Volume interactions in the statistical physics of a polymer macromolecule

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Theoretical approaches to the spatial structure of linear macromolecular chains are reviewed. The associated problems are found to be essentially different when repulsion and attraction between chain elements are respectively dominant. In the case of attraction, the chain condenses on itself and forms a globule with a definite structure which can be analyzed in the self-consistent field approximation. In the case of repulsion, the result is a coil with a fluctuating structure and, in this situation, one must use the methods of scaling theory. The coil-globule transition is also analyzed.

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CONTENTS

1. INTRODUCTION

A. Basic Concepts

1) Linear memory and volume interactions. Current interest in the statistical theory of polymers and, in particular, of polymer solutions, is supported by the needs of applied chemistry and biology. There is, in addition, a further reason for the interest in this theory: there is an analogy with many topical problems in theoretical physics, first and foremost with the physics of phase transitions and critical phenomena.

Apart from the particular quantitative analogy between certain problems in these subjects (see below), there is an analogy insofar as the overall approach to these problems is concerned. Many problems in the theory of polymer solutions are similar to problems in the theory of phase transitions in that they can be formulated in a way that is both general and useful. In this, they differ from such related fields as the theory of complex molecules and the statistical theory of liquids. To a considerable extent, this situation has arisen because the system has two large parameters that can be explicitly taken into account.

Thus, firstly, the molecular system exhibits a hierarchy of interactions: the covalent bond energies E_1 are much greater than all other energies E_2 in the system, i.e., $E_1/E_2 \gg 1$. In relation to a polymer chain, this means that the sequence of links in the chain is determined by the high energies of the longitudinal valence bonds, and the relative position of each link in the chain is fixed once and for all. This is conveniently indicated by saying that a polymer chain has a fixed linear memory.

Secondly, the other large parameter is the total number of links in the chain $N \gg 1$. In common synthetic polymers, $N \sim 10^4 - 10^5$, and in the DNA macromolecules, $N \sim 10^5 - 10^7$.

The above two large parameters enable us to approach the theory of polymer solutions as follows. Firstly, since $N \gg 1$, the polymer chain may be looked upon as a mcaroscopic system. Effective utilization of

the methods of statistical physics is thus found to simplify the theory of polymers as compared with the mechanical theory of ordinary molecules. Secondly, the hierarchy of interactions frequently enables us to look upon a polymer chain as a one-dimensional thermodynamic system. This has led to the elucidation of very many important phenomena ranging from the elasticity of rubber-like polymers to the coil-globule transition in proteins and nucleic acids (see the classic monographs by Vol'kenshtein,[1] Birshtein and Ptitsyn,[2] and Flory[3]). Finally, the availability of the above two large parameters enables us, independently of the statistical theory of liquids, to consider even problems for which the fact that the polymer chain is a three-dimensional system is an essential feature.

We are concerned here with phenomena in which the so-called volume interactions, i.e., interactions between distant links in the chain, which are brought closer together in space as a result of the flexure of the chain, are important. We shall examine these phenomena in the present review.

2) Scope of the review. The statistical physics of volume interactions in polymer solutions is a very large subject which cannot be adequately examined in a single review paper. We shall therefore confine our attention to the statistics of volume interactions within a single isolated macromolecule, i.e., we shall discuss the theory of dilute polymer solutions when the individual macromolecules may be looked upon as noninteracting. Moreover, we shall confine our review to a homogeneous sequence of links along the chain (we shall refer to this type of chain as homopolymeric) and, even then, we shall be interested only in geometric characteristics such as root mean square separation between the ends of the chain, $\langle R^2 \rangle$, and the density distribution $n(\mathbf{x})$ in the system.

Throughout this review, we shall speak of the interaction between monomers, apparently ignoring the presence of the solvent molecules. It will then, of course, be important to remember that we shall be dealing with the effective interaction between monomers, which is renormalized by the presence of the solvent molecules. Whether or not this type of effective interaction can be introduced will be discussed below.

3) Flexibility of a polymer chain. The importance of volume interactions in the physics of a polymer macromolecule lies in the fact that the natural configuration of a polymer chain is not rectilinear, but takes the form of a coil tangled up in space. The flexibility of the chain is responsible for this state of affairs.

Rotational isomerization[1] is the main mechanism for the flexibility of ordinary polymer chains. The essence of this phenomenon is that, if we consider a particular link in a particular state, the next link can be found with the same order of probability in one of several states, namely, the rotational isomers. There is now a well-developed theory of the flexibility of polymer chains due to rotational isomerization.[1-3] These questions are not directly related to volume interactions and we shall not examine them here.

It is clear that, whatever the mechanism responsible for the flexibility of the chain, the mean value of the cosine of the angle ϑ between two parts of the chain seperated by a sufficiently large distance s measured along the chain must decrease exponentially with s:

$$\langle \cos \vartheta (s) \rangle \sim \exp \left(-\frac{s}{l} \right);$$ (1.1)

where l is the so-called persistence length and is an important characteristic of the chain stiffness. Its meaning is as follows: a segment of the chain that is short in comparison with l will behave as a solid rod, and different segments l can rotate practically independently of one another.

4) Unperturbed characteristics of a macromolecule. Calculations on the mechanism of chain flexibility can be used[1-3] to determine the conditional probability $g(\alpha_j, \alpha_{j+1})$ that the $j+1$-th link is in the state corresponding to the rotational isomer α_{j+1}, given that the j-th link is in the state corresponding to the rotational isomer α_j. We emphasize that all the links in the homopolymeric chain are characterized by the single matrix g (α_j and α_{j+1} are the matrix indices). Once this probability has been determined, we have to calculate the characteristics of the macromolecule as a whole (for example, the mean square end-to-end distance $\langle R^2 \rangle$). When volume interactions are ignored, this calculation yields the unperturbed characteristics of the macromolecule.

The evaluation of these characteristics presents no basic difficulty, and the problem can now be regarded as solved.[1-3] By suitably defining an elementary link in the polymer chain, we can ensure that the state α_{j+1} of the next link will depend only on the state α_j of the preceding link. This means that the migration of the polymer chain in space may be looked upon as a simple Markov process, and the macroscopic characteristics of the chain can be determined by the usual methods used to describe, for example, the one-dimensional Ising model, or the Brownian motion of a particle (further details can be found in the literature[1-3]).

In particular, in the case of the analogy between a polymer chain and a Brownian particle, the distance from the origin measured along the polymer chain corresponds to time, and the persistence length corresponds to the diffusion coefficient. It is clear from this analogy that the mean end-to-end distance $\langle R^2 \rangle_0$ (the subscript indicates that we are here dealing with unperturbed quantities) is given by the following order-of-magnitude relation:

$$\langle R^2 \rangle_0 \sim N l^2.$$ (1.2)

The theory outlined in Refs. 1-3 can then be used to calculate the persistence length l for each model of the polymer chain, and to determine the numerical factor in (1.2).

5) Gibbs distribution for a polymer macromolecule. It is clear from the foregoing that the Gibbs distribution for the polymer macromolecule with linear memory and volume interaction is

$$\rho (\Gamma) = \exp \left[\frac{F - \varepsilon (\Gamma)}{T} \right] \prod_j g (\alpha_{j+1}, \alpha_j),$$ (1.3)

where $\Gamma = \{\alpha_1, \ldots, \alpha_N\}$ is a point in the configuration space of the system, $\varepsilon(\Gamma)$ is the energy associated with the volume interactions in the configuration Γ, and F is the free energy of the system.

To establish important connections with the fund of knowledge now available on real gases and liquids, we shall find it convenient to represent the given form of volume forces by thermodynamic functions for a system of particles that are not linked in a chain but interact through these forces. These thermodynamic functions can be calculated from the Gibbs distribution

$$\rho_0(\Gamma) = \exp\left[\frac{F_0 - \varepsilon(\Gamma)}{T}\right]. \tag{1.4}$$

A system with this distribution will be referred to as a broken-link system.

B. Models of a polymer chain

A theoretical approach to the study of complicated systems such as polymer solutions necessarily involves model representations of the structure of the macromolecules under discussion. Since a sufficient set of clear physical representations is not yet available in the theory of polymers, it is useful to begin by considering models for which simple and mathematically acceptable formulations can be introduced. The natural starting point is to consider the two opposite limiting cases, namely, the discrete model, in which the links are looked upon as localized particles (beads on a string), and the continuous model in which the chain is uniform along its entire length.

1) Beads-on-string model. Here, the polymer chain is looked upon as a set of beads on a weightless string, the beads being the monomers (Fig. 1a). The state of each monomer is then completely defined by the position $\mathbf{x}$ of its center. The linear memory of this model is specified by the function $g(\mathbf{x}_{j+1} - \mathbf{x}_j)$, i.e., the conditional probability that the $j+1$-th monomer is at the point $\mathbf{x}_{j+1}$ provided the j-th monomer is at $\mathbf{x}_j$. Volume interactions are determined by the potential $u(|\mathbf{x}_i - \mathbf{x}_j|)$ for the interaction between monomers i and j. For homopolymers, to which we shall confine our attention, the functions g and u are independent of i and j.

Since $g(\mathbf{x}_{j+1} - \mathbf{x}_j) = g(\mathbf{y})$ is a probability, we have

$$\int g(\mathbf{y}) \, d^3y = 1. \tag{1.5}$$

The mean square distance a' between two monomers that are adjacent in the chain is an important characteristic and is given by

$$a'^2 = 6a^2 = \int \mathbf{y}^2 g(\mathbf{y}) \, d^3y. \tag{1.6}$$
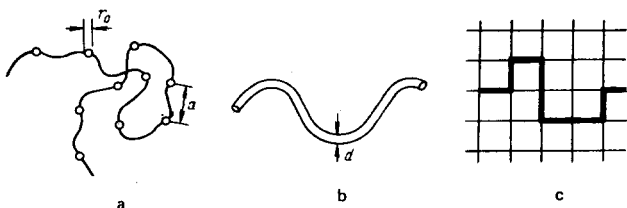
As a rule, theoretical studies use a function g that depends on $|\mathbf{y}|$ only. The Gaussian function

$$g(|\mathbf{y}|) = (4\pi a^2)^{-3/2} \exp\left(-\frac{y^2}{4a^2}\right) \tag{1.7}$$

is an example of such a function. This type of correlation is obtained when the individual beads are connected by a long and perfectly flexible string.

The potential $u(r) = u(|\mathbf{x}_i - \mathbf{x}_j|)$ is usually assumed to correspond to strong repulsion at small distances and attraction at large distances (Fig. 2). There is little point in providing a more detailed description of $u(r)$ because it describes the effective interaction, including the contribution of the solvent molecules. We shall assume a short-range potential with a characteristic range r_0 and characteristic volume $v \sim r_0^3$.

The physical realization approaching the beads-on-string model is a copolymer with large side groups embedded in a thin main chain.

2) Persistent model. Here, the polymer chain is looked upon as a long flexible elastic "hose" of diameter d and persistence length l (Fig. 1b). Segments of this chain interact with one another with a certain linear interaction density which depends on their mutual disposition. This model is obtained by smoothing out the properties of the polymer chain at the microscopic level.

3) Lattice model. This model is usually employed in the simulation of the properties of polymer macromolecules on a computer. The polymer chain is represented by a random-walk trajectory on some space lattice (Fig. 1c). The function g, which describes the linear memory, is then defined on a discrete set of points. Volume interactions are specified by demanding that the random walk must not cross itself (repulsion) and by assigning an energy $-\varepsilon < 0$ to each pair of sites separated by one lattice constant (attraction).

4) Connection between models of polymer chains. Standard Gaussian model. The following questions naturally arise: What is the relationship between the above models among themselves and with real chains? Are the results sensitive to the choice of a particular model of a chain? Answers to these questions may be found in the ensuing account.

For the moment, we merely note that, under certain definite conditions, the behavior of a polymer macromolecule is universal, i.e., it does not depend on the particular structure of the chain and, consequently, on the choice of its model. It follows that, when these conditions are satisfied, the model can be chosen on the basis of mathematical convenience alone. In fact, the beads-on-string model with the correlation given by (1.7) and the monomer interaction potential shown in Fig. 2 is the most convenient for our purposes. We

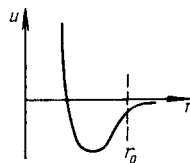FIG. 1. Models of a polymer chain: beads-on-string (a), persistent model (b), lattice (c).

FIG. 2. Example of the potential $u(r)$.

shall refer to this model of the polymer chain as the standard Gaussian model.

Unless stated to the contrary, we shall throughout this paper discuss volume interactions within the framework of the standard Gaussian model. Insofar as the universal, i.e., model-independent, behavior of the macromolecule is concerned, we shall indicate a method of transferring the results obtained for the standard model to the other models of the polymer chain. Whenever the results obtained for the standard Gaussian model are qualitatively invalid for other models, this will be explicitly stated.

C. Polymer coil and polymer globule

1) Definition of coil and globule. It is well known that a polymer globule is defined in molecular biology as a dense three-dimensional structure from the core of which practically all the solvent has been displaced by the monomers of the chain.[4] As a rule, such a structure is biochemically highly active. Heating of the globule results in denaturation, the dense structure is destroyed, and biochemical activity ceases. The globule is then said to transform into a coil.

However, more precise definitions are essential for the development of a quantitative theory. Analysis of the possible macroscopic states of the homopolymer chain suggests that the following definitions will be convenient.

A globule is a state of the polymer macromolecule with a definite thermodynamically stable spatial structure in which density fluctuations are small compared to the density itself, and their correlation length is much smaller than the size of the whole macromolecule.

Conversely, a coil is a state of the macromolecule without a stabled spatial structure. In this state the density fluctuations are of the order of the density itself, and their correlation length is of the same order as the size of the macromolecule.

2) The coil-globule transition. Terminology. Thus, according to our definition, the globule and the coil differ from one another by their fluctuational state. From the standpoint of statistical physics, it is natural to refer to such very different states as phases, and the transition between them as a phase transition. However, it is important to remember that, in statistical physics, phase states and transitions between them are rigorously defined only for $N \to \infty$. On the other hand, real polymer chains have large, but not infinite, values of N (this number may even be very small in comparison with the classical applications of thermodynamics). A given finite chain cannot, therefore, always be assigned to a particular phase state. This means that there is a definite transition width ΔT (to be specific, we consider a transition occurring as the temperature T is varied) which separates regions that can be reliably assigned to different phases, i.e., regions in which one of the phases provides the dominant contribution to the partititon function.

We shall adhere to the following terminology in the classification of transitions occurring for finite N. A conformational transition will be called a phase transition if its width ΔT tends to zero for $N \to \infty$. A phase transition is said to be of the first order if, in the transition region, there are two free-energy minima and, correspondingly, two stable states in the space of the macrovariables, each of which is thermodynamically stable on one side of the transition point and metastable on the other. A phase transition is said to be of the second order if, in the transition region, there is only one free-energy minimum in the space of the macrovariables, i.e., there are no metastable states on the other side of the transition point. This terminology is reasonable from the physical point of view and from the point of view of analyses of experimental data.

3) Macromolecule without volume interaction—the polymer coil. Depending on the strength and nature of the volume interactions, a polymer macromolecule can exist either in the coil or the globular state. As an example, we consider the possible state of a macromolecule in the absence of any volume interactions, i.e., when $u(r) = 0$.

We recall that, unless stated to the contrary, we are dealing with the standard model. We can then use (1.7) to show quite easily that the mean square end-to-end distance for a chain of $N+1$ links is given by

$$\langle R^2 \rangle_0 = 6Na^2. \tag{1.8}$$

If we place the initial (zeroth) link of the chain at the origin, we find that the distribution function for the k-th link is

$$p_k(x_k) = (4\pi ka^2)^{-3/2} \exp\left(-\frac{x_k^2}{4ka^2}\right). \tag{1.9}$$

We now introduce the microscopic monomer number density

$$n_{\Gamma}(\mathbf{x}) = \sum_{k=1}^{N} \delta(\mathbf{x} - \mathbf{x}_k) \tag{1.10}$$

and the mean density

$$n(\mathbf{x}) = \langle n_{\Gamma}(\mathbf{x}) \rangle = \sum_{k=1}^{N} \langle \delta(\mathbf{x} - \mathbf{x}_k) \rangle = \sum_{k=1}^{N} p_k(\mathbf{x}). \tag{1.11}$$

Replacing summation by integration, we find that

$$n(\mathbf{x}) = (4\pi a^2)^{-3/2} N^{-1/2} \int_0^1 dq\, q^{-3/2} \exp\left(-\frac{\xi^2}{q}\right), \tag{1.12}$$

where $\xi = x/(\langle R^2 \rangle_0)^{1/2}$. For $1/N \ll \xi \ll 1$, this density falls off as $1/\xi$, i.e., the characteristic length related to the density distribution is $\xi \sim 1$.

To characterize the density fluctuations, we must find the correlation function. By analogy with (1.12), we have

$$\langle n_{\Gamma}(\mathbf{x}_1)\, n_{\Gamma}(\mathbf{x}_2) \rangle = \frac{1}{(4\pi a^2)^3 N} \int_0^1 \int_0^1 dq_1\, dq_2\, \frac{\exp[-(\xi_1^2/q_1) - (|\xi_1 - \xi_2|^2/|q_1 - q_2|)]}{q_1^{3/2}|q_1 - q_2|^{3/2}} \tag{1.13}$$

from which it is clear that the correlation length for the density fluctuations, i.e., the characteristic length corresponding to the correlation function

$$\frac{\langle n_{\Gamma}(\mathbf{x}_1)\, n_{\Gamma}(\mathbf{x}_2) \rangle}{\langle n_{\Gamma}(\mathbf{x}_1) \rangle \langle n_{\Gamma}(\mathbf{x}_2) \rangle} - 1, \tag{1.14}$$

is of the same order as the characteristic size of the

macromolecule. This, in turn, means that the unperturbed chain is in the coil state.[5]

In Sec. 2, we shall examine the theory of macromolecules in the coil state, in Sec. 3 in the globular state, and in Sec. 4 the theory of the coil-globule transition. The range of problems which we shall examine is seriously restricted, as indicated in subsection A, para. 1). The approach on which our account of the theory of the globular state is based was suggested by Lifshits[5] and was developed in a number of subsequent papers.[6-8]

2. VOLUME INTERACTIONS IN POLYMER COILS

A. Universal behavior of polymer coils

1) The Θ point. When volume interactions are present, distance segments of the chain will either attract or repel as they approach one another as a result of flexure. If the potential $u(r)$ is as shown in Fig. 2, repulsion between the monomers will predominate at high temperatures and attraction at low temperatures.

The fundamental concept in the statistical physics of volume interactions in a macromolecule is the concept of the Θ point. According to Flory,[9] this is the temperature at which attraction and repulsion between the segments of the chain are completely compensated and all the characteristics of the macromolecule assume the values found in the state unperturbed by the volume interactions. Repulsion between the monomers that predominates for $T > \Theta$ (good solvent region) and attraction predominates for $T < \Theta$ (poor solvent region).

In this chapter, we shall consider the region $T > \Theta$. It was shown at the end of the last chapter that, in the absence of volume interactions, i.e., for $T = \Theta$, the macromolecule exists in the coil state. It is clear that, for $T > \Theta$, the additional forces of repulsion will only make the structure of the macromolecule much looser, so that it will correspond more closely to the coil state.

2) Role of binary interactions. Simple estimates can readily be used to establish the origin of the virtually complete compensation of volume interactions at the particular temperature $T = \Theta$. Let us imagine that the macromolecule is a cloud of monomers within a volume $\sim R^3$, where R is the size of the molecule. For $T = \Theta$, we have $R \sim aN^{1/2}$ [see (1.8)], and for $T > \Theta$, $R > aN^{1/2}$, because the presence of repulsion facilitates an increase in the size of the coil. The mean monomer number density in this cloud for $T \geqslant \Theta$ is $n \sim N/R^3 \leqslant a^{-3}N^{-1/2}$. It is clear that, when $N \gg 1$, the density is exceedingly low, i.e., the monomer cloud becomes very tenuous. Consequently, in this case, the number of binary collisions between monomers (described by the second virial coefficient B) predominates over the number of higher-order collisions (described by the third, fourth, and so on, virial coefficients C, D, ...), so that the higher-order interactions can be neglected with a high degree of accuracy. Thus, for $T \geqslant \Theta$, the conformational properties of polymer coils for large N are determined by binary interactions between monomers and, consequently, depend only on the second virial coefficient $B(T)$.

From this point of view, the Θ point is the inversion temperature for $B(T)$, i.e., $B(\Theta) = 0$. This is the temperature at which the contribution of the binary interactions is reduced to zero, the contributions of higher-order interactions are small, and, consequently, the characteristics of the macromolecule assume the unperturbed values.

3) Universality. It is clear from the foregoing that the conformational characteristics of polymer macromolecules do not depend for $T \geqslant \Theta$ on the detailed shape of the volume interaction potential $u(r)$, but depend only on one of its integral characteristics, namely, the second virial coefficient $B(T)$. This is indeed a reflection of the universal behavior of polymer coils, namely, the fact that its properties depend on B in a universal fashion, independently of the particular nature of the forces contributing to this virial coefficient (these properties also depend on the parameters N and a, which are not related to the volume interactions[1]).

4) Quasimonomers. The above analysis does not, however, take into account one important fact, namely, that the monomers are linked in a chain and are not, therefore, independently distributed within the coil. Hence, despite the fact that the mean monomer number density in the coil for large N is low, the local density of other monomers in the neighborhood of the given monomer is not at all small, and does not decrease with increasing N.[10] This high local density is due to neighboring monomers in the chain. It would appear that, because of the high density of monomers, it will not be enough to take into account only the second virial coefficient for their interaction, so that the universal character of the behavior of polymeric coils becomes doubtful, at least as formulated above.

It is, however, clear intuitively that if the mean monomer number density in the coil is small, this should lead to a degree of universality. This does indeed turn out to be the case.[11] If we consider not the interaction among the monomers in a polymer coil but the interaction between distant segments of the chain, the fact that the mean density in the coil is low signifies that binary interactions between the segments predominate over higher-order interactions. It has been shown[11,13] that this predominance leads to a universal behavior analogous to that obtained above, but this universal property is due to the representation of the polymer coil not by a cloud of N uncoupled monomers but by a cloud of N uncoupled quasiparticles (quasimonomers). Quasimonomers differ from monomers by the fact that they interact with the *renormalized* characteristics that effectively take into account the linking of the monomers into a chain (in particular, they involve the effective second virial coefficient B^* and not B). The representation of a polymer coil by a cloud of quasimonomers is possible because each monomer in a chain is in a standard environment of other monomers, mainly its nearest neighbors in the chain.[11-13] This "standard environment" is, in fact, responsible for the renormalization

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[1]We recall that, unless the converse is explicitly stated, we are dealing with the standard Gaussian model of the polymer chain.

of the properties of each monomer, so that it reflects the presence of volume interactions in the macromolecule by behaving as a quasiparticle whose characteristics are different from the characteristics of the original monomer.

It follows that all the foregoing discussion remains in force except that B must be replaced by the renormalized coefficient B^*. Henceforth, we shall assume that this renormalization has been carried out.

The idea of quasimonomers has been very useful in the analysis of inhomogeneous polymer chains (finite chains, chains containing defects, branched chains, and so on[11-13]). If the chain is not homogeneous, the standard environment of all the monomers is modified but, for most monomers, this change is small and can be regarded as being a linear function of the change in the local density of the monomers around the given monomer, Δn_{loc}. The characteristics of the interactions of a quasimonomer based on a given monomer are modified in the same way, i.e., linearly in Δn_{loc}. Once the change in these characteristics has been found, it is a relatively simple matter to obtain any other quantity describing the volume interactions by starting with the polymer coil, looked upon as a gas of quasimonomers with known interaction characteristics suitably modified to take into account the inhomogeneity of the chain.[11-13]

5) *Expansion factor of a macromolecule.* The mean square end-to-end distance can be written in the form

$$\langle R^2 \rangle = \alpha^2 \langle R^2 \rangle_0, \qquad (2.1)$$

where $\langle R^2 \rangle_0$ is the unperturbed value of $\langle R^2 \rangle$, defined by (1.8). The quantity α is the expansion factor of the macromolecule, and it is clear that, for $T > \Theta$, for which repulsive forces predominate, $\alpha > 1$.

It is clear from the foregoing that α^2 is a universal function of N, a, and B^*:

$$\alpha^2 = \alpha^2(N, a, B^*) = \alpha^2 \left(N, \frac{B^*}{a^3} \right) \qquad (2.2)$$

(the last equation follows from dimensional considerations). We shall now try to evaluate α^2 by considering the volume interaction as a perturbation.[14-16]

The partition function of a chain of $N+1$ monomers with the initial (zeroth) link at the origin and the last link at the point R can be written in the form [see (1.3)]

$$Z\left(\begin{smallmatrix} 0 & N \\ 0 & R \end{smallmatrix}\right) = \int \delta(x_0)\, \delta(x_N - R) \exp\left[-\frac{\varepsilon(\Gamma)}{T} \right] \prod_{j=1}^{N} g(x_j - x_{j-1})\, d\Gamma, \qquad (2.3)$$

where Γ is a point in the configuration space of the macromolecule and $\varepsilon(\Gamma)$ is the microscopic volume interaction energy in the given configuration, i.e., $\varepsilon(\Gamma) = \sum_{1 \leq i < j \leq N} u(|x_i - x_j|)$. We now introduce the Mayer function

$$f_{ij}(|x_i - x_j|) = \exp\left[-\frac{u(|x_i - x_j|)}{T} \right] - 1 \qquad (2.4)$$

and, if we expand the integrand in (2.3) in powers of f, we obtain

$$Z\left(\begin{smallmatrix} 0 & N \\ 0 & R \end{smallmatrix}\right) = \int \delta(x_0)\, \delta(x_N - R) \prod_{j=1}^{N} g_j \left(1 + \sum_{1 \leq i < j \leq N} f_{ij} + \sum f_{ij} f_{kl} + \dots \right) d\Gamma, \qquad (2.5)$$

where the p-th order of perturbation theory corresponds to the retention in (2.5) of terms involving the product of p Mayer functions, i.e., it is equivalent to taking into account p simultaneous binary collisions.

In addition, we assume that

$$f_{ij} \sim -\delta(x_i - x_j), \qquad (2.6)$$

which means that $u(r)$ is a short-range potential. It has been shown[11] that the proportionality factor in (2.6) is the renormalized coefficient B^*.

Next, we can evaluate all the integrals in (2.5) taking (2.6) and (1.7) into account. The quantity α^2 is given by

$$\alpha^2 = \int R^2 Z\left(\begin{smallmatrix} 0 & N \\ 0 & R \end{smallmatrix}\right) d^3R \Big/ \int Z\left(\begin{smallmatrix} 0 & N \\ 0 & R \end{smallmatrix}\right) d^3R \, \langle R^2 \rangle_0 \qquad (2.7)$$

so that the final series for α^2 is[17]

$$\alpha^2 = \alpha^2(z) = 1 + k_1 z + k_2 z^2 + \dots, \qquad (2.8)$$

where $z = B^* N^{1/2}/a^3$ and k_i are numerical coefficients.

This series shows that the expansion coefficient α^2 is a function of a single real variable, namely, z. The series is, however, suitable for the evaluation of α^2 only for $|z| \ll 1$, whilst the quantity z contains the large factor $N^{1/2}$, so that $|z| \ll 1$ holds only in a small neighborhood of the Θ point, i.e., the temperature for which $B^* = 0$ [the convergence of the series given by (2.8) is discussed in the literature[18-20]]. Thus, despite the fact that the mean monomer number density in the coil is small, the effect of the volume interactions on the coil size cannot, in general, be taken into account within the framework of perturbation theory.

The function $\alpha^2(z)$ can be evaluated for the entire domain of z only by more sophisticated methods which are described in subsection C.

6) *Two-parameter theory.* It follows that $\langle R^2 \rangle$ for a polymer chain depends on the basic parameters N, a, and B^* in the form of the following two combinations: Na^2 and $N^{1/2}B^*/a^3$. Similarly, it can be shown that any other conformational characteristic of a polymer coil, for example, $\langle R^p \rangle$ with $p \neq 2$, depends on N, a, and B^* for $T \geq \Theta$ only in the form of these two combinations.[17] It is therefore usual to speak of the two-parameter theory of dilute polymer solutions: all the macroscopic conformational characteristics are functions of the two parameters Na^2 and $N^{1/2}B^*/a^3$ only.

B. Connection between the models of a polymer chain in the universal region

1) *Equivalent standard Gaussian chain.* The universal behavior of polymer coils is a consequence of the predominance of binary interactions between the chain segments as compared with the higher-order interactions and, in this sense, it should be valid for any model of a polymer chain. This means that, for any model, one can introduce the effective second virial coefficient B^* for the interactions between the chain segments, after which the polymer coil can be represented by a tenuous cloud of quasimonomers interacting with this virial coefficient. Next, one can choose a standard Gaussian chain of beads for which the parameters of the cloud of

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quasimonomers are the same as for the model. This beads-on-string chain will be referred to as the equivalent standard chain. It is clear that all the macroscopic conformational characteristics of the original and the standard coils will be equal.

It is thus clear that there is no loss of generality if we confine our attention to the standard Gaussian model in the universality region $T \geq \Theta$ because any polymer chain can be associated with an equivalent standard chain, and the results obtained for the standard model can be used to evaluate the macroscopic characteristics.

2) Method of constructing the equivalent chain. We must first consider how we can associate a given coil with its equivalent standard coil, i.e., a standard coil whose macroscopic characteristics are the same as the characteristics of the original macromolecule.[21]

All macroscopic conformational properties in the standard model depend only on the two parameters Na^2 and $N^{1/2}B^*/a^3$ (see subsection A, para. 6) and these two parameters have a particular physical interpretation: Na^2 is $\langle R^2 \rangle_0$, and $z = N^{1/2}B^*/a^3$ is a single-valued function of α^2. Hence, it is clear that, if we take the parameters N, a, and B^* of the equivalent standard model so that $\langle R^2 \rangle_0$ and a^2 (or z) for the equivalent chain are equal to those for the original chain, all the other characteristics of the original and equivalent chains will be equal.

Since we must specify the three parameters N, a, B^* in order to define completely the properties of the standard chain, and we subject this choice to only two conditions, one of them can be chosen arbitrarily. This means that the original chain can be divided in arbitrary fashion into the monomers, i.e., one can arbitrarily select N, but, thereafter, the parameters a and B^* are unambiguously fixed. The choice of the elementary monomer is restricted by a single condition, namely, it must not interact through the volume forces with itself since, otherwise, it would not, of course, be elementary. For example, the length of the elementary monomer along the chain cannot be greater than the persistence length.

3) Equivalent standard chain for the persistent model. We shall illustrate the above general discussion of the reduction to the equivalent standard chain by taking the persistent model as an example (see Fig. 1b). We must first define the partition of the persistent chain into monomers. Since we have two characteristic length parameters d and l for the chain, it is natural to divide the chain either into pieces of length l or pieces of length d. In these two cases, we reduce the persistent chain to two different but equivalent standard chains.

Suppose that we have divided the chain into pieces of length l (case 1). Let N_1 be the number of persistence lengths in the chain, i.e., $N_1 = L/l$ (where L is the total length of the chain. Since, in this case, $\langle R^2 \rangle_0 \sim N_1 l^2$ [see (1.2)] and $\langle R^2 \rangle_0$ for the persistent chain and for its equivalent standard chains must be equal, we must take $a_1 \sim l$. The order of magnitude of B^* in this case must, clearly, be the same as that of the second virial coefficient for the interaction between cylinders of diameter d and length l, i.e., we may write $B_1^* \sim dl^2 \tau$, where $\tau = (T - \Theta)/\Theta$. All the parameters of the equivalent standard chain are thus determined. An analysis of the properties of the persistent model in the case of a rigid chain with the aid of the equivalent standard model defined above can be found in the literature.[22]

Let us now divide the persistent model into pieces of length l (case 2). Since, in this case,

$$\langle R^2 \rangle_0 \sim N_2 \frac{d}{l} l^2 \sim N_2 p d^2, \tag{2.9}$$

where $N_2 = L/d$ and $p = l/d$, we must take $a_2 = p^{1/2}d$. The coefficient B_2^* for this case can be found from the condition that the values of z in the above two cases must be equal:

$$\frac{N_1^{1/2}B_1^*}{a_1^3} = \frac{N_2^{1/2}B_2^*}{a_2^3}, \tag{2.10}$$

and, hence, $B_2^* \sim d^3 \tau$.

Either representation of the persistent chain with the aid of the equivalent standard chain can be used for any particular application.

Let us finally estimate the ration v/a^3, where v is the monomer volume in the equivalent standard chain in the case of flexible ($p \sim 1$) and stiff ($p \gg 1$) persistent chains. Since for the usual potentials $u(r)$ (see Fig. 2) we have $B^* \sim v\tau$, and if we compare the above expressions for B^* for the equivalent standard chain, we find that, in the case of the flexible chains, $v \sim a^3$, whereas, for stiff chains, $v \ll a^3$ in both representations. Hence, for flexible chains, the equivalent standard chain is as shown in Fig. 3, whereas, for stiff chains, it is as shown in Fig. 1a.

The reduction of the stiff persistent chain to the standard model is, of course, only possible in the absence of effects connected with orientational ordering, i.e., in the absence of the liquid-crystal phase.

C. Evaluation of the function $\alpha^2(z)$. Polymer-magnet analogy

1) Excluded volume problem and early approaches to it. We now return to the standard model and consider the evaluation of the function $\alpha^2(z)$ which describes the effect of volume interactions on the size of the polymer coil.

We begin by considering a long polymer macromolecule in a good solvent. We then have $B^* \sim v$ and $z \sim N^{1/2}v/a^3 \gg 1$. Consequently, in this region, we must know the asymptotic behavior of $\alpha^2(z)$ for $z \gg 1$. The problem of the asymptotic behavior is known as the self-avoiding random walk problem, or the excluded volume problem.

Extensive literature is now devoted to this subject. The most important advances prior to the establishment of the analogy between polymers and magnets were due
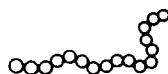

FIG. 3. Equivalent chain of beads for $v \sim a^3$.

to Flory[23] and Edwards.[24] Flory's method is described by Tsvetkov *et al.*[25] and Edwards' ideas are developed in detail by Freed.[26] An elementary derivation of Edwards' results is given by de Gennes.[27]

Both the Flory and Edwards methods yield the same result for the asymptotic form of $\alpha^2(z)$ for $z \gg 1$, namely:

$$\alpha^2(z) \sim z^{2/5}. \qquad (2.11)$$

This is hardly surprising since both theories are essentially self-consistent field theories.

2) Analogy with the problem of second-order phase transitions. It is, however, clear that, since the polymer coil is a highly fluctuating system (the density fluctuations are of the order of the density itself), the self-consistent field approach is not exact. In this sense, the situation is analogous to that arising in the case of second-order phase transitions (to be specific, in magnets): the fluctuations become so large near the transition point that the Landau self-consistent field theory ceases to be valid. The above analogy becomes deeper if we compare the universal behavior of polymer coils with the universal behavior of magnets near second-order phase transition points.

It is well known that the renormalization group method is the basic method for the description of phenomena occurring near second-order phase transition points.[28] The ideas upon which this method is founded have recently been used in connection with polymer coils.[29] De Gennes[29] has, in fact, used the well-known renormalization group approach to describe volume interactions.[29] Part of a chain of g successive monomers was combined into a single effective monomer with new interaction characteristics, so that a chain of N monomers was reduced to an effective chain of N/g monomers. The procedure was then repeatedly applied to the system and, by suitably choosing the parameters, it was possible to establish the recurrence relations that gave the required point when the number of iterations tended to infinity, which, as is well known, is the basis of universality (further details will be found in the de Gennes paper[29]).

All these facts indicate that the analogy between the polymer coil and a magnet near the second-order phase transition point should be quantitative and not merely qualitative. This has, indeed, been shown to be the case: de Gennes has demonstrated[30] that the correlation function for a magnet is equal to a generating function of

$$Z \begin{pmatrix} 0 & N \\ 0 & R \end{pmatrix},$$

if the number of components of the elementary spin in the magnet is formally set equal to zero (see next paragraph).

3) Connection between the correlation function of a magnet and the partition function of a chain with fixed ends. There are several different methods of deriving this connection.[30-34] The simplest and most elegant derivation is given in the appendix to the paper by Daoud *et al.*[32] Here, we shall briefly outline the original method put forward by de Gennes.[30]

It is well known[28] that the central feature of the theory of second-order phase transitions is the analysis of fluctuations in the field φ with the Landau Hamiltonian:

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_{\rm int},$$

$$\mathscr{H}_0 = \int d^d x \left[\frac{\alpha}{2} \sum_{j=1}^n \varphi_j^2 + \frac{\beta}{2} \sum_{i=1}^d \sum_{j=1}^n \left(\frac{\partial \varphi_j}{\partial x_i} \right)^2 \right], \quad \mathscr{H}_{\rm int} = \frac{\gamma}{4} \int d^d x \left(\sum_{j=1}^n \varphi_j^2 \right)^2, \qquad (2.12)$$

where $\alpha = (T - T_0)/T_0$ is the dimensionless deviation from the transition point, d is the dimensionality of the space, and n is the number of independent components of the order parameter. To evaluate the correlation function

$$G_{ij}(\mathbf{R}) = \langle \varphi_i(\mathbf{x}) \varphi_j(\mathbf{x} + \mathbf{R}) \rangle = \delta_{ij} \mathscr{G}(\mathbf{R}) \qquad (2.13)$$

we must apply the Fourier transformation which converts $\mathscr{H}_0$ to the sum of the Hamiltonians of the independent oscillators. The next step is to expand $\exp(\mathscr{H}_{\rm int})$ into a series and to average each of the terms of this series with the aid of Wick's theorem. It is easily verified that the ingoing and outgoing lines on each of the diagrams obtained in this way have the same polarization index, and this has already been reflected in (2.13) by the presence of the δ-function δ_{ij}. However, the diagrams with closed loops are connected to other parts of the diagram only by interaction lines contain summation over the loop polarizations, i.e., simply the factor n (since nothing depends on the loop polarization index). Hence, we may formally substitute $n = 0$ and thus obtain the diagram series without closed loops.

This series differs from the perturbation theory series for the partition function of a polymer chain [see (2.5)] only by the absence of the condition of constant chain length between the end points 0 and R. This length must be fixed by a special chemical potential, and we then obtain

$$\mathscr{G}(\mathbf{R})|_{n=0} = \sum_N \exp[-(\alpha + \mu)N] Z \begin{pmatrix} 0 & N \\ 0 & R \end{pmatrix}. \qquad (2.14)$$

The phase transition point corresponds to $\alpha = 0$, i.e., an infinitely long chain $N \to \infty$. The polymer quantities a and B correspond to the field quantities β and γ.

The fundamental result given by (2.14) was first obtained by de Gennes.[30] It provides a relatively complete characterization of the function

$$Z \begin{pmatrix} 0 & N \\ 0 & R \end{pmatrix}.$$

It is well known that, near the second-order transition point, the function $\mathscr{G}$ is scale-invariant, i.e., it has the form

$$\mathscr{G}(\mathbf{R}) = |\mathbf{R}|^{-d+2-\eta} f\left(\frac{R}{\xi}\right), \qquad \xi \sim \alpha^{-\nu}, \qquad (2.15)$$

where ξ is the correlation length, ν, η are the critical exponents, and f is a universal function with known asymptotic behavior. From (2.14) and (2.15), we obtain analogous expressions for Z:

$$Z \begin{pmatrix} 0 & N \\ 0 & R \end{pmatrix} = N^{\nu(-d+2-\eta)-1} a^{-d} h\left(\frac{R}{aN^\nu}\right) \exp(N\mu), \qquad (2.16)$$

where h is a new universal function with the following asymptotic behavior:

$$h(\mathbf{x}) = \begin{cases} {\rm const} \cdot \exp(-|\mathbf{x}|) & \text{for} \quad |\mathbf{x}| \gg 1, \\ {\rm const} \cdot |\mathbf{x}|^{-d+2-\eta} & \text{for} \quad |\mathbf{x}| \ll 1. \end{cases} \qquad (2.17)$$

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The critical exponents have been calculated[35] as functions of d and n in the general formulation of the problem of second-order phase transitions. For real polymers, $d = 3$ and $n = 0$. The exponent ν turns out to be[30] very close to 3/5 and $\eta \lesssim 0.05$.

The expression given by (2.16) can be used to find any characteristic of the coil in the good-solvent region. In particular, the mean size of the coil turns out to be $\langle R^2 \rangle \sim N^{2\nu}$. The corresponding asymptotic form of α^2 turns out to be (quite fortuitously) close to but not identical with the asymptotic form given by (2.11).

4) Form of $\alpha^2(z)$ for $z \sim 1$. We thus see that, when $|z| \ll 1$, the function $\alpha^2(z)$ can be described with the aid of perturbation theory [see (2.8)], whereas, for $z \gg 1$, the asymptotic behavior of $\alpha^2(z)$ is close to that indicated by (2.11). To describe the behavior of the polymer coil near the Θ point, we must also know the form of the function $\alpha^2(z)$ for $a \sim 1$.

There is a large number of published attempts to determine $\alpha^2(z)$ for the intermediate values of z. Most of them have been reviewed by Yamakawa.[17] However, all these conclusions are based on certain arbitrary and generally invalid assumptions and, as a rule, are incapable of describing the behavior of real polymers.

A purely pragmatic approach to this problem has been formulated by Domb and Barett.[36] They suggest that one should simply tabulate the universal function $\alpha^2(z)$ for some particular simple model, for example, the lattice model (cubic lattice). They then use the data obtained for this model as a basis for the following simple interpolation formula for $\alpha^2(z)$:

$$\alpha^5 = 1 + \frac{20}{3}z + 4\pi z^2. \tag{2.18}$$

Such an approach to the problem seems to be the most reasonable at present, and subsequent studies[37-38] have confirmed the validity of (2.18).

5) Analogy between the Θ point and the tricritical point. Within the framework of the above analogy between the polymer coil and the zero-component magnet, the Θ point turns out to be similar to the tricritical point.[39]

We shall not demonstrate this analogy in detail here, and will confine our attention to the following. In ordinary systems, the tricritical point (i.e., the point at which the line of second-order phase transitions goes over into the line of first-order phase transitions) corresponds to transitions from the developed fluctuational behavior to the thermodynamically stable behavior. The tricritical region, with the intermediate behavior of the system, occurs near this point. In the case of the polymer coil, the Θ region also corresponds to the transition from strong fluctuations in the coil surrounded by a good solvent to the thermodynamically stable globular state of the macromolecule (see Sec. 4). The asymptotic laws are then intermediate between the two regions.

In the three-dimensional case, the critical exponents near the tricritical points agree with the values obtained by the Landau self-consistent field method.[40] It follows

that, in the Θ region, the polymer chain is also correctly described by the self-consistent critical exponent. On the other hand, when $d = 3$, there are logarithmic corrections to the self-consistent behavior near the tricritical point. These corrections must also be introduced for the polymer in the Θ region.[41] Physically, they represent ternary collisions between chain segments.

3. VOLUME INTERACTIONS IN THE GLOBULAR STATE

A. Polymer macromolecule in a compressive external field

1) Formulation of the problem. At temperatures lower than those discussed in the last chapter, attractive forces begin to predominate in the volume interaction. The tenuous, highly fluctuating, polymer coil may then "condense on itself" and assume a dense and weakly fluctuating (i.e., in our definition, globular) conformation. This conformation is stabilized by the self-consistent compressive field due to the attractive forces between the monomers. (In contrast to the polymer coil, the idea of the self-consistent field is valid for the weakly fluctuating polymer globule, so that the theory of the polymer globule given below is of the self-consistent field type.)

The first step in the derivation of the self-consistent equations for polymer globules is to consider the problem of the polymer chain without volume interactions in an external compressive field $\varphi(\mathbf{x})$. The concepts formulated in the course of this turn out to be subsequently useful in the solution of the self-consistent field problem.

We note, by the way, that the solution of the problem of a polymer chain in an external compressive field is not only an important auxiliary step, but is frequently of physical interest in its own right. The compressive field is not necessarily a real physical field such as, for example, the electric field. It can be any effective thermodynamic characteristic reflecting the spatial inhomogeneity of the solvent, the presence of phase separation boundaries or inhomogeneous particles in it, and so on.

The equations for the polymer globules were first obtained by Lifshits[5] and a more rigorous derivation was given subsequently.[8] In this review, however, we have tried to achieve simplicity and brevity rather than rigor.

2) Partition function for a polymer chain without volume interactions in a compressive external field. Suppose that the zeroth link of the chain lies at the point η, whilst the N-th (final) link is at the point ξ. The partition function for the chain is then of the form [see (2.3)]

$$Z\begin{pmatrix} 0 & N \\ \eta & \xi \end{pmatrix} = \int \delta(x_0 - \eta)\, \delta(x_N - \xi) \prod_{j=1}^{N} g(x_j - x_{j-1}) \prod_{j=0}^{N} \exp\left(-\frac{q(x_j)}{T}\right) d\Gamma. \tag{3.1}$$

We now add the $N + 1$-th link to the chain, which gives us the recurrence relation

$$Z\begin{pmatrix}0&N+1\\ \eta& \xi\end{pmatrix} = \exp\left(-\frac{\varphi(\xi)}{T}\right) \int g(\xi-\xi')\, Z\begin{pmatrix}0&N\\ \eta&\xi\end{pmatrix} d^3\xi'. \tag{3.2}$$

The solution of this is the bilinear expansion[5]:

$$Z\begin{pmatrix}0&N\\ \eta&\xi\end{pmatrix} = \sum_k \Lambda_k^N \psi_k(\xi)\, \psi_k^*(\eta), \tag{3.3}$$

where ψ_k and Λ_k are the eigenfunctions and the corresponding eigenvalues of the equation

$$\hat{g}\psi = \Lambda \exp\left(\frac{\varphi}{T}\right)\psi. \tag{3.4}$$

where $\hat{g}$ is defined to be the integral operator

$$\hat{g}\psi = \int g(x-x')\,\psi(x')\, d^3x'. \tag{3.5}$$

If the largest eigenvalue of (3.4) belongs to the discrete spectrum, and is separated from the next eigenvalue by a finite gap, the corresponding term dominates (3.3). Next, using the symmetry of

$$Z\begin{pmatrix}0&N\\ \eta&\xi\end{pmatrix}$$

in η and ξ, we can readily show that, in this case,

$$Z\begin{pmatrix}0&N\\ \eta&\xi\end{pmatrix} \approx \Lambda^N \psi(\eta)\,\psi(\xi), \tag{3.6}$$

where Λ and ψ are the largest eigenvalue and corresponding eigenfunction of (3.4), respectively.

It is clear, that the partition function (3.6) has split into a product of factors. This means that, in the state with the discrete spectrum, the ends of the chain are statistically independent. This can be expected in the state in which the correlation length is much less than the size of the molecule, i.e., in view of the earlier definition (see subsection 1C), in the globular state. Consequently, we may conclude that the existence of the discrete spectrum in (3.4) signifies that the compressive field $\varphi(\mathbf{x})$ is so strong that it produces a globular structure.

By increasing the temperature, one can always ensure that φ/T in (3.4) is so small that the discrete spectrum in this equation is lost. Consequently, the external field can produce a globular state only when the temperature is low enough.

From (3.6), we find that the free energy in the state with a discrete spectrum is

$$F = -TN \ln \Lambda \tag{3.7}$$

where we have retained only thermodynamically additive terms proportional to N.

3) Density. The macroscopic state of a polymer globule will be defined by specifying the smooth density function $n(\mathbf{x})$. The smoothing volume ω is chosen as the smallest of the volumes within which fluctuations in the monomer number density are small in comparison with the density itself. By virtue of the definition of the globular state (see subsection 1C), the volume ω must be much smaller than the size of the macromolecule, so that it is meaningful to speak of a function $n(\mathbf{x})$ corresponding to a set of macrovariables.

The density $n(\mathbf{x})$ can be found as follows. It is clear from (3.6) that $\psi(\mathbf{x})$ is proportional to the probability density for finding the end link at $\mathbf{x}$. On the other hand, the function $n(\mathbf{x})$ is proportional to the probability of finding at $\mathbf{x}$ the link M that is well away from the end of the chain ($M \gg 1$, $N-M \gg 1$), since it is precisely such links that provide the main contribution to $n(\mathbf{x})$ for $N \gg 1$. We now introduce the quantity

$$Z\begin{pmatrix}0&M&N\\ \eta&\mathbf{x}&\xi\end{pmatrix},$$

i.e., the partition function for a chain with three fixed points. By writing this function in terms of the partition functions for the chains $(1, M)$ and (M, N), and applying the result (3.6) to them, we find that

$$n(\mathbf{x}) = \psi^2(\mathbf{x})\exp\left[\frac{\varphi(\mathbf{x})}{T}\right]. \tag{3.8}$$

The function ψ is normalized so that the coefficient in (3.8) is equal to unity and

$$\int n(\mathbf{x})\, d^3x = N. \tag{3.9}$$

For the state with the discrete spectrum, we can also evaluate the correlation function for the densities (1.14) at two macroscopically different points (in different smoothing volumes ω), and show that it goes to zero as $1/N$ as $N \to \infty$.[5,8] This finally demonstrates that the state with the discrete spectrum corresponds to the globular structure.

4) Configurational entropy. We shall now evaluate the configurational entropy $S\{n\}$ corresponding to the macrostate with fixed smoothed density $n(\mathbf{x})$. To do this, we write the free energy (3.7) in the form

$$F = -TN \ln \Lambda = E\{n\} - TS\{n\}, \tag{3.10}$$

where $E\{n\}$ is the energy of the monomers in the field $\varphi(\mathbf{x})$ that produces the density $n(\mathbf{x})$. It is clear that

$$E\{n\} = \int \varphi(\mathbf{x})\, n(\mathbf{x})\, d^3x \tag{3.11}$$

and, therefore,

$$S\{n\} = \int \left(\frac{\varphi}{T} + \ln \Lambda\right) n(\mathbf{x})\, d^3x. \tag{3.12}$$

Eliminating φ from (3.12) with the aid of (3.6) and (3.8), we have

$$S\{n\} = \int n(\mathbf{x})\ln\left(\frac{\hat{g}\psi}{\psi}\right) d^3x, \tag{3.13}$$

where $\psi(\mathbf{x})$ can be expressed in terms of $n(\mathbf{x})$, as follows:

$$\Lambda n(\mathbf{x}) = \psi(\mathbf{x})\hat{g}\psi. \tag{3.14}$$

The last two formulas determine the entropy of the macromolecule corresponding to the macrostate with the given density $n(\mathbf{x})$ whether or not this density has been produced by the external or the self-consistent field (field φ is not present in these two expressions). The particular value of Λ is unimportant for $S\{n\}$. This number only affects the normalization of the function ψ.

To establish the connection between (3.13) and the usual expression for entropy, we consider the limiting case in which all the monomers are localized by the field in a small volume of size $R \ll a$. We then have

$$\hat{g}\psi \approx g(0) \int \varphi(\mathbf{x})\, d^3x,$$

and hence (3.13)–(3.14) yield

$$S\{n\} = -\int n \ln\left(\frac{n}{e}\right) d^3x + N \ln g(0) + N \ln\left(\frac{N}{e}\right).$$

This has a simple interpretation. Since bonds do not

restrict the motion of the monomers within the limits of the small volume, the entropy of the system differs from the entropy of the Boltzmann gas (first term) by the presence of the additional terms which correspond to the factor $[g(0)]^N N!$ in the partition function. This factor is due to the N-fold return of the chain to the same point and the fixed numeration of the monomers in the chain.

The expression given by (3.13) will be needed later (in subsection B).

B. Polymer globule formed by the self-consistent field

1) Equation for the equilibrium density. Consider a polymer globule formed by the volume interaction, and suppose that the smoothed density in this globule is $n(\mathbf{x})$. The free energy corresponding to this smoothed density will be written in the form $F\{n\} = E\{n\} - TS\{n\}$, i.e., we shall isolate the entropy part (3.13). The quantity $E\{n\}$ will then describe the contribution of volume interactions to the free energy of the system and will play the role of the energy (although, of course, it is not equal to the usual energy).

The equilibrium function $n(\mathbf{x})$ can be determined by minimizing the functional $F\{n\}$ under the additional condition (3.9). Hence, the minimization equation has the form $\delta F/\delta n = \lambda$, where λ is an undetermined Lagrange multiplier.

The variational derivative $\delta S/\delta n$ can be readily evaluated when (3.13) and (3.14) are taken into account:

$$\frac{\delta S}{\delta n} = \ln \frac{\hat{g}\psi}{\psi}. \tag{3.15}$$

The Euler equation for the minimization of the functional $F\{n\}$ then assumes the form

$$\hat{g}\psi = \Lambda\psi \exp\left(\frac{\delta E/\delta n}{T}\right), \quad \Lambda = \exp\left(-\frac{\lambda}{T}\right). \tag{3.16}$$

If we now compare (3.16) with (3.4), we readily see that $\delta E/\delta\{n\}$ plays the role of the self-consistent field. Incidentally, when an external field is present and there is no volume interaction, $E\{n\}$ assumes the form given by (3.11) and (3.16) transforms directly into (3.4).

2) Self-consistent field. The next problem is, therefore, to find the self-consistent field $\delta E/\delta n$ that must be substituted into the equation for ψ instead of the external field $\varphi(\mathbf{x})$. We note that the field $\varphi(\mathbf{x})$ is the energy that must be expended in order to bring the test monomer from infinity to the point $\mathbf{x}$. In the case of the self-consistent field, this energy is obviously the chemical potential of the monomer less the component corresponding to the perfect gas.

A more rigorous analysis shows that,[5,8] when $r_0 \ll a$ [2] [we recall that r_0 is the characteristic range of the volume interaction potential $u(r)$], the self-consistent field $\delta E/\delta n$ can be expressed in terms of the chemical potential $\mu(n, T)$ of the set of broken links, i.e., a system of monomers interacting through the potential $u(r)$ but not

linked to one another:

$$\frac{\delta E}{\delta n} = \mu^*(n(\mathbf{x}), T) = \mu(n(\mathbf{x}), T) - \mu_{id}(n(\mathbf{x}), T), \tag{3.17}$$

where μ_{id} is the part of μ corresponding to the perfect gas, i.e., $\mu_{id} = T \ln n$. From (3.17), we have

$$E\{n\} = \int f^*(n(\mathbf{x}), T) d^3x, \tag{3.18}$$

where $f^*(n,T) = f(n, T) - f_{id}(n, T)$ is the free energy per unit volume of the set of broken links less the component corresponding to the perfect gas, $\mu^* = \delta f^*/\delta n$.

Lifshits and Grosberg[42] have shown how (3.17) is modified when the solvent molecules are explicitly taken into account. We shall not consider this point here and will merely note that the net result is that μ^* is replaced by μ^*_{eff}, which is a complicated and nonmonotonic function of temperature. However, the overall structure of the equations remains the same (see Sec. 1).

3) The complete set of equations for a globule. Substituting (3.17) in (3.16), we obtain

$$\hat{g}\psi = \Lambda\psi \exp\left(\frac{\mu^*(n)}{T}\right). \tag{3.19}$$

The functions n and ψ are related through (3.14). Taking (3.19) into account, we have

$$n = \psi^2 \exp\left(\frac{\mu^*}{T}\right). \tag{3.20}$$

Equations (3.19) and (3.20) taken together with the normalization condition (3.9) form the complete set of two equations and one additional condition for the determination of the two unknown functions n and ψ are the unknown number Λ.

The equilibrium free energy of the globule is

$$F = E - TS = \int \left[f^* - Tn \ln\left(\frac{\hat{g}\psi}{\psi}\right) \right] d^3x = -TN \ln \Lambda - \int p^* d^3x. \tag{3.21}$$

In this equation, in which (3.19) has been taken into account, $p^*(n, T) = p(n, T) - p_{id}(n, T)$ is the pressure of the set of broken links minus the perfect-gas component $p_{id} = nT$; $p^* = n\mu^* - f^*$.

Equation (3.19) is a nonlinear integral equation with a difference kernel [see (3.4)]. It is substantially simplified when the characteristic length over which there is a change in density in the system is large in comparison with a. Using the spherical symmetry of g together with (1.5)–(1.6), we obtain

$$\hat{g}\psi = \int g(\mathbf{y}) \left[\psi(\mathbf{x}) + \mathbf{y}\nabla\psi + \frac{1}{2}(\mathbf{y}\nabla)^2\psi + \dots \right] d^3y \approx \psi(\mathbf{x}) + a^2\Delta\psi. \tag{3.22}$$

In this case, therefore, the operator $\hat{g}$ in (3.19) can be replaced by $1 + a^2\Delta$, so that the equation becomes a second-order nonlinear differential equation.

C. Solution of equations for a large polymer globule

We shall now consider a method of solving (3.19)–(3.20) for the most important case of a large globule, i.e., a globule whose size R is much greater than a. When $r_0 \sim a$ (see Fig. 3), this condition is always satisfied for $N \gg 1$, whereas, for $r_0 \ll a$ (see Fig. 1a), the above inequality is valid provided the somewhat stronger condition $N \gg a^3/v$ is satisfied (we recall that $v \sim r_0^3$).

1) Nature of density distribution. It is clear that the equilibrium structure of the globule will consist of a

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[2] When $r_0 \sim a$, Eq. (3.17) is not, in general, valid but it can be used for qualitative purposes.[8] We shall therefore use the resulting equations in this case as well.

dense nucleus surrounded by a region of decreasing density which tends to zero at infinity (Fig. 4). When $|\mathbf{x}| \to \infty$, the density can either continuously decrease over distances $\sim R_0$ (Fig. 4a) or it may remain practically constant within the globule and then sharply fall on its surface (the characteristic length for this reduction is $l \ll R_0$; see Fig. 4b). We shall now consider which of these two cases occurs in reality.

We begin by considering the expression for $S\{n\}$ given by (3.13). Since the density varies smoothly in the system, we may substitute $\hat{g} \to 1 + a^2$ in (3.13). Using the same replacement in (3.14), where we can substitute simply $\hat{g} \to 1$, and eliminating ψ from (3.13)–(3.14), we obtain

$$S \approx -a^2 \int (\nabla n^{1/2})^2 \, d^3x. \tag{3.23}$$

It follows that, if the density varies as shown in Fig. 4a, we have $S \sim -Na^2/R^2 \sim -N^{1/3}(n_0 a^3)^{2/3}$, where n_0 is of the order of the monomer number density in the globule. If, on the other hand, n varies as shown in Fig. 4b, we have $S \sim -N/lR \sim -N^{2/3} n_0^{1/3} a^2/l$. In both cases, S is proportional to N to a power less than unity.

At the same time, the functional $E\{n\}$ [see (1.18)] is proportional to N, and this means that the leading approximation to the free energy for a long enough chain is

$$F\{n\} = E\{n\} - TS\{n\} \approx E\{n\} = \int f^*(n) \, d^3x. \tag{3.24}$$

Since this functional is local and does not contain derivatives, its minimum under the condition given by (3.9) will correspond to the step function shown in Fig. 4b. This function will be "smeared out" because of the neglect of the entropy terms in (3.24).

The density profile of a large globule is thus seen to take the form of the "smeared out" step function shown in Fig. 4b.

2. Volume approximation. To achieve a rough description of the structure of the globule, we may introduce the volume approximation in which the density profile is replaced by the sharp step function, i.e., we neglect the surface entropy terms. The density n_0 in the globule in this approximation corresponds to the minimum of (3.24), i.e., to the minimum of

$$F\{n\} = V_0 f^*(n_0) = \frac{Nf^*(n_0)}{n_0}, \tag{3.25}$$

where V_0 is the volume of the globule. Minimization yields the following condition for n_0:

$$p^*(n_0) = 0. \tag{3.26}$$

This condition is then used to determine the density at the center of the large globule. The free energy of this globule can be obtained from (3.21):
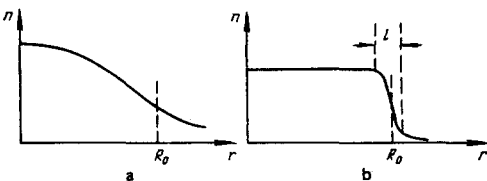
$$F = -TN \ln \Lambda = N\mu^*(n_0). \tag{3.27}$$

FIG. 4. Possible density profiles for a globule.

Condition (3.26) can also be written in the form

$$0 = -p^*(n_0) = f^*(n_0) - n_0\mu^*(n_0) = \int_0^{n_0} [\mu^*(n) - \mu^*(n_0)] \, dn. \tag{3.28}$$

The geometric interpretation of this condition is that the shaded areas in Fig. 5 are equal when this condition is satisfied. The free energy per particle corresponds to the intercept cut by the horizontal line on the ordinate axis.

3. Surface effects. If we do not neglect the entropy term in the free energy, we have to consider the question as to what is the density profile near the surface of the globule, i.e., we have to examine the smoothing out of the step function.

It will be convenient to introduce the parametrically defined function $v(\psi)$:

$$v(\psi) = \exp\left[\frac{\mu(n, T)}{2T}\right], \quad n = \psi v. \tag{3.29}$$

Equation (3.19) can then be written in the simple form

$$\hat{g}\psi = \Lambda v(\psi) \tag{3.30}$$

where we have used the fact that $\mu_{1d} = T \ln n$.

We note that, since $R \gg a$, the problem of evaluating the density profile is essentially one-dimensional. We now introduce the radial coordinate x ($x = 0$ for $R = R_0$) and replace $\hat{g}$ by $1 + (a^2 d^2/dx^2)$. Equation (3.30) then assumes the form

$$a^2 \frac{d^2\psi}{dx^2} = \Lambda v(\psi) - \psi. \tag{3.31}$$

This can be integrated easily, and the result is

$$x = -a \int_{\psi(0)}^{\psi(x)} \left[2 \int_0^\psi (\Lambda v(\psi) - \psi) d\psi\right]^{-1/2} d\psi. \tag{3.32}$$

It is readily verified that this result does, in fact, lead to the simple density profile shown in Fig. 4b. In particular, as $x \to \pm\infty$, we obtain the simple exponential asymptotic behavior

$$\psi(x)|_{x\to+\infty} \approx \text{const} \cdot \exp\left(-\frac{\vartheta_+ x}{a}\right), \quad \vartheta_+ = (\Lambda - 1)^{1/2}, \tag{3.33}$$

$$\psi(x)|_{x\to-\infty} \approx \psi_0 + \text{const} \cdot \exp\left(\frac{\vartheta_- x}{a}\right), \quad \vartheta_- = \left[\Lambda \left(\frac{\partial v}{\partial \psi}\right)_{\psi_0} - 1\right]^{1/2}.$$

By virtue of (3.27), the free energy of the globule, including the surface terms (3.21), can be written in the form

$$F = N\mu^*(n_0, T) - \int p^*(n) \, d^3x \tag{3.34}$$

since $p^* = 0$ at the center of the globule, the last term in (3.34) is proportional to the surface area of the globule, i.e., it is a kind of entropy surface tension. If we use $\sigma(T)$ to represent the corresponding surface tension, we have

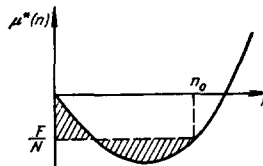$$F = N\mu^*(n_0, T) + 4\pi R_0^2 \sigma(T), \tag{3.35}$$

FIG. 5. Graphical determination of the density n_0 and free energy of a large globule in the volume approximation.

and, since the problem is essentially one-dimensional, we have

$$\sigma(T) = -\int_{-\infty}^{+\infty} p^*(n(x), T)\, dx. \tag{3.36}$$

It is now a relatively simple matter to calculate $\sigma(T)$ from the solution (3.32) of the problem of the structure of the surface. The result is

$$\sigma = aT \int_0^{\psi_0} \frac{2\int_0^\psi v(\psi)\,d\psi - v\psi}{[2(\psi_0 v_0)\int_0^\psi v(\psi)\,d\psi - \psi^2]^{1/2}}\, d\psi \tag{3.37}$$

and this gives σ explicitly in terms of the thermodynamic functions of the equivalent broken-link system. Simple estimates show that $\sigma \sim aT/v \sim (T/a^2)a^3/v$.

D. Other results for globular and similar structures

In this section, we shall give a brief review of other results obtained as a result of studies of polymer globules and other systems for which equations analogous to (3.19)–(3.20) are obtained.

1) If the temperature T is less than the critical temperature T_{cr} for phase separation in the system of broken links, there is a range of densities corresponding to absolutely unstable states of the system. It is natural to expect that the density in the globule never assumes values corresponding to this interval, i.e., the globule must take the form of a peculiar two-phase system with a sharply defined boundary between the core and the envelope.[6] We then have the problem of the additional boundary conditions that must be satisfied on the separation boundary. It turns out that these additional conditions are: a) continuity of chemical potential $\mu(n, T)$ across the boundary,[6] and b) continuity of the local pressure $p(n, T)$ across the boundary.[8] We note that the suggestion made by Lifshits and Grosberg[6] that the function p is not continuous across the boundary has turned out to be incorrect. An analysis of the structure of a globule with a density discontinuity has been given in previous papers.[6,8]

2) It is occasionally useful to consider the situation—at first sight extremely exotic—where the range of the potential $r_0 \sim v^{1/3}$ in the chain is so small (or a is so large) that not only $v \ll a^3$ but also

$$\frac{r}{a^3} \ll \frac{1}{N} \ll 1. \tag{3.38}$$

For $T < T_{cr}$, this kind of chain can form the so-called small globule,[6] the core of which occupies the volume $V_0 \ll a^3$ and is separated from the envelope by a sharp boundary.

The small globule is an advantageous formation because, firstly, the various effects connected with the polymer nature of the chain are then well defined and are, in fact, the leading effects (and not the secondary, surface effects as in the large globule). Secondly, the mathematical description of small globules is much simpler. This means that, whenever some particular effect is examined, it is best to begin with the case of the small globule which frequently turns out to be sufficient to achieve a qualitative understanding of the gen-

eral case as well. Examples of this can be found in the literature.[6,43–45]

The above device has been used[43,44] to investigate the interaction between a globule and a foreign solid particle. This may be regarded as a very approximate model of an enzyme-substrate complex.

Here, we shall confine our attention to a brief analysis of the structure of an isolated small globule. The decisive point is that the density and the ψ-function may be looked upon as constants within the confines of the small core of the globule, and equal to their boundary values n_- and ψ_-.

In view of the above boundary conditions, the two boundary densities n_- and n_+ may be regarded as known functions of temperature because they are equal to the densities of the coexisting phases of the system of broken links in equilibrium.

If, for simplicity, we neglect the volume interaction outside the core of the globule, we immediately obtain $n_+ = \psi_+^2$, $n_- = \psi_+\psi_-$ (so that ψ_- and ψ_+ are also known), whereas, outside the core, we have $n_{out}(x) = \psi_{out}^2(x)$.

The basic equation (3.19) can be easily rewritten in the form of a linear equation for ψ_{out}, and this eventually yields

$$\psi_{out}(x) = \frac{V_0(\psi_- - \psi_+)}{(2\pi)^3} \int \exp(-i k x) \frac{g_k}{\Lambda - g_k}\, d^3k. \tag{3.39}$$

To determine the constants V_0 and Λ, we must use the normalization conditions and $\psi_{out}(0) = \psi_+$. The final results can be easily shown to be

$$NQ(\Lambda) = n_+ a^3, \tag{3.40}$$

$$NP(\Lambda) = V_0(n_- - n_+),$$

where P and Q are uniquely determined by g:

$$P = \frac{J_1}{J_1 + J_2}, \qquad Q = \frac{J_1^2}{J_1 + J_2}, \tag{3.41}$$

$$J_q = \left(\frac{a}{2\pi}\right)^3 \int \left(\frac{g_k}{\Lambda - g_k}\right)^q d^3k.$$

The equilibrium free energy turns out to be

$$F = NT[P(\Lambda) - \ln \Lambda]. \tag{3.42}$$

The functions P and Q have been tabulated for the Gaussian core, and graphs of them can be found in a previous paper.[8]

3) The structure of a polymer globule formed by hydrogen-type bonds saturated in pairs was examined in an earlier paper.[7] It was found that, when the excluded volume of the monomer was small enough, the monomers were capable of forming bonds that were both relatively rare in the chain and bonds that were sufficiently strong, and the polymer chain formed a globule of volume a^3, for which the density profile could be evaluated exactly, i.e., one could find the exact solution of the corresponding nonlinear integral equation (3.19). Further details can be found in Ref. 7 (Sec. 2).

4) When equations such as (3.4) or (3.19) do not have a discrete spectrum, the inclusion of only the largest eigenvalue in the partition function (3.3) is not enough. When this is so, we can look upon N in (3.2) as a con-

tinuously varying quantity, and easily find the equation for Z:

$$\frac{\partial Z}{\partial N} + Z = \exp\left(-\frac{\mu^*}{T}\right)\hat{g}\,Z. \qquad (3.43)$$

Here, instead of the external field $\varphi(\mathbf{x})$, we have substituted the self-consistent field $\mu^*[n(\mathbf{x})]$. If the density profile $n(\mathbf{x})$ is a continuous function, we can substitute $\hat{g} \to 1 + a^2\Delta$ in (3.43) and this gives

$$\frac{\partial Z}{\partial N} = a^2\Delta Z - \left[1 - \exp\left(-\frac{\mu^*}{T}\right)\right]Z. \qquad (3.44)$$

This equation was used by Edwards[24] for the self-consistent solution of the excluded volume problem (Sec. 2, Subsection C, para. 1). The density in the coil is then small and $\mu^* \approx 2nBT$, where $B \sim v$ is the second virial coefficient for the interaction between the monomers in a good solvent. Equation (3.44) then assumes the form

$$\frac{\partial Z}{\partial N} = a^2\Delta Z - 2n\,BZ. \qquad (3.45)$$

This is the Edwards equation.[24] We note, however, that, as shown in Sec. 2, the self-consistent solution of the excluded volume problem cannot lead to an exact result.

5) The globular structure formed by a compressive external field has been examined[5] for a chain without volume interaction, and in the general case.[45]

In the case of the ideal chain, interesting results have been obtained for the case of an extended and deep potential well $\varphi(\mathbf{x})$. In this case, $\psi(\mathbf{x})$ is identical with the quantum-mechanical wave function for a particle of mass $\hbar^2/2T$ in the field $\varphi(\mathbf{x})$. This enables us to calculate the pressure exerted by the chain on the surrounding walls for a spherical well of both infinite[5] and finite[8] depth, and to analyze the pressure distribution over the surface of a nonspherical potential well.[46]

In the presence of repulsive volume interactions, the structure of the system for $Nv \ll V$, when all the monomers lie within the well V, is very different from the case where $Nv \gg V$, when the well contains only a relatively small number of monomers.[45]

6) An important example of the problem of a polymer chain in a compressive external potential field is that of the adsorption of a polymer on an attractive surface. The external field $\varphi(\mathbf{x})$ then consists of the impenetrable surface and a potential well localized on it. Equation (3.4) (usually with $\hat{g} \to 1 + a^2$) is well known in adsorption theory[8,27,47,48] (see also the references in Refs. 27 and 48).

We note particularly the paper by de Gennes.[48] This not only provides a review and a simple derivation of the results of the self-consistent field theory as applied to the adsorption problem, but also gives a qualitative discussion of the scaling corrections which must be taken into account because of the presence of developed fluctuations in a broad adsorption layer (in the case of weak adsorption[48]).

7) Problems that are particularly close to the theory of globules arise in the analysis of separation boundaries between immiscible polymer materials in a block, and also the phase separation boundary in a polymer solution. The theory of such inhomogeneous polymer

systems has been substantially advanced in recent years, mainly as a result of the work of Helfand et al.[49,50-53]

It is clear that the polymer macromolecules in such systems are located in the inhomogeneous self-consistent field of the other macromolecules, so that we have equations such as (3.19). As a rule, such systems are weakly fluctuating, so that correlations between the ends of the chain are split, and ψ is independent of N.

Since problems on separation boundaries are one-dimensional, the substitution $\hat{g} \to 1 + (a^2 d^2/dx^2)$ is made in (3.19). Helfand et al.[50-53] have treated, essentially, the solution of this type of equation. An analysis of the results is given in Ref. 49.

8) Another important example of the application of equations of the same type is the theory of block copolymers of the form $A - A - \ldots - A - B - B - \ldots - B$, the block components of which are immiscible.[49,54-56] The block components will tend toward phase separation and this will be impeded by the presence of chemical valence bonds between A and B. The result is the appearance of a microdomain structure with one-, two-, or three-dimensional periodicity, depending on the relative length of the two blocks.[49]

It is clear that the theory describing this microdomain structure must operate with equations such as (3.19). Periodic boundary conditions[54] are imposed on these equations and this substantially modifies the nature of their solution. We shall not go into the details of this interesting problem, the theory of which is not, in our opinion, anywhere near completion. Readers interested in specific derivations and preliminary results are referred to the literature.[54-56]

4. THEORY OF THE COIL-GLOBULE TRANSITION

A. Formulation of the problem

The theories of the globular and coil states were discussed in the preceding chapters independently of each other. In this chapter, we consider the theory of the coil-globular transition in the homopolymeric macromolecule.

This problem arose historically in connection with the denaturation of a protein globule. It is well known that this is a rapid cooperative transition with a well defined heat effect. The question was whether this cooperative denaturation was a feature of the highly specific structure of the protein globule or whether the rapid coil-globule transition could be observed in any, including the homopolymeric, macromolecule. This formulation of the problem attracted considerable attention to the coil-globule transition and considerable literature is now devoted to it.

We recall that the definitions of coil and globule, and the terminology used to describe the phase transition in a finite system, are given in Subsection C of Sec. 1.

We start by stating the basic assumptions of the theory of the coil-globule transition. In the last section, we investigated the structure of a polymeric globule and

found its configurational free energy F. It is easily seen that this free energy was expressed as an increment on the free energy of an ideal coil without volume interactions. Consequently, the coil-globule transition point can be found directly from the condition $F = 0$.[3]

The transition width can be estimated as follows. According to the foregoing theory, the globular state corresponds to the splitting of correlations in (3.1). It is readily seen that the condition for the segregation of the main term (3.6) of the bilinear series is $|F| \gg T$. This means that the higher eigenfunctions which modify the fluctuation state must be included in the region $|F| \lesssim T$. The width of this region is, in fact, the transition width ΔT:

$$F(T_c) = 0, \qquad |F(T_c - \Delta T)| \sim T \ll NT. \tag{4.1}$$

B. Coil-globule transition in a long chain

1) Volume approximation. We begin by considering the volume approximation in which, according to (3.27), we have $F = N\mu^*(n_0)$. Consequently, in this approximation, the transition temperature can be determined from the condition $\mu^*(n_0, T_c) = 0$.

The most realistic form of the function $\mu^*(n, T)$ is shown in Fig. 5 (the alternative graph is shown in Fig. 9 and will be discussed in Subsection D). The transition temperature T_c can be determined graphically from the condition that the horizontal cutting line coincides with the abscissa axis. It is clear from Fig. 5 that, as $T \to T_c$, the density n_0 in the globule tends to zero. This enables us to use the following virial expansions for the thermodynamic functions near T_c:

$$\mu^* \approx 2nTB(T) + 3n^2 TC(T), \tag{4.2}$$

$$p^* \approx n^2 TB(T) + 2n^3 TC(T),$$

and hence achieve a universal description of the transition in terms of the second and third virial coefficients for the interaction between monomers, B and C.[4]

The expansions given by (4.2) readily yield explicit formulas in the volume approximation. The core density is given by

$$n_0 = -\frac{B}{2C} \qquad (p^*(n_0) = 0), \tag{4.3}$$

the free energy of the globule by

$$F = -\frac{NTB^2}{4C}, \tag{4.4}$$

and, according to (3.27),

$$\Lambda = 1 + \frac{B^2}{4C}. \tag{4.5}$$

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[3] This condition will still be satisfied even when volume interactions are present in the coil at the point of transition because F is proportional to N and the difference between the free energies of two coils is proportional to N^α ($\alpha < 1$) since the monomer number density in the coil is small.

[4] Of course, these virial coefficients must be renormalized because the monomers are linked in a chain, so that we must write B^* and C^* but the asterisks will be omitted in this section for simplicity. The renormalization of the virial coefficients in the theory of polymeric globules is discussed in Ref. 8.

All this also readily yields the radius of the globule: $R = (3N/4\pi n_0)^{1/3}$.

It is clear that $F = 0$ when $B = 0$. Thus, in the volume approximation, the coil-globule transition temperature T_c coincides with the Θ point. The coefficients B and C can be written in the following form near the Θ point:

$$B(T) \approx \frac{b(T - \Theta)}{\Theta} = b\tau, \tag{4.6}$$

$$C(T) \approx C > 0.$$

We now see that $F \sim -\tau^2$, i.e., in the volume approximation, the coil-globule transition is a second-order phase transition.

2) Inclusion of surface terms. The above analysis does not, however, take into account surface effects which are very important near the transition point. As a matter of fact, as $T \to \Theta$, Eq. (4.5) shows that $\Lambda \to 1$, i.e., the width $\sim a/(\Lambda - 1)^{1/2}$ of the surface layer increases [see (3.33)]. The formula given by (3.37) also predicts that, when T approaches Θ,

$$\sigma \approx \frac{aB^2 T}{8C^{3/2}}. \tag{4.7}$$

Consequently, the total free energy (3.35) becomes

$$F = -NT \frac{b^2}{4C} \tau^2 \left[1 - \left(\frac{\tau_c}{|\tau|} \right)^{2/3} \right], \tag{4.8}$$

$$\tau_c = 1 - \frac{T_c}{\Theta} = (18\pi)^{1/2} \frac{a^{3/2} C^{1/4}}{bN^{1/2}}. \tag{4.9}$$

The point T_c is the coil-globule transition point because $F(T_c) = 0$. We note that it is precisely at the point T_c that the radius R of the globule and the thickness of the surface layer $a/(\Lambda - 1)^{1/2}$ become equal to within an order of magnitude. This means that the negative volume and positive surface parts of the free energy become equal at this point. As indicated by the volume approximation, the transition point tends to the Θ point as $N \to \infty$, and $\tau_c \to 0$.

We shall now use (4.1) to determine the transition width. It is readily seen that

$$\Delta T \sim \frac{(\Theta - T_c) C^{1/2}}{a^3} \sim \frac{\Theta C^{3/4}}{a^{3/2} b N^{1/2}}. \tag{4.10}$$

As $N \to \infty$, it is clear that $\Delta T \to 0$. Consequently, according to Subsection C of Sec. 1, the coil-globule transition is a phase transition. When $C^{1/2} \ll a^3$, we have $\Delta T \ll (\Theta - T_c)$: the transition occurs at the point T_c and the narrow transition region is clearly separate from the Θ point. When $C^{1/2} \sim a^3$, the transition smears out and includes the Θ point.

If v is the characteristic volume of the monomer, we have the following order of magnitude expressions for the usual potentials (see Fig. 2): $b \sim v$, $C \sim v^2$, i.e., $C^{1/2}/a^3 \sim v/a^3$. Consequently, the above dependence of the nature of the transition on the quantity $C^{1/2}/a^3$ is really determined by whether $v \ll a^3$ (see Fig. 1a) or $v \sim a^3$ (see Fig. 3). The formulas given by (4.9) and (4.10) can be written in the following form in terms of v and a^3:

$$\tau_c \sim \left(\frac{a^3}{Nv} \right)^{1/2}, \qquad \Delta T \sim \Theta \left(\frac{v}{a^3 N} \right)^{1/2}.$$

It is clear from (4.8) that the character of the transition is somewhat unusual. When $1 \gg |\tau| \gg \tau_c$, F is proportional to τ^2 and the system behaves in a way characteristic of a second-order phase transition, namely,

the density (4.3) gradually decreases and the globule spreads out (R increases). However, within the minis-cule region near the transition point, $|\tau| - \tau_c \ll \tau_c$ and the behavior of the system changes. In this region,[5] we have $F \sim -(T_c - T)a^3/C^{1/2}\tau_c$. This type of dependence on $T_c - T$ is typical for first-order transitions but, in fact, we have a second-order transition because the coefficient in front of $T_c - T$ is proportional to $N^{1/2}$ and not to N, i.e., the heat of the transition per monomer

$$\frac{\Delta Q}{N} = \left(\frac{\pi}{2}\right)^{1/2}\Theta\frac{a^{3/2}b}{C^{3/4}N^{1/4}} \sim \Theta\left(\frac{a^3}{Nv}\right)^{1/2} \qquad (4.11)$$

tends to zero as $N \to \infty$.

The density in the globule at the transition point is

$$n_g = \left(\frac{\pi a^3}{2C^{3/4}N}\right)^{1/3} \sim \frac{1}{v}\left(\frac{a^3}{Nv}\right)^{1/2}, \qquad (4.12)$$

i.e., the dependence on N is such that the globule dens-ity falls to a value of the order of the coil density at the transition point. On the other hand, the binary vol-ume interaction parameter z in a coil at the transition point is $z \sim N^{1/2}B/a^3 \sim C^{1/4}a^{-3/2} \sim (v/a^3)^{1/2} \ll 1$. Conse-quently, for the case $v \ll a^3$ which we are discussing (see footnote 5), the coil can be looked upon as Gaus-sian at the transition point with density $n_c \sim a^{-3}N^{-1/2}$. The relative change in the density during the transition is

$$\frac{n_g - n_c}{n_c} \sim \left(\frac{a^3}{v}\right)^{3/2}. \qquad (4.13)$$

It follows that, as $N \to \infty$, the density increases only by a finite factor at the transition point, and the number of contacts made is relatively small. Further reduction in the temperature is accompanied by a gradual in-crease in the density of the globule, tending to close packing: $n \sim 1/v$ (for which the entire free solvent is displaced from the globule).

Even when $v \sim a^3$, Eq. (4.12) and extrapolation of the above transition characteristics obtained for $v \ll a^3$ show that a gradual transition from the globular to the coil state occurs in this case in the region around the Θ point of width $\Delta T \sim \Theta/N^{1/2}$. This transition can be naturally identified with a second-order transition.

Figure 6 shows the mean densities for $v \ll a^3$ and $v \sim a^3$ as functions of temperature. The reason for the difference between these two cases is essentially that the free energy has two minima in the space of the macrovariables when $v \ll a^3$, and the probability func-tion for the system is "pumped through" from one min-imum into the other during the transition. On the other hand, when $v \sim a^3$, there is only one such minimum, and the minimum is gradually displaced from the globular to the coil region during the transition. In accordance with the terminology described in Subsection C, the coil-globule transition for $v \ll a^3$ is a first-order tran-sition, whereas the transition corresponding to $v \sim a^3$ is a second-order transition.

3) Coil-globule transition in the persistent model.

[5]This form of the free energy is meaningful only if $|F| \gg T$ in this region since, otherwise, we would have to take into ac-count the contribution of coil states. The necessary condition in this case is $a^3 \gg C^{1/2}$ of $v \ll a^3$, which we shall assume un-less stated to the contrary.
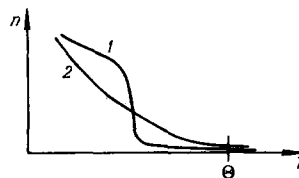
FIG. 6. Temperature dependence of mean density within the limits of a macromolecule in the region of the coil-globule transition: $1 - v \ll a^3$, $2 - v \sim a^3$.

We have seen in Sec. 2 that, because the monomer num-ber density within the coil is small, its properties are universal, i.e., results obtained for the standard model can easily be converted to the results for any other model, including the persistent model. Formally, this was ensured by the fact that the macroscopic charac-teristics of the polymer coil depended only on the single parameter B connected with the volume interactions.

Conversely, the monomer number density in the poly-mer globule, considered in Sec. 3, is not in general small, so that the results obtained in that section are valid only within the framework of the standard model.

We shall show in this section that the globule density becomes very small near the transition point, so that it is natural to expect a degree of universality, i.e., model independence, for the coil-globule phase transi-tion picture as well. However, in this case, universal-ity involves two parameters connected with the volume interaction, which correspond to B and C in the stand-ard model.

It was pointed out in Subsection B of Sec. 2 that the second virial coefficient for the interaction between cylinders of thickness d and length l $(B \sim dl^2\tau)$ could be taken as an estimate for B in the persistent model. It is natural to suppose that the third virial coefficient for the interaction between such cylinders can be taken as an estimate for C. This yields $C \sim d^3l^3\ln(l/d)$ (see Ref. 57). These expressions for B and C must then be sub-stituted in all the formulas of this subsection to esti-mate the characteristics of the coil-globule transition in the persistent model.[6] In particular, it is readily seen that the transition picture for $v \ll a^3$ corresponds to $p = l/d \gg 1$ (stiff chain) in the persistent model; $v \sim a^3$ corresponds to $p \sim 1$ (flexible chain).

4) Conclusions.

a) When $v \ll a^3$, or when the chain is stiff, the coil globule transition is a rapid first-order phase transi-tion with a finite density change (4.13), which lies just below the Θ point (4.10). However, in some ways, this transition is close to a second-order transition, for example, the heat of transition (4.11) is small.

b) When $v \sim a^3$, or in the case of a flexible chain, the coil-globule transition is similar to a gradual second-order phase transition extending throughout the Θ re-gion.

[6]This will, naturally, yield the correct estimates but only for the isotropic globular phase. The possibility of liquid-crys-tal order in the globule must be considered separately.

C. Conditions for the existence of globules in solution

The main difficulty in the experimental verification of the coil-globule transition in homopolymer solutions is the fact that the polymers precipitate out below the Θ point. This results in a gain in the free energy because of the reduction in the area of contact between the globular phase and the pure solvent ($\sim \sigma R^2$). However, there is an attendant loss in the free energy associated with the relative motion of the globules per macromolecule, $\sim T \ln(n_0/c)$, where c is the mean concentration of the monomers in solution (since N/n_0 is the volume of the globule and N/c is the volume per globule in the solution, we find that n_0/c is the fraction of volume occupied by globules in the solution). Consequently, precipitation does not occur [see (4.7) and (4.3)] if

$$\left| \ln \frac{cv}{\tau} \right| \gtrsim N^{2/3} \left(\frac{a^3}{v} \right)^{1/3} \tau^{4/3} \qquad (4.14)$$

In particular, precipitation at the transition point will not occur [see (4.9)] if

$$\left| \ln c \left(\frac{N C^{1/2}}{a^3} \right)^{1/2} \right| \gtrsim \frac{a^3}{C^{1/2}}. \qquad (4.15)$$

It is clear that the more sharp the transition, the smaller the parameter v/a^3, the more stringent is the condition imposed on the concentration c of the solution which ensures that the globules are formed and do not precipitate. Hence, the main difficulty for the experimental verification of the above transition is that the various effects to be observed in the case of very dilute solutions are very weak.

The formulas given by (4.9) and (4.14) define the region of existence of homopolymeric globules in solution. Figure 7 shows the state diagram for a polymer solution on the T, c plane. The shaded region corresponds to the existence of globules in solution.

D. Other possible intramolecular phase transitions

1) The function $\mu^*(n)$ may have several extrema at low temperatures and these may be connected, in particular, with the presence of different phases in the system of separate monomers.

When additional extrema are present, the equation given by (3.26) for the density n_0 in the globule may have a number of solutions. These solutions correspond to globules with different core densities and different free energies, $N\mu^*(n_0^{(1)})$ and $N\mu^*(n_0^{(2)})$. If the difference between these energies changes sign as a result of a change in temperature, we have a first-order globule-globule phase transition connected with a rearrangement in the structure of the core. The situation illustrated in Fig. 8 corresponds to the transition point.
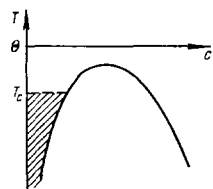

FIG. 7. Simplest state diagram for a polymer solution. Shaded region corresponds to the existence of isolated globules in solution.
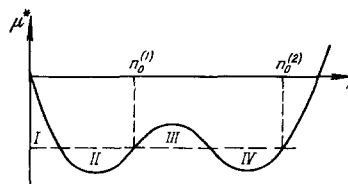

FIG. 8. Graph of $\mu^*(n)$ at the globule-globule transition temperature (area I is equal to area II, and area III is equal to area IV).

2) Another possibility is that when the function $\mu^*(n)$ has the form shown in Fig. 9. Here, the coil-globule transition takes place for $T_c > \Theta$, as may be seen from the figure, and the density in the globule is very high at the transition point ($n_0 \sim 1/v$). The transition itself is a rapid cooperative first-order transition. It is possible that the denaturation of a protein globule occurs through an analogous mechanism.

3) At sufficiently low temperatures, when a density discontinuity occurs on the surface of the globule, another type of transition takes place, namely, the so-called globule-with-fringe to globule-without-fringe transition,[6] which is a first-order transition in which all the monomers in the chain condense into a dense "drop" without a gaseous envelope of any kind.[6]

4) For a small globule (see Sec. 3, Subsection D, para. 1), the coil-globule transition takes the form of a rapid first-order phase transition well below the Θ point. When the small globule appears, the density undergoes a large discontinuity, reaching a value corresponding to the expulsion of the solvent.[6,8]

5) If the polymer chain is stiff enough, and if the attractive forces between chain segments are strong enough, orientational ordering in the macromolecule, i.e., the appearance of liquid crystal structure, becomes possible. The conditions for the appearance of macromolecules with orientational order, and their properties, are outside the scope of the present review and will be examined elsewhere.

6) The formation of a globular structure from a chain without volume interactions under the influence of a compressive external field was described in a previous paper,[5] where it was shown that the corresponding phase transition was a second-order transition.

In particular, adsorption of a coil when attraction to the surface can be reduced to a potential field is also a second-order phase transition. On the other hand, if the interaction between the polymer chain and the surface cannot be described in terms of a potential field, for example, the adsorption of macromolecules with nonalternating dipole moments by a charged surface,[58]
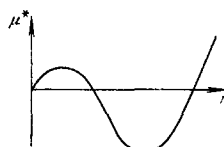

FIG. 9. Example of the function $\mu^*(n)$ for which the coil-globule transition is a first-order phase transition.

the adsorption process can also occur as a first-order transition. We draw attention to the fact that Skvortsov et al.[59,60] have analyzed the effect of chain stiffness on adsorption which is, in effect, outside the framework of the standard model. It turns out that, although the adsorption process remains a second-order phase transition as the stiffness increases, the jump in the specific heat and T_c both increase.

7) The formation of a globular structure from a chain with a repulsive volume interaction under the influence of an external compressive field was discussed in a previous paper.[45] It was found that the introduction of this volume interaction affected neither the temperature nor the type of the transition, and there was only a change in the jump in the specific heat. In particular, this result is valid in the case of adsorption.

8) The adsorption of globules was discussed by Grosberg,[61,62] who constructed the state diagram on the (T, φ_0) plane, where φ_0 is the depth of the surface potential well.

E. Comparison with the results of other approaches and with laboratory and computer experiments

As already noted, there is considerable literature devoted to the determination of the characteristics of the coil-globule transition.

1) Theoretical approaches. As far as we know, the first attempt at a theory of the coil-globule transition is due to Ptitsyn and Éĭzner.[63] This was subsequently developed further by Éĭzner.[64] A similar approach to this problem was developed by de Gennes.[39] These papers were based on a modification of Flory's method for the determination of the expansion coefficient α^2, but allow an examination to be made of the region $\alpha^2 < 1$. It was concluded[39,64] that, for small v/a^3, a sharp conformational transition occured below the Θ temperature, whereas, for $v/a^3 \sim 1$, the transition was more gradual. This conclusion agrees with our analysis. However, the approach adopted in Refs. 39 and 64 will not yield more detailed information on the nature of the transition.

Oono[20] has shown rigorously that $\langle R^2 \rangle \sim N^{2/3}$ is always the case when $T < \Theta$ as $N \to \infty$. Saito et al.[65] have shown that $T_c \to \Theta$ as $N \to \infty$. All these conclusions are also predicted by the theory given above.

Massih and Moore[66] have discussed the lattice model of a polymer chain with volume interactions in which the chain is represented by a random walk on a "Bethe cactus" type lattice for which an exact solution can be obtained. It was found that a second-order phase transition existed for this model at a certain temperature. However, this model represents the polymer chain not in ordinary three-dimensional space but rather in an infinite-dimensional space.[67] Therefore the result obtained is not related to the usual coil-globule transition.

In a recent paper, Moore[67] reported an attempt to construct a theory of the coil-globule transition which is essentially analogous to our theory[7] (see above). However, Moore noted correctly right from the start

that the phase transition as such could occur only for infinite N and did not proceed to the discussion and classification of conformational transitions for finite N. It seems to us that this approach is unsuitable in the case of macromolecules in which the number of monomers is not all that large (10^4-10^5). Our terminology (see Introduction, Subsection C) seems physically more reasonable for such systems. When applied to the coil-globule transition, Moore's approach has led to an essentially incorrect result, namely, that the coil-globule transition is always (even for $v \sim a^3$) a second-order transition.

2) Computer experiments. We now consider the results obtained for the coil-globule transition in the lattice model (Fig. 1b) of the polymer chain obtained by the Monte Carlo method on a computer.

The most complete investigation of the coil-globule transition by this method was reported in a series of papers by Kron et al.[68-70] This work differs from other similar computer experiments in that a study was made of the transition characteristics as functions of the chain stiffness. The basic conclusion was that the coil-globule transition occurred in stiff chains in the form of a rapid first-order transition whereas, in flexible chains, it took the form of a more gradual transition that was not of the first order. These results are generally in agreement with other theoretical predictions. However, some of the theory is insufficient for detailed comparisons because, in many of the cases examined on the computer,[68-70] the coil-globule transition turns out to be closely related to intramolecular orientational ordering which is outside the framework of the standard model. A comparison of the results of numerical experiments[68-70] with the theory of the intramolecular liquid crystal phase will be given elsewhere.

Domb[71] used an analysis of computer data as a basis for the proposal that the coil-globule transition was always a first-order transition occurring at a certain critical temperature $T_c < \Theta$ (as $N \to \infty$). This conclusion appears to be due to an incorrect extrapolation of computer data.

Finsy et al.[72] have concluded that a first-order phase transition occurs at a temperature T_c much smaller than Θ in the case of a chain simulated on a cubic lattice.

If more detailed analyses confirm this conclusion, this will mean that the globule-globule type transition described in para. 1 of Subsection D of this section occurs for this type of chain.

3) Experiments with real macromolecules. As already noted, the main difficulty in experiments designed to verify the coil-globule transition is that one has to work with low concentrations of the polymer in solution. The picture is distorted by polydispersion, the presence of defects, branching, and so on. The polymers must therefore be carefully prepared. Studies of the conformation of such "pure" polymer chains below the Θ point began only relatively recently, using the well-studied system of polystyrene in cyclohexane.[73,74] It was found[74] that, when the temperature was reduced by 1.5° below

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the Θ point, the coefficient α^2 of the polymer chain ($N = 4.5 \times 10^5$) fell by a factor of three. This system was also studied by Nierlich et al.,[75] who used small-angle neutron scattering. Collapse was observed at 19° below the Θ point. Its width was ~1° and the expansion factor of the coil at the transition point was about 0.9. The density was found to increase linearly with temperature below the transition point. These data are, in general, in agreement with the above results.

Various conformational transitions in the neighborhood of the Θ point have frequently been reported in the literature and are occasionally identified with the coil-globule transition. However, in each specific case, the reality of the alleged coil-globule transition requires thorough examination and, in particular, one must be sure that the intermolecular interaction is small in comparison with the intramolecular interaction. Analysis of such experiments is beyond the scope of this review.

In conclusion, we may say that the present-day theory of volume interactions in polymer systems provides a qualitatively correct description of homopolymeric macromolecules in sufficiently simple situations, and can be used as a basis for further more realistic approximations.

Biopolymers must be particularly noted. From the physical point of view, their main distinguishing feature is the heterogeneity of primary structure. It follows that the theory developed for a homopolymer is not directly applicable to biopolymers. On the other hand, this theory may, firstly, facilitate the formulation of new questions relating to biopolymers and, secondly, it may lay claim to be useful in the description of properties that do not depend on the details of the primary structure.

However, it is not as yet clear as to whether there are some properties of a biomacromolecule that are insensitive to variations in its primary structure. Biological activity itself is, of course, due precisely to the unique primary structure which leads to an equally unique spatial (ternary) structure. Hence, studies of the biological functioning of macromolecules (for example, in the course of enzyme reactions) must be based on fundamentally new formulations of the various questions. Lifshits and Grosberg[6] have mapped out some of the possible approaches to these problems.

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