Phase transition in a solution of heteropolymers

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A two-field model is set up which describes a binary solution of linear heteropolymers in chemical equilibrium. The region of low concentrations and large mean molecular lengths is investigated. It is shown by the renormalization group method that in first-order approximation in ε a phase transition of first order in the monomer activity occurs in the solution. It is also shown that a sufficiently long heteropolymer molecule in such a solution forms a globule. Results are presented of calculations for a solution containing cyclopolymers.

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§1. INTRODUCTION

The analogy between a solution of linear homopolymers and the n-component field theory in the limiting case $n\to 0$ (Refs. 1 and 2) has made it possible to go beyond the framework of the mean-field theory and to track, using very simple polymer models, the irregularities in the behavior of solutions of long molecules. The thermodynamic characteristic of the solution and the average dimensions of the molecules are obtained in this case directly from microscopic characteristics of the monomers.

For heteropolymers, however, there is no such theory and the existing studies do not go beyond the framework of the mean-field approximation. Many of them pertain to melts and to concentrated solutions, and are based on a phenomenological approach. This phenomenological approach is inapplicable to investigations of dilute and semidilute solutions of long heteropolymers.

The present paper makes use of a method similar to the des Cloizeaux formalism for homopolymers. It constitutes a simplified variant of a formalism developed by Erukhimovich in his dissertation.[3] The polymer is represented as consisting of beads (monomers) strung on flexible bodiless filaments. For simplicity it is assumed that the monomers are located at the sites of a primative cubic lattice with a period a. When setting up such a model with real polymers, the polymer segment (two beads connected by a filament) corresponds not to an individual link of the molecular chain, but to a statistical Kuhn segment, i.e., the distance along the chain on which the orientations of the links do not influence each other. We consider the simplest case, when there are only two different monomer species. The difference between the properties of the monomers manifests itself in the different bead-interaction energy (the radius of the interaction is the same and equals a) and different lengths of the segments. The employed formalism, just as the des Cloizeaux formula, is applicable only to solutions that are in chemical equilibrium with respect to the breaking and formation of bonds between the monomers (segments). Thus, polymers in a solution are statistical and have no definite primary structure. The partition function of such a solution can be reduced to the partition function of the two-field model. The renormalization group equations of this model are solved in the first ε-approximation. The solution at high values of the correlation radius lie outside the region of the physical stability, thus pointing to the existence of a first-order phase transition. This result is confirmed by a calculation of the equation of state of the model. This is followed by a "reconstruction" of the solution of the polymer problem on the basis of the results obtained for the field model. The physical conditions under which this phase transition can take place are investigated.

The article is arranged as follows. In §2 is described the field model and relations between the polymer and field quantities are given. The Hamiltonian of the dilute solution is determined in §3. The physical meaning of the results are investigated in §4 and certain quantitative estimates are made. The results are presented for a solution containing cyclopolymers.

§2. DESCRIPTION OF MODEL. CORRESPONDENCE BETWEEN FIELDS AND POLYMERS

We consider a solution of linear two-component heteropolymers. The polymers in the solution can be torn up into shorter strings and connected into longer molecules. It is assumed that equilibrium with respect to this reaction and with respect to all the thermodynamic degrees of freedom has been established in the solution. In addition, it is assumed that the volume considered is part of a large reservoir, i.e., a grand canonical ensemble is formed. This ensemble is completely specified by the corresponding chemical potentials μ_i or by the activities

$$f_i=\exp(\mu_i/T).$$

Its partition function is

$$Z=\sum\exp\Big[\Big(-E+\sum_i\mu_i N_i\Big)\Big/T\Big], \qquad (2.1)$$

where E is the configuration energy and N_i are the numbers of the chemical bonds and polymer ends. The summation is over all the different configurations of all possible polymers that can be produced for the given N_i, and also over all the N_i; Z is also the generating functional for a solution with definite N_i.

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In the approach of the present paper we write Z in the form of the partition function of a certain field model with Hamiltonian H:

$$Z=\int \exp[-H(\varphi_j(\mathbf{x}))]\prod_{j,\mathbf{x}} D\varphi_j(\mathbf{x}).$$

This allows us to use the results obtained in field theory.

Real physical systems, which can be approximately described by such a model, are solutions of chains in which the chemical composition (in this case the species of the monomer) changes little over distances of the order of the persistence length (the Coulomb segment). The most suitable physical realization of the model is an equilibrium solution of polymers, in which the lateral groups can be joined. If the density of the lateral appendages is small and the probability of two appendages landing on one Kuhn segment can be neglected, such a system is sufficiently well described by the model constructed.

The two monomer species will hereafter be designated one and two. The corresponding polymer segments (the statistical Kuhn segments) will be designated 11, 12, and 22. Let $I_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})$ be the distribution function of the lengths of an isolated polymer segment $\Delta\Delta'$, and

$$f_{\Delta\Delta'}=\exp(\mu_{\Delta\Delta'}/T)$$

its statistical weight (or activity); T is the solution temperature. The activity of the terminal monomer of species Δ is h_Δ. We specify the interaction of the monomers in the solution as follows:

$$\begin{aligned} &U_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})=0 \ \text{at}\ \mathbf{x}\neq\mathbf{y},\\ &U_{22}(\mathbf{x}-\mathbf{y})=\infty \ \text{at}\ \mathbf{x}=\mathbf{y},\\ &U_{12}(\mathbf{x}-\mathbf{y})=U_{11}(\mathbf{x}-\mathbf{y})=U_0 \ \text{at}\ \mathbf{x}=\mathbf{y}. \end{aligned} \tag{2.2}$$

Here $U_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})$ is the energy of the interaction of monomers Δ and Δ' located at the points $\mathbf{x}$ and $\mathbf{y}$.

We choose the Hamiltonian H in the form (see Refs. 3 and 4)

$$\begin{aligned} H=&-\sum_{\mathbf{x}}\ln\Big[1+\sum_{\Delta}(\varphi_\Delta^2(\mathbf{x})/2+h_\Delta\varphi_{\Delta1}(\mathbf{x}))\\ &+{}^1/_8\varkappa(\varphi_1^2(\mathbf{x}))^2+{}^1/_4\varkappa\varphi_1^2(\mathbf{x})\varphi_2^2(\mathbf{x})\Big]\\ &+{}^1/_2\sum_{\mathbf{x},\mathbf{y},\alpha,\Delta,\Delta'}\varphi_{\Delta\alpha}(\mathbf{x})\varphi_{\Delta'\alpha}(\mathbf{y})J^{-1}_{\Delta\Delta'}(\mathbf{x}-\mathbf{y}); \end{aligned} \tag{2.3}$$

$$\varkappa=e^{-U_0/T}<1,\quad \varphi_\Delta^2=\sum_{\alpha=1}^{n}\varphi_{\Delta\alpha}^2,\quad n\to 0.$$

The subscripts Δ and Δ' label the monomer species. The matrix $J_{\Delta\Delta}^{-1}(\mathbf{x}-\mathbf{y})$ is defined by the condition

$$\begin{aligned} &\sum_{\Delta',\mathbf{y}} J_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})J^{-1}_{\Delta'\Delta''}(\mathbf{y}-\mathbf{z})=\delta_{\Delta\Delta''}\delta_{\mathbf{x},\mathbf{z}},\\ &J_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})=f_{\Delta\Delta'}I_{\Delta\Delta'}(\mathbf{x}-\mathbf{y}). \end{aligned}$$

The partition function of the model is of the form

$$\begin{aligned} Z=\int\prod_{\mathbf{x}}\Big[&1+\sum_{\Delta}({}^1/_2\varphi_\Delta^2(\mathbf{x})+h_\Delta\varphi_{\Delta1}(\mathbf{x}))+{}^1/_8\varkappa(\varphi_1^2(\mathbf{x}))^2\\ &+{}^1/_4\varkappa\varphi_1^2(\mathbf{x})\varphi_2^2(\mathbf{x})\Big]\exp[-H_0(\varphi_\Delta(\mathbf{x}))]\prod_{\Delta,\mathbf{x},\alpha}D\varphi_{\Delta\alpha}(\mathbf{x}), \end{aligned}$$

where H_0 is the quadratic Gaussian Hamiltonian:

$$H_0={}^1/_2\sum_{\mathbf{x},\mathbf{y},\alpha}\varphi_{\Delta\alpha}(\mathbf{x})J^{-1}_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})\varphi_{\Delta'\alpha}(\mathbf{y}).$$

Expanding the sum in the brackets in the expression for Z and averaging all the products of the fields φ_Δ with the Hamiltonian H_0, we obtain expression (2.1). An analogous procedure is described in greater detail in Ref. 4, where all the missing details can be found. The density of the segments $\Delta\Delta'$ is $\rho_{\Delta\Delta'}=\partial\ln Z/\partial\ln f_{\Delta\Delta'}$. The correlator

$$G_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})=Z^{-1}\partial^2 Z/\partial h_\Delta(\mathbf{x})\partial h_{\Delta'}(\mathbf{y})$$

is the correlation function of the terminal monomers of species Δ and Δ'. To investigate the behavior of the solution at low densities, we expand H in powers of φ_Δ up to terms of fourth order. We obtain the following expression:

$$\begin{aligned} H=&-\sum_{\mathbf{x},\Delta}(\varphi_\Delta^2(\mathbf{x})/2+h_\Delta\varphi_\Delta(\mathbf{x}))\\ &+{}^1/_2\sum_{\mathbf{x},\mathbf{y},\alpha,\Delta,\Delta'}\varphi_{\Delta\alpha}(\mathbf{x})J^{-1}_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})\varphi_{\Delta'\alpha}(\mathbf{y})\\ &+{}^1/_8\sum_{\mathbf{x}}[(\varphi_1^2(\mathbf{x})+\varphi_2^2(\mathbf{x}))^2(1-\varkappa)+\varkappa(\varphi_2^2(\mathbf{x}))^2]. \end{aligned} \tag{2.4}$$

The Hamiltonia (2.4) is not connected with the particular form of the potential (2.2) and is determined by the second virial coefficients

$$B_{22}=a^3,\quad B_{12}=B_{11}=(1-\varkappa)a^3,$$

where a is the lattice period and a^3 is the volume of the unit cell. On the other hand, if we land in the region of high densities, to obtain qualitative results it suffices to take into account the third virial coefficients.

In first order in the monomer density (a small quantity) we can write the following relations. The density of the monomers of species Δ is the mean value

$$c_\Delta=\langle\varphi_\Delta^2/2+h_\Delta\varphi_{\Delta1}\rangle. \tag{2.5}$$

The mean value

$$F(\mathbf{x}-\mathbf{y})=\langle\varphi_{\Delta\beta}(\mathbf{x})\varphi_{\Delta'\beta}(\mathbf{y})\rangle,\quad \beta\neq 1 \tag{2.6}$$

is the correlation function of the terminal monomers of species Δ and Δ' belonging to one and the same molecule. All these relations are obtained exactly in the same manner as in Ref. 4, where a similar Hamiltonian is used. For convenience in the calculation we put

$$\theta=\varkappa/(1-\varkappa),$$

so that the fourth-order terms in (2.4) take the form

$${}^1/_8(1-\varkappa)\sum_{\mathbf{x}}[(\varphi_1^2(\mathbf{x})+\varphi_2^2(\mathbf{x}))^2+\theta(\varphi_2^2(\mathbf{x}))^2].$$

We change in (2.4) to the momentum representation:

$$\varphi_{\Delta\alpha}(\mathbf{q})=\sum_{\mathbf{x}} e^{i\mathbf{q}\mathbf{x}}\varphi_{\Delta\alpha}(\mathbf{x}), \quad J_{\Delta\Delta'}(\mathbf{q})=\sum_{\mathbf{y}} e^{i\mathbf{q}(\mathbf{x}-\mathbf{y})}J_{\Delta\Delta'}(\mathbf{x}-\mathbf{y}).$$

The terms quadratic in φ_Δ in H are diagonalized by the transformation

$$\begin{aligned}\varphi_{1\alpha}(\mathbf{q})&=\psi_{1\alpha}(\mathbf{q})\cos\chi(\mathbf{q})-\psi_{2\alpha}(\mathbf{q})\sin\chi(\mathbf{q}),\\ \varphi_{2\alpha}(\mathbf{q})&=\psi_{1\alpha}(\mathbf{q})\sin\chi(\mathbf{q})+\psi_{2\alpha}(\mathbf{q})\cos\chi(\mathbf{q}),\end{aligned} \tag{2.7}$$

where

$$\operatorname{tg} 2\chi(\mathbf{q})=2J_{12}(\mathbf{q})/(J_2(\mathbf{q})-J_1(\mathbf{q})).$$

We put for simplicity $a = 1$; then, after replacing the summation by integration, the Hamiltonian of the fields $\psi_{\Delta\alpha}$ takes the form

$$\begin{aligned}H=&{}^1/_2\int\sum_{\alpha,\Delta}\tau_\Delta(\mathbf{q})|\psi_{\Delta\alpha}(\mathbf{q})|^2d^3\mathbf{q}/(2\pi)^3\\ &+\int\delta\Bigl(\sum_{i=1}^{4}\mathbf{q}_i\Bigr)\sum_{\alpha,\beta}[\Gamma_{4.0}(\mathbf{q}_i)\psi_{1\alpha}(\mathbf{q}_1)\psi_{1\alpha}(\mathbf{q}_2)\psi_{1\beta}(\mathbf{q}_3)\cdot\\ &\cdot\psi_{1\beta}(\mathbf{q}_4)+\Gamma_{3.1}(\mathbf{q}_i)\psi_{1\alpha}(\mathbf{q}_1)\psi_{1\alpha}(\mathbf{q}_2)\psi_{1\beta}(\mathbf{q}_3)\psi_{2\beta}(\mathbf{q}_4)\\ &+\Gamma_{2.2}(\mathbf{q}_i)\psi_{1\alpha}(\mathbf{q}_1)\psi_{1\alpha}(\mathbf{q}_2)\psi_{2\beta}(\mathbf{q}_3)\psi_{2\beta}(\mathbf{q}_4)\\ &+\Gamma_{2/2}(\mathbf{q}_i)\psi_{1\alpha}(\mathbf{q}_1)\psi_{2\alpha}(\mathbf{q}_2)\psi_{1\beta}(\mathbf{q}_3)\psi_{2\beta}(\mathbf{q}_4)\\ &+\Gamma_{1.3}(\mathbf{q}_i)\psi_{1\alpha}(\mathbf{q}_1)\psi_{2\alpha}(\mathbf{q}_2)\psi_{2\beta}(\mathbf{q}_3)\psi_{2\beta}(\mathbf{q}_4)\\ &+\Gamma_{0.4}(\mathbf{q}_i)\psi_{2\alpha}(\mathbf{q}_1)\psi_{2\alpha}(\mathbf{q}_2)\psi_{2\beta}(\mathbf{q}_3)\psi_{2\beta}(\mathbf{q}_4)]\\ &\times\prod_i(d^3\mathbf{q}_i/(2\pi)^3)+h_1'\psi_{11}(0)+h_2'\psi_{21}(0),\end{aligned} \tag{2.8}$$

where the integral is taken over the reciprocal-lattice cell and

$$\begin{gathered}\tau_{1,2}(\mathbf{q})=\{{}^1/_2(J_1(\mathbf{q})+J_2(\mathbf{q}))\pm[{}^1/_4(J_1(\mathbf{q})-J_2(\mathbf{q}))^2\\ +J_{12}^2(\mathbf{q})]^{1/2}\}^{-1}-1, \quad \tau_1(\mathbf{q})<\tau_2(\mathbf{q}),\\ h_1'=h_1\cos\chi(0)+h_2\sin\chi(0), \quad h_2'=h_2\cos\chi(0)-h_1\sin\chi(0).\end{gathered}$$

This Hamiltonian differs from the Hamiltonian considered by Pokrovskiĭ, Lyuksyutov, and Khmel'nitskiĭ[5] of the two-field model with an artitrary number of field components in that, owing to the diagonalization operation, the unusual vertices $\Gamma_{1.3}$, $\Gamma_{2/2}$, and $\Gamma_{3.1}$ appear.

It is easy to show that $\tau_2(\mathbf{q})$ has at $\mathbf{q} = 0$ an absolute minimum, i.e., at small q we have

$$\tau_1(\mathbf{q})=\tau_1+s^2q^2.$$

In order of magnitude

$$s^2=\max_{\Delta,\Delta'}(f_{\Delta\Delta'}l_{\Delta\Delta'}^2),$$

$$l_{\Delta\Delta'}=\sum_{\mathbf{y}}|\mathbf{x}-\mathbf{y}|^2I_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})\Big/\sum_{y}I_{\Delta\Delta'}(\mathbf{x}-\mathbf{y})$$

is the mean squared length of the segment $\Delta\Delta'$. The Ginzburg number of the model is $1/s^3$ (Ref. 4). At $\tau_1 \ll s^{-3}$ the field fluctuates strongly and the scaling relations are valid.

We consider the case $\tau_2 \gg \tau_1$. The role of the weakly fluctuating field ψ_2 reduces then only to a renormalization of the parameters of the field ψ_1.

If we multiply all the $f_{\Delta\Delta'}$ by x,

$$f_{\Delta\Delta'}\to f_{\Delta\Delta'}x,$$

each polymer enters in $F(\mathbf{x} - \mathbf{y})$ of (2.6) with an additional factor x^L, where L is its length. At $h = 0$ only one polymer, starting at the point $\mathbf{x}$ and ending at the point $\mathbf{y}$, contributes to $F(\mathbf{x} - \mathbf{y})$. Therefore, the correlation functions of a polymer of fixed length are obtained by taking the inverse Laplace transform of (2.6) with respect to $\ln x$ at $h = 0$. Just as in Ref. 2, we find that in the strong-fluctuation region the average length of the polymer is

$$\bar{L}\sim(x-x_{cr})^{-1}\sim(\tau_1-\tau_{1cr})^{-1}.$$

§3. DILUTE SOLUTION OF LONG MOLECULES

In this section we consider the case $\bar{L} \gg 1$, i.e., $\tau_1 \ll 1/s^3$. In this region, the correlation radius r_c of the field ψ_1 is large and the system is close to a second-order transition in τ_1. A similar situation was considered in Ref. 5.

We consider the Hamiltonian obtained by excluding the strongly fluctuating field ψ_1. To this end we integrate in the expression for the partition function

$$Z=\int\exp[-H(\psi_1,\psi_2)]\prod_{\mathbf{q},\alpha}D\psi_{1\alpha}(\mathbf{q})D\psi_{2\alpha}(\mathbf{q})$$

over all the fields $\psi_{1\alpha}(\mathbf{q})$, where $q \geqslant \lambda$, and represent the result in Hamiltonian form[6]:

$$Z=\int\exp[-H(\psi_1,\psi_2,\lambda)]\prod_{\mathbf{q},\alpha}D\psi_{2\alpha}(\mathbf{q})\prod_{\beta,q'<\lambda}D\psi_{1\beta}(\mathbf{q}').$$

This integration can be carried out up to $\lambda \sim r_c^{-1}$. In the Hamiltonian $H(\psi_1,\psi_2,\lambda)$ we are interested here in vertices of fourth order at small external momenta. The calculations are carried out in first-order approximation in $\varepsilon = 4 - d$, where d is the dimensionality of the lattice (in the final answer we must put $d = 3$ and $\varepsilon = 1$). We put $\Gamma_{i.k} = \Gamma_{i.k}(\mathbf{q}_j)$ at $\mathbf{q}_j = 0$. This integration yields the renormalized quantities $\Gamma_{i.k}$ as functions of r_c. In place of λ we introduce the new variable

$$\xi=S_d(\lambda^{-\varepsilon}-1)/(2\pi)^ds^4\varepsilon,$$

where S_d is the area of a d-dimensional sphere. For $\Gamma_{i.k}(\xi)$ we obtain the following renormalization-group equations (the dot denoted differentiation with respect to ξ):

$$\begin{gathered}\dot\Gamma_{4.0}=-32\Gamma_{4.0}^2, \quad \dot\Gamma_{3.1}=-32\Gamma_{4.0}\Gamma_{3.1},\\ \dot\Gamma_{2.2}=-2\Gamma_{3.1}^2-8\Gamma_{4.0}\Gamma_{2.2}-4\Gamma_{4.0}\Gamma_{2.2},\\ \dot\Gamma_{2/2}=-6\Gamma_{3.1}^2-8\Gamma_{2/2}\Gamma_{4.0}, \quad \dot\Gamma_{1.3}=-6\Gamma_{2/2}\Gamma_{3.1}-4\Gamma_{2.2}\Gamma_{3.1},\\ \dot\Gamma_{0.4}=-\Gamma_{2/2}^2-2\Gamma_{2/2}\Gamma_{2.2}.\end{gathered} \tag{3.1}$$

Equations (3.1) can be easily solved. The solution is of the form

$$\begin{gathered}\Gamma_{4.0}=\Gamma(\xi)=\Gamma_{4.0}(0)/(1+32\Gamma_{4.0}(0)\xi),\\ \Gamma_{3.1}=c_0\Gamma(\xi), \quad \Gamma_{2/2}={}^1/_4c_0^2\Gamma(\xi)+c_{2/2}\Gamma^{1/4}(\xi),\\ \Gamma_{2.2}={}^1/_8c_0^2\Gamma(\xi)+c_{2.2}\Gamma^{1/4}(\xi)-{}^1/_8c_{2/2}\Gamma^{1/4}(\xi)\ln(\xi+\xi_0),\\ \Gamma_{1.3}={}^1/_2c_0(\Gamma_{2.2}+\Gamma_{2/2}-{}^1/_4c_0^2\Gamma(\xi))+c_{1.3},\\ \Gamma_{0.4}={}^1/_8\Gamma_{2.2}\Gamma_{2/2}/\Gamma(\xi)-{}^3/_{32}\Gamma_{2/2}^2/\Gamma(\xi)+{}^1/_8c_0^2({}^3/_4\Gamma_{2.2}+\Gamma_{2/2})\\ -({}^{15}/_{512})c_0^4\Gamma(\xi)+c_{0.4}, \quad \xi_0=(32\Gamma_{4.0}(0))^{-1},\end{gathered} \tag{3.2}$$

where c_0, $c_{2/2}$, $c_{2.2}$, $c_{1.3}$, $c_{0.4}$ are constants that depend on the initial conditions. The asymptotic form of $\Gamma_{i.k}(\xi)$ as $\xi\to\infty$ takes the form

$$\Gamma_{4.0}=\Gamma(\xi)\approx(32\xi)^{-1},\quad \Gamma_{2.2}\approx-{}^1/_8c_{2/2}\Gamma^{1/4}(\xi)\ln\xi,$$
$$\Gamma_{0.4}\approx c_{2/2}^2\ln\xi/(64\Gamma^{1/2}(\xi)),\quad \Gamma_{2/2}\approx c_{2/2}\Gamma^{1/4}(\xi)\ll\Gamma_{2.2}.$$

For the terms of fourth order in ψ in the Hamiltonian $H(\psi_1,\psi_2,\lambda)$ to be positive definite, it is essential to satisfy the condition $\Gamma_{2.2}\geqslant0$ or

$$\Gamma_{2.2}<0,\quad \Gamma_{2.2}^2/(4\Gamma_{4.0}\Gamma_{0.4})<1.$$

Inasmuch as in the region of large ξ we have

$$\Gamma_{2.2}^2/4\Gamma_{4.0}\Gamma_{0.4}\approx{}^1/_4\ln(\xi+\xi_0)\gg1,$$

there appears in the system $\xi\to\infty$ an instability that can lead to a first-order phase transition. Interest attaches precisely to this case, which corresponds to $\varkappa>0(\theta>0)$ in (2.4).

To calculate the equation of state, we make the transformation

$$\psi_{1\alpha}=\psi_{1\alpha}'-c_0\psi_{2\alpha}/4, \tag{3.3}$$

which eliminates the term $\psi_1^2\psi_{1\alpha}\psi_{2\alpha}$ from the Hamiltonian (2.8). In addition, this transformation eliminates from the solution (3.2) all the terms containing c_0. The Hamiltonian $H(\psi_1,\psi_2,\lambda)$ has a minimum with respect to ψ_1' at

$$\psi_{1\alpha}'=z\psi_{2\alpha},$$

where z is the point of absolute minimum of the expression

$$P(x)=\Gamma_{4.0}x^4+(\Gamma_{2.2}+\Gamma_{2/2})x^2+c_{1.3}x+\Gamma_{0.4}.$$

The field h is assumed weak, and we consider the region

$$\Gamma_{2/2}\psi_2^2\gg\tau_1.$$

We assume the direction of the vector $\psi_{2\alpha}$ to be the axis 1. We put

$$\zeta_1=\psi_{11}'-z\psi_{21},\quad \zeta_\beta=\psi_{1\beta}',\quad \beta\neq1$$

and assume that the weakly fluctuating field ψ_2 does not depend on the coordinates. In the Hamiltonian of the field ζ and ψ_2 we retain terms of order not higher than second in ζ. The result is the expression

$$\begin{aligned}H(\zeta,\psi_2)=\int[&\tau_1\zeta^2(x)/2+\tau_2\psi_2^2/2+s^2(\nabla\zeta)^2/2\\&+(\psi_2^2)^2(\Gamma_{0.4}+c_{1.3}z+(\Gamma_{2.2}+\Gamma_{2/2})z^2+\Gamma_{4.0}z^4)\\&+(\Gamma_{2/2}+\Gamma_{2.2}+6\Gamma_{4.0}z^2)\zeta_1^2\psi_2^2-c_{1.3}\psi_2^2\zeta_\beta^2/(2z)]\,d^d\mathbf{x}.\end{aligned}\tag{3.4}$$

We shall show that the coefficient g at $(\psi_2^2)^2$ is negative. From the definition of z it follows that $c_{1.3}z<0$. We put

$$x_0=-(-{}^1/_2\Gamma_{2.2}/\Gamma_{4.0})^{1/2}c_{1.3}/|c_{1.3}|.$$

Inasmuch as at large ξ we have

$$|x_0|<|c_{1.3}|/\Gamma_{2/2},$$

it follows that

$$c_{1.3}x_0+\Gamma_{2/2}x_0^2<0.$$

Consequently

$$y=\min_x P(x)\leqslant P(x_0)=\Gamma_{0.4}+\Gamma_{4.0}x_0^4+\Gamma_{2.2}x_0^2+\Gamma_{2/2}x_0^2+c_{1.3}x_0$$
$$<\Gamma_{0.4}+\Gamma_{4.0}x_0^4+\Gamma_{2.2}x_0^2=\Gamma_{0.4}-\Gamma_{2.2}^2/4\Gamma_{4.0}<0.$$

To calculate the free energy of the condensate it is necessary to integrate over the field ζ in the statistical integral with Hamiltonian (3.4). The resultant corrections to τ_2 and g must be excluded, since they have already been taken into account by Eqs. (3.1).[5,6]

Since Eqs. (3.1) are valid only in first-order approximation in ε, it is likewise necessary to retain in the integration only the first order in ε. In fact, we can put $\varepsilon=0$, since allowance for the first order in ε does not change anything substantially. As a result we get

$$\begin{aligned}\Phi(\psi_2)=&\tau_2\psi_2^2/2+g(\psi_2^2)^2+(64\pi^2)^{-1}(\psi_2^2)^2\\&\times\{(8\Gamma_{4.0}z^2-c_{1.3}/z)^2\ln[(8\Gamma_{4.0}z^2-c_{1.3}/z)\\&\times\psi_2^2/\tau_1]-(c_{1.3}/z)^2\ln(-c_{1.3}\psi_2^2/(z\tau_1))\}.\end{aligned}\tag{3.5}$$

It is more convenient to reduce $\Phi(\psi_2)$ to the form

$$\Phi(\psi_2)=\tau_2\psi_2^2/2+g(\psi_2^2)^2+\gamma(\psi_2^2)^2\ln(\lambda\psi_2^2/\tau_1),$$
$$\gamma=(4\Gamma_{4.0}^2z^4-\Gamma_{4.0}c_{1.3}z)/4\pi^2.$$

In the region of large ξ we have $\lambda\sim\gamma$. The transition line is defined by the conditions

$$\Phi(\psi_2)=0,\quad \partial\Phi/\partial\psi_2=0.$$

The density discontinuity in the transition is

$$\psi_2^2/2=\tau_2/4\gamma \tag{3.6}$$

The equation of the transition line is of the form

$$\gamma+g+\gamma\ln(\tau_2\lambda/(2\tau_1\gamma))=0. \tag{3.7}$$

It is seen from (3.6) that $\psi_2^2\gtrsim1$, and it is necessary to take into account in $\Phi(\psi_2)$ the higher virial coefficients, which correspond to vertices of sixth order and higher in the Hamiltonian (2.8). These vertices, however, are weakly renormalized, and since $g\to-\infty$, the transition will take place.

The same holds true also for a magnetic field. A weak magnetic field does not change r_c, meaning also ξ. In addition, it is easy to show that introduction of a sufficiently weak magnetic field in $\Phi(\psi_2)$ does not cause the transition to vanish.

§4. PHYSICAL MEANING OF THE PHASE TRANSITION

Let us make clear what corresponds in "polymer language" to a phase transition in the field model. In "polymer language" a solution of heteropolymers is characterized by densities $\rho_{\Delta\Delta'}$ of segments $\Delta\Delta'$ and by densities ρ_Δ of terminal monomers of species Δ. The field parameters are the activities $f_{\Delta\Delta'}$ (or the chemical potentials $\mu_{\Delta\Delta'}$). The density discontinuity in the phase transition means in the model that these descriptions are not equivalent: certain values of $\rho_{\Delta\Delta'}$ and ρ_Δ do not correspond to any solution in chemical equilibrium. Indeed, consider in the space $\rho_{\Delta\Delta'}$, ρ_Δ an arbitrary curve whose points correspond to the states of an equilibrium solution of heteropolymers. If this curve lies entirely in the region of large $\bar{L}$ and joins states with large and small monomer density, then at $\theta > 0$ it cannot be continuous, since it crosses a first-order transition line.

The physical cause of this phenomenon is easiest to understand using as an example a concrete physical realization of the model (see §2), namely, a linear-polymer solution containing molecules adsorbed on the polymer chains. A monomer on which the molecule is adsorbed is repelled (in a good solvent) from other monomers more strongly than the single monomer. Therefore, the adsorbed molecules increase the sizes of the polymer coils. Let us fix the density of the monomers and then increase the average length of the chains in the solution. The coils begin to overlap, so that the configuration entropy of the polymers decreases. Under these conditions, it is thermodynamically more favorable to eject part of the adsorbed molecules from the region occupied by the polymers. The coils then decrease in size and the degree of their overlap decreases. The decrease of the entropy of the adsorbed molecules is offset by an increase in the entropy of the coils.

The new result compared with the mean-field theory is the statement that the transition is of first order. A finite fraction of the molecules is immediately desorbed. Similar results were obtained recently by Grossberg,[7] who considered the globulization of an adsorbed polymer chain. It was found that there exists a range of parameters in which the "coil–globule" transition is accompanied by an avalanche-like desorption. This leads to a jumplike character of the transition which is of first order even an infinitely long chain.

In the presence of a first-order transition, a region of phase stratification exists in the system. In our case this stratification takes place if the numbers N_m of the monomers and N_a of the adsorbate molecules in the solution are fixed. If N_m and N_a were not fixed and were determined by chemical potentials, a jumplike change of N_m and N_a would take place in the solution with increasing average length of the polymers, and the number N_a/N_m of adsorbate molecules per monomer would then decrease. When N_m and N_a are fixed (we have in mind, as before, a solution in chemical equilibrium) we would have instead the subdivision of the solution into regions of more concentrated and less concentrated phases. The excess of adsorbate molecules would go over to the less concentrated phase. Of course, it is necessary that N_m/N_a in the solution exceed the equilibrium value for the more concentrated phase, otherwise there would be no excess adsorbate and no stratification at all.

A similar stratification could be observed in experiment by lowering the temperature of the solution described above. The activities $f_{\Delta\Delta'}$ would then increase and the average length of the polymer would increase. However, the stratification, as will be shown below, sets in at a very high degree of polymerization, and the corresponding time of establishment of the chemical equilibrium may turn out to be unattainable.

An equilibrium solution always contains cyclopolymers, but allowance for them does not lead to vanishing of the effect.

It may seem that the fact that the effective vertex g for the field ψ_2 is negative should lead to a "coil–globule" transition for one isolated molecule. Such fluctuation-induced transitions are discussed in Ref. 8. This conclusion, however, is refuted when account is taken of the gradient terms in $\Phi(\psi_2)$ (see (3.5)). If ψ_2 depends on the coordinates, then $\Phi(\psi_2)$ takes at $h = 0$ the form

$$\Phi(\psi_2) = \int [\tau_2 \psi_2^2(\mathbf{x})/2 + \lambda (\nabla \psi_2(\mathbf{x}))^2$$

$$+ \text{ terms of higher order }]\, d^d\mathbf{x}.$$

Since $\tau_2 \sim 1$ and the correlation radius of the field ψ_2 is equal to r_c, we have $\lambda \sim r_c^2$. It is seen from this that if a globule were produced the thickness of the surface layer would be of the order of r_c, i.e., the dimension of the globule would at any rate be not less than r_c. At the same time, as already indicated, the field ψ_2 fluctuates weakly and the critical exponents in our model are the same as in the des Cloizeaux model:

$$r_c \sim \tau_1^{-\nu} \sim L^\nu,$$

i.e., an isolated molecule can form only a non-Gaussian coil.

It is clear from this reasoning that in a dilute solution, where the polymer coils do not interact and the molecules behave as isolated unit, no transition will take place. For a transition to occur it is necessary that the coils interact, i.e., the transition can be observed in a semi-dilute solution or in the transition region from the dilute to the semi-dilute solution.

The effective attraction in the solution of heteropolymers leads to one more interesting phenomenon. We consider such a solution near the point of transition to a less dense phase. We denote the average length of the molecules in the solution by $\overline{L}$. We place in the solution a singled-out molecule of length $L \gg \overline{L}$. Its dimensions are much larger than the correlation radius in the solution. It can be shown, by using the method of singled-out molecules,[4] that the sections of the chain of the singled-out long molecule are subjected at scales of the order of the correlation radius to the same effective attraction as the molecules in the solution. This result is obvious if it is recognized that sections of length of the order $\overline{L}$ form "blobs"[9] of size r_c and behave as individual molecules. At the same time, at sufficiently large $L/\overline{L}$ the effective attraction is capable of forming a globule out of the singled-out chain. This effect is similar to compactization of DNA in a polyethylene glycol solution.[8]

For quantitative estimates it is necessary to express the solution (3.2) in terms of the initial conditions for the vertex functions $\Gamma_{i,k}$. It turns out that the transition line is very close to the $\Gamma_{2,2}(\xi) = 0$ line. The point is that the condition $\Gamma_{2,2}(\xi) = 0$ is satisfied only at such large ξ that the equation (3.7) is subsequently satisfied at a small relative increase of ξ. From this we easily obtain estimates for ξ and r_c at the transition point. At $\theta \ll 1$ we obtain utterly unrealistic numbers, and at $\theta \gtrsim 1$ the change of r_c is small. At $\theta \approx 1$ we have

$$r_c \sim 10^3\ s^4.$$

As is known from similarity theory,[6] the regions of strong and weak fields are characterized by the parameter $k = h\tau^{-(\beta+\gamma)}$. For a strong field $k \gg 1$, and for a weak one

$k \ll 1$. In "polymer" language $1/k$ is the average number of "blobs" in a molecule located in a dilute solution. Since k is a dimensionless parameter, the transition vanishes at $k \sim 1$. From this we obtain an estimate for the necessary degree of polymerization of the solution:

$$\bar{L} \sim 10^6\, s^6. \tag{4.1}$$

For the reasons indicated in §5, this estimate is probably too high.

The degree of polymerization needed for the existence of a transition is lowered if the formation of cyclopolymers is assumed. In a real equilibrium solution, cycles are always present. It is known[3] that the number of field components plays the role of the activity of the cyclopolymers. Allowance for the cycles leads thus to the fact that the number n of the field components φ_Δ differs from zero. At $n \neq 0$ we can also write equations similar to (3.1), which contain n. These equations can be solved and it turns out that a first-order phase transition takes place at any $n \geqslant 0$.

Equilibrium between cyclopolymers and linear polymers corresponds to a value $n = 1$. In this case the transition takes place at an average polymerization degree of the order of 10^5.

For a better understanding of the difference between our results and those of the mean-field theory, we can briefly list the main results of the latter.

When the activities $f_{\Delta\Delta'}$ increase, a second-order phase transition takes place in the system and

$$\langle \psi_1 \rangle \gg \langle \psi_2 \rangle.$$

The density of the monomers undergoes no jumps whatever. All the densities $\rho_{\Delta\Delta'}$ are continuous functions of the osmotic pressure, i.e., everything takes place as in a solution of homopolymers.

§6. CONCLUSION

The results are of interest in themselves. However, from the purely theoretical point of view it is interesting also that they can be obtained in principle from neither the mean-field-theory, nor perturbation, nor simplest scaling considerations. In the investigated region, only the renormalization-group method is applicable, and this method has so far been little used in polymer theory.

The tremendous lengths of the molecules involved in calculations for linear polymers are generally speaking arbitrary. The point is that even in the four-dimensional space Eqs. (3.1) determine only the asymptotic forms of the functions $\Gamma_{i.k}(\xi)$ at large ξ. It is possible to use here the initial conditions for $\Gamma_{i.k}(\xi)$ at $\xi = 0$ only in very rough estimates. Since the equation for the transition line contains $\ln \xi$ (this is precisely the reason for so large a value of $\bar{L}$ in (4.1)), the possible error increases exponentially. The solution of the renormalization-group equations for the case $n = 1$ (equilibrium of linear and cyclic polymers) does not contain logarithms, and the corresponding estimate is therefore more reliable. The final answer for the question can apparently be obtained only by experiment.

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