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Extended description of a solution of linear polymers based on a polymer-magnet analogy

E. S. Nikomarov and S. P. Obukhov

L. D. Landau Institute of Theoretical Physics, Academy of Sciences of the USSR

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It is shown that the problem of the behavior of a long polymer molecule in a solution of other linear polymers can be reduced to the problem of the correlation functions of an anisotropic magnet. Expressions are obtained for the correlation function of the ends of a probe molecule. The condition for globule formation, the mean size of the polymer coil, etc., are also determined. The case when the polymers are adsorbed on a surface (two-dimensional polymer solution) is considered separately. It is shown that in this case the familiar results obtained for two-dimensional magnets can be employed. Other problems are mentioned in which the analogy between a polymer solution and a magnet can be applied.

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1. INTRODUCTION

The analogy between a solution of linear polymers and a magnet with zero number of components (first established by des Cloizeaux)[1] makes it possible to relate the average parameters for the given solution to the thermodynamic averages of the zero-component Heisenberg model. Des Cloizeaux used this analogy to determine the scaling relationships between the parameters characterizing a strongly fluctuating polymer solution, and connected them with the already familiar scaling relationships for a magnet near the phase-transition point. The state of the magnet is unambiguously given by two parameters—the temperature and the magnetic field—in terms of which we may express all the remaining correlation radii of the longitudinal and transverse fluctuations, the free energy, etc. In exactly the same way, given any two parameters which characterize the polymer solution—say, the monomer density and the average degree of polymerization—we may determine the correlation radius in solution, the average separation between ends of the polymer, and the entropy. Here, within the framework of the "polymer solution–magnet" analogy, we cannot obtain in principle more detailed characteristics of the solution—the equilibrium polymer length distribution, the average separation between ends of a polymer of a given length—let alone obtain an expression for the correlation function of a polymer placed into the given solution and having other chemical and physical properties.

In this work, we present a method which allows us to obtain all these detailed characteristics: the probe molecule method. We consider a magnet composed of two interacting subsystems; using one subsystem we will describe the polymer solution, and using the other subsystem we will describe an isolated polymer molecule in this solution. We find that the problem is reduced to calculation of the correlation functions of an anisotropic magnet with double the number of components—a well-known simple problem.[2] The polymer-magnet analogy is used in our work not only in the region of strongly fluctuating solutions of linear polymers, but also to describe concentrated solutions (melts) and solutions containing cyclic polymers. The results obtained for melts agree with the familiar results[3] obtained by ordinary perturbation theory methods. The case of a two-dimensional solution of polymers (polymers which are adsorbed on a surface) is an exception for which perturbation theory is not applicable. In this case, the polymer–magnet analogy makes it possible to use the results obtained by Polyakov for two-dimensional magnets with an arbitrary number of components to describe the polymer solution.

2. HEISENBERG MODEL IN THE LIMITING CASE $n\to 0$. CORRESPONDENCE BETWEEN A MAGNET AND A POLYMER

Let us consider a lattice[1)] with classical n-component spins of length $n^{1/2}$ at the lattice points. We write the spin interaction Hamiltonian as

$$H=-\sum_{i,k,\alpha} J_{ik}S_\alpha(\mathbf{x}_i)S_\alpha(\mathbf{x}_k)-\sum_i h_1(\mathbf{x}_i)S_1(\mathbf{x}_i). \tag{2.1}$$

Here $J_{ik}=J(\mathbf{x}_i-\mathbf{x}_k)$ is the interaction parameter between spins located at the lattice points i and k; the index α takes on values from 1 to n; h is the external magnetic field, directed along the 1 axis. The summation is over all the lattice points.

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The partition function of the system is

$$Z=\langle e^{-H/T}\rangle_g, \tag{2.2}$$

where $\langle\ldots\rangle_g$ means geometric averaging over all the spin orientations

$$\langle\ldots\rangle_g=\int\ldots\prod_i d\Omega_i\Big/\int\prod_i d\Omega_i,$$

where Ω_i is the solid angle in n-dimensional spin space.

In order to change from the variables S_α, on which the condition $\Sigma_\alpha S_\alpha^2=n$ is imposed, to the usual field variables, it is convenient to use the Stratonovich-Hubbard identity:

$$\exp\Big[\frac{1}{T}\sum_{i,k,\alpha}J(\mathbf{x}_i-\mathbf{x}_k)S_\alpha(\mathbf{x}_i)S_\alpha(\mathbf{x}_k)+\sum_{i,\alpha}\frac{h_\alpha(\mathbf{x}_i)}{T}S_\alpha(\mathbf{x}_i)\Big]$$
$$=(\det J_{ik})^{n/2}\Big(\frac{2\pi}{T}\Big)^{nN/2}\int\prod_{i,\alpha}D\psi_\alpha(\mathbf{x}_i)\exp\Big[-\frac{T}{2}\sum_{i,k,\alpha}\psi_\alpha(\mathbf{x}_i)\psi_\alpha(\mathbf{x}_k)J_{ik}^{-1}$$
$$+\sum_{i,\alpha}\Big(\psi_\alpha(\mathbf{x}_i)+\frac{h_\alpha(\mathbf{x}_i)}{T}\Big)S_\alpha(\mathbf{x}_i)\Big], \tag{2.3}$$

where $J_{ik}{}^{-1}$ is the matrix which is the inverse of J_{ik}. Substituting Eq. (2.3) into Eq. (2.2), we may average over $S_\alpha(\mathbf{x}_i)$. For this, we use the relation

$$\Big(\int d\Omega\Big)^{-1}\int\exp\Big(\sum_{\alpha=1}^{n}k_\alpha S_\alpha\Big)d\Omega=\Big(\frac{in^{1/2}k}{2}\Big)^{1-n/2}\Gamma\Big(\frac{n}{2}\Big)J_{(n-2)/2}(in^{1/2}k). \tag{2.4}$$

Here Γ is a gamma function and $J_{(n-2)/2}$ is a Bessel function of order $(n-2)/2$. In the limit $n\to0$, the right-hand side of Eq. (2.4) becomes $1+k^2/2+O(n)$. Using this relation, which allows us to neglect terms which vanish as $n\to0$, we obtain the following expression for the partition function:

$$Z=\int\prod_{i,\alpha}D\psi_\alpha(\mathbf{x}_i)\prod_i\Big(1+\frac{1}{2}\Sigma(\mathbf{x}_i)\Big)\exp\Big[-\frac{T}{2}\sum_{i,k,\alpha}\psi_\alpha(\mathbf{x}_i)\psi_\alpha(\mathbf{x}_k)J_{ik}^{-1}\Big],$$
$$\Sigma(\mathbf{x}_i)=\sum_\alpha(\psi_\alpha(\mathbf{x}_i)+h_\alpha(\mathbf{x}_i)/T)^2. \tag{2.5}$$

Writing Eq. (2.5) as

$$Z=\int e^{-H(\psi)}D\psi,$$

we find that in the new variables the Hamiltonian of the system is

$$H(\psi)=\frac{T}{2}\sum_{i,k}\psi_\alpha(\mathbf{x}_i)\psi_\alpha(\mathbf{x}_k)J_{ik}^{-1}-\sum_i\ln\Big[1+\frac{1}{2}\Sigma(\mathbf{x}_i)\Big].$$

The average value $\langle S_\alpha(\mathbf{x})\rangle$ of the spin at the point $\mathbf{x}$, the spin correlation functions $\langle S_\alpha(\mathbf{x}_i)S_\beta(\mathbf{x}_k)\rangle$, etc., may be obtained by differentiating $\ln Z$ with respect to $h_\alpha(x)$:

$$\langle S_\alpha(\mathbf{x})\rangle=\Big\langle(\psi_\alpha(\mathbf{x})+h_\alpha(\mathbf{x})/T)\Big/\Big(1+\frac{1}{2}\Sigma(\mathbf{x})\Big)\Big\rangle.$$

In Eq. (2.5) we change variables:

$$\psi_\alpha'(\mathbf{x})=\psi_\alpha(\mathbf{x})(1+h^2/2T^2)^{-1/2},\quad T'=T(1+h^2/2T^2),\quad h'=h(1+h^2/2T^2)^{1/2}$$

(we set $h_1=h, h_\beta=0, \beta\neq1$). We obtain

$$Z(h,T)=\Big(1+\frac{h^2}{2T^2}\Big)^N\int\prod_{i,\alpha}D\psi_\alpha'(\mathbf{x}_i)\prod_i\Big(1+\frac{1}{2}\sum_\beta(\psi_\beta'(\mathbf{x}_i))^2$$
$$+\frac{h'}{T'}\psi_1'(\mathbf{x}_i)\Big)\exp\Big[-\frac{T'}{2}\sum_{j,k,\alpha}\psi_\alpha'(\mathbf{x}_j)\psi_\alpha'(\mathbf{x}_k)J_{jk}^{-1}\Big]. \tag{2.6}$$

The expression obtained may be represented as the sum of averages of the form $\langle\psi_\alpha(\mathbf{x}_i)\psi_\beta{}^2(\mathbf{x}_j)\ldots\psi_\gamma(\mathbf{x}_k)\rangle_{H_0}$, calculated with the free-field Hamiltonian

$$H_0=\frac{T'}{2}\sum_{j,k,\alpha}\psi_\alpha(\mathbf{x}_j)\psi_\alpha(\mathbf{x}_k)J_{jk}^{-1}.$$

Using Wick's theorem and the obvious equality

$$\langle\psi_\alpha(\mathbf{x})\psi_\beta(\mathbf{y})\rangle_{H_0}=\delta_{\alpha\beta}\frac{J(\mathbf{x}-\mathbf{y})}{T'}$$

we may reduce the partition function to the form

$$Z=\Big(1+\frac{h^2}{2T^2}\Big)^N Z_{pol}. \tag{2.7}$$

Here

$$Z_{pol}=\sum_{N_m,N_p}\Big(\frac{J_0}{T'}\Big)^{N_m}\Big(\frac{h'}{T'}\Big)^{2N_p}Z(N_m,N_p), \tag{2.8}$$

where $Z(N_m, N_p)$ is the number of different configurations from N_m segments forming N_p linear polymers. A statistical weight J_{ik}/J_0 ($J_0=\Sigma_k J_{ik}$) is assigned to the segment with ends at the points $\mathbf{x}_i$ and $\mathbf{x}_k$; i.e., the probability of two monomers occupying mutually the points $\mathbf{x}_i$ and $\mathbf{x}_k$ if there is a chemical bond between them is given by J_{ik}/J_0. Each segment enters with the factor J_0/T' and each end of the polymer with h'/T'. The condition of non-self-intersection is imposed on the configuration: two monomers cannot occupy the same point. Configurations including cyclic polymers drop out, since due to the summation over α they acquire the additional factor n, but $n\to0$.

Furthermore, for convenience we will assume that the monomeric unit is taken to be the segment (i.e., the chemical bond, and not the atom). Except when speaking of the virial coefficient, the term "monomer" will be used specifically in this sense--i.e., to designate a "polymer segment".

We designate h' and T' respectively as h_p and T_p. From Eq. (2.7) it is not difficult to see that the parameters $-\ln(J_0/T_p)$ and $-2\ln(h_p/T_p)$ play the role of the chemical potentials of the monomer and polymer, and completely characterize the polymer ensemble. The relationship between h_p and T_p and the "magnetic" parameters h and T is one-to-one; the transformation from h_p, T_p to h, T has the form

$$h=h_p(1-h_p{}^2/2T_p{}^2)^{1/2},\quad T=T_p(1-h_p{}^2/2T_p{}^2). \tag{2.9}$$

Equations (2.7) and (2.9) differ from the corresponding formulas of des Cloizeaux,[1] in which no distinction is made between h, h_p, Z, and Z_{pol}. These differences are insignificant only at small h/T, while at $h/T\sim1$ they strongly change the results. Since at low T, the region $h/T\sim1$ corresponds to the melting of long ($L\sim T^{-1/2}$) polymers, these differences must not be neglected.

Let us write the correspondence equations between the polymer and the magnetic parameters. We assume hereafter $J_0=1$. Then from Eq. (2.8) we may write for the average number of polymers N_p and for the average number of monomers N_m

$$N_p={}^1/_2h\,\partial\ln Z_{pol}/\partial h_p, \tag{2.10}$$
$$N_m=-T_p\,\partial\ln Z_{pol}/\partial T_p-2N_p. \tag{2.11}$$

In practice, however, it is much more convenient to obtain the equations for the polymer parameters directly from the diagrams obtained on calculation of $Z(h, T)$ according to Eq. (2.6). For example, for the concentrations of the polymers and monomers (per unit cell of the lattice) we obtain

$$\rho_p(\mathbf{x}) = (h/2T)\langle\psi_1(\mathbf{x})/(1+{}^1/_2\Sigma(\mathbf{x}))\rangle, \tag{2.12}$$

$$\rho_m(\mathbf{x}) = {}^1/_2\left\langle\sum_\alpha \psi_\alpha{}^2(\mathbf{x})/(1+{}^1/_2\Sigma(\mathbf{x}))\right\rangle + \rho_p(\mathbf{x}). \tag{2.13}$$

The correlation function for the transverse components of S_α determines the correlations between the ends of the same molecule:

$$\langle S_\beta(\mathbf{x})S_\beta(\mathbf{y})\rangle = \left\langle\frac{\psi_\beta(\mathbf{x})}{[1+{}^1/_2\Sigma(\mathbf{x})]}\frac{\psi_\beta(\mathbf{y})}{[1+{}^1/_2\Sigma(\mathbf{y})]}\right\rangle = \frac{T^2}{h^2}G(\mathbf{x}-\mathbf{y}), \quad \beta\neq 1, \tag{2.14}$$

where $G(\mathbf{x}-\mathbf{y})$ is the correlation function for the ends of the polymer chain, averaged over all molecules. Analogously, the statistical average

$$\langle(S_1(\mathbf{x})-hS_1{}^2(\mathbf{x})/T)(S_1(\mathbf{y})-hS_1{}^2(\mathbf{y})/T)\rangle = \left\langle\frac{\psi_1(\mathbf{x})}{[1+{}^1/_2\Sigma(\mathbf{x})]}\frac{\psi_1(\mathbf{y})}{[1+{}^1/_2\Sigma(\mathbf{y})]}\right\rangle = \frac{T^2}{h^2}\mathcal{G}(\mathbf{x}-\mathbf{y})$$

gives the correlation function $\mathcal{G}(\mathbf{x}-\mathbf{y})$ for the ends of all the polymer chains.

If in Eq. (2.6) we leave n finite and omit the factor $(1+h^2/2T^2)^N$ and the primes on h and T, then

$$Z(h,T)\Big/\left(\prod_\mathbf{q}\frac{\pi J(\mathbf{q})}{T}\right)^{1/2}$$

will give the partition function for a solution containing linear and cyclic polymers. Each cyclic polymer will enter with the factor n stemming from the summation over α. Such a system, however, is no longer equivalent to any Heisenberg magnet. It is necessary to require also that

$$J_{ik}>0 \quad \text{at} \quad i=k,$$

since otherwise the matrix J_{ik}^{-1} is defined. At $n=0$, an addition to J_{ik} of the form $\lambda\delta_{ik}$ did not change the properties of the system; at $n\neq 0$ this is already not so. The parameter J_{ik}/J_0 at $i=k$ gives the probability of congruence of the ends of an isolated segment. Since we admit of cycle formation, the probability may be different from zero. The Hamiltonian of the system has the form

$$H(\psi) = {}^1/_2T\sum_{i,k,\alpha}\psi_\alpha(\mathbf{x}_i)\psi_\alpha(\mathbf{x}_k)J_{ik}^{-1} - \sum_i \ln(1+{}^1/_2\Sigma_1(\mathbf{x}_i)),$$

$$\Sigma_1(\mathbf{x}_i) = \sum_\alpha \psi_\alpha{}^2(\mathbf{x}_i) + h_1\psi_1(\mathbf{x}_i)/T.$$

For the average numbers of polymers and monomers, Eqs. (2.10)–(2.13) hold as before. Equation (2.14) also holds. At $h=0$ it determines the correlation function of the probe chain (see Sec. 4). For the average number of cycles we obtain a formula analogous to Eq. (2.10):

$$N_c = n\frac{\partial \ln Z(h,T)}{\partial n} - \frac{nNa^3}{2(2\pi)^3}\int \ln(\pi J(\mathbf{q})/T)\,d^3q.$$

The correlation function for the density of monomers entering into the cyclic polymers is expressed in terms of the average value of the fields ψ_α according to the formula

$$\langle\rho_{mc}(\mathbf{x})\rho_{mc}(\mathbf{y})\rangle = {}^1/_4\left\langle\frac{\psi_\beta{}^2(\mathbf{x})}{[1+{}^1/_2\Sigma_1(\mathbf{x})]}\frac{\psi_\beta{}^2(\mathbf{y})}{[1+{}^1/_2\Sigma_1(\mathbf{y})]}\right\rangle, \quad \beta\neq 1,$$

and the correlation function of monomers of the same cyclic polymer is expressed according to the formula

$$G_c(\mathbf{x}-\mathbf{y}) = {}^1/_4\left\langle\!\!\left\langle\frac{\psi_\beta{}^2(\mathbf{x})}{[1+{}^1/_2\Sigma_1(\mathbf{x})]}\frac{\psi_\beta{}^2(\mathbf{y})}{[1+{}^1/_2\Sigma_1(\mathbf{y})]}\right\rangle\!\!\right\rangle, \quad \beta\neq 1,$$

where the double angle brackets mean the irreducible average.

3. SELF-CONSISTENT-FIELD APPROXIMATION

We assume that the fluctuations of the fields ψ_α are small. We introduce new variables $\varphi_\alpha(\mathbf{x}_i)$, reckoned from the average values of $\psi_\alpha(\mathbf{x}_i)$:

$$\psi_1(\mathbf{x}_i) = \Delta + \varphi_1(\mathbf{x}_i), \quad \psi_\beta(\mathbf{x}_i) = \varphi_\beta(\mathbf{x}_i).$$

We write the Hamiltonian up to terms of second order in φ_α (we consider linear polymers, i.e., the model with $n=0$)

$$H = H_\Delta + H_\varphi$$

$$H_\Delta = TN\Delta^2/2 + N\ln(1+\xi^2/2),$$

$$H_\varphi = {}^1/_2\sum_\mathbf{q}[T/J(\mathbf{q}) - (1+\xi^2/2)^{-1} + \xi^2/(1+\xi^2/2)^2]|\varphi_1(\mathbf{q})|^2 + {}^1/_2\sum_{\mathbf{q},\alpha\neq 1}(T/J(\mathbf{q}) - 1/(1+\xi^2/2))|\varphi_\alpha(\mathbf{q})|^2. \tag{3.1}$$

Here

$$\xi = \Delta + h/T, \quad \varphi_\alpha(\mathbf{q}) = N^{-1/2}\sum_j \varphi_\alpha(\mathbf{x}_j)\exp(i\mathbf{q}\mathbf{x}_j),$$

$$J(\mathbf{q}) = \sum_k J_{jk}\exp[i\mathbf{q}(\mathbf{x}_j-\mathbf{x}_k)], \quad J_0 = J(0) = 1,$$

N is the number of lattice points. The minimum H_Δ is achieved for

$$T\Delta = (\Delta + h/T)/[1+{}^1/_2(\Delta+h/T)^2]. \tag{3.2}$$

Taking into account Eq. (3.2), we write

$$H_\Delta = TN\Delta^2/2 + N\ln(1+\xi^2/2),$$

$$H_\varphi = {}^1/_2\sum_\mathbf{q}(1/J(\mathbf{q}) - 1 + h/T\xi + T\Delta^2)|\varphi_1(\mathbf{q})|^2 + {}^1/_2T\sum_{\mathbf{q},\beta\neq 1}(1/J(\mathbf{q}) - 1 + h/T\xi)|\varphi_\beta(\mathbf{q})|^2. \tag{3.3}$$

The mean square fluctuation of φ_α is

$$\begin{aligned}\langle\varphi_1{}^2(\mathbf{x})\rangle &= \frac{a^3}{(2\pi)^3T}\int\left[\frac{1}{J(\mathbf{q})} - 1 + \frac{h}{T\xi} + T\Delta^2\right]^{-1}d^3q,\\ \langle\varphi_\beta{}^2(\mathbf{x})\rangle &= \frac{a^3}{(2\pi)^3T}\int\left[\frac{1}{J(\mathbf{q})} - 1 + \frac{h}{T\xi}\right]^{-1}d^3q, \quad \beta\neq 1.\end{aligned} \tag{3.4}$$

Here we have changed from summation over $\mathbf{q}$ to integration over the reciprocal-lattice cell, a^3 is the volume of the unit cell of the lattice.

If we introduce the mean square length of the segment l^2:

$$l^2 = \left(\sum_k J_{ik}\right)^{-1}\sum_k J_{ik}|\mathbf{x}_i - \mathbf{x}_k|^2,$$

then for small $\mathbf{q}$

$$J(\mathbf{q}) = 1 - q^2l^2/2d. \tag{3.5}$$

Substituting Eq. (3.5) in (3.4), we obtain

$$\langle\varphi_1{}^2(\mathbf{x})\rangle \approx \langle\varphi_\alpha{}^2(\mathbf{x})\rangle \sim a^3/l^3T.$$

For $h=0$ we obtain for Δ^2:

$$\Delta^2=2(1/T-1).$$

Thus, the condition for small fluctuations is

$$a^3/l^3 \ll (T_c-T)/T_c, \qquad T_c=1.$$

We see that a^3/l^3 is the Ginzburg number and will be considered in this section as a small parameter.

In the zeroth order in the fluctuations, using Eqs. (2.12), (2.13), and (3.2), we obtain for the polymer and monomer densities

$$\rho_p^{(0)}=h\Delta/2T(1+\xi^2/2), \qquad \rho_m^{(0)}=T\Delta^2/2. \tag{3.6}$$

From this the average degree of polymerization of the molecules in solution is:

$$\bar{L}^{(0)}=\rho_m^{(0)}/\rho_p^{(0)}=T\xi/h \quad \text{or} \quad \bar{L}^{(0)}-1=T\Delta/h. \tag{3.7}$$

We also note that small h and T correspond to the situation in which the density is close to unity (melt):

$$\bar{L}\approx T^{1/2}/h, \qquad \rho_m=1-T. \tag{3.8}$$

From Eq. (3.1) we obtain for the transverse correlation function or, which is the same thing, for the correlation function of the ends of the polymer:

$$G(q)=(q^2l^2/2d+1/L)^{-1}, \tag{3.9}$$

d is the dimensionality of the space.

For the mean square separation between the ends of the polymer chains, we obtain

$$\langle R^2\rangle=l^2T\xi/h \tag{3.10}$$

or, taking into account Eq. (3.7),

$$\langle R^2\rangle=l^2\bar{L}. \tag{3.11}$$

Thus, the self-consistent-field approximation corresponds to the approximation of a solution of Gaussian chains.

Let us find the equation of state for a solution of Gaussian chains. For this we use the familiar relation[4]

$$PV=k\tau\ln Z_{pol},$$

k is the Boltzmann constant and T is the temperature of the solution. Substituting the value $Z(h, T)=e^{-H\Delta}$ in Eq. (2.7) for Z_{pol}, we obtain

$$PV=-k\tau\frac{V}{a^3}\left[\rho_m+\ln\frac{1-\rho_m(\bar{L}+1)}{\bar{L}}\right]-\frac{k\tau}{2}\ln\frac{V}{a^3}$$
$$+\frac{k\tau}{2}\left[\ln\left(1-\frac{1}{\bar{L}}\right)-\ln\left(2\rho_m+\frac{1}{\bar{L}}\right)-\ln\left(1-\frac{\rho_m\bar{L}}{(\bar{L}-1)}\right)\right]. \tag{3.12}$$

A similar equation of state for a polymer solution was first obtained by Flory.[5] For the case $n\neq 0$, we consider the simplest situation: $h=0$ and the system is above the transition point, i.e., there are no linear polymers. Then in first order in the fluctuations:

$$\rho_m^{(0)}=\frac{n}{2}\frac{a^3}{(2\pi)^3}\int\left(\frac{T}{J(\mathbf{q})}-1\right)^{-1}d^3q, \tag{3.13}$$

$$\rho_c^{(0)}=\frac{n}{2}\frac{a^3}{(2\pi)^3}\int\ln\frac{T/J(\mathbf{q})}{T/J(\mathbf{q})-1}d^3q, \tag{3.14}$$

where the integration is carried out over the cell of the reciprocal lattice. Thus, the density of cyclic polymers is proportional to the Ginzburg number Gi. The equation of state of the solution of cyclic polymers in this approximation is

$$PV=k\tau N_c. \tag{3.15}$$

In the next approximation with respect to the fluctuations, Eqs. (3.14), (3.15) appear as follows:

$$\rho_m^{(1)}=\frac{n}{2}\frac{a^3}{(2\pi)^3}\int\left[\frac{T}{J(\mathbf{q})}-1+\frac{n+2}{n}\rho_m^{(0)}\right]^{-1}d^3q-\frac{n+2}{n}(\rho_m^{(0)})^2,$$

$$\rho_c^{(1)}=\rho_c^{(0)}-\frac{n+1}{n}(\rho_m^{(0)})^2, \tag{3.16}$$

$$PV=k\tau(N_c+N_m\rho_m/2).$$

4. AN ISOLATED CHAIN IN THE POLYMER SOLUTION

To describe the statistical properties of a single isolated chain located in a solution of other polymers we consider, in addition to the n-component field used to describe the polymer solution, another n-component field interacting with it and use it to describe the isolated chain. Distinguishing the parameters characterizing these n-component fields by the indices 1 and 2 respectively, we write the partition function of such a system as

$$Z=\int\prod_{i,\alpha}D\psi_{1\alpha}(\mathbf{x}_i)D\psi_{2\alpha}(\mathbf{x}_i)\left\{1+\frac{1}{2}\sum_\beta\left[\left(\psi_{1\beta}(\mathbf{x}_i)+\frac{h_{1\beta}}{T_1}\right)^2\right.\right.$$
$$\left.\left.+\left(\psi_{2\beta}(\mathbf{x}_i)+\frac{h_{2\beta}}{T_2}\right)^2\right]\right\}\exp\left\{-\frac{T_1}{2}\sum_{i,k,\alpha}\psi_{1\alpha}(\mathbf{x}_i)\psi_{1\alpha}(\mathbf{x}_k)J_{1ik}^{-1}\right.$$
$$\left.-\frac{T_2}{2}\sum_{i,k,\alpha}\psi_{2\alpha}(\mathbf{x}_i)\psi_{2\alpha}(\mathbf{x}_k)J_{2ik}^{-1}\right\}. \tag{4.1}$$

If $h_2\to 0$, then the density of the polymers described by the second field tends to zero. Thus, in this limit the average $\langle\psi_{2\beta}\psi_{2\beta}\rangle$ is the correlation function of the ends of a linear polymer, each segment of which is assigned a weighting factor J_{2ik}/T_2, and the monomer density and the number of polymers in the surrounding solution are determined by the parameters J_1/T_1 and h_1/T_1.

On the other hand, using the identity (2.3) it is not difficult to see that the partition function (4.1) has a simple physical meaning, as the partition function of a $2n$-component anisotropic magnet with a Hamiltonian

$$-\beta H=\sum_{i,k,\alpha,\Delta}\frac{J_{\Delta ik}}{T_\Delta}S_{\Delta\alpha}(\mathbf{x}_i)S_{\Delta\alpha}(\mathbf{x}_k)+\sum_{i,\alpha}\frac{h_{1\alpha}}{T_1}S_{1\alpha}(\mathbf{x}_i). \quad \Delta=1,2. \tag{4.2}$$

We shall verify later that for the description of long molecules, the anisotropy should be small compared with J_0; therefore it is convenient to write Eq. (4.2) in the form

$$-\beta H=\sum_{i,k,\alpha,\Delta}J_{ik}S_{\Delta\alpha}(\mathbf{x}_i)S_{\Delta\alpha}(\mathbf{x}_k)+\lambda\sum_{i,\alpha}(S_{2\alpha}(\mathbf{x}_i))^2+\sum_i hS_{11}(\mathbf{x}_i), \tag{4.3}$$

$$J_{ik}=\frac{J_{1ik}}{T_1}, \qquad \lambda=\frac{J_{20}}{T_2}-\frac{J_{10}}{T_1}, \qquad h=\frac{h_1}{T_1}.$$

Thus, the problem of the correlation function of the probe molecule is reduced to the problem of the transverse correlation function of an anisotropic magnet.

The average $\langle S_{1\beta}(\mathbf{x}_i)S_{1\beta}(\mathbf{x}_k)\rangle\sim\langle\psi_{1\beta}(\mathbf{x}_i)\psi_{1\beta}(\mathbf{x}_k)\rangle$, $\beta\neq 1$, is as before the correlation function for the ends of a polymer in a solution. The transverse correlation functions of an anisotropic magnet in the region of weak fluctuations have the form[2]

$$G_{1\alpha}=(h/M+ck^2)^{-1}, \quad \alpha\neq 1, \tag{4.4}$$
$$G_{2\alpha}=(h/M-\lambda+ck^2)^{-1}, \tag{4.5}$$

where $c\sim r_c^2\approx l^2/2d\rho_m$ (r_c is the correlation radius of the longitudinal fluctuations, d is the dimensionality of the space), and M is the magnetic moment.

In order to obtain the expression for the correlation function of chains of length L, we must perform an inverse Laplace transformation from the variable λ to L. Then

$$G_L(k)\sim\text{const}\cdot\exp(-Lck^2-hL/M). \tag{4.6}$$

From this, $h/M=1/\bar{L}$ (this also follows from the results of Sec. 3), since $G_L(k)$ is at $k=0$ the length distribution function of polymers in solution[5]:

$$G_L\sim\text{const}\cdot\exp(-L/\bar{L}). \tag{4.7}$$

In the coordinate representation

$$G_L(x)\sim(G_L/L^{3/2})\exp(-x^2/4Lc).$$

In the region of strong fluctuations, we may use the scaling relations.[6] In this case, Eqs. (4.4), and (4.5) are replaced at $kr_c\ll 1$ by

$$G_{1\alpha}\sim(h^R/M^R+(kr_c)^2)^{-1}, \tag{4.8}$$
$$G_{2\alpha}\sim(h^R/M^R-\lambda^R+(kr_c)^2)^{-1}. \tag{4.9}$$

From the scaling relations it follows that

$$\lambda^R\sim\lambda(r_c/l)^{1/\nu},$$

where ν is the critical exponent of the correlation radius ($\nu\approx 3/5$). Performing an inverse Laplace transformation with respect to λ in Eq. (4.9), we obtain the correlation function of the ends of the probe chain:

$$G_L(k)\sim\text{const}\cdot\exp\left\{-L\left(\frac{r_c}{l}\right)^{-1/\nu}\left(\frac{h^R}{M^R}+(kr_c)^2\right)\right\}. \tag{4.10}$$

From Eq. (4.10) we obtain for the average length of the molecule in solution the relation

$$\bar{L}=\left(\frac{r_c}{l}\right)^{1/\nu}\frac{M^R}{h^R}.$$

For small h (i.e., for large $\bar{L}$)

$$\rho_m\approx\frac{1}{T}\frac{\partial\ln Z}{\partial T}\sim\left(\frac{T-T_c}{T_c}\right)^{1-\alpha}$$
$$r_c\sim\left(\frac{T-T_c}{T_c}\right)^{-\nu}$$

and, using the relation between α and ν,

$$\alpha=2-d\nu,$$

we obtain

$$(r_c/l)^{1/\nu}\sim\rho_m r_c^d.$$

For the mean square size of the molecule in solution we then obtain

$$\langle R^2\rangle=\bar{L}r_c^2/\rho_m r_c^d.$$

If we introduce the quantities

$$c^R\approx r_c^2, \quad \bar{L}^R\approx\bar{L}(\rho_m r_c^d)^{-1}. \quad L^R\approx L(\rho_m r_c^d)^{-1},$$

then Eqs. (4.6)–(4.8) will be satisfied, if we take c, L, and $\bar{L}$ to mean c^R, L^R, and $\bar{L}^R$. If $h^R/M^R-\lambda^R\ll(h^R/M^R)^2$ then the major role is played by the fluctuations associated with a phase transition that is of second order in λ. In this region, $L^R\gg(\bar{L}^R)^2$ and the length distribution function G_L has the form

$$G_L\sim(L^R)^{\gamma-1}\exp(-L^R/\bar{L}^R),$$

γ is the critical exponent of the susceptibility.

Equations (4.4) and (4.5) describe the Gaussian behavior of the "average" molecule in solution, and also the Gaussian behavior of the isolated molecule of length $L\sim(h/M-\lambda)^{-1}$. Corrections to Eqs. (4.4), (4.5) arise only when account is taken of the interaction of long-wavelength transverse fluctuations. The magnitude of this interaction is proportional to the magnitude of the external magnetic field. From Eq. (3.7) it follows that a weak magnetic field $h\sim 1/\bar{L}$ corresponds to the case of a solution of long molecules. In polymer language this means that the effective second virial coefficient of the interaction of quasimonomers in solution decreases in inverse proportion to the average length of the molecules in solution.[5]

An accurate value for the second virial coefficient may be obtained by writing down the first correction with respect to the fluctuations for the mean square separation between the ends of the probe molecule. Simple calculations (which we omit) give to first order in a^3/l^3 ($L\gg 1$):

$$\langle R^2(L)\rangle=l^2[L+(a^3/l^3)(L-1)(I_1+I_2L^{1/2})]. \tag{4.11}$$

where

$$I_1=\int\left\{\left[1-J\left(\frac{\mathbf{k}}{l}\right)\right]\left[\left(J\left(\frac{\mathbf{k}}{l}\right)\right)^{-1}-1+2\rho_m\right]\right\}^{-1}\frac{d^3k}{(2\pi)^3},$$
$$I_2=3\sqrt{6}[4\pi\bar{L}(2\rho_m+1/\bar{L})]^{-1}.$$

The I_1 term in Eq. (4.11) describes the effective increase in the length of each segment

$$l_2^2=l^2[1+(a^3/l^3)I_1], \tag{4.12}$$

and the I_2 term determines the effective repulsion of monomers in solution. This repulsion is substantial only for very long molecules $L\gg a^6(\bar{L})^2/l^6$, which, as seen from Eq. (4.7), do not contribute to the average characteristics of the solution. Equation (4.9) is obtained as the average separation between the ends of molecules of average length L, distributed according to (4.7) with $\bar{L}=L$. Knowing the form of this distribution, we may obtain for $R^2(L)$:

$$R^2(L)=l_R^2(L+(4a^3/3\sqrt{\pi}\,l^3)(L-1)I_2L^{1/2}). \tag{4.13}$$

Comparing Eq. (4.13) with the usual series of perturbation theory for an isolated non-self-intersecting molecule (see Ref. 7)

$$R^2(L)=l^2(L+{}^4/_3(3L/2\pi)^{3/2}B/a^3),$$

we obtain for the effective virial coefficient in solution;

$$B=\pi({}^2/_3)^{3/2}a^6I_2/l^3. \tag{4.14}$$

For weakly fluctuating solutions, the parameter B agrees with the value calculated from ordinary perturbation theory.[3] For strongly fluctuating solutions, we must take L, $\bar{L}$, ρ_m, and a^3/l^3 in Eqs. (4.13) and (4.14) to mean the renormalized values

$$L^R\approx L\rho_m^{1/(d\nu-1)}, \quad \bar{L}^R\approx\bar{L}\rho_m^{1/(d\nu-1)}, \quad \rho_m^R\sim 1, \quad (a^3/l^3)^R\sim 1. \tag{4.15}$$

Here ρ_m is the true concentration of the monomers in the solution.

The form of Eqs. (4.13)–(4.14) demonstrates the validity of the representation of the molecules in a strongly fluctuating solution (proposed by de Gennes[8]) as a Gaussian chain of "blobs," each of which has a size on the order of the correlation radius $r_c \sim \rho_m^{-\nu/(d\nu-1)}$ and contains $\rho_m r_c^d \sim \rho_m^{1/(d\nu-1)}$ monomers. This chain occurs in the melt ($\rho_m \approx 1$) of other such chains of "blobs." As is evident from Eq. (4.14), such a representation is applicable to molecules whose length is not very great: $L^R \ll (\bar{L}^R)^2$ (in blob units). When the inverse inequality is satisfied, obviously we must sum the entire perturbation-theory series. Just as for a separate long molecule with repulsion,[9] this leads to the familiar law $R^2(L) \sim L^{2\nu}$.

Until now we have considered the situation in which the probe molecule has the same properties as the surrounding solution molecules. We note that in Eq. (4.1) we may introduce different quantities J_{1ik} and J_{2ik} to describe the two different types of segments—segments of the probe molecule and segments of the solution molecule. Below, we analyze the general case, when not only are J_{ik} and J_{2ik} different, but the quantities characterizing the interaction of the monomers among themselves are different. Since the case of strong fluctuations is the most interesting, we write the Hamiltonian of two interacting subsystems, confining ourselves to terms up to ψ^4:

$$\beta H = \int d^d\mathbf{x}\{\tau_1\psi_1^2(\mathbf{x}) + c_1(\nabla\psi_1(\mathbf{x}))^2 + u_{11}(\psi_1^2(\mathbf{x}))^2 + \tau_2\psi_2^2(\mathbf{x}) + c_2(\nabla\psi_2(\mathbf{x}))^2 + u_{22}(\psi_2^2(\mathbf{x}))^2 - h_1\psi_{11}(\mathbf{x}) + 2u_{12}\psi_1^2(\mathbf{x})\psi_2^2(\mathbf{x})\},$$

where

$$\psi_\Delta^2 = \sum_\alpha \psi_{\Delta\alpha}^2, \quad (\nabla\psi_\Delta)^2 = \sum_\alpha (\nabla\psi_{\Delta\alpha})^2.$$

Here u_{11}, u_{12}, and u_{22} are field-interaction constants. Each type of monomer is characterized by its own stiffness c_Δ, which is proportional to the square of its persistent length.[2)]

We note that by the simple transformation

$$\psi_\Delta' = \sqrt{2}c_\Delta^{1/2}\psi_\Delta$$

the Hamiltonian of such a system is transformed to

$$\beta H = \int d^d\mathbf{x}\{\tau_1'\psi_1^2(\mathbf{x})/2 + (\nabla\psi_1(\mathbf{x}))^2/2 + \tilde{u}_{11}(\psi_1^2(\mathbf{x}))^2 + \tau_2'\psi_2^2(\mathbf{x})/2 + (\nabla\psi_2(\mathbf{x}))^2/2 + \tilde{u}_{22}(\psi_2^2(\mathbf{x}))^2 + 2\tilde{u}_{12}\psi_1^2(\mathbf{x})\psi_2^2(\mathbf{x}) - \tilde{h}_1\psi_{11}(\mathbf{x})\}, \tag{4.16}$$

where $\tilde{u}_{11} = c_1^{-2}u_{11}/4$, $\tilde{u}_{22} = c_2^{-2}u_{22}/4$, and $\tilde{u}_{12} = c_1^{-1}c_2^{-1}u_{12}/4$. We note that when any stiffness (for example, c_1) is large, the corresponding interaction constants u_{11} and $\tilde{u}_{12}$ are small.

Since it is always assumed that the concentration of probe molecules in solution is as small as desired, they obviously do not affect the state of the solution. We consider the case in which the average separation between the ends of the probe molecule is greater than the correlation radius in the solution (in the opposite limiting case, the correlation function of the probe molecule is the same as for the isolated polymer chain). In this case, it is convenient at first to integrate in the Hamiltonian (4.16) over scales that are smaller than the correlation radius. Renormalizations of such a Hamiltonian were considered by Pokrovskiĭ, Lyuksyutov, and Khmel'nitskiĭ[10] for the case of an arbitrary number of components of the fields ψ_1 and ψ_2. If the number of components of each field is zero, the renormalization equations obtained in Ref. 10 may be written to first order in $\varepsilon = 4 - d$ as

$$\begin{gathered}\frac{\partial u_{11}^R}{\partial\xi} = \varepsilon u_{11}^R - 32(u_{11}^R)^2,\\ \frac{\partial u_{22}^R}{\partial\xi} = \varepsilon u_{22}^R - 32(u_{22}^R)^2,\\ \frac{\partial u_{12}^R}{\partial\xi} = \varepsilon u_{12}^R - 8u_{12}^R(u_{11}^R + u_{22}^R) - 16(u_{12}^R)^2.\end{gathered} \tag{4.17}$$

Here $\xi = \ln(R/1)$, a is the interaction radius of monomers (in the lattice model—the cell size), R is the scale up to which the renormalization is carried out.

Solving Eq. (4.17) with initial conditions (4.16), we obtain

$$\begin{gathered}u_{11}^R = (R/a)^\varepsilon\tilde{u}_{11}(32\tilde{u}_{11}x+1)^{-1}, \quad u_{22}^R = (R/a)^\varepsilon\tilde{u}_{22}(32\tilde{u}_{22}x+1)^{-1},\\ u_{12}^R = (R/a)^\varepsilon\tilde{u}_{12}\left[16\tilde{u}_{12}f(x)\int_0^x (f(x))^{-1}dx + f(x)\right]^{-1},\\ x = \varepsilon^{-1}[(R/a)^\varepsilon - 1)], \quad f(x) = [(32\tilde{u}_{11}x+1)(32\tilde{u}_{22}x+1)]^{1/4}.\end{gathered} \tag{4.18}$$

Thus, depending on the relationship between $\tilde{u}$ and r_c, the following situations are possible:

a) if r_c is sufficiently large and $\tilde{u}_{12} > 0$, then all the u^R take the universal form $u^R = \varepsilon/32$, and in this case the results of the preceding discussion for chains of identical monomers are applicable;

b) if r_c is not very large, then the u^R are as usual not equal to each other.

After we have taken into account all the fluctuations of the field ψ_1 using renormalizations, we may completely integrate over it, i.e., take into account the effect of the solution on the probe polymer chain. For this we expand the Hamiltonian (4.16), considering all the parameters in it to be renormalized, close to the minimum with respect to ψ_1 ($\psi_{11} = M$) up to terms on the order of $(\psi_1 - M)^2$. Next, integrating $e^{-\beta H}$ with respect to ψ_1, we obtain for the field ψ_2 the effective Hamiltonian

$$\beta H(\psi_2) = \int\left\{\frac{\tau_2^*\psi_2^2(\mathbf{x})}{2} + \frac{(\nabla\psi_2(\mathbf{x}))^2}{2} + \left(u_{22}^R - \frac{4(u_{12}^R)^2M^2}{\tau_1^R/2 + 6u_{11}^RM^2}\right)(\psi_2^2(\mathbf{x}))^2\right\}d^d\mathbf{x}.$$

Using the equation of state of the field ψ_1

$$\tau_1^RM + 4u_{11}^RM^3 - h^R = 0, \tag{4.19}$$

we obtain the following expression for the effective peak of the field ψ_2:

$$u_{22}^{\text{eff}} = u_{22}^R - (u_{12}^R)^2/u_{11}^R(1 + h_1^R/(8M^3u_{11}^R)).$$

We note that from the results obtained in the beginning of the section and Eq. (4.19), it follows that

$$\frac{h_1^R}{8M^3u_{11}^R} \approx \frac{1}{\bar{L}^R\tau_1^R} \sim \frac{1}{\bar{L}^Rr_c^{1/\nu}} \sim \frac{1}{\bar{L}},$$

where $\bar{L}^R$ is the average length of the polymer in solution in "blob" units

$$\bar{L}^R \sim \bar{L}\rho_m^{1/(d\nu-1)} \sim \bar{L}r_c^{-1/\nu}.$$

Depending on the sign of u_{22}^{eff}, two types of limiting behavior of the foreign molecule in solution are possible. if $u_{22}^{\rm eff}>0$, then, starting from $L^R \gg (u_{22}^{\rm eff} r_c^{-3})^2$ (L^R is the number of effective monomers of lengths r_c in the probe molecule), the average size of the probe molecule is given by $R^2 \sim L^{2\nu}$. If $u_{22}^{\rm eff}<0$ then starting from $L^R \sim (u_{22}^{\rm eff} r_c^{-3})^2$, the molecule transforms into the globular state[3] (similar to the coil-globule transition, see the review by Lifshitz, Grosberg, and Khoklov[11]).

5. TWO-DIMENSIONAL CASE (LINEAR POLYMERS, ADSORBED ON A SURFACE)

In the preceding section we saw that the representation of the molecule in solution as a Gaussian chain of "blobs" gives the correct result for molecules that are not very long. Below we shall see that in the two-dimensional case, such a chain is non-Gaussian. This is connected with the fact that for $d=2$ the non-self-intersection condition is more complex than in a space of greater dimensionality. Thus, for example, in the situation represented on Fig. 1, at $d>2$ this condition only forbids superposition of two parts of the chain on one another, while at $d=2$ it furthermore forbids penetration into the whole region A. Formally, the fact that $d=2$ is a special case is evident from the fact that in Eqs. (3.4) in the two-dimensional case, the simplest corrections due to the transverse fluctuations diverge logarithmically as $h\to 0$ (for sufficiently long chains). An interesting characteristic of a magnet with $n=0$ is that the corrections to the magnetic moment, arising from the transverse fluctuations, are positive. In contrast to the usual magnets with $n=2$ and 3, the fluctuations in this case lead to an increase and not to a decrease in the average moment.

The first to take systematic account of the renormalizations arising in the two-dimensional case for an arbitrary n-component magnet was Polyakov.[13] We use the results of Ref. 13, bearing in mind that they are applicable even for $n=0$. The Hamiltonian of the magnet is conveniently written as

$$H=\int\left[c_0\sum_{\alpha=1}^{n}(\nabla S_\alpha(\mathbf{x})-hS_1(\mathbf{x})\right]d^2\mathbf{x}. \qquad (5.1)$$

Here, $c_0 \sim r_c^2$ is the effective stiffness. As S_α we will take the magnetic moment averaged over a volume with dimensions $r_c \sim \rho_m^{-\nu/(\nu d-1)}$, where ν is the exponent in the functional dependence $R^2 \sim L^{2\nu}$ for an isolated non-self-intersecting two-dimensional chain.

As shown in Ref. 13, at $h=0$, the averaging over the transverse fluctuations for separations larger than r_c and less than some scale R lead to logarithmic renormalization of the average moment

$$S(R)=S(r_c)\left(1-(n-2)\frac{a^2T}{2\pi c_0S^2(r_c)}\ln\left(\frac{R}{r_c}\right)\right)^{(n-1)/2(n-2)} \qquad (5.2)$$

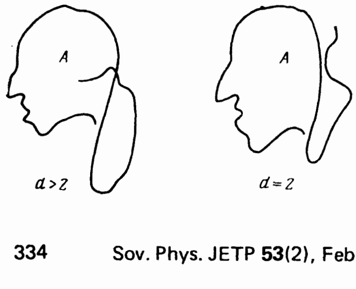

FIG. 1.

and of the effective stiffness

$$c(R)=c_0\left(1-(n-2)\frac{a^2T}{2\pi c_0S^2(r_c)}\ln\left(\frac{R}{r_c}\right)\right)^{-1/(n-2)}. \qquad (5.3)$$

The magnetic field h and the temperature T are not renormalized. In the case $\rho_m \sim 1$, i.e., for low temperatures, to estimate $T[c_0S^2(r_c)]^{-1}$ we may use the formulas of self-consistent-field theory:

$$c_0\approx l^2/d\rho_m, \qquad S^2(r_c)\approx 2T\rho_m,$$

whence

$$T/(c_0S^2(r_c))\approx a^2/2l^2\sim \mathrm{Gi}.$$

Furthermore, we will designate the coefficient $(2-n)T/[2\pi c_0S^2(r_c)]$ as A. In the case of a melt, $A\approx a^2/\pi l^2$, and in the case of strong fluctuations $A\approx 1$.

If $h\neq 0$, then renormalizations (5.2), (5.3) are significant only up to scales in which the magnetic field term is of first order in the gradient term:

$$R_h\sim(c_0S(r_c)/h)^{1/2}\approx(\bar{L}^Rr_c^2)^{1/2},$$

where $\bar{L}^R$ is the average length of the polymers in solution in "blob" units. For the correlation radius of the transverse fluctuations we obtain the estimate

$$R^2\sim\frac{c(R_h)S(R_h)}{h}\sim\frac{c_0S(r_c)}{h}\left(1+A\ln\frac{R_h}{r_c}\right)^{3/4}. \qquad (5.4)$$

According to Eq. (2.14), this is the average separation between the ends of the linear molecule. The polymer density is

$$\rho_p=S(R_h)h\approx S(r_c)h[1+A\ln(R_h/r_c)]^{1/4}. \qquad (5.5)$$

The monomer density is not renormalized, since the major contribution to $T\partial\ln Z/\partial T$ comes from a region of separations less than r_c. Writing the right-hand side of Eq. (5.4) using Eq. (5.5) in terms of polymer quantities, we obtain

$$\langle R^2\rangle=\left(1+\frac{A}{2}\ln\bar{L}^R\right)R^2_{\rm Gaussian}\,. \qquad (5.6)$$

The correlation function of the isolated chains may be determined by making the field S_α $2n$-component $[S=(S_{1\alpha}, S_{2\beta})]$ and adding to the Hamiltonian (5.1) the term $\lambda\Sigma S_\alpha^2$ [see Eq. (4.2)]. Then, besides R_h, another characteristic scale $(J/\lambda)^{1/2}$ appears. If

$$J/\lambda\ll JS/h,$$

then this is the size of the probe chain. In this case the renormalizations are carried out up to separations on the order of $(J/\lambda)^{1/2}$. Then from Eq. (5.3) we obtain for the size of the probe chain the formula

$$R^2=\left(1+\frac{A}{2}\ln L^R\right)^{1/3}R_{\rm Gaussian}\,. \qquad (5.7)$$

At first glance, such a result contradicts Eq. (5.6). In fact, however, the discrepancy arises from the change (compared with the three-dimensional case) in the molecule length distribution function. For the correlation function of the transverse components of the moment, we obtain

$$G(x)=\langle S_{2\alpha}(\mathbf{x})S_{2\alpha}(0)\rangle\sim G^{(0)}(x)\left(1+A\ln\frac{x}{2}\right)^{1/2}.$$

From this the length distribution of molecules in solution is

$$G_L \sim [\ln(L/\bar{L})]^{1/2} \exp[-L/(\bar{L} \ln^{1/4} L^R)]. \qquad (5.8)$$

Calculating the average size of the molecule in solution using Eqs. (5.7) and (5.8), we obtain a result which agrees with Eq. (5.6).

6. CONCLUSION

We have given a short description of a method which allows us to reduce practically any problem in polymer solution theory to a corresponding magnetic problem, which as a rule has already been solved. In addition to the problems considered in our work, the polymer-magnet analogy may be applied to the description of a mixture of polymers of different composition, and also to solutions of polymers with a non-equilibrium length[4)] distribution[4)] or with a spatially inhomogeneous distribution. Due to lack of space, we could not dwell at length on the description of cyclic polymers, or on mixtures of cyclic and linear polymers.

Finally, we point out an interesting correspondence between the problem of polymer behavior in a limited volume and the problems of magnetism of small particles, and the analogy between surface effects in a solution and in magnets, etc.

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[1)] Here we introduce the lattice only for simplicity in formulation of the model. We can easily generalize to a continuous model.

[2)] By the persistent length we mean the distance along a chain, over which the orientation of one link ceases to affect the orientation of another.

[3)] The result that long rigid moleucles in a fluctuating solution of flexible molecules go over into the globular state has been obtained independently by Grosberg, Erukhimovich, and Shakhnovich.[12] This corresponds to the particular case $c_1 \gg c_2$, as a consequence of which $\tilde{u}_{11}$ and $\tilde{u}_{12}$ are small and are not renormalized; then $u_{11} - \tilde{u}_{12}^2/u_{22}^R < 0$.

[4)] With the condition, that this distribtuion may be represented as an aggregate of equilibrium distributions. Our method is inapplicable to a monodispersed polymer solution.

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An estimate of the percolation probability in inhomogeneous media

M. I. Shvidler

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A universal lower estimate of the probability of percolation is obtained for a random system containing subregions of a conductor and of an insulator. The estimate depends on macroscopic functionals: the effective and mean conductivities of the system, and for anisotropic systems also on the direction of the mean field-intensity vector; that is, on characteristics that can be determined quite simply experimentally.

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We consider a heterogeneous system consisting of subregions occupied by a uniform and isotropic conductor, with conductivity σ_0, and of subregions of zero conductivity (insulators). It is known that with a sufficiently irregular and complicated structure of the medium, there may exist isolated regions of the conductor that do not take part in the transport process. For estimation of the size of such regions, in the theory of percolation[1,2] a quantitative characteristic has been introduced: the percolation probability P, interpreted as the fraction of the conductor volume that takes part in transport. In its essence, the value of P is a char-