in (19), which describes the interaction of the units in an incompressible system, takes its simplest form,

$$\Omega^*/T=\rho\int d\mathbf{x}[u(\mathbf{x})+v^2(\mathbf{x})/2\chi], \tag{45}$$

in terms of the variables u and v, which are related to the parameters z_i in (19) by

$$z_1^*=\exp(u+\pi_2v), \quad z_2^*=\exp(u-\pi_1v). \tag{46}$$

Expressions (45) and (46) are found in the lattice model by taking the limit $\rho \to v^{-1}$ in (20) and (19). The function $v(\mathbf{x})$ is proportional to the deviation $\Delta\rho_1(\mathbf{x})$ of the density of the monomer units of the first type at the given point $\mathbf{x}$ from its mean value over the volume:

$$v(\mathbf{x})=\chi\Delta\rho_1(\mathbf{x})/\rho, \quad \Delta\rho_1(\mathbf{x})=\pi_2\rho_1(\mathbf{x})-\pi_1\rho_2(\mathbf{x}). \tag{47}$$

The densities of units M_i are therefore

$$\rho_1(\mathbf{x})=\pi_1\rho+\Delta\rho_1(\mathbf{x}), \quad \rho_2(\mathbf{x})=\pi_2\rho-\Delta\rho_1(\mathbf{x}).$$

Substituting (45), (46) and (43), (44) into (18), we find, in the mean-field approximation,

$$\Omega_{dm}/\rho VT=\text{const}-\sum_{k=1}^{m} f(u^{(k)}, v^{(k)})-\sum_{k\neq k'} f_{int}(v^{(k)}, v^{(k')})+\dots, \tag{48}$$

$$f(u, v)=\sum_{\mathbf{q}\neq 0}\{[1/2\chi-\pi_1\pi_2(g_{2\mathbf{q}}+{}^1/_2)]v_{\mathbf{q}}v_{-\mathbf{q}}-{}^1/_2 u_{\mathbf{q}}u_{-\mathbf{q}}\}$$

$$-(\pi_2-\pi_1)\sum_{\mathbf{q},\mathbf{q}'\neq 0} g_{2\mathbf{q}}g_{2\mathbf{q}'}v_{\mathbf{q}}v_{\mathbf{q}'-\mathbf{q}}v_{-\mathbf{q}'}-\sum_{\mathbf{q}\neq 0} g_{1\mathbf{q}}\xi_{\mathbf{q}}\xi_{-\mathbf{q}},$$

$$\xi_{\mathbf{q}}=u_{\mathbf{q}}-\pi_1\pi_2\sum_{\mathbf{q}'}(g_{2\mathbf{q}'}+{}^1/_2)v_{\mathbf{q}'+\mathbf{q}}v_{-\mathbf{q}'},$$

$$f_{int}(v, v')=\pi_1{}^2\pi_2{}^2\sum_{\mathbf{q},\mathbf{q}'\neq 0,\mathbf{q}+\mathbf{q}'\neq 0} g_{1\mathbf{q},\mathbf{q}'}(g_{2\mathbf{q}}+{}^1/_2)(g_{2\mathbf{q}'}+{}^1/_2)$$

$$\times v_{\mathbf{q}}v_{-\mathbf{q}}v'_{\mathbf{q}'}v_{-\mathbf{q}'},$$

$$g_{1\mathbf{q},\mathbf{q}'}\equiv g_{1\mathbf{Q}}, \quad \mathbf{Q}=(\mathbf{q}, \mathbf{q}', 0, \dots, 0). \tag{49}$$

Here it is assumed that all the momenta $\mathbf{q}$ and $\mathbf{q}'$ lie in the d-dimensional space. Minimizing expression (48) with respect to $u_{\mathbf{q}}^{(k)}$, we find

$$u_{\mathbf{q}}^{(k)}=g_{1\mathbf{q}}(g_{1\mathbf{q}}+{}^1/_2)^{-1}\pi_1\pi_2\sum_{\mathbf{q}'}(g_{2\mathbf{q}'}+{}^1/_2)v_{\mathbf{q}+\mathbf{q}'}^{(k)}v_{-\mathbf{q}'}^{(k)} \tag{50}$$

Substituting (50) into (48), we find a functional Ω_{dm} which depends only on the field v. We are interested below in the momentum region $\bar{l}^{-1} \ll a^2q^2 \ll \nu_{12}+\nu_{21}$. In other words, we are interested in characteristic dimensions q^{-1} which are small in comparison with the size of the macromolecule, $R=a\bar{l}^{1/2}$, but large in comparison with the characteristic dimension $a(\nu_{12}+\nu_{21})^{-1/2}$ of one of its blocks. Restricting the discussion to the terms linear in q^2 in the expansion of the functions $g_{i\mathbf{q}}$ in (42) in this approximation, and introducing the dimensionless variables

$$v_{\mathbf{q}}=\frac{\tau(\nu_{12}+\nu_{21})c_{\mathbf{p}}}{[\pi_1\pi_2(1-\nu_{12}-\nu_{21})]^{1/2}}, \quad \tau=1-\frac{\chi_c}{\chi},$$
$$\mathbf{q}=\frac{\mathbf{p}}{a}\gamma^{1/2}\tau^{1/2}, \quad \gamma=\frac{(\nu_{12}+\nu_{21})(2-\nu_{12}-\nu_{21})}{2(1-\nu_{12}-\nu_{21})}, \tag{51}$$

we find the following expression for the functional Ω_{dm}:

$$\Omega_{dm}/\rho VT=\gamma\tau^3\sum_{k=1}^{m}\Big[\sum_{\mathbf{p}\neq 0}c_{\mathbf{p}}^{(k)}c_{-\mathbf{p}}^{(k)}(-1+\mathbf{p}^2)-\Delta$$
$$\times\sum_{\mathbf{p},\mathbf{p}'\neq 0,\mathbf{p}+\mathbf{p}'\neq 0}c_{\mathbf{p}}^{(k)}c_{-\mathbf{p}-\mathbf{p}'}^{(k)}c_{\mathbf{p}'}^{(k)}\Big]$$
$$-\sum_{k\neq k'}\sum_{\mathbf{p},\mathbf{p}'\neq 0}\frac{c_{\mathbf{p}}^{(k)}c_{-\mathbf{p}}^{(k)}c_{\mathbf{p}'}^{(k')}c_{-\mathbf{p}'}^{(k)}}{p^2+p'^2},$$
$$\Delta=\frac{2(\pi_2-\pi_1)}{2-\nu_{12}-\nu_{21}}\left(\frac{1-\nu_{12}-\nu_{21}}{\pi_1\pi_2}\right)^{1/2}. \tag{52}$$

We restrict the discussion below to the solution $c_{\mathbf{q}}^{(k)}=c_{\mathbf{p}}$, symmetric with respect to replicas, of the equations which describe the conditions for a minimum of functional (52). A nontrivial analytic solution, which exists at $\tau>0$, can be found as a power series in the parameter $|\Delta|$. In the leading approximation in $|\Delta|$, we find

$$c_{\mathbf{p}}=c\sum_{i=1}^{6}[\Delta(\mathbf{p}-p_0\mathbf{e}_i)+\Delta(\mathbf{p}+p_0\mathbf{e}_i)], \tag{53}$$

$$c=\frac{\operatorname{sgn}\Delta}{3^{3/2}\cdot 2^{1/2}}\left(1+\left(\frac{2}{3}\right)^{1/2}|\Delta|\right), \quad p_0=\frac{1}{3^{1/2}}\left(1+\frac{|\Delta|}{6^{1/2}}\right), \tag{54}$$

where $\mathbf{e}_i$, $i=1,\dots,6$, are unit vectors directed along the edges of a regular tetrahedron. Solution (53) corresponds to an absolute minimum of the free-energy functional (52) with $\Delta\neq 0$. Solutions of this sort, which belong to a rhombohedral (trigonal) crystal symmetry system,[12] could not be derived in Refs. 4–8, where periodic structures in heteropolymer systems were studied theoretically. It is not difficult to see that solution (53) is stable at small values $|\Delta|\ll 1$. In the following orders in $|\Delta|$ in the sum in (53), higher harmonics with wave vectors $\Sigma n_i\mathbf{e}_i$ (the n_i are integers) of the reciprocal rhombohedral lattice contribute to sum (53). A solution of this type exists only under the condition $|\Delta|<\Delta_c\sim 1$. For the quantity Δ_c it is a simple matter to derive an upper estimate $\Delta_c<(3/2)^{1/2}$, through the use of the variational principle with the trial function (53).

The condition $a^2q^2\ll\nu_{12}+\nu_{21}$ for the applicability of expansion (52) holds only at $\tau\ll 1$. At $\tau\sim 1$, the amplitude of the superstructure, $\Delta\rho_1(\mathbf{x})$ in (47), (51), reaches values on the order of the total density ρ, and its period reaches values on the order of the size of a block. In expansion (52) of the thermodynamic potential, at $\tau\gtrsim 1$, we should thus retain only the small terms of higher order in $v^{(k)}$ and $u^{(k)}$. This solution is a clearly defined domain structure with a period equal to the size of a block. Similar spatial structures have been described in previous theoretical papers,[4–6] based on models different from our own. However, a description of such structures goes beyond the scope of our Ginzburg-Landau approach.

The difference between the free energies of a state with superstructure (53) and the spatially homogeneous state, (22), is

$$\Delta F/\rho VT=-(2\gamma\tau^3/27)(1+2^{3/2}|\Delta|/3^{1/2}), \quad |\Delta|\ll 1. \tag{55}$$

Since the cubic invariants of the order parameter (53) are finite, the expansion of the free energy in (55) contains odd powers of $|\Delta|$. Because of the factor τ^3, the transition in which we are interested here is a third-order phase transition in the parameter τ, even if the functional (52) contains terms which are cubic in v. This situation, which is a totally unusual one for the conventional Ginzburg-Landau approach, stems from the long-range nature of the fourth-order term f_{int} in (49), which describes the interaction of the different replicas. The presence of a term of this sort, which incorporates configurational disorder, was also demonstrated in Ref. 13, in the description of an isolated, statistically random macromolecule of a heteropolymer, although in the symmetric case we have $\pi_1=\pi_2=1/2$.

The conclusion, reached in that previous study, that there exists a spatial structure in a heteropolymer system with Bernoulli statistics for the distribution of units in the macromolecule contradicts the results of the present paper. According to the present results, such a structure could arise only if there were long-range correlations in the order of alternation of the types of units along the chain. There is absolutely no such correlation in Bernoulli heteropolymers. This discrepancy between results apparently stems from the incorrect use in Ref. 13 of a continuum model for the chain in a description of Bernoulli heteropolymers. In particular, the conclusions reached in that earlier paper are extremely sensitive to the length scale of the bulk interactions, but that scale has no bearing on the polymer specifics of the problem under consideration.

Erukhimovich[14] and Leibler[15] have also developed a theory for domain structures in heteropolymers. They assumed that the magnitude of the wave vector of the superstructure, q, can be found by analyzing terms of the Ginzburg-Landau functional which are quadratic in the order parameter. However, the value found for q_0 by that approach applies only to the transition point itself, $\tau = 0$. We have shown that at this point we have $q_0 = 0$ but that the characteristic value of q (of the reciprocal-lattice vector of the structure) increases in proportion to $\tau^{1/2}$ with distance from this point, with increasing τ.

The mean-field theory used in this section of the paper is valid only in the case in which the benefit achieved in terms of the free energy of the superstructure, (55), over a length scale equal to the period of this structure, $2\pi/q$, is large in comparison with the temperature T. This condition imposes a restriction on the values of the parameter τ:

$$\tau \gg \tau_G \approx \gamma^{1/3} (v^{1/3}/a)^2. \tag{56}$$

For real polymers we would have $v^{1/2} \lesssim a$, so the Ginzburg number in (56) would always be small ($\tau_G \ll 1$) in the case of block copolymers. Consequently, except for a narrow fluctuation region $\tau \lesssim \tau_G$ the mean-field theory gives a correct description of the periodic superstructure.

CONCLUSION

In this paper we have proposed a new and fairly general approach to the description of solutions and melts of polymers of arbitrary chemical structure. We have discussed in detail the important case of Markovian linear heteropolymers, and we have studied the possibility that they would form periodic structures. It has been shown that it is impossible in principle for structures of this sort to form in the case of Bernoulli heteropolymers, which is a case of practical importance. In block copolymers, the period of the structure depends on the strength of the interaction between the monomer units. It may be much larger than the spatial size of one block. An incommensurable superstructure of this sort stems from the presence of configurational disorder, and it cannot exist in the case of chemically regular copolymers.

Another important distinction between (on the one hand) real multiblock heteropolymers and (on the other) the chemically regular copolymers and block copolymers with small numbers of blocks in a macromolecule which have been studied previously is in the nature of their transition to a state with a periodic structure. In the latter cases, this is a first-order phase transition, which can give way to a second-order transition only at the symmetry point $\pi_1 = \pi_2 = 1/2$ (Ref. 15). As we showed above, this transition is a third-order phase transition in Markovian heteropolymers, even if there are terms in Ginzburg-Landau functional (48) which are cubic in the order parameter. To describe this unusual fact let us examine the Ginzburg-Landau functional which depends only on the amplitude $\Delta\rho$ of the superstructure and which is found by minimizing (48) with respect to the magnitude of the wave vector q. Substituting the value $q^2 \sim |\Delta\rho|$, found as a result of this minimization, into (48), we find that the coefficient of the cubic term, $|\Delta\rho|^3$, is positive in the case $\Delta < \Delta_c$. Consequently, a nontrivial solution $\Delta\rho \neq 0$ which minimizes the Ginzburg-Landau functional exists only under the condition $\tau > 0$, which is the condition under which the quadratic form of this functional loses its positive definite nature, and $\Delta\rho$ is not discontinuous at the transition point.

The Ginzburg-Landau functional method which has been used in all studies of phase transitions in heteropolymer systems of which the present authors are aware, makes it possible to describe only those first-order phase transitions which are approximately of second order. The formalism developed above makes it possible to go beyond that limitation. This flexibility is important in practical calculations on specific polymer systems. In addition to heteropolymer systems of linear macromolecules, the general approach proposed here can describe branched polymers. As an example, we give a closed expression for the thermodynamic potential [expression (B2) in Appendix B] in replica space. That potential makes it possible to find an exhaustive statistical description of solutions of tree-shaped polymers, which are frequently encountered in practice. In principle, incorporating the fluctuations of the functions z_i^* in (18) would make it possible to carry out a correct study of fluctuation effects in polymer systems with a given arbitrary distribution of numbers of macromolecules, $\{n(C)\}$.

APPENDIX A

Let us evaluate the functional Ω^* defined by the expression

$$\exp\left[-\frac{\Omega^*\{z^*\}}{T}\right] \equiv \left\langle \prod_i \delta[z_i^*(\mathbf{x}) - \exp[-v_i(\mathbf{x})/T]] \right\rangle_{\mathbf{v}}. \tag{A1}$$

Representing the δ-function as an integral over the complex field $z_i(\mathbf{x})$ and transposing the average over v and the integration over z_i, we rewrite (A1) as

$$\int Dz_i(\mathbf{x}) \exp\left[-\sum_i \int d\mathbf{x}\, z_i(\mathbf{x}) z_i^*(\mathbf{x}) - \Omega^{\text{pз}}\{z_i(\mathbf{x})\}/T\right], \tag{A2}$$

where we have used the representation[3] of the partition function of the system of ruptured bonds as an average over the fields $\mathbf{v}(\mathbf{x})$,

$$\exp\left[-\frac{\Omega^{\text{pз}}\{z_i(\mathbf{x})\}}{T}\right] = \left\langle \exp \sum_i \int d\mathbf{x}\, z_i(\mathbf{x}) z_i^*(\mathbf{x}) \right\rangle \tag{A3}$$

At this point we assume that the system of ruptured units is far from its critical point. Since the density fluctuations of such a system are small, the integral in (A2) over the variables $z_i(\mathbf{x})$ can be evaluated by the method of steepest descent without difficulty. The result of these calculations can be put in the form in (19).

APPENDIX B

Let us evaluate the functional Ω_{dm}^{xc} in (17) for a system of tree-shaped macromolecules obtained through a polycondensation of M_i units which have respectively $f_{\alpha i}$ functional groups of type α. The mean numbers of these macromolecules, $\bar{n}(C)$, are described by the Flory distribution:

$$\bar{n}(C) = \bar{n}\nu(z_i, y_{\alpha\beta}) \prod_i z_i^{l_i} \prod_{\alpha\beta} y_{\alpha\beta}^{m_{\alpha\beta}}, \tag{B1}$$

where $\bar{n}$ is their total number, l_i and $m_{\alpha\beta}$ are respectively the number of M_i units and the number of the bonds between groups α and β, and the functional dependence of the normalization factor ν on the parameters z_i and $y_{\alpha\beta}$ $(0 < z_i,\ y_{\alpha\beta} < 1)$ is derived below. These parameters may be thought of as the activities of the units and bonds of a dm-dimensional system at chemical equilibrium. The thermodynamic potential of such a system, (17), can be written in the form

$$\Omega_{dm}^{xc}\{z_i^*\}/\bar{n}T\nu(z_i, y_{\alpha\beta}) = {}^1/_2 \sum_{\alpha\beta} (\mathbf{y}^{-1})_{\alpha\beta} \int d\mathbf{X}\, d\mathbf{X}' (\lambda_{dm}^{-1})(\mathbf{X}-\mathbf{X}') \times \varphi_\alpha(\mathbf{X})\varphi_\beta(\mathbf{X}') - \sum_i \int d\mathbf{X}\, z_i z_i^*(\mathbf{X}) \prod_\alpha (1+\varphi_\alpha(\mathbf{X}))^{f_{\alpha i}}/f_{\alpha i}!\ , \tag{B2}$$

where $\mathbf{y}^{-1}$ is the matrix which is the inverse of $\mathbf{y}$, and the function λ_d^{-1} is related to λ_d by an equation like (10). The function $\varphi_\alpha(\mathbf{X})$ should be found from the condition which minimizes the right side of (B2).

According to definition (17), the thermodynamic potential in (B2) can be expressed in the case $m = 0$ in terms of the total number of macromolecules, $\bar{n}$. Setting $m = 0$ in (B2), we find the following expression for the normalization factor ν in (B1):

$$\nu^{-1}(z_i, y_{\alpha\beta}) = \sum_i \theta_i - {}^1/_2 \sum_{\alpha\beta} (\mathbf{y}^{-1})_{\alpha\beta} \varphi_\alpha^{(0)} \varphi_\beta^{(0)}, \tag{B3}$$

$$\theta_i \equiv z_i \prod_\alpha (1+\varphi_\alpha^{(0)})^{f_{\alpha i}}/f_{\alpha i}!,$$

where the parameters $\varphi_\alpha^{(0)}$ are found from the solution of the equations

$$\sum_\beta (\mathbf{y}^{-1})_{\alpha\beta}\varphi_\beta^{(0)} = \sum_i \partial\theta_i/\partial\varphi_\alpha^{(0)}. \tag{B4}$$

Expression (B2), along with general relation (18), can be used as the starting point for constructing a microscopic theory of solutions of branched polymers, in the same way that expression (34) was used in the main body of this article to describe linear heteropolymers. As a very simple example of the use of (B2), we will calculate the structure function (27) for a spatially homogeneous system. It is not difficult to show that the minimum of (B2) in the limit $m \to 0$ is reached with the solution $\varphi_\alpha(\mathbf{X}) = \varphi_\alpha^{(0)}$ and that we have

$$\rho_i^{(0)} = \bar{n}\nu(z_j, y_{\alpha\beta})\theta_i/V^{(0)}. \tag{B5}$$

Differentiating free energy (15), (B2) with respect to h, we find the Fourier component of the structure function (27):

$$g_{ij\mathbf{q}} = \frac{\bar{n}\nu(z_k, y_{\alpha\beta})}{V^{(0)}} \left[\delta_{ij}\theta_i + \sum_{\alpha\beta} \frac{\partial\theta_i}{\partial\varphi_\alpha^{(0)}} \varkappa_{\alpha\beta\mathbf{q}} \frac{\partial\theta_j}{\partial\varphi_\beta^{(0)}}\right], \tag{B6}$$

where the matrix which is the inverse of $\varkappa_\mathbf{q}$ is

$$(\varkappa_\mathbf{q}^{-1})_{\alpha\beta} = (\mathbf{y}^{-1})_{\alpha\beta}\lambda_\mathbf{q}^{-1} - \sum_i \partial^2\theta_i/\partial\varphi_\alpha^{(0)}\, \partial\varphi_\beta^{(0)}. \tag{B7}$$

It can be shown that (B6) and (B7) can be put in the form which was found previously for the case of a concentrated system in chemical equilibrium,[3] if we switch from z_i and $y_{\alpha\beta}$ to the new variables $\rho_i^{(0)}$ in (B5) and $p_{\alpha\beta}$:

$$p_{\alpha\beta} = \frac{y_{\alpha\beta}}{1+\varphi_\alpha^{(0)}} \sum_i \frac{\partial\theta_i}{\partial\varphi_\beta^{(0)}}. \tag{B8}$$

This result seems quite natural, since in this case the molecular-structure distribution is the same as (B1).

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