Some problems of the statistical physics of polymer chains with volume interaction

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The present state of the theory of volume effects in a polymer chain is reviewed. The theory of coils (i.e., chains with predominately repulsive volume interaction of monomers) and the analogy between the excluded volume problem and the theory of second-order phase transitions are briefly described. The theory of globules, formed by attractive interaction of monomers or by external attractive fields, is considered in greater detail. The coil-globule transition under various conditions is analyzed. A theory is constructed for the simplest model of the polymer chain—the model of "interacting beads on a flexible string." The connection of this model with more realistic ones is discussed. This review is based on the approach proposed by I. M. Lifshitz in 1968. While attention is focused on the physical aspects of the problems, some questions concerning biological applications are discussed in the conclusion.

CONTENTS

I. INTRODUCTION

A. Scope and aim of the work

Polymer physics is one of the youngest fields of the physics of condensed matter. It began to develop in the 1930's under the influence of chemical and biological applications. Soon it was realized that a large number of problems in polymer physics can be formulated directly for the individual polymer chain, which is considered simultaneously as a molecule and as a macroscopic system (macromolecule). Research into the nature of the chain flexibility and the methods of the physics of one-dimensional systems (one-dimensional Ising model) led to a great number of impressive advances, from the explanation of rubber elasticity to the creation of the theory of helix-coil transitions in proteins and nucleic acids.

An exhaustive review of the methods and results of this stage of the theory can be found in the well-known books by Flory (1953), Volkenshtein (1959), Birshtein and Ptitzyn (1964), and Flory (1969).

It is hard to consider as accidental the fact that, in the next stage of the theory, difficulties appear which are similar to those occurring in other fields of physics—because these problems are related to each other. We refer here to the problem of interactions which are not weak and which can not be considered in the framework of perturbation theory. In the polymer context this is the problem of accounting for interactions of segments far apart along the chain, which approach each other due to the chain flexibility. These so-called volume interactions determine the three-dimensional spatial organization of a polymer chain and are responsible for a large number of various phenomena. The best-known and most shining example of this kind is the phenomenon of enzyme catalysis.

In this article we attempt to develop the simplest theory of the spatial structure of a polymer chain with volume interaction. We do not discuss the applicability of this theory to any specific polymer; our efforts are concentrated on analyzing its basic features. Assuming that our readers will be primarily physicists, we use physical terminology and apparatus and discuss only the physical aspects of the problems. No earlier special knowledge of polymer physics or chemistry is expected; the next sections of the introduction present the necessary information briefly.

B. The polymer chain as a statistical system

1. Linear memory

Linear polymer molecules are extremely long chains formed from low-molecular-weight monomer units, as a result of a chemical reaction. The molecular weights of polymer chains can reach ~10^7-10^9 (in the case of DNA, for example), while the molecular weight of monomers is usually ~10^2. Clearly such a large system can be described in several respects as a statistical-thermodynamical one.

It must be noted that in the majority of cases the primary (chemical) structure of a polymer chain can be considered as fixed—in these cases there is no destruction of the chain. (For example, in the living cell the synthesis of the protein is separated from its biological functioning). This means that the equilibrium state of a polymer chain is in fact a state of partial equilibrium with a fixed linear memory. In other words, each segment of the chain has a definite number in the sequence of monomers in the chain, and this sequence is fixed.

The general method of describing partial equilibrium states is to select regions in the phase space and to attribute suitable weights to them. In this case the role of weights is played by the conditional probabilities $g_j(\alpha_j, \alpha_{j+1})$ of finding the $(j+1)$th link in the state α_{j+1}, provided the jth one is in the state α_j. The matrices $g_j(\alpha_j$ and α_{j+1} are the matrix indices) give a complete phenomenological description of the primary structure of the chain, i.e., of the linear memory.

Thus the Gibbs distribution for the chain has the form:

$$\rho(\Gamma) = \exp\left(\frac{F - E(\Gamma)}{T}\right) \prod_{j=1}^{N} g_j \,. \tag{1.1}$$

Here Γ is a point in the configurational space of the chain, $E(\Gamma)$ is the energy of the configuration (besides the energy of longitudinal bonds, already taken into account by the correlations g), F is the free energy of the system, and N is the number of links.

2. Flexibility and volume interactions

Thermal motion in macromolecules at the usual temperatures produces small deformations of valent bonds and angles and causes rotamerization, i.e., rotation around the single σ bonds. It is clear that for long molecules such fluctuations will lead to significant changes in the mutual spatial arrangement of atoms which are far from each other along the chain. If the temperatures are not too high the long wave variations are dominant; thus the chain can be interpreted as an elastic filament (the so-called persistent model). It is easy to show that in this model the mean value of cosine of the angle θ between the two parts of the chain, separated along the chain by a sufficiently large distance l, is

$$\langle \cos\theta(l)\rangle \sim \exp(-l/\tilde{l}) . \tag{1.2}$$

The so-called persistent length $\tilde{l}$ is an important characteristic of the chain stiffness. Its meaning is as follows: the part of the chain shorter than $\tilde{l}$ can be interpreted as a practically rigid rod, while the different $\tilde{l}$ segments can rotate practically independently for each other. In this sense the flexibility of extremely long chains can be considered.

It is important to bear in mind that the basic mechanism of chain flexibility is rotation around the single σ bonds of the main chain. This enables one to formulate the rotational-isomeric approximation (Volkenshtein, 1959), which allows one to undertake effective calculations for specific chains.

From Eq. (1.2) it is clear that a long polymer chain never takes a rectilinear conformation. The irregular occasional bending produces the conformation of an entangled coil.

Obviously, monomers which are distant from each other along the chain can approach and touch each other in space. In this case the forces of volume interaction are acting between these monomers. These forces differ essentially from the interactions between adjacent segments. It is the energy of volume interactions that appears as $E(\Gamma)$ in Eq. (1.1).

Interactions between monomers which are distant from each other along the chain (covalent or hydrogen bonds, vanderWaals or multipole forces, etc.) are essentially the same as those acting between the atoms of a real gas. These interactions include the strong repulsion on the scale $r_{\rm rep}$ of atomic distances which makes it impossible for two monomers to occupy the same place in space, i.e., the so-called excluded volume effect, and the weaker attraction on the larger distance scale $r_{\rm attr}$.

In order to establish relations which will increase our fund of knowledge about the real gases we shall often consider as a suitable representation of a given volume interaction, the thermodynamic functions of the system of monomers which are not adjacent in the chain, but which interact with the forces of volume interaction. We shall call this system the gas of separate monomers.

3. Formulation of the "beads on a string" model

The general analysis of the distribution (1.1) is very complex. In order to analyze its main specific features it is useful to simplify considerably the set of variables characterizing the state of a link. More precisely, we shall consider the model of a chain in which each link can be represented as a material point, i.e., its state is completely defined if its position in space is given. An illustrative sample of such a system is an elastic flexible string on which beads are strung (Fig. 1).

The correlations in this model are represented by a single function, which describes the elastic properties of the chain and which depends in the simplest case only on the spatial distance between the adjacent beads

$$g_j \equiv g(|\mathbf{y}_j|); \quad \mathbf{y}_j = \mathbf{x}_{j+1} - \mathbf{x}_j . \tag{1.3}$$

Here $g(\mathbf{y})$ is a probability, so

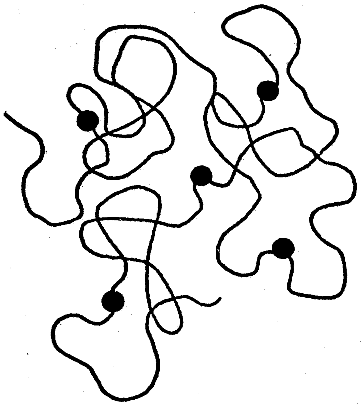

FIG. 1. The "beads on a string" model.

$$\int g(\mathbf{y}) d^3y = 1 . \tag{1.4}$$

The important characteristic of the function $g(\mathbf{y})$ is the mean square spatial distance a^2 between the adjacent monomers (for convenience we shall use $\frac{1}{6}$ of this value):

$$a^2 = \frac{1}{6} \int y^2 g(\mathbf{y})\, d^3y . \tag{1.5}$$

As an example of the function $g(\mathbf{y})$ we shall sometimes use the function

$$g(y) = \frac{1}{(4\pi a^2)^{3/2}} \exp(-y^2/4a^2) . \tag{1.6}$$

Such a correlation function for adjacent monomers can be used in the case when the beads are connected by a long flexible immaterial string. The copolymer consisting of flexible pieces of the chain with rare strongly interacting groups is the simplest realization of the "beads" model.

In a large number of problems (see Secs. II.D and V.B) some part of the chain can be considered as a material point and thus the real polymer chain can be represented as an effective chain of beads. In other cases (see Sec. VI.B) such a representation is incorrect.

In this article we shall consider basically the bead model. This model is implied everywhere if the opposite is not explicitly indicated.

C. Macroscopic states of a polymer chain

1. Definition of coil and globule

It is well known that the functioning of biopolymers and primarily of proteins in a living cell is determined by a unique spatial ternary structure formed by volume interaction (Volkenshtein, 1975). This structure is called the protein globule. It is also well known that when the protein is heated its denaturation occurs, the globular spatial structure being destroyed and the biochemical activity ceasing. In this case one says that the globule is transformed into the coil.

Similar phenomena can be observed in simple nonbiological polymers.

In order to develop the theory we must give a more precise definition to the terms "coil" and "globule." In the literature in the majority of cases (Volkenshtein, 1975) the globule is defined as a dense three-dimensional structure from which almost all solvent molecules are ousted by the monomers of the chain.

Proceeding from analogy with the proteins, in which the main property of a globule is its function, we shall adopt another definition (Lifshitz, 1968). We shall call a globule the state of a macromolecule in which it has a definite thermodynamically reliable spatial structure. In other words, the density fluctuations in a globule are less than the density itself, or the range of density correlations is finite when $N \to \infty$.

In contrast, a coil is the state of a macromolecule without any spatial structure. The coil pulsates macroscopically, the density fluctuations in it are of the same order as the density itself, and the radius of correlation is of the same order as the dimensions of the coil, i.e., it tends to infinity when $N \to \infty$.

2. Coil-globule transition. The terminology

Thus, according to our definition, the globule and the coil have different fluctuation regimes. From the point of view of statistical physics it is natural to call such significantly different states the phases, and the transition between them the phase transition.

However, it will be recalled that phase states and the phase transitions between them are strictly defined in statistical physics only in the limit $N \to \infty$. At the same time, the real polymer chains have a great but not infinite (and even very small in comparison with usual applications of thermodynamics) number of monomers. In this case it is sometimes impossible to relate a given finite chain to a particular phase state. This means that there is a finite transition width ΔT separating the regions which can be confidently related to different phases (i.e., the regions within which one of the phases gives an overwhelming contribution to the partition function).

In order to classify the transitions occurring at finite N we shall employ terminology which has been used for a long time in biophysics (which often deals with finite systems). Namely, the conformational transition is called a phase transition if its width ΔT tends to zero as $N \to \infty$; the phase transition is called a first-order phase transition if in the transition region there exist two free energy minima and, correspondingly, two states in the space of macro variables; each of these two states is thermodynamically stable on one side of the transition region and metastable on the other side; the phase transition is called a second-order phase transition if in the transition region there exists only one minimum in the space of macrovariables, i.e., if there are no metastable states on the other side of the transition region. This terminology is reasonable from the physical point of view and from the point of view of the treatment of experimental data.

If in the system there exists, in addition to N, another large parameter $\tilde{N}$, then it is sometimes useful to consider the intermediate asymptotics $1 \ll N \ll \tilde{N}$. The transitions in this case are classified as above.

The theory of polymeric coils has achieved considerable successes in the past few years. An extensive literature is devoted to this subject, in particular, the reviews by Berry and Casassa (1970), Freed (1972), and McKenzie (1976), and the book by Yamakawa (1971). That is why in our review only Sec. II deals with the polymeric coils. This section does not pretend to completeness, the choice of problems under consideration depending only on the authors' tastes; for a more thorough introduction to the theory of coils, the reader is referred to the above-mentioned works. The subsequent chapters of this review deal with different questions of the theory of globules and the coil-globule phase transition. The basic approach to this theory was proposed by Lifshitz (1968) and was developed in some subsequent works.

Throughout this review we shall consider, as a rule, the isolated homopolymer chain surrounded by solvent. An understanding of processes occurring in the isolated chain is necessary for the consideration of the more general case of the solution of chains. Furthermore, it is the consideration of an isolated chain that is important, as a rule, for biological applications.

We underline once more that the list of references to this work does not pretend to completeness.

II. BRIEF DESCRIPTION OF THE THEORY OF A POLYMERIC COIL

A. Chain without volume interactions (ideal coil)

1. Gaussian distribution

Let us consider first the simplest model of the polymer chain which takes into account the bonding of monomers in the chain but does not take into account the volume interactions,[1] and let us show that such a polymer takes the coil conformation.

In the absence of volume interactions the bending of a polymer chain in space can be described as a Markovian process: the position of each monomer depends only on the positions of some nearest neighbors along the chain. The problem of determining the properties of such a chain is analogous to the problem of describing Brownian motion. The distance from the end of the chain plays the role of the time; the persistent length plays the role of the diffusion coefficient. It is clear from this analogy that the mean square end-to-end distance $\langle R^2 \rangle$ is proportional to the length of the chain and the distribution function for this distance is Gaussian.

For example, for the model which is described by Eq. (1.6) it can be shown that

$$\langle R^2 \rangle = 6Na^2 \,. \tag{2.1}$$

The inequality $R \sim \langle R^2 \rangle^{1/2} \ll L = Na$ means that the bending chain is highly entangled. If the first monomer of this chain is fixed at the origin, the distribution function of the Kth monomer (when $K \gg 1$) is

$$p_K(\mathbf{x}) = (4\pi K a^2)^{-3/2} \exp(-x^2/4Ka^2) \tag{2.2}$$

For a chain with fixed center of mass (rather than fixed

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[1] A situation close to this model is realized at the θ point (see below).

position of the first monomer) a similar result has been shown to be correct (Yeh and Isihara, 1969) with somewhat more complex dependence on K [K in (2.2) must be replaced in this case by $N/3 - K(N-K)/N$].

2. Density and density fluctuations

In order to characterize the spatial organization of a coil the density distribution of the monomers is usually used. If the microscopic density is

$$n_\Gamma(\mathbf{x}) = \sum_{k=1}^{N} \delta(\mathbf{x} - \mathbf{x}_k), \tag{2.3}$$

then the average density is

$$n(\mathbf{x}) = \langle n_\Gamma(\mathbf{x}) = \sum_{k=1}^{N} \langle \delta(\mathbf{x} - \mathbf{x}_k)\rangle = \sum_{k=1}^{N} p_k(\mathbf{x}). \tag{2.4}$$

Changing the sum to an integral, we find

$$n(\mathbf{x}) = (4\pi a^2)^{-3/2} N^{-1/2} \int_0^1 ds \cdot s^{-3/2} \exp(-\xi^2/s), \tag{2.5}$$

where $\xi^2 = x^2/\langle R^2\rangle$. In the region $1/N \ll \xi \ll 1$ this density decreases as $1/\xi$, i.e., the characteristic length connected with the density distribution ξ is ~1.

In order to characterize the density fluctuations it is necessary to find the correlation function. Analogously to Eq. (2.5) it is easy to show that

$$\langle n_\Gamma(\mathbf{x}_1) n_\Gamma(\mathbf{x}_2)\rangle = (4\pi a^2)^{-3} N^{-1} \int_0^1 \int_0^1 ds_1 ds_2 \exp\left(-\frac{\xi_1}{s_1} - \frac{|\xi_1 - \xi_2|^2}{|s_1 - s_2|}\right) \Big/ s_1^{3/2} |s_1 - s_2|^{3/2}. \tag{2.6}$$

One may see from (2.6) that the range of density correlations, i.e., the characteristic radius of the correlation function

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

is of order $\xi \sim 1 (x \sim \langle R^2\rangle^{1/2})$, i.e., of the same order as the dimensions of the system. The correlation radius tends to infinity when $N \to \infty$. Thus the ideal chain is in the coil state (Lifshitz, 1968).

The described model of a Gaussian coil is the simplest and historically the first model of the spatial organization of a polymeric coil.

B. Flory's θ temperature. Universality of coil behavior at $T > \theta$

1. θ temperature, good and poor solvents

If the possibility of collisions or interactions between distant parts of the chain is taken into account, then the problem of mathematical description of a polymer becomes essentially non-Marcovian. The properties of the system depend significantly on the character of these interactions.

The fundamental concept in the theory of polymer chains with volume interactions is the concept of the θ temperature. According to Flory (1949), at this temperature the attraction and the repulsion of the distant parts of the chain compensate each other completely, and as a result the chain takes the conformation of the Gaussian coil. When $T > \theta$ the repulsion between the monomers is dominant (the so-called region of good solvent), when $T < \theta$ attraction plays the most important role (the region of poor solvent).[2] It is clear that in the repulsion region $T > \theta$ (in the good solvent) the chain is in the conformation of a coil of dimensions greater than (2.1) and has significant density fluctuations.

2. Role of binary collisions

By means of simple estimations it is easy to understand the reason for almost complete compensation of volume interactions at the definite temperature $T = \theta$. Let us imagine the polymeric coil as a cloud of monomers located in the volume $\sim R^3 \sim \langle R^2\rangle^{3/2} \gtrsim a^3 N^{3/2}$. The monomer density in this volume is $n \sim N/R^3 \lesssim 1/a^3 N^{1/2}$ [compare with Eq. (2.5)]. Correspondingly, the average number of simultaneously occurring binary collisions is of order $\sim Nnv \lesssim (v/a^3) N^{1/2}$, where $v \sim r_{\text{rep}}^3$ is the cube of the characteristic radius of volume interaction, i.e., a value of the same order as the excluded volume. Analogously, the average number of ternary collisions is $\lesssim N \cdot (nv)^2 \sim v^2/a^6$, of four-body collisions $\lesssim N \cdot (nv)^3 \sim v^3/a^9 N^{1/2}$, etc. Thus the number of simultaneously occurring collisions of third and higher order is $\lesssim 1$, and they cannot significantly affect the chain conformation. The

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[2] In real cases the chain is surrounded by the solvent. In this case besides the interactions between the monomers there exist also interactions between the monomers and the molecules of solvent and interactions between the molecules of solvent. The net effect appears to be the balance of all these kinds of interaction. This may lead to decrease of repulsion with increase of temperature. Solvents with a low critical mixing temperature $T > \theta$ correspond to poor solvents (attraction) and those with $T < \theta$ to good ones (repulsion). More complex situations with several θ points are also possible. In this paper we shall consider, for simplicity, only solvents with one upper critical mixing temperature and, correspondingly, with one θ point.

conformation is determined by the binary collisions and so it depends only on the second virial coefficient $B(T)$.

From this point of view the θ temperatue is the point of inversion of the second virial coefficient (the Boyle point) $B(\theta)=0$. At this point the contribution from binary collisions vanishes; the contribution from higher-order collisions is always small; thus at the θ point the chain conformation is close to the Gaussian coil.

3. Collisions of the parts of the chain

The following question may arise concerning the above estimations: is the picture of a cloud of monomers independently distributed in the region $\sim R^3$ the correct representation of a polymeric coil? The fact that the monomers are tied together determines in this picture only the value of $\langle R^2\rangle$, but does not affect the characteristics of the collisions. At the same time, the collisions in the polymeric coil are not merely between monomers, but rather between parts of the chain; thus the fact that the monomers are tied together must affect the characteristics of the collisions: these characteristics must be renormalized due to the increase in probability of additional collisions near the two colliding monomers. The method and the results of this renormalization have been analyzed by Khokhlov (1977). It turned out that the polymeric coil may be qualitatively represented as a cloud of "quasimonomers" with the renormalized characteristics of interaction (in the framework of the mean-field approximation). In particular, for the characterization of the polymeric coil it is important to know not the value of B itself, but the renormalized value B^*—the effective second virial coefficient of the interaction between parts of the chain.[3] In the future, when we refer to monomer interaction we shall imply such a renormalization.

4. Expansion factor of a polymer chain at $T>\theta$

The repulsive interaction in the region $T>\theta$ leads to an increase of the coil dimensions $\langle R^2\rangle$, i.e., the so-called expansion factor of a coil

$$\alpha^2 = \langle R^2\rangle / \langle R^2\rangle_0 \tag{2.7}$$

is more than unity when $T>\theta$ (in $\langle R^2\rangle_0$ the index zero indicates the absence of volume interaction). The value of α^2 is one of the main characteristics of the coil.

From the above it is clear that α^2 depends only on B among all the characteristics of volume interaction; in addition to this α^2 depends on the linear structure of the chain, i.e., on a and N. Thus the problem consists in the calculation of the function

$$\alpha^2 = \alpha^2(N, B, a^3) = \alpha^2(N, B/a^3)\,. \tag{2.8}$$

This equation follows from the dimensionality arguments.

To solve similar problems, we need to know the probability distribution of the end-to-end distance $P_N(\mathbf{R})$. This distribution coincides, apart from the numerical coefficient, with the partition function of a chain whose ends are fixed at a distance $\mathbf{R}$ one from another, i.e., with the Green's function

$$P_N(\mathbf{R}) = \mathrm{const}\, Z\left(\begin{array}{c|c} 1 & N \\ 0 & \mathbf{R}\end{array}\right). \tag{2.9}$$

The first attempts to calculate these functions were made in the framework of perturbation theory (Zimm, 1946; Teramoto, 1951a, b, c; Fixman, 1955). In this method the distribution function of a chain (2.9) [see also Eq. (1.1)] is written in the form

$$\begin{aligned} Z\left(\begin{array}{c|c} 1 & N \\ 0 & \mathbf{R}\end{array}\right) &= \int \delta(\mathbf{x}_1)\delta(\mathbf{x}_N-\mathbf{R})\prod_j g_j \prod_{1\le i<j\le N}(1+f_{ij})\,d\Gamma \\ &= \int \delta(\mathbf{x}_1)\delta(\mathbf{x}_N-\mathbf{R})\prod_j g_j \Big\{1+\sum_{1\le i<j\le N} f_{ij} \\ &\qquad + \sum f_{ij}f_{kl}+\cdots\Big\}\,d\Gamma\,, \end{aligned} \tag{2.10}$$

where $f_{ij}=\exp(-V_{ij}/T)-1$ is a Mayer function. The pth order of the perturbation theory corresponds to the terms in (2.10) involving p Mayer functions, i.e., to the consideration of p simultaneously occurring binary collisions.

In addition the following supposition is introduced

$$f_{ij} = -B\delta(\mathbf{x}_i-\mathbf{x}_j)\,. \tag{2.11}$$

This supposition means that we neglect the renormalization of the coefficient B (Khokhlov, 1977). Thus if (2.11) is supposed, the renormalization is to be made in the final result.

It is easy to understand from the above consideration of the number of binary collisions in a coil that as a result of a perturbation procedure we shall get an expansion in powers of the parameter

$$Z = BN^{1/2}/a^3\,. \tag{2.12}$$

In particular, for the expansion factor we have

$$\alpha^2 = \alpha^2(Z) = 1 + K_1 Z + K_2 Z^2 + \cdots\,, \tag{2.13}$$

where K are the numerical coefficients. The coefficient K_1, for instance, is equal to $(8/3)\pi^{3/2}$.

A complete review of the perturbation theory method has been given by Yamakawa (1971), so we shall not comment on it further here.

The result (2.13) shows that the expansion factor is a universal function of one real variable Z. But Eq. (2.13) is not practical for the calculation of this function because, as was shown recently by Edwards (1975) and Oono (1975), this expansion has a radius of convergence practically equal to zero in the most important limiting cases. Calculation of the function $\alpha^2(Z)$ is possible only by means of somewhat more refined methods, which are described in Sec. C.

5. Universality of the laws of a polymeric coil

The results described above may be summarized as follows. First of all, the expansion factor of a poly-

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[3] B^* in contrast to B represents the collective property of all the monomers of the chain.

meric coil and other conformational properties do not depend on the details of volume interaction potential, but depend only on one integral characteristic—on the second virial coefficient B. Furthermore, the expansion factor depends on a single combination Z of the volume interaction (B) parameter and the parameters of the linear structure a and N. These facts mean that all the different chains in the region of good solvent $T > \theta$ show universal behavior: the conformational characteristics of a coil are the universal functions of one parameter.

C. Excluded volume problem and its connection with the problem of the second-order phase transition

1. Early approaches to the excluded volume problem

Let us consider the behavior of a long polymer chain in a good solvent. In this solvent $B \sim v$ and $Z \sim vN^{1/2}/a^3 \gg 1$. Thus in this region it is necessary to know the asymptotic form of $\alpha^2(Z)$ at $Z \gg 1$. The problem of determining this asymptotic form is known as the excluded volume problem or as the problem of self-avoiding walks.

A great deal of work has been done on this problem. The most important advances have been made by Flory (1949), Edwards (1965), and de Gennes (1972).

The basic concept of Flory's method is the image of the polymeric coil as a cloud of monomers, distributed in the volume $\sim(\alpha^2\langle R^2\rangle_0)^{3/2}$. The difference between the free energies of the polymeric coil expanded with the factor α and of the ideal coil is assumed to include two parts:

$$\Delta F(\alpha) = \Delta F_{\mathrm{el}}(\alpha) + \Delta F_{\mathrm{mix}}(\alpha)$$

where $\Delta F_{\mathrm{el}}(\alpha)$ is the free energy of elastic deformation of an ideal polymer coil which has been expanded uniformly by the factor α, and $\Delta F_{\mathrm{mix}}(\alpha)$ is the free energy of mixing of the monomers with the molecules of the solvent in the volume of the coil. Once this difference is known, the equilibrium value of α can be found by minimizing $\Delta F(\alpha)$ with respect to α:

$$\partial \Delta F(\alpha)/\partial\alpha = 0\,. \tag{2.14}$$

Here $\Delta F_{\mathrm{el}}(\alpha)$ can be easily calculated because the corresponding problem is Markovian. $\Delta F_{\mathrm{mix}}(\alpha)$ depends on the monomer interaction; if we take into account only binary interactions of monomers with the second virial coefficient B, then Eq. (2.14) will take the form

$$\alpha^5 - \alpha^3 = C_1 Z\,, \tag{2.15}$$

where C_1 is the numerical coefficient. Thus, when $Z \gg 1$,

$$\alpha^2(Z) = \mathrm{const}\, Z^{2/5}\,. \tag{2.16}$$

For a more detailed derivation of (2.15) see the book by Flory (1953).

Flory's method was based on some physically incorrect assumptions; thus in subsequent years it was subjected to significant criticism (see, for example, des Cloizeaux, 1970, 1976). But the asymptotic form (2.16) itself is now considered to be very close to the correct one.

Edwards (1965) applied consistently the mean-field method to the excluded volume problem. His calculation confirmed the result (2.16). A detailed exposition of Edwards' approach has been given by Freed (1972), and an elementary derivation of his results can be found in the review by de Gennes (1969).

2. Analogy with the problem of the second-order phase transition

However, it is clear that the self-consistent field method is not exact because the polymeric coil is a highly fluctuating system. The situation is somewhat analogous to that occurring in the theory of second-order phase transitions, for example in magnetic systems—the fluctuations near the transition point become so great that Landau's self-consistent field theory becomes inapplicable. To describe such highly fluctuating systems a formalism based on the renormalization group method has been developed in the past few years [see the reviews by Wilson and Kogut (1974) and by Fisher (1974)]. This formalism has also been shown to be useful for polymeric coils (de Gennes, 1972).

The analogy between the behavior of a polymer and that of a magnet near a second-order phase transition is based on the one hand on the universality of the coil behavior and on the other hand on the universality of magnetic properties in the vicinity of the second-order phase transition. In both cases the universality is in fact due to the dominant role of the interaction between long wavelength flucutations.

This analogy is not purely qualitative. In the next section we shall show that the correlation function of a magnet is equal to the generating function $Z\left(\begin{smallmatrix}1\\0\end{smallmatrix}\middle|\begin{smallmatrix}N\\\mathbf{R}\end{smallmatrix}\right)$ if the number of components of an elementary spin in the magnet is formally equated with zero.

3. Relation between the correlation function of a magnet and the probability distribution of the end-to-end distance of a polymer

In the literature there exist many different methods of deriving this relation (de Gennes, 1972; Emery, 1975; Daoud *et al.*, 1976; Bowers and McKerrell, 1973; des Cloizeaux, 1975). Here we shall briefly describe one of them.

It is well known (Wilson and Kogut, 1974) that the central point of the theory of second-order phase transitions is the analysis of fluctuations of the field φ with the Landau Hamiltonian

$$H = H_0 + H_{\mathrm{int}}\,,$$

$$H_0 = \int d^dx\left\{\frac{\alpha}{2}\sum_{j=1}^{n}\varphi_j^2 + \frac{\beta}{2}\sum_{i=1}^{d}\sum_{j=1}^{n}\left(\frac{\partial\varphi_j}{\partial x_i}\right)^2\right\}, \tag{2.17}$$

$$H_{\mathrm{int}} = \frac{\gamma}{4}\int d^dx\left[\sum_{j=1}^{n}(\varphi_j)^2\right]^2,$$

where $\alpha = (T - T_0)/T_0$ is the relative deviation from the transition temperature, d is the dimensionality of space, n is the number of independent components of the order parameter. In order to calculate the correlation function

$$G_{ij}(\mathbf{R}) = \langle \varphi_i(\mathbf{x}) \varphi_j(\mathbf{x}+\mathbf{R}) \rangle = \delta_{ij} \mathcal{G}(\mathbf{R}) \tag{2.18}$$

it is necessary to perform a Fourier transformation which reduces H_0 to the sum of Hamiltonians of independent oscillators. Then one must expand $\exp(H_{\text{int}})$ and use the Wick theorem when each term is averaged. It is easy to find that the input and output lines of the diagrams obtained in such a way have the same polarization index; this is already shown in Eq. (2.18) by the δ function δ_{ij}. But the diagrams having close loops, which are connected with other parts of the diagram only by interaction lines, contain the summation over the polarizations of loops, i.e., simply the factor n (because nothing depends on the polarization index of a loop). Thus if we formally allow n to be zero we can obtain the diagram expansion without close loops.

This expansion differs from the perturbation theory expansion of the Green's function of a polymer chain [see Eq. (2.10)] only by the absence of the condition of constant chain length connecting the points 0 and R. This length must be fixed by means of a special chemical potential, thus

$$\mathcal{G}(\mathbf{R})\big|_{n=0} = \sum_N e^{-\alpha N} Z_N(\mathbf{R}), \tag{2.19}$$

where we have denoted for the sake of brevity $Z\left(\begin{smallmatrix}1\\0\end{smallmatrix}\middle|\begin{smallmatrix}N\\\mathbf{R}\end{smallmatrix}\right) = Z_N(\mathbf{R})$. The point of the phase transition corresponds to $\alpha = 0$, i.e., to an infinitely long chain $N \to \infty$. The field values β and γ correspond to the polymer values a and B.

The fundamental result (2.19) was obtained by de Gennes (1972). It allows us to characterize the function $Z_N(\mathbf{R})$.

It is well known that the Green's function $\mathcal{G}$ has scale-invariant properties near the transition point, i.e., it behaves as

$$\begin{gathered} \mathcal{G}(\mathbf{R}) = |\mathbf{R}|^{-d+2-\eta} f(\mathbf{R}/\xi), \\ \xi \sim \alpha^{-\nu}, \end{gathered} \tag{2.20}$$

where ξ is the radius of correlation, ν and η are the critical exponents and, f is some universal function. It is easy to find from (2.19) and (2.20) the analogous expression for $Z_N(\mathbf{R})$:

$$Z_N(\mathbf{R}) = N^{\nu(-d+2-\eta)-1} \frac{1}{a^3} h\left(\frac{\mathbf{R}}{aN^\nu}\right), \tag{2.21}$$

where h is the new universal function asymptotically equal to

$$h(x) = \begin{cases} \text{const.}\, e^{-x} & x \gg 1 \\ \text{const.}\, x^{-d+2-\eta} & x \ll 1 \end{cases}. \tag{2.22}$$

In the general theory of second-order phase transitions the critical exponents are calculated as functions of d and n (Brézin *et al.*, 1973); for the real polymers we must take $d=3, n=0$. The exponent ν in this case appears to be very close to $\frac{3}{5}$ (de Gennes, 1972); the Fisher exponent η is always small $\eta \leqslant 0.05$.

From (2.21) one can find any characteristic of a coil in the region of universality $T > \theta$. In particular, the mean square end-to-end distance appears to be $\langle R^2 \rangle \sim N^{2\nu}$, $\nu \approx 0.6$; this is very close to (2.16).

4. The function α^2 (Z) at $Z \sim 1$. Analogy between the θ point and the tricritical point

The coefficient $B(T)$ near the θ point can be written as

$$B = v[(T-\theta)/\theta] = v\tau, \tag{2.23}$$

where v is of the same order as the cube of the radius of interaction. Correspondingly, $Z = \tau N^{1/2} v/a^3$, and it is clear that near the θ point we need to know the function $\alpha^2(Z)$ at intermediate $Z \sim 1$.

The literature contains a great number of attempts to describe the form of the function $\alpha^2(Z)$ at $Z \sim 1$.[4] A review of the majority of them has been written by Yamakawa (1971). All these derivations are based on some arbitrary and generally incorrect assumptions and so they do not allow us to describe the behavior of real polymers.

A pragmatic approach to this problem was formulated by Domb and Barrett (1976). They proposed to tabulate the universal function $\alpha^2(Z)$ for some simple model, for example, for self-avoiding walks on the cubic lattice with the energy of the nearest-neighbor attraction ϵ [in this system θ point corresponds to $\epsilon/T \approx 0.275$ (McCrackin, Mazur, and Guttman, 1973)]. Then for any other polymer the function $\alpha^2(Z)$ will be known and the problem will consist only in establishing the relation between Z and the experimentally given variables τ and N.

When $\tau \ll 1$, Z is of order $Z \sim N^{1/2} v\tau/a^3$, i.e., the value of Z is uniquely determined by N and τ apart from the factor v/a^3 which is different for different polymers. Thus, for any polymer chain near the θ point, the graphs $\alpha^2(\tau)$ at $N = \text{const}$ [or $\alpha^2(N)$ at $\tau = \text{const}$] differ one from another only by the scale of the τ axis (or N axis). This scale is determined by the value v/a^3.

As a result, in order to describe completely the dimensions of a polymer chain at $\tau \ll 1$, one must know in addition to the tabulated function $\alpha^2(Z)$ only one number v/a^3 for each real polymer. This number is a constant for a given polymer–solvent system.

When one moves away from the θ point ($\tau \sim 1$) the linear dependence (2.23) is broken down in an individual way for each polymer–solvent system. Thus, to give a complete description of the expansion of a specific polymer chain in a wide temperature range it is necessary to know the function $B(T)$ and not only one number v/a^3. The form of this function can be restored using data on the coil dimensions—after the determination of the universal function $\alpha^2(Z)$ from real or computer experiments at $\tau \ll 1$.

As to analogy with the zero-component magnet, the θ point of a polymer system is similar to the tricritical point (de Gennes, 1975).

It will be recalled that the tricritical point is the point at which the line of second-order phase transition converts into a line of first-order phase transitions. The tricritical point corresponds to the change from the strongly fluctuating behavior which characterizes second-order phase transitions to the thermodynamically stable behavior which characterizes first-order phase

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[4] Flory's formula (2.15) is historically the first among these attempts.

transitions. Near this point there exists a tricritical region with its own special behavior.

In our case there is an analogous θ region, corresponding to $Z \ll 1$. In this region the behavior of the system differs qualitatively from that in the good solvent region; the asymptotic laws at $Z \ll 1$ are different from those at $Z \gg 1$. At $Z \sim 1$ the crossover occurs.

It is well known (Fisher, 1974) that a new variable becomes relevant near the tricritical point. In our case, as is clear from the above, the second virial coefficient B plays the role of this new variable.

In the three-dimensional case the tricritical exponents, describing the behavior of magnetic systems in the tricritical region, coincide with those calculated by means of the self-consistent Landau field theory (Fisher, 1974). That is why a polymer chain in the θ region is correctly described by self-consistent critical exponents. On the other hand there are logarithmic corrections to the self-consistent behavior in the tricritical region of magnetic systems. These corrections exist also for a polymer in the θ region. They have been calculated by Stephen (1975). Physically they account for the ternary collisions.

D. Connection between the models of a polymer chain in the universality region $T > \theta$

In this section we shall show how to reformulate the results obtained earlier for the "interacting beads on a flexible string" polymer model to take account of a more realistic "persistent model."

The persistent model is characterized by two parameters, the width d and the persistent length $\tilde{l} \sim a$; the bead model is characterized by the parameters v and a. The unperturbed dimensions in both models are determined by the parameter a. Volume effects in the bead model depend on the parameter v/a^3. The question arises, what parameter is qualitatively analogous to v/a^3 for the persistent model?

From the definition of the persistent length it is clear that pieces of the chain having length $\sim a$ collide and interact almost as rigid cylinders [when one divides the chain into links $\sim a$, renormalization does not change qualitatively their interactions (Khokhlov, 1977)]. The second virial coefficient in the gas of cylinders of diameter d and length a is of order da^2. Correspondingly near the θ point

$$B \sim da^2\tau, \; Z \sim N^{1/2}B/a^3 \sim N^{1/2}\tau d/a \sim \tau N^{1/2}/M \,, \qquad (2.24)$$

where the ratio $M = a/d$ is the persistent length in units of d. $M \gg 1$ corresponds to stiff chains, $M \sim 1$—to flexible ones (see also Birshtein, Skvortzov, and Sariban, 1975).

From (2.24) it is seen that in the universality region $(T > \theta)$ all qualitative results for the persistent model can be obtained from the analogous results for the bead model by means of the substitution

$$\frac{v}{a^3} \to \frac{1}{M} \,. \qquad (2.25)$$

III. EQUATIONS FOR THE DESCRIPTION OF THE GLOBULAR STATE OF A POLYMER CHAIN

A. General scheme of the derivation

In this section we shall describe briefly the main steps in deriving equations for globules (Lifshitz, 1968). Detailed derivation is given in the subsequent sections.

1. Entropy of a state with a given density distribution

The density distribution in a globular state is a well-defined thermodynamic quantity. This allows us to describe the macrostate of the system by the density distribution $n(\mathbf{x})$, smoothed over the volume ω. On the one hand, the smoothing volume must contain a large number of monomers, and, on the other hand, the mean density $\langle n_\Gamma(\mathbf{x})\rangle$ must not vary significantly within ω. The smoothing procedure in this case does not differ from the usual one. Since the number of monomers in each smoothing volume is large $(n\omega \gg 1)$, the assignment of the smoothed density fixes only a relatively small number of variables in the configurational space. Thus, a large volume in the configurational state corresponds to the macrostate with fixed $n(\mathbf{x})$. The logarithm of this volume is the configurational entropy of the macrostate,[5]

$$S\{n(\mathbf{x})\} = \ln \int \delta(n_\Gamma(\mathbf{x}) - n(\mathbf{x})) \prod_j g_j d\Gamma \,, \qquad (3.1)$$

where $n_\Gamma(\mathbf{x})$ is the exact microscopic density (2.3).

Our first problem will be the calculation of the function $S\{n\}$ (Sec. III.B). The method of calculation is based on the fact that the generating function of the statistical weight $\exp(S\{n\})$ is the partition function of the chain without volume interactions in an external field $\varphi(\mathbf{x})$

$$Z\{\varphi\} = \int \exp\left[-\frac{\sum_j \varphi(\mathbf{x}_j)}{T}\right] \prod_j g_j d\Gamma$$

$$= \int \exp\left[-\frac{\int \varphi(\mathbf{x}) n(\mathbf{x}) d^3x}{T}\right] \exp[S\{n\}] \mathfrak{D}n \,. \qquad (3.2)$$

Here $\int \cdots \mathfrak{D}n$ denotes functional integration over the smoothed density $n(\mathbf{x})$. The last equation follows from the fact that $\exp[S]$ is, as usual, the Jacobian of the transition from the integration over the configurational space to the integration over the smoothed macrovariables. It is natural that, in order for the density $n(\mathbf{x})$ to correspond to the globular state, the external field must be attractive.

Thus, in order to calculate $S\{n\}$, it suffices to solve the problem of the ideal polymer chain in an external attractive potential field. The solution of this problem will not only prepare us for subsequent consideration of the self-consistent situation, but can also in some cases be of physical interest in itself (see Sec. VI).

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[5] It will be recalled that the bead model is always implied unless some other model is explicitly indicated.

2. Accounting for volume interactions

In the presence of volume interactions the free energy of a macrostate with a given smoothed density is equal to

$$F\{n(\mathbf{x})\} = -T\ln\int \exp\left\{-\frac{E(\Gamma)}{T}\right\}\delta(n_\Gamma(\mathbf{x}) - n(\mathbf{x}))\sum_j g_j\,d\Gamma\,, \tag{3.3}$$

where $E(\Gamma)$ is the energy of monomer interaction in the microconfiguration Γ [see (1.1)].

The quantity

$$E\{n(\mathbf{x})\} = F\{n\} + TS\{n\} \tag{3.4}$$

describes the contribution of volume interactions to the free energy of the system and will play the role of the internal energy in our description (although this quantity is not equal to the internal energy as defined in the usual way). The calculation of $E\{n\}$ is performed in Sec. III.C. In some limiting cases this function can be expressed through the thermodynamic characteristics of the gas of separated monomers (for the definition see Sec. I.B.2). Knowing $S\{n\}$ and $E\{n\}$ allows us to calculate $F\{n\}$, i.e., the free energy of the chain in a state with fixed $n(\mathbf{x})$.

3. Equilibrium density

The free energy of a chain in equilibrium is

$$F = -T\ln\int \exp\left[-\frac{F\{n\}}{T}\right]\mathfrak{D}n. \tag{3.5}$$

In the globular state the density is a weakly fluctuating, well-defined thermodynamic quantity. The mathematical expression of this physical fact is the existence of the saddle point n_{eq} in the functional integral (3.5). Thus, for a globule

$$F \cong \min F\{n\} = F\{n_{\text{eq}}\}\,; \tag{3.6}$$

i.e., to determine the equilibrium density distribution we must minimize the function $F\{n\}$. The minimization procedure will be performed in Sec. III.C. This will allow us to get a closed system of equations for determining the equilibrium density in a globule, i.e., for describing the homopolymer globule structure.

The fact that the steepest descent method is used in the derivation of the equations means, as usual, that the corresponding theory is self-consistent. Thus, for polymeric globules, in contrast to polymeric coils (see Sec. II), the self-consistent field theory appears to be applicable on the whole. Nevertheless, in the external regions of the globule, where the density is low and density fluctuations are significant, the picture may differ in some way from the self-consistent one. But even in this case the self-consistent consideration is a step towards the construction of a more exact theory. In the future we shall not, as a rule, overstep the limits of the self-consistent equations. The applicability of these equations is discussed in greater detail in Appendix B.

B. Ideal polymer chain in an attractive external field

1. Method of describing a globule formed by an external field

As has already been noted, in the absence of volume interactions the bending of a polymer chain has the character of a Markovian process and it can therefore be described analogously to the description of Brownian motion. The key function in the approach to such a problem is the Green's function; in our case the role of a Green's function is played by the partition function of the chain with fixed end points [compare with Eqs. (2.9) and (2.10)]

$$Z\left(\begin{array}{c|c} 1 & N \\ \eta & \xi \end{array}\right) = \int\prod_{j=1}^{N}\left[g_j\exp\left(-\frac{\varphi(\mathbf{x}_j)}{T}\right)\right]\delta(\mathbf{x}_1-\eta)\delta(\mathbf{x}_N-\xi)\,d\Gamma\,. \tag{3.7}$$

In order to derive an equation analogous to the diffusion equation for which (3.7) plays the role of the Green's function, we must pass from a chain with N links to a chain with $(N+1)$ links. This will give us a recurrence relation of the form

$$Z\left(\begin{array}{c|c} 1 & N+1 \\ \eta & \xi \end{array}\right) = \exp\left(-\frac{\varphi(\xi)}{T}\right)\int g(\xi-\xi')Z\left(\begin{array}{c|c} 1 & N \\ \eta & \xi' \end{array}\right)d^3\xi'\,. \tag{3.8}$$

Below in order to write the analogous formulas we shall use the designation $\hat{g}$ for the integral operator

$$\hat{g}\psi = \int g(\mathbf{x}-\mathbf{x}')\psi(\mathbf{x}')d^3x'. \tag{3.9}$$

Equation (3.8) plays the role of the diffusion equation. It is natural to search for its Green's function (3.7) in the form of a bilinear expansion

$$Z\left(\begin{array}{c|c} 1 & N \\ \eta & \xi \end{array}\right) = \sum_k \Lambda_k^N\psi_k(\xi)\psi_k^+(\eta)\,, \tag{3.10}$$

ψ_k and Λ_k being the eigenfunctions and the corresponding eigenvalues of the equation

$$\hat{g}\psi = \Lambda\exp[\varphi/T]\psi\,. \tag{3.11}$$

If the largest eigenvalue of this equation belongs to a discrete spectrum and is separated by a finite interval from the next eigenvalue, then the corresponding term dominates in (3.10). Using the symmetry of the expression $Z\left(\begin{smallmatrix}1 & N\\ \eta & \xi\end{smallmatrix}\right)$ in ξ and η we easily obtain

$$Z\left(\begin{array}{c|c} 1 & N \\ \eta & \xi \end{array}\right) = \Lambda^N\psi(\eta)\psi(\xi)\,, \tag{3.12}$$

where Λ and ψ are the largest eigenvalue and the corresponding eigenfunction of Eq. (3.11).

From (3.12) it follows that in a discrete spectrum the free energy of the system (more exactly, the change in the free energy with respect to the free energy level of the ideal coil) is equal to

$$F\{\varphi\} = -TN\ln\Lambda\{\varphi\} \equiv N\lambda\{\varphi\}\,;\quad \Lambda = \exp(-\lambda/T)\,. \tag{3.13}$$

We see that confining ourselves to the first term in the bilinear expansion, is equivalent to considering only terms linear with respect to N in the free energy.

It should be noted that the discrete spectrum of Eq. (3.11) appears only if the external field φ is attractive and if the corresponding potential well φ/T is deep enough. When the temperature is increased, the depth of the well decreases, and at some temperature T_c the discrete level disappears. Physically this corresponds to the fact that the potential well at $T > T_c$ cannot hold the chain. The phenomena near T_c will be considered in Sec. VI.

2. Density and density correlations

Let us now find the expression for the monomer density $n(\mathbf{x})$, and let us show that, if Eq. (3.11) has a discrete spectrum, the chain takes on a globular conformation.

It is seen from (3.12) that the function $\psi(\mathbf{x})$ is proportional to the probability density of finding the end link of the chain at $\mathbf{x}$.[6] At the same time, the density $n(\mathbf{x})$ in a given field is proportional to the probability of finding the Mth link at point $\mathbf{x}$ (where M satisfies the conditions $M \gg 1, N-M \gg 1$, so the Mth link is remote from the chain ends), because it is these links that give the main contribution to n if $N \gg 1$. Let us introduce the function

$$Z\begin{pmatrix} 1 & M & N \\ \eta & \mathbf{x} & \xi \end{pmatrix},$$

the partition function of the chain with three fixed points. Expressing this function through the partition functions of the chains $(1, M)$ and (M, N), and applying to them the result (3.12) we find

$$n(\mathbf{x}) = \psi^2(\mathbf{x}) \exp(\varphi(\mathbf{x})/T). \tag{3.14}$$

Here we chose to normalize the function ψ, in order that coefficient in (3.14) be equal to unity, taking into account

$$\int n(\mathbf{x}) d^3x = N. \tag{3.15}$$

The result (3.14) can be obtained with equal success by calculating the variational derivative

$$n(\mathbf{x}) = \frac{T}{Z} \frac{\delta Z}{\delta\varphi(\mathbf{x})} = \frac{\delta F}{\delta\varphi(\mathbf{x})} = N \frac{\delta\lambda}{\delta\varphi(\mathbf{x})}. \tag{3.16}$$

The advantage of this method is that it allows the generalization of the density correlator to

$$\langle n_\Gamma(\mathbf{x}_1) n_\Gamma(\mathbf{x}_2)\rangle = \frac{T^2}{Z} \frac{\delta^2 Z}{\delta\varphi(\mathbf{x}_1)\delta\varphi(\mathbf{x}_2)}$$

$$= N^2 \frac{\delta\lambda}{\delta\varphi_1} \frac{\delta\lambda}{\delta\varphi_2} - NT^2 \frac{\delta^2\lambda}{\delta\varphi_1\delta\varphi_2}. \tag{3.17}$$

It will be recalled that $\langle\!\langle n_\Gamma(\mathbf{x})\rangle\!\rangle = n(\mathbf{x})$. So the density correlator is equal to

$$\frac{\langle\!\langle n_\Gamma(\mathbf{x}_1) n_\Gamma(\mathbf{x}_2)\rangle\!\rangle - \langle\!\langle n_\Gamma(\mathbf{x}_1)\rangle\!\rangle\langle\!\langle n_\Gamma(\mathbf{x}_2)\rangle\!\rangle}{\langle\!\langle n_\Gamma(\mathbf{x}_1)\rangle\!\rangle\langle\!\langle n_\Gamma(\mathbf{x}_2)\rangle\!\rangle} = -\frac{T}{N} \frac{\delta^2\lambda/\delta\varphi_1\delta\varphi_2}{(\delta\lambda/\delta\varphi_1)(\delta\lambda/\delta\varphi_2)}$$

$$\sim \frac{1}{N}. \tag{3.18}$$

It is seen that the density correlation tends to zero as $N \to \infty$. Hence the presence of a discrete spectrum actually corresponds to a globular state with thermodynamically reliable spatial structure.

3. Configurational entropy

Let us now calculate the configurational entropy $S\{n\}$ for a chain in a state with a given density distribution $n(\mathbf{x})$. For this purpose let us consider the field $\varphi(\mathbf{x})$, in which $n(\mathbf{x})$ is just the equilibrium density. We shall assume that the density $n(\mathbf{x})$ corresponds to a field $\varphi(\mathbf{x})$ for which the greatest eigenvalue of Eq. (3.11) belongs to a discrete spectrum. This means that the density $n(\mathbf{x})$ fluctuates weakly and consequently the integral (3.5) has a saddle point at equilibrium (i.e., just at the given) density $n(\mathbf{x})$, thus

$$F\{\varphi\} = -T \ln Z\{\varphi\} = \int \varphi(\mathbf{x}) n(\mathbf{x}) d^3x - TS\{n\} \tag{3.19}$$

[compare with (3.6)]. From the expression for $F\{\varphi\}$ (3.13) we find

$$S = \int \frac{\varphi(\mathbf{x}) - \lambda}{T} n(\mathbf{x}) d^3x. \tag{3.20}$$

Now we must express the entropy directly in terms of the density $n(\mathbf{x})$. This can be easily done by eliminating φ with the help of (3.11) and (3.14). As a result we get (Lifshitz, 1968)

$$S\{n\} = \int n(\mathbf{x}) \ln \frac{\hat{g}\psi}{\psi} d^3x, \tag{3.21}$$

where $\psi(\mathbf{x})$ is related to $n(\mathbf{x})$ by

$$\Lambda n(\mathbf{x}) = \psi(\mathbf{x}) \hat{g}\psi. \tag{3.22}$$

The number Λ here is generally arbitrary and determines the normalization of the ψ function.

As expected, the expression for the entropy is nonlocal; the nonlocality enters through the operator $\hat{g}$, i.e., it is determined by the linear memory.

4. Analysis of the expression for the entropy

In order to illustrate Eq. (3.21) it is useful to consider two limiting cases:

(1) First let all the monomers be located in a small volume of dimensions $R \ll a$. In this case $\hat{g}\psi \cong g(0) \int \psi(\mathbf{x}) d^3x$ and thus we have from (3.21) and (3.22)

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

The interpretation of this result is simple. Since within a small volume the bonds do not restrict the motion of monomers, the entropy of the system differs from the entropy of Boltzmann gas (the first item) by the additional items which correspond in the partition function to the factor $[g(0)]^N \cdot N!$. This factor originates from the return of the chain N-times to one place and the

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[6] The fact that the function Z in (3.12) splits into a product of factors means that the chain end points are statistically independent in a state with a discrete spectrum.

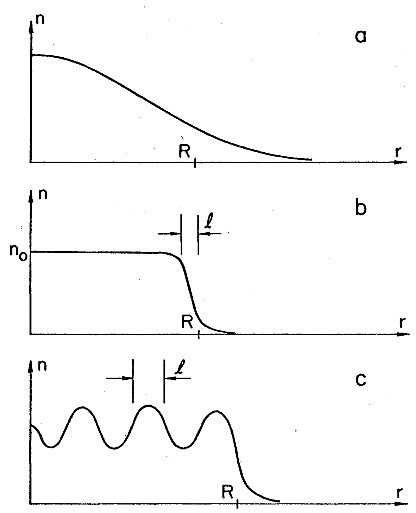

FIG. 2. Possible forms for the density versus distance from the center of a globule. (a) Uniformly varying density. (b) Density distribution with smoothed boundary. (c) Density distribution with microstructure.

presence of a fixed order in which the particles are strung on the chain.

(2) Let us consider now the opposite limiting case $R \gg a$. In the case of a smoothly varying function ψ, taking into account the spherical symmetry of $\hat{g}$ and conditions (1.4)–(1.5), we get

$$\hat{g}\psi = \int g(y)\{\psi(x) + \mathbf{y}\nabla\psi + \tfrac{1}{2}(\mathbf{y}\nabla)^2\psi + \cdots\}d^3y \cong \psi(\mathbf{x}) + a^2\Delta\psi$$

i.e., the substitution $\hat{g} \to 1 + a^2\Delta$ can be made. After this it is easy to find

$$S \cong -a^2 \int [\nabla n^{1/2}]^2 d^3x .$$

Three variants are possible: uniform density variation along the system [Fig. 2(a)]; constant density in the interior of the system and rapid by varying density in a surface layer of width l [Fig. 2(b)]; microstructure with the characteristic length l [Fig. 2(c)]. In these cases we obtain, respectively, (a) $S \sim -Na^2/R^2$; (b) $S \sim -Na^2/lR$; (c) $S \sim -Na^2/l^2$.

For the system with ideal coil dimensions, $R \sim a \cdot N^{1/2}$ and $S \sim 1$ in case (a). This means that there is no coil structure with significant entropy advantages. It is for this reason that the coil pulsates macroscopically.

C. Self-consistent theory of a globule with volume interaction

1. Equation for the equilibrium density

As has already been noted in Sec. III.A, the self-consistent equations for determing the equilibrium density $n(\mathbf{x})$ in a polymeric globule formed by volume interactions are the minimization equations for the function $F\{n\} = E\{n\} - TS\{n\}$. In the process of minimization, however, one must take into account the additional condition (3.15). Hence the equation which determines the minimum of $F\{n\}$ will have the form $\delta F/\delta n = \lambda$, where λ is the indefinite Lagrange multiplier.

The variational derivative of the entropy (3.21) can be explicitly calculated taking into account (3.22)

$$\frac{\delta S}{\delta n} = \ln \frac{\hat{g}\psi}{\psi} . \tag{3.23}$$

Thus the Euler equation for the minimization of the function $F\{n\}$ takes on the form

$$\hat{g}\psi = \Lambda\psi \exp\left\{\frac{\delta E}{\delta n}\Big/T\right\} , \tag{3.24}$$

where the normalizing constant Λ is chosen to be equal to

$$\Lambda = \exp(-\lambda/T) \tag{3.25}$$

[compare with Eq. (3.13)].

Comparing (3.24) with (3.11) we see that $\delta E/\delta n$ plays the role of the self-consistent field. In the presence of an external field and in the absence of volume interaction Eq. (3.24) transforms directly into (3.11) because in this case

$$E = \int \varphi(\mathbf{x})n(\mathbf{x})d^3x; \quad \delta E/\delta n = \varphi(\mathbf{x}) .$$

Thus our next problem is the calculation of $E\{n\}$

$$E\{n\} = -T \ln \frac{\int e^{-E(\Gamma)/T}\delta(n - n_\Gamma) \sum_j g_j d\Gamma}{\int \delta(n - n_\Gamma) \sum_j g_j d\Gamma} . \tag{3.26}$$

2. Method of accounting for the volume interactions (Lifshitz, 1968)

It will be recalled that the forces of volume interaction include strong repulsion (impenetrable core) over small distances $r_{\text{rep}} \sim v^{1/3}$ and attraction over larger distances $r_{\text{attr}} > r_{\text{rep}}$. In all cases, clearly $r_{\text{rep}} < a$, i.e., $v < a^3$. We shall consider first the case $r_{\text{attr}} \sim v^{1/3} \ll a^3$, i.e., $v \ll a^3$ (to be compared with Sec. II).

In this case, if we assume for the sake of simplicity[7] that $na^3 \gg 1$, then we can choose the smoothing volume ω satisfying the condtion $\omega \ll a^3$. For such smoothing the nuclei g can be considered as constant in (3.26) in comparison with the rapidly varying factor $\exp(-E(\Gamma)/T)$, i.e.,

$$E\{n\} \cong E_0\{n\} = -T \ln \frac{\int e^{-E(\Gamma)/T}\delta(n - n_\Gamma)d\Gamma}{\int \delta(n - n_\Gamma)d\Gamma} . \tag{3.27}$$

One may see that the functional $E\{n\}$ can be expressed through the simple thermodynamic function of the gas of separate monomers with the same interaction $E(\Gamma)$ but without the linear memory.

It is convenient to introduce the following notation. Let $f(n, T)$ be the free energy per unit volume of the equivalent system of separate monomers at temperature T and with density n; let $\mu(n, T) = \partial f/\partial n$ be the chemical potential of this system; and let $p(n, T) = n\mu - f$ be the pressure. Let us introduce the analogous values for the

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[7] A more detailed analysis shows (see Appendix B) that Eq. (3.27) for $E\{n\}$ is always valid if $v \ll a^3$, irrespective of the condition $na^3 \gg 1$.

ideal gas: $f_{id}=Tn\ln n/e$; $\mu_{id}=T\ln n$; $p_{id}=nT$, and, finally, let us write:

$$f^*(n,T)=f-f_{id};\quad \mu^*(n,T)=\mu-\mu_{id}=\partial f^*/\partial n;\qquad p^*(n,T)=p-p_{id}=n\mu^*-f^*. \tag{3.28}$$

In this notation (3.27) takes the form

$$E\{n\}=\int f^*(n(\mathbf{x})d^3x \tag{3.29}$$

and, consequently,

$$\delta E/\delta n=\mu^*(n(\mathbf{x})). \tag{3.30}$$

Thus for short-range forces ($v\ll a^3$) Eq. (3.24) takes the form

$$\hat{g}\psi=\Lambda\psi\exp\{\mu^*(n)/T\}. \tag{3.31}$$

The density n is related to ψ by means of (3.22). From (3.31) and (3.22) we get

$$n=\psi^2\exp\{\mu^*(n)/T\}. \tag{3.32}$$

From (3.32) one can see why it is convenient to choose the normalization of the ψ function in the form (3.25): in this case the connection between the equilibrium values of n and ψ appears to be the local one. A typical plot $\psi(n)$ is shown in Fig. 3.

Equations (3.31) and (3.32) together with the normalizing condition (3.15) form a complete system of two equations and one auxiliary condition for the determination of two unknown functions n and ψ and one unknown number Λ.

The equilibrium free energy of a globule (3.6) can be written in the form

$$F=\int\{f^*(n)-Tn\ln(\hat{g}\psi/\psi\}d^3x=-TN\ln\Lambda-\int p^*d^3x. \tag{3.33}$$

It will be recalled that F corresponds to the globule free energy with respect to the free energy level of an ideal coil.

Sometimes it is useful to write Eqs. (3.31) and (3.32) in the form:

$$\hat{g}\psi=\Lambda\exp\{\mu(n,T)/2T\} \tag{3.34}$$

$$n=\psi\exp\{\mu(n,T)/2T\}. \tag{3.35}$$

It is equally simple to generalize the obtained equations to the case in which, alone with the short range forces ($v\ll a^3$) there exist also long-range forces within whose radius of interaction a large number of particles are situated. In this case the exact expression for the energy of the interaction with the potential $\mathcal{U}(\mathbf{x}-\mathbf{x}')$ can be obtained directly through the smoothed density

$$U=\frac{1}{2}\int n_\Gamma(\mathbf{x})\mathcal{U}(\mathbf{x}-\mathbf{x}')n_\Gamma(\mathbf{x}')d^3xd^3x'$$

$$\cong\frac{1}{2}\int n(\mathbf{x})\mathcal{U}(\mathbf{x}-\mathbf{x}')n(\mathbf{x}')d^3xd^3x'.$$

Let us reserve, for simplicity, the notation $E(\Gamma)$ for the short-range part of the energy; then we must have in (3.27) the energy $E(\Gamma)+U$. But within the limits of the integration $U=U\{n\}$ is constant, so $\exp(U/T)$ can be carried out of the integral. Thus in the presence of long-range forces we get once more Eqs. (3.31) and (3.32) with the substitution

$$\mu^*(n)\rightarrow\mu^*(n)+\hat{U}n,$$

where $\hat{U}$ is the operator with the nucleus $\mathcal{U}(\mathbf{x}-\mathbf{x}')$. In this case we must add to the free energy (3.33) the term $\frac{1}{2}U\{n\}$.

Unfortunately, for the most important real case $v\sim a^3$ the function $E\{n\}$ cannot be found in simple form. The only information obtainable in this case is by extrapolation of the results obtained from the Eqs. (3.31) and (3.32), which are valid in the case $v\ll a^3$. The error made during this extrapolation is of order unity; thus the equations give for the case $v\sim a^3$ the correct orders of magnitude. In addition to this, it is natural to assume that no qualitatively new features in the solution can appear during this extrapolation. Hence, considering below the solutions of Eqs. (3.31) and (3.32), we shall assume that these equations are quantitatively correct for the case $v\ll a^3$ (to within v/a^3) and only qualitatively correct for the case $v\sim a^3$ (see also Appendix B).

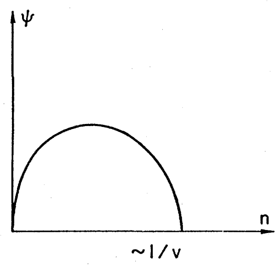

FIG. 3. Typical plot of the relation between ψ and n, resulting from Eq. (3.32). The quantity $n(\mathbf{x})$ is the polymer density at point $\mathbf{x}$, while $\psi(\mathbf{x})$ is proportional to the probability of finding the end link of the chain at $\mathbf{x}$.

D. Explicit consideration of the influence of solvent (Lifshitz and Grosberg, 1975)

As can be seen from the above, the spatial structure of a globule is determined by the volume interaction of monomers. Under some assumptions the role of this interaction can be described by means of the function $\mu(n,T)$. The solvent has an influence on the character of volume interactions between monomers, thus $\mu(n,T)$ is an effective value, including the indirect interaction of monomers through the solvent. In order to determine the influence of such solvent parameters as pressure $\mathcal{P}$, acidity pH, etc. on the globule, it is necessary to obtain the explicit expressions for the effective thermodynamic values.

First of all it should be noted that the configurational entropy of the chain does not depend on the presence or absence of a solvent and is determined by Eqs. (3.21) and (3.22).

Let us introduce in addition to the monomer density distribution $n(\mathbf{x})$ the density distribution of the solvent molecules $n_s(\mathbf{x})$ and let us consider as known the thermodynamic functions of the solution of monomers without linear memory: the free energy per unit volume $f(n,n_s,T)$, the chemical potential of monomers

$\mu(n, n_s, T) = \partial f/\partial n$, the chemical potential of the molecules of solvent $\mu_s(n, n_s, T) = \partial f/\partial n_s$, and the pressure $p(n, n_s, T) = n\mu + n_s\mu_s - f$.

If we assume once more that the characteristic radius of interaction is much less than a, then the change E in the energy due to the volume interaction

$$E(\{n\}, \{n_s\}) = TS + F(\{n\}, \{n_s\}, V, T) \tag{3.36}$$

can be calculated by means of the same method as in the previous section. The result has the form

$$E(\{n\}, \{n_s\}) = \int_V \{f(n_s, n, T) - Tn\ln(n/l)\} d^3x. \tag{3.37}$$

We shall assume that the whole volume of the system V is much larger than the volume of the globule, so that the monomer density on the periphery is equal to zero; the density of the pure solvent far from the chain will be denoted by $n_{s\infty}$. Since most of the pure solvent surrounding the chain has no influence on its state, it is expedient to exclude the volume of the system V and the number of solvent molecules N_s from the thermodynamic functions.

First of all, minimizing the free energy with respect to $n_s(\mathbf{x})$ at constant N_s, we obtain the standard condition of the constancy of the chemical potential of the solvent

$$\mu_s(n(\mathbf{x}), n_s(\mathbf{x}), T) = \mu_s(0, n_{s\infty}, T) = \mu_s(\mathcal{P}, T), \tag{3.38}$$

$$\mathcal{P} = p(0, n_{s\infty}, T), \tag{3.39}$$

which reflects the fact that the solvent density at each point is determined by the monomer density: $n_s(\mathbf{x}) = \tilde{n}_s(n(\mathbf{x}), \mathcal{P}, T)$.

Now we must pass from the free energy to the thermodynamic Gibbs potential $F + \mathcal{P}V$. In order to express the volume in terms of other variables, we shall write it in the form

$$V = \frac{N_s}{n_{s\infty}} + \int \frac{n_{s\infty} - n_s(\mathbf{x})}{n_{s\infty}} d^3x, \tag{3.40}$$

where the integration can be performed over all space and not only over the volume V.

The quantity $v(n) = (n_{s\infty} - \tilde{n}_s)/n_{s\infty}n$, expressed according to (3.38) as a function of n, is the volume per monomer of the ousted solvent. At high densities the solvent does not penetrate between the monomers ($n_s \ll n_{s\infty}$) and $v(n) \cong 1/n$; at low densities $v(n)$ becomes equal to the effective volume of the monomer v_0 (see below for the exact formula)

$$\frac{\tilde{n}_s - n_{s\infty}}{n_{s\infty}} \equiv nv(n) = \begin{cases} 1 & n_s \to 0 \\ nv_0 & n \to 0 \end{cases}. \tag{3.41}$$

It is clear that $v(n)$ depends parametrically on the external pressure and the temperature.

With the help of Eqs. (3.36) and (3.40) we find the Gibbs potential of the solvent with the globule $F + \mathcal{P}V$.

Since the entropy of the chain is determined with respect to the entropy level of an ideal coil, it is natural to determine the energy term (3.37) similarly. In order to do this one must subtract the Gibbs potential for the solvent with an ideal coil from the Gibbs potential for the solvent in the case of a globule. Since linear memory does not affect the monomer-solvent interaction, one obtains for the Gibbs potential of solvent with coil

$$N_s\mu_s(\mathcal{P}, T) + N\chi(\mathcal{P}, T), \tag{3.42}$$

where χ is the coefficient of the term linear in n in the expansion, with respect to n, of the integrand in (3.37).

Differentiating (3.42) with respect to $\mathcal{P}$, it is easy to find the volume which is occupied by the solvent in the case of the coil. Comparing the result with (3.40) and (3.41), we find that

$$v_0 = \partial\chi/\partial\mathcal{P}. \tag{3.43}$$

When we substract the Gibbs potential of the solvent with the coil from the Gibbs potential of the solvent with the globule we automatically pass from the variable N_s to the variable μ_s due to the term $N_s\mu_s$. Taking into account all the above, we obtain the following expression for the thermodynamic potential of a solvent with a globule:

$$\begin{aligned}\Phi(T, \mathcal{P}, \{n\}) = \int\Big\{ & f(n, \tilde{n}_s, T) - \frac{\tilde{n}_s}{n_{s\infty}} f(0, n_{s\infty}, T) + \Big(\mathcal{P}\frac{\partial\chi}{\partial\mathcal{P}} - \chi\Big) \\ & - Tn\ln\frac{n}{e}\Big\} d^3x - T\int n\ln\frac{\hat{g}\psi}{\psi} d^3x \\ & + \mathcal{P}\int n[v(n) - v_0] d^3x, \end{aligned} \tag{3.44}$$

where the integration is to taken over all space.

The equation for the monomer density distribution can now be derived by minimizing the thermodynamic potential (3.44) with the constant number of monomers $N = \int nd^3x$; as a result we obtain the equation

$$\hat{g}\psi = \Lambda \exp\{\mu_{\text{eff}}/T\} \tag{3.45}$$

[compare with Eq. (3.34)], where the effective chemical potential is determined by the relation

$$\mu_{\text{eff}}(n) = \mu(n, \tilde{n}_s, T) - \chi(\mathcal{P}, T). \tag{3.46}$$

Here the solvent density is supposed to be expressed in terms of the monomer density according to (3.38). We should remember that exclusion of n_s by means of (3.38) can lead to a complex nonmonotonic dependence of $\mu_{\text{eff}}(n)$ on the temperature. It is well known, that in the case $n \to 0$ we have

$$\mu \cong T\ln n + n\chi. \tag{3.47}$$

Equations (3.44) and (3.45) give for the equilibrium value of the thermodynamic potential

$$\Phi = -TN\ln\Lambda - \int (p - nT - \mathcal{P}) d^3x. \tag{3.48}$$

This is the natural generalization of Eq. (3.33).

Thus the description of a polymer globule when we take into account the influence of the solvent differs from its description in the absence of the solvent only by the redefinition (3.46). Hereafter we shall assume that this renormalization is made and we shall omit the sign eff from $\mu_{\text{eff}}(n)$.

E. Some analogous problems in polymer physics

The Eqs. (3.31) and (3.32) were derived in order to construct a self-consistent theory of polymeric globules. Analogous equations are used in some other problems of polymer physics. Here we shall discuss some examples of this kind.

It is natural that when systems with linear memory are described, equations with operator $\hat{g}$ appear. However, most work in this field replaces $\hat{g}$ with the approximation $\hat{g} \to 1 + a^2\Delta$. This is equivalent to substituting for the $3N$-dimensional integral (3.7) the functional Wiener integral (Freed, 1972). Equation (3.31), for example, in this case takes the form

$$a^2\Delta\psi - (\Lambda e^{[\mu^*(n)/T]} - 1)\psi = 0\,, \tag{3.49}$$

i.e., becomes a second-order differential equation.

In a great number of cases (in the absence of a discrete spectrum, for example) we cannot confine ourselves only to calculating the contribution from the greatest eigenvalue to the partition function (3.10). Considering N in (3.8) as a continuous variable it is easy to find in this case the equation for the Green's function Z (which is analogous to the nonstationary diffusion equation)

$$\partial Z/\partial N + Z = e^{-\mu^*/T}\,\hat{g}Z\,. \tag{3.50}$$

Here the external field $\varphi(x)$ is replaced by the self-consistent field $\mu^*(n(x))$. Under the same assumptions as in (3.49) we obtain

$$\partial Z/\partial N = e^{-\mu^*(n)/T}\,a^2\Delta Z - (1 - e^{-\mu^*(n)/T})Z\,. \tag{3.51}$$

The second equation, which expresses n in terms of Z and which is necessary in order that the system of equations be closed, is obtained in each specific case in a different way.

Equations of the type (3.49)–(3.51) are often encountered in the polymer physics literature. Here we give some examples.

Equation (3.49) (with the replacement $\mu^* \to \varphi$) is well known in the theory of ideal coil adsorption (see Sec. VI).

If the density in the system is low and $\mu^*/T = 2nB \ll 1$, then Eq. (3.51) takes the form

$$\partial Z/\partial N = a^2\Delta Z - 2nBZ\,. \tag{3.52}$$

This equation was derived by Edwards (1965) in order to obtain a self-consistent solution of the excluded volume problem. Here $B \sim v$ is the second virial coefficient of monomer interaction in a good solvent.

Problems similar to those in the globule theory appear in the theory of boundary interfaces in inhomogeneous polymer materials and in the theory of interfaces between phases in phase-separated polymer solutions. Recent significant advances in the theory of such inhomogeneous polymer systems are due mainly to the work of Helfand and his collaborators (Helfand, 1975a, b, c, d, 1976; Helfand and Tagami, 1972, Helfand and Sapse, 1975, 1976; Helfand and Wasserman, 1976; Weber and Helfand, 1976). In these works equations quite similar to (3.51) appear. In order to derive the closing equation for the system of equations, considerations analogous to that given before Eq. (3.14) are used. Due to the splitting of correlations (for the polymer in bulk and in the concentrated phase of the solution) the main equation in these cases becomes an ordinary second-order differential equation, and the closing equation algebraic.

It should be noted that in the expression for the self-consistent field in Helfand's work there exist along with the local term $\mu^*(n)$ nonlocal terms proportional to Δn. These terms are due to the nonlocality of monomer interactions. This nonlocality actually always exists and must be compared with nonlocality due to bonding of monomers in the chain, which is expressed by the presence of the operator $\hat{g}$ in the main equations. A comparison of the two types of nonlocality made in Appendix B shows that nonlocality due to monomer interactions is less than that due to bonding of monomers by a factor $(v/a^3)^2$. Thus, as explained in Sec. III.C, such nonlocal terms do not appear in our equations.

The substitution $\hat{g} \to 1 + a^2\Delta$ is valid only for smooth enough density profiles. Hence, for sharp boundary interfaces (at temperatures significantly less than the critical one) it is necessary to solve an integral (and not a differential) equation [of the same type as (3.31)]. Another alternative approach was proposed by Helfand (1975c). His method consists in introducing the lattice model for a given system. In the lattice interpretation the integral is replaced by the sum and the integral equation amounts to the system of a great number of algebraic equations. These algebraic equations can be solved numerically. The shortcomings of this method are the well-known internal imperfections of the lattice model, and the main advantage is the fact that both types of nonlocality mentioned above are taken into account.

IV. SPATIAL STRUCTURE OF A GLOBULE

In this section we shall discuss the solutions of Eqs. (3.31)–(3.32) far from the points of conformational transitions. The problems connected with conformational transitions are discussed in the next section.

A. Large globule: The volume approximation (Lifshitz, 1968)

1. Character of the density distribution

First of all we shall consider the case of the so-called large globule, i.e., the globule whose dimensions R_0 are much more than $a (R_0 \gg a)$. For this condition to be fulfilled, the polymer chain must be long enough.

It is clear that the equilibrium structure of a globule includes the dense core, going out from which the density decreases and tends to zero at infinity. The density can *a priori* either decrease smoothly at distances $\sim R_0$ [Fig. 2(a)], or remain practically constant within the globule, decreasing sharply on its boundary [the characteristic length of this decrease is $l \ll R_0$ Fig. 2(b)].

It will be recalled that in both cases

$$S\{n\} \sim N^{\alpha}\,, \tag{4.1}$$

where α is equal to $\frac{1}{3}$ or $\frac{2}{3}$, i.e., is always less than unity (see Sec. III.B). At the same time the function $E\{n\}$ defined by (3.29) is proportional to N. Thus for long enough chains the free energy is equal in a first approximation to

$$F\{n\} = E\{n\} - TS\{n\} \approx E\{n\} = \int f^*(n)\,d^3x\,. \tag{4.2}$$

In view of the local character of the function (4.2) and the absence of derivatives in it, its minimum under the condition (3.15) corresponds to a step function of the type shown in Fig. 2(b). The smoothing of this function occurs owing to the entropy terms neglected in Eq. (4.2).

Hence the density profile of a large globule is a smoothed step function [Fig. 2(b)].

2. Volume approximation

In order to describe roughly the structure of a large globule one can introduce the volume approximation, in which the density profile is considered as an abrupt "step." This approximation neglects entropic surface terms. The density n_0 in the globule corresponds in this approximation to the minimum of Eq. (4.2), i.e., to the minimum of

$$F\{n\} = V_0 f^*(n_0) = (N/n_0) f^*(n_0)\,, \tag{4.3}$$

where V_0 is the volume of the globule. As a result of minimization we get

$$p^*(n_0) = 0\,. \tag{4.4}$$

The condition (4.4) determines the density in the core of a large globule. The free energy of this globule can be determined from (3.33):

$$F = -NT\ln\Lambda = N\mu^*(n_0)\,. \tag{4.5}$$

The last equality follows from (3.31), if we assume in (3.31) $\hat{g}\psi = \psi$ (we can assume this because of the constant density in the core of the globule). The condition (4.4) can be written in the form

$$0 = p^*(n_0) = f^*(n_0) - n_0\mu^*(n_0) = \int_0^{n_0} [\mu^*(n) - \mu^*(n_0)]\,dn\,. \tag{4.6}$$

The graphic interpretation of this condition is the coincidence of the shaded areas in Fig. 4. The free energy per monomer corresponds to the segment cutoff by the horizontal secant on the μ^* axis.

If one takes into account the external pressure $\mathcal{P}$ in the solvent, the condition (4.4) takes on the form

$$p(n_0) = n_0 T + \mathcal{P}\,. \tag{4.7}$$

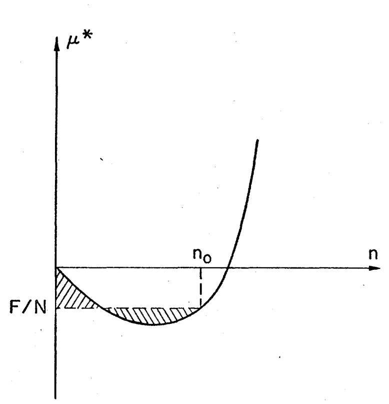

FIG. 4. Graphic determination of the density n_0 in the core of a globule and of the free energy of a large globule in the volume approximation.

B. Large globule: The surface terms (Lifshitz and Grosberg, 1973)

1. Formulation of the problem

If the entropy term in the free energy is not neglected, then the problem of determining the density profile near the boundary of the globule arises. In other words, we should like to know how the "step" is smoothed.[8] The answer to this question depends on the termperature: is $T > T_{\rm cr}$ or $T < T_{\rm cr}$, where $T_{\rm cr}$ is the critical temperature of the phase separation in the gas of separate monomers?[9]

If $T > T_{\rm cr}$, then all the values of density from zero to n_0 can be realized in the gas of separate monomers and the density profile has the form shown in Fig. 2(b). If $T < T_{\rm cr}$, then there is an interval of densities corresponding to the absolutely unstable states of the gas of separate monomers. It is natural to expect that the density in the globule never takes values in this interval, i.e., the globule is a sort of two-phase system with a sharp boundary between the core and the "fringe" (Fig. 5).

In the case $T < T_{\rm cr}$ there must be some additional conditions on the boundary for the equations to be closed. One of these conditions can be obtained from (3.34): from the definition of the operator $\hat{g}$ it follows that the function $\hat{g}\psi$ must be continuous, hence [see Eq. (3.34)] the chemical potential $\mu(n, T)$ must also be a continuous function:

$$\mu(n_+) = \mu(n_-)\,. \tag{4.8}$$

It can be shown that the second boundary condition is continuity of the local pressure (see Appendix A):

$$p(n_+) = p(n_-)\,. \tag{4.9}$$

The conditions (4.8) and (4.9) are the same as in the gas of separate monomers. Hence the boundary densities n_+ and n_- in the globule are the same as the densities of the coexisting phases in the gas of separate monomers. Thus n_+ and n_- can be considered as the known functions of temperature in the globule.

Let us pass now to the quantitative determination of the surface structure. Using Eqs. (3.33) and (4.5) it can be shown that the free energy of a globule is equal to

$$F = N\mu^*(n_0, T) - \int p^*(n)\,d^3x\,. \tag{4.10}$$

Since in the core of the globule $p^* = 0$, the last term in (4.10) is proportional to the surface area of the globule. This is a sort of entropic surface tension due to the linear memory. Denoting the corresponding surface tension coefficient by $\sigma(T)$ we can write

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[8] It is meaningful to determine the macroscopic density profile of the globule surface only when the width of the surface l is much larger than the interatomic distance, $v^{1/3}$. But it turns out (see below), that far from the θ point $l \sim a$. Hence analysis of the surface structure makes sense in this case only when $v \ll a^3$. At the same time, when T is close to θ it turns out that $l \gg a$ (see Sec. V). Hence, in this region, analysis of the surface structure is valid even when $v \sim a^3$.

[9] It should be noted that for the usual interactions $T_{\rm cr} < \theta$.

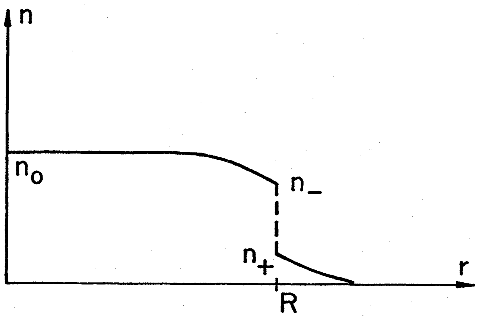

FIG. 5. Density distribution in the two-phase globule.

$$F=N\mu^*(n_0,T)+4\pi R_0^2\sigma(T)\,. \tag{4.11}$$

When there exists in addition a discontinuity in the density at the surface (Fig. 5) we must add to this expression a term corresponding to the ordinary surface tension: $4\pi R_0^2\sigma_0$. Since conditions (4.8) and (4.9) are the same as in a system without linear memory, σ_0 equals the surface tension in this system.

It should be noted also that the problem of determining the density profile in the case $R_0 \gg a$ is essentially one-dimensional. Introducing the coordinate x along the radius ($x=0$, when $R=R_0$), we obtain the following expression for the surface tension

$$\sigma(T)=-\int_{-\infty}^{+\infty} p^*(n(x),T)dx\,. \tag{4.12}$$

The problem of determining the surface structure can be formulated as follows: starting from Eqs. (3.31) and (3.32) determine the one-dimensional density profiles $n(x)$ and $\psi(x)$ and the surface tension σ. Let us consider the main steps in the solution of this problem as presented by Lifshitz (1968) (at $T>T_{\rm cr}$) and by Lifshitz and Grosberg (1973) (at $T<T_{\rm cr}$).

It should be noted beforehand that the problem under consideration is equivalent to the problem of determining the interphase surface structure in the phase-separated polymer solution. Thus the obtained results can also be applied to this last problem (see also Sec. IV.E).

2. The case $T>T_{\rm cr}$

Here it is convenient to use the local relation between n and ψ (3.35) and introduce the parametrically defined function $\nu(\psi)$

$$\nu=\exp(\mu(n,T)/2T)\,;\quad n=\psi\nu\,. \tag{4.13}$$

The approximate plot of this function at $T>T_{\rm cr}$ is shown is Fig. 6.

Using the function $\nu(\psi)$ we can write Eq. (3.34) in the outwardly simple form:

$$\hat{g}\psi=\Lambda\nu(\psi)\,. \tag{4.14}$$

When $T>T_{\rm cr}$ it is natural to expect that the density in the large globule changes smoothly. Thus we can replace the operator $\hat{g}$ by $1+a^2\Delta$. The obtained differential equation

$$a^2(d^2\psi/dx^2)=\Lambda\nu(\psi)-\psi \tag{4.15}$$

is easily integrated and the result has the form

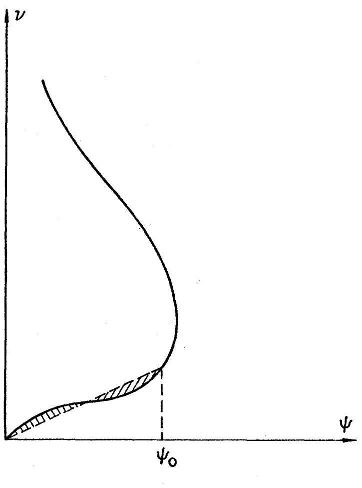

FIG. 6. Typical plot $\nu(\psi)$ at $\theta>T>T_{\rm cr}$. The value of ψ_0 in the core of the globule is determined by the equality of the shaded areas.

$$x=-a\int_{\psi(0)}^{\psi(x)}\left[2\int_0^{\psi}\{\Lambda\nu(\psi)-\psi\}d\psi\right]^{-1/2}d\psi\,. \tag{4.16}$$

In order to interpret this result we note that the formulas $\mu^*(n_0)=-T\ln\Lambda$ and $p^*(n_0)=0$ can be written in the form: $\Lambda\nu_0=\psi_0$ and $\int_0^{\psi_0}(\Lambda\nu(\psi)-\psi)d\psi=0$. Hence their graphic interpretation in Fig. 6 is the equality of the shaded areas.

It is easy to show that (4.16) actually leads to a simple density profile of the type shown in Fig. 2(b). In particular, when $x\to\pm\infty$ we obtain the simple exponential asymptotic forms

$$\psi(x)|_{x\to\pm\infty}\cong \text{const.}\exp[\mp\theta_\pm(x/a)]+\psi(\pm\infty)\,.$$

$$\psi(+\infty)=0\,;\psi(-\infty)=\psi_0\,.$$

$$\theta_+=(\Lambda-1)^{1/2}\,;\quad \theta_-=\left(\Lambda\left(\frac{\partial\nu}{\partial\psi}\right)_{\psi_0}-1\right)^{1/2}\,. \tag{4.17}$$

The result (4.16) allows us also to write the simple closed expression for the surface tension coefficient

$$\sigma=aT\int_0^{\psi_0}\left(2\int_0^{\psi}\nu(\psi)d\psi-\nu\psi\right)\Big/\left(2\frac{\psi_0}{\nu_0}\int_0^{\psi}\nu(\psi)d\psi-\psi^2\right)^{1/2}d\psi\,. \tag{4.18}$$

Equation (4.18) expresses σ explicitly through the thermodynamic functions of the equivalent system of separate monomers, i.e., gives the dependence $\sigma(T)$. A simple estimate shows that $\sigma\sim aT/v=(a^3/v)\cdot T/a^2$.

3. The case $T<T_{\rm cr}$

Now let us consider the case $T<T_{\rm cr}$, when the density profile has the bound shown in Fig. 5. In this case the chemical potential in the gas of separate monomers becomes the nonmonotonic function of n (Fig. 7), and as a result the plot of function $\nu(\psi)$ takes the form shown in Fig. 8.

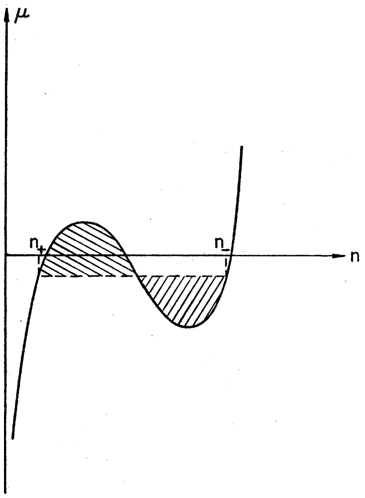

FIG. 7. Typical plot of $\mu(n)$ at $T < T_{cr}$. The equilibrium densities of the coexisting phases n_+ and n_- are determined by the equality of the shaded areas (Maxwell's rule).

The values of density n_+ and n_- can be determined from the well-known Maxwell's rule (see Fig. 7). It is easy to show that in Fig. 8 we have a rule analogous to Maxwell's: the equilibrium values of ψ_+ and ψ_- can be determined from the equality of the horizontally and vertically shaded areas.

The presence of a surface bounding the system can be taken into account in Eq. (4.15) by introducing the corresponding source term (Lifshitz and Grosberg, 1973). However, when the temperature is lowered the situation becomes more complex: according to the volume approximation the value of ψ_0 in the core of the globule is determined, as usual, by the equality of the obliquely shaded areas (Fig. 8), and it is seen that at low temperatures the point (ψ_0, ν_0) is situated on the decreasing brach of the function $\nu(\psi)$. In this case the singular point of Eq. (4.15), which corresponds to $x \to -\infty$, becomes the focus and not the saddle. This corresponds to the oscillating regime of the approach of $\psi(x)$ to $\psi(-\infty) = \psi_0$. In this situation the approximation $\hat{g} \to 1 + a^2\Delta$ is not valid and a more exact approximation is required—at least to account for the fourth derivative. The numerical solution of the integral equation for the simplest cases confirms the presence of the oscillating regime (Fig. 9). The physical reason for the oscillations is clear already from Fig. 2: in a region in which the density of monomers approaches the highest possible density, the probability of finding a given specific monomer (and, in particular, the end monomer) decreases.

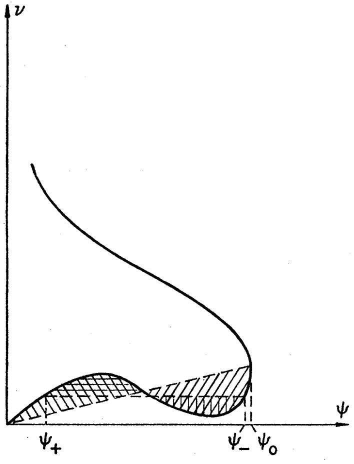

FIG. 8. Typical plot $\nu(\psi)$ at $T < T_{cr}$. The equilibrium boundary values of ψ_+ and ψ_- are determined by the equality of the vertically and horizontally shaded areas. The value of ψ_0 in the core of the globule is determined by the equality of obliquely shaded areas.

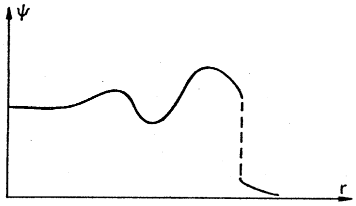

FIG. 9. The oscillating profile of ψ at low temperatures.

C. Small globule (Lifshitz and Grosberg, 1973)

In this section we shall consider the situation, on the face of it very exotic, of a chain in which the effective range of $v^{1/3}$ is so small (or a is so large), that not only is $v \ll a^3$, but in addition

$$\frac{v}{a^3} \ll \frac{1}{N} \ll 1 \tag{4.19}$$

or $N \ll \tilde{N} \sim a^3/v$. Such a chain can at $T < T_{cr}$ form a so-called small globule. The core of this globule occupies the volume $V_0 \ll a^3$ and is separated from the "fringe" by a sharp boundary (Fig. 10).

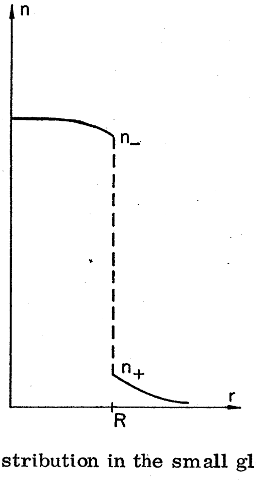

FIG. 10. Density distribution in the small globule.

The consideration of this situation is useful for two reasons. First, effects connected with the polymeric nature of the chain become more apparent in a small globule and are the main ones (and not the secondary or surface effects as in the large globule). Second, the mathematical description of small globules is relatively simple. Owing to these facts it is sometimes useful when considering a specific effect to analyze it first for the small globule; this often appears to be enough for a qualitative understanding of the general situation. Examples of analyses of this kind can be found in Lifshitz and Grosberg (1973), Grosberg and Liberol (1976), Grosberg (1976a), and Lifshitz, Grosberg, and Khokhlov (1976a). Here we shall consider a method of solving Eqs. (3.31) and (3.32) for the case of the small globule.

Since the characteristic length of the density variation is a, in the zeroth approximation the density in the core of the small globule may be considered to be constant and equal to its boundary value n_-. This is also the case for the ψ function.

Let us denote by $\psi_{\text{out}}(\mathbf{x})$ the function which is equal to $\psi(\mathbf{x})$ outside the core and to ψ_+ within the core. Thus $\psi_{\text{out}}(\mathbf{x})$ is a continuous function. In addition to this the interactions in the "fringe" will be neglected for simplicity $[\nu(\psi)=\psi$ when $\psi<\psi_+]$. Then Eq. (4.14) can be written in the form

$$\hat{g}\psi_{\text{out}}+V_0(\psi_- - \psi_+)g(\mathbf{x})=\Lambda_0\psi_{\text{out}}(\mathbf{x}) \tag{4.20}$$

(the index zero corresponds to the zeroth approximation). This linear integral equation with the nucleus $g(\mathbf{x}-\mathbf{x}')$ can be easily solved with the help of the Fourier transformation. The result has the form

$$\psi_{\text{out}}(\mathbf{x})=\frac{V_0(\psi_- - \psi_+)}{(2\pi)^3}\int e^{-i\mathbf{k}\mathbf{x}}\frac{g_{\mathbf{k}}}{\Lambda_0-g_{\mathbf{k}}}\,d^3k\,. \tag{4.21}$$

In order to determine the constants Λ_0 and V_0 it is necessary to use the normalization condition (3.15) and the equality $\psi_{\text{out}}(0)=\psi_+$. Simple calculations give

$$NQ(\Lambda_0)=n_+a^3\,, \tag{4.22}$$

$$V_0=NP(\Lambda_0)/(n_- - n_+)\,, \tag{4.23}$$

where the following definitions are introduced

$$J_m(\Lambda)=\left(\frac{a}{2\pi}\right)^3\int\left(\frac{g_{\mathbf{k}}}{\Lambda-g_{\mathbf{k}}}\right)^m d^3k\,;\quad P(\Lambda)=\frac{J_1}{J_1+J_2}\,;$$

$$Q(\Lambda)=J_1P\,.$$

Now let us find the free energy of the small globule in this approximation. Since outside the core $p^*=0$ and inside it $p^*(n_-)=p(n_-)-Tn_-=T(n_+-n_-)$, we have according to (3.33)

$$F_0=NT(P(\Lambda_0)-\ln\Lambda_0)\,. \tag{4.24}$$

The functions $P(\Lambda)$ and $Q(\Lambda)$ are determined by the form of the linear memory $g(\mathbf{x})$. (For the Gaussian nucleus they are given in Fig. 11.) One may say that if the function $n_+(T)$ is given, (4.22) determines $\Lambda_0(T)$ and then (4.24) determines $F_0(T)$. This is illustrated in Fig. 11. For the mutual arrangement of the plots in Fig. 11 it is essential that

$$\frac{P(\Lambda)}{Q(\Lambda)}\,\frac{dQ}{d\Lambda}=\frac{d}{d\Lambda}\,(P(\Lambda)-\ln\Lambda)\,. \tag{4.25}$$

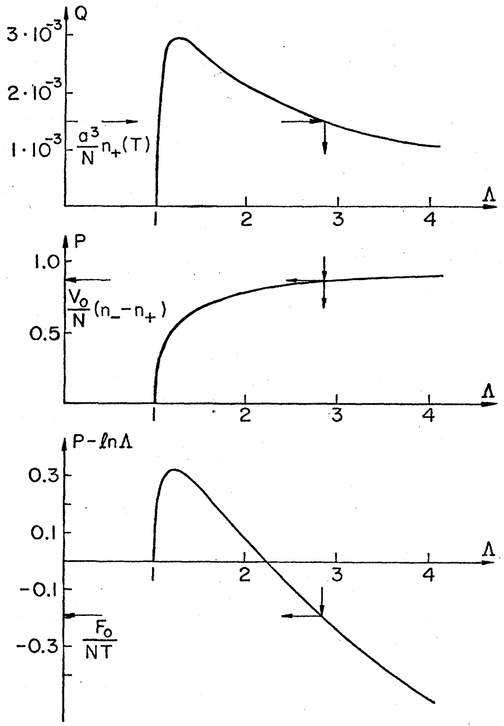

FIG. 11. Graphic representation of results for the small globule.

Due to this equality the maxima of functions $Q(\Lambda)$ and $P(\Lambda)-\ln\Lambda$ occur at the same value of Λ.

Let us return to the result (4.21). Expanding it in powers of $1/\Lambda_0$ we find

$$\psi_{\text{out}}=\sum_m\frac{V_0(\psi_- - \psi_+)}{\Lambda_0^m}\,\rho_m(\mathbf{x}) \tag{4.26}$$

$$\rho_m(\mathbf{x})=\int g(\mathbf{x}_1-0)g(\mathbf{x}_2-\mathbf{x}_1)\cdots g(\mathbf{x}-\mathbf{x}_{m-1})d^3x_1\cdots d^3x_{m-1} \tag{4.27}$$

Here $\rho_m(\mathbf{x})$ is the distribution function of the end point of a chain with m monomers and with the beginning fixed at the origin. Since ψ_{out} is the distribution function of the end point of the chain with N monomers, it is clear that the coefficient at ρ_m in (4.26) determines the probability of the existence in the fringe of the "tail" of m monomers. With the help of the equality $n_{\text{out}}=\psi^2_{\text{out}}$ one can find the probabilities of formation of the "loop" of m monomers.

The solution can be made exact by accounting for the next terms of the expansion in powers of the parameter $R_0/a\ll 1$. It turns out that the density distribution in the core follows approximately $g(\mathbf{x})$, in particular, the signs of the values $\Delta n(\mathbf{x})|_{x=0}$ and $\Delta g(\mathbf{x})|_{x=0}$ coincide. However, even when $n(\mathbf{x})$ is monotonic, $\psi(\mathbf{x})$ can be a nonmonotonic function. This function can make one or several oscillations in the core (Grosberg and Liberol, 1976). It will be recalled that a similar phenomenon is possible in the large globule.

It is clear that the zeroth approximation with respect to R_0/a corresponds to complete neglect of the influence of linear memory within the core of the globule. Thus we need the further approximations to determine the situation in such cases as, for example, the interaction of a small globule with the hard macroparticle (Grosberg and Liberol, 1976; Grosberg, 1976a).

D. Polymeric globule formed by saturating bonds

In the case of a globule of intermediate dimensions $V_0 \sim a^3$ general methods do not exist, and one must solve the general system of nonlinear integral equations (3.31)–(3.32) in each specific case. As a rule, only a numerical solution is possible. However, for one special interaction an analytical solution was found (Lifshitz, Grosberg, and Khokhlov, 1976b). This is the case of a globule formed by strong mutually saturating bonds widely spaced along the chain between the monomers, in the case when the excluded volume of monomers is small.

In this case the gas of separate monomers is a mixture of monatonic and diatomic ideal gases and its thermodynamic functions [in particular, $\mu^*(n, T)$] can be calculated exactly. As a result Eqs. (3.31), (3.32), and (3.15) take the form

$$\hat{g}(\tilde{\nu} + \tilde{\nu}^3) = \Lambda \nu , \tag{4.28}$$

$$n = (1/2K)(\tilde{\nu}^2 + \tilde{\nu}^4) , \tag{4.29}$$

$$\int (\tilde{\nu}^2 + \tilde{\nu}^4) d^3\xi = \beta ; \quad \beta = 2NK/a^3 , \tag{4.30}$$

where $\tilde{\nu} = \nu(2K)^{1/2}$, $\xi = \mathbf{x}/a$, and K is the monomer bonding constant [$K \sim \exp(-U/T)$, where U is the energy of a bond]. The system of Eqs. (4.28) and (4.30) contains only one parameter β. The simplest solution can be found in the case $\beta \to \infty$, when $\tilde{\nu}$ is large everywhere in the region of the particles, and, thus, $\tilde{\nu}$ can be neglected in comparison with $\tilde{\nu}^3$ and $\tilde{\nu}^2$ can be neglected in comparison with $\tilde{\nu}^4$. The obtained simplified system of equations has for a Gaussian nucleus a solution in the form of a Gaussian function. The calculation gives for the density profile

$$n(x) = \frac{N}{a^3}\left(\frac{2}{3\pi}\right)^{3/2} \exp\left(-\frac{2x^2}{3a^2}\right) , \tag{4.31}$$

and for the free energy

$$F = \tfrac{1}{2} NT \left[1 - \ln\left(\frac{2}{27\pi}\right)^{3/2} \beta\right] . \tag{4.32}$$

Let us consider now the region of applicability of the obtained results.

In fact these equations were obtained, firstly, by neglecting the excluded volume of monomers—thus requiring that $n(0)v \sim Nv/10a^3 \ll 1$—and, secondly, by neglecting $\tilde{\nu}$ with respect to $\tilde{\nu}^3$ in the region where the majority of monomers is located. The later condition means that the number of monomers outside the radius R, where $Kn(R) \sim 1$, must be negligible. Numerical analysis shows that this condition is fulfilled when $\beta \gg 1000$. Thus the region of applicability of the used approximation is

$$\frac{v}{10} \ll \frac{a^3}{N} \ll \frac{2K}{1000} .$$

In the described limit the width of the density profile does not depend on the temperature and on the length of the chain. The numerical solution of the system (4.28)–(4.30) at $\beta < 1000$ shows the slow dependence of n on T and N (Lifshitz, Grosberg, and Khokhlov, 1976b).

E. Spatial structure of some other polymer systems

In Sec. III.E some situations in polymeric systems, which are described by equations analogous to (3.31) and (3.32), were mentioned. The description of globular structures formed by external fields will be considered in Sec. VI; the excluded volume problem was considered in Sec. II; here we shall describe briefly the results, obtained by Helfand and co-workers, for the spatial structure of inhomogeneous polymer systems.

In several works (Helfand and Tagami, 1972; Helfand and Sapse, 1975; Helfand, 1975b) the structure of the boundary between weakly immiscible polymer materials in bulk was considered. As has already been noted, from the mathematical point of view this problem amounts to an ordinary differential equation of the second order. For the specific solution a special, but realistic, form of the potential $\mu^*(n_A, n_B)$ was chosen (n_A and n_B are the densities of the immiscible polymer components). An exact analytical solution was obtained in the case of low compressibility of polymer materials; the general case was considered numerically.

If we characterize the mixability of polymer materials by the Flory parameter χ [the energy (in units of T) necessary to exchange the positions of monomers A and B, if initally these monomers were situated in pure substances consisting only of A and B] then at small χ the width of the surface layer is $\sim\chi^{-1/2}$ and the surface tension is $\sim\chi^{1/2}$ (Helfand and Tagami, 1972; Helfand and Sapse, 1975).

The interphase boundary in phase-separated polymer solutions was considered by Helfand (1976), Helfand and Sapse (1976), and Weber and Helfand (1976). The results and the method [in the work by Helfand and Sapse (1976)] do not differ significantly from those described in Sec. III.B.2. In the future it will be important to calculate in more detail the structure of the interphase boundary surface near the critical point of precipitation of the solution, bearing in mind that the self-consistent theory is longer valid near this point.

One more important example of the application of equations of the same type is the block-copolymer theory (Helfand, 1975c; Helfand and Wasserman, 1976). Helfand and Wasserman have considered block copolymers of the type A-A-...-A-B-B-...-B in bulk. If the monomers A and B are immiscible, they will tend toward phase separation, but the presence of the valent chemical bond between A and B will prevent this. As a result, a microdomain structure is formed. If the number of monomers types A and B are approximately equal, then lamellar structure becomes the most advantageous (Fig. 12). The theory developed by Helfand (1975c) and Helfand and Wasserman (1976) allows us to determine the period of such a structure and the form of the density profile.

In this case an equation of the type (3.51) is solved with periodic boundary conditions: the values of Z, n,

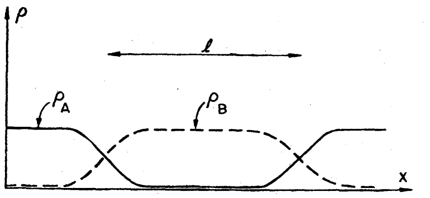

FIG. 12. Schematic image of the lamellar structure of a block-copolymer in bulk.

etc. are considered to vary in some direction periodically with the period d. From equations with this sort of boundary conditions the free energy $F(d)$ is found. Then $F(d)$ is minimized with respect to d in order to determine the equilibrium value of d.

We shall not go more deeply into this interesting problem because, from our point of view, the construction of the theory is far from being completed. The reader who is interested in specific calculations and the first results can find them in the cited references.

V. THEORY OF THE COIL-GLOBULE TRANSITION

A. Formulation of the problem

The problem of describing the transition of a polymer chain from the globular state to the coil arose historically in connection with the problem of the denaturation of a protein globule (Volkenshtein, 1975). It will be recalled that protein denaturation occurs as a sharp cooperative transition with a pronounced heat effect (Joly, 1965). As a result of denaturation the highly specific spatial structure of a protein globule is completely destroyed, this being manifested in the disappearence of enzyme activity. The question arises as to what extent the cooperativity of the protein denaturation may be explained on the basis of the coil-globule transition in a homopolymer. This formulation of the problem attracted attention to coil-globule transitions, and a large number of works is devoted to their analysis.

It will be recalled (Sec. I.C) that, according to the accepted definition, the coil and the globule are different macroscopic phases and the coil–globule transition is a phase transition (when $N\to\infty$). If N is finite, this transition is a more or less sharp cooperative transition with the width ΔT and it can be classified according to Sec. I.C.

Let us describe the main premises of coil-globule transition theory. In the previous section we considered for some limiting cases the structure of a globule, and we calculated its free energy F with respect to the free energy level of an ideal coil. Thus, for these cases, we can find directly the transition point from the condition $F=0$.[10]

The width of the transition can be obtained from the following considerations. According to the formulated theory, the globular state corresponds to the splitting of correlations in (3.7). It is easy to see that the validity condition for (3.12) has the form $F\sim NT\gg T$. Thus, in the region $F\lesssim T$, it is necessary to take into account the influence of the next eigenfunctions. These eigenfunctions change the fluctuation regime: so the width of the region where $F\lesssim T$ is just the width of the transition ΔT:

$$F(T_c)=0;\quad F(T_c-\Delta T)\sim T\ll NT. \tag{5.1}$$

B. Coil-globule transition in the long chain ($R_0 \gg a$) (Lifshitz, Grosberg, and Khokhlov, 1976b)

1. Volume approximation

Let us consider first the volume approximation. In this case, according to (4.5), $F=N\mu^*(n_0,T)$ and thus the transition temperature can be determined from $\mu^*(n_0,T_c)=0$. The most realistic form of the function $\mu^*(n,T)$ is shown in Fig. 4 (an alternative plot is shown in Fig. 15 and will be considered in Sec. D). Graphically the transition temperature can be determined from the condition of coincidence of the horizontal secant with the x axis. From Fig. 4 it is clear that as $T\to T_c$ the density in the globule tends to zero: $n_0\to 0$. This allows us to use for the thermodynamic functions μ^* and p^* the virial expansion

$$\begin{aligned}\mu^*&=2nTB(T)+3n^2TC(T),\\ p^*&=n^2TB(T)+2n^3TC(T).\end{aligned} \tag{5.2}$$

Owing to this fact the universal description of the transition in terms of the second and third virial coefficients of monomer interaction B and C becomes possible.

Starting from (5.2) it is easy to obtain explicit formulas for the volume approximation. The density in the core of the globule is equal to

$$n_0=-B/2C\quad (p^*(n_0)=0), \tag{5.3}$$

and the free energy of a globule

$$F=-NTB^2/4C, \tag{5.4}$$

and, according to (4.5),

$$\Lambda=1+B^2/4C. \tag{5.5}$$

The globule radius $R_0=(3N/4\pi n_0)^{1/3}$ can be found from (5.3).

It is seen that $F=0$ at $B=0$. Thus in the volume approximation the temperature of the coil-globule transition T_c coincides with the θ temperature. Near the θ point B and C can be expressed in the form:[11]

$$\begin{aligned}B(T)&=b(T-\theta)/\theta=-b\tau,\\ C(T)&\cong C>0.\end{aligned} \tag{5.6}$$

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

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[10] Even if at the transition point the coil is not ideal, but is the coil with excluded volume, this condition is conserved, because $F\sim NT$, and the difference between the free energies of any two coils is always much less than NT.

[11] It should be noted that in this section τ differs in sign from that used in Sec. 11.

2. Consideration of surface terms

However, the above consideration does not take into account the surface effects, which are essential near the transition point. Actually, when $T \rightarrow \theta$ we have, according to (5.5), $\Lambda \rightarrow 1$, i.e., according to (4.17), the width of the surface layer $\sim a/(\Lambda - 1)^{1/2}$ increases. From (4.18) it can be found that in this case

$$\sigma = aB^2 T/8C^{3/2}\,. \tag{5.7}$$

Thus we obtain for the total free energy (4.11)

$$F = -N\,\frac{T\,b^2}{4C}\,\tau^2\left\{1 - \left(\frac{\tau_c}{\tau}\right)^{2/3}\right\}, \tag{5.8}$$

$$\tau_c = 1 - \frac{T_c}{\theta} = (18\pi)^{1/2}\,\frac{a^{3/2}\cdot C^{1/4}}{b\cdot N^{1/2}}\,. \tag{5.9}$$

The point T_c is the point of the coil–globule transition, because $F(T_c) = 0$. We note that just at T_c the values of the globule radius R_0 and of the width of the surface layer $\sim a/(\Lambda - 1)^{1/2}$ are of the same order of magnitude; this means that at this point the negative volume part of the free energy and the postive surface part are equal to each other. When $N \rightarrow \infty$ the point of the transition tends to θ point.

Let us determine the width of the transition from (5.1). It is easy to find

$$\Delta T \sim (\theta - T_c)\,\frac{C^{1/2}}{a^3} \sim \theta\,\frac{C^{3/4}}{a^{3/2} b N^{1/2}}\,. \tag{5.10}$$

In the case $C^{1/2} \ll a^3$ we have $\Delta T \ll \theta - T_c$, thus the transition occurs at the point T_c and the transition region is separated from the θ point. In the case $C^{1/2} \sim a^3$ the transition occurs in the region including the θ point.

If v is the characteristic volume of a monomer, then for ordinary interactions $b \sim v$; $C \sim v^2$; i.e., $C^{1/2}/a^3 \sim v/a^3$. It was shown in Sec. II that the parameter v/a^3 plays an important role in the coil structure. Now we see that it determines also the picture of the coil–globule transition. Equations (5.9) and (5.10) can be written in terms of v and a^3

$$\tau_c \sim (a^3/Nv)^{1/2}\,; \quad \Delta T \sim \theta(v/a^3 N)^{1/2}\,.$$

We saw in Sec. II that in the region of universality ($T > \theta$) all the results for the persistent model can be obtained from the results for the "bead" model by means of the substitution $v/a^3 \rightarrow 1/M$. Since, in addition to this, for the persistent model we have $C^{1/2}/a^3 \sim M^{-3/2}\ln^2 M$ (Onsager, 1949), then in the description of the coil-globule transition we may also use this substitution for qualitative purposes. Thus, in order to obtain corresponding results for the persistent model, the substitution $v/a^3 \rightarrow 1/M$ [see Eq. (2.25)] is to be made in all the formulas of this chapter. In particular, the case $v/a^3 \ll 1$ corresponds to stiff chains and the case $v \sim a^3$ to flexible ones.

The character of the transition, as is clear from Eq. (5.8), is unusual. In the region $1 \gg \tau \gg \tau_c$ we have $F \approx -\mathrm{Const}.N\tau^2$ and the behavior of the system is typical for the second-order phase transition: the density (5.3) decreases gradually and the globule broadens (R_0 increases). But within the small region near the transition point $\tau - \tau_c \ll \tau_c$ the behavior of the system changes: in this region[12] $F \sim (T_c - T)a^3/C^{1/2}\tau_c$. Such a dependence on $(T_c - T)$ is typical for a first-order phase transition, but in this case the transition is close to second-order, since the coefficient at $(T_c - T)$ is proportional to $N^{1/2}$ and not to N, i.e., the heat of the transition per monomer

$$\frac{\Delta Q}{N} = \left(\frac{\pi}{2}\right)^{1/2}\theta\,\frac{a^{3/2} b}{C^{3/4} N^{1/2}} \sim \theta\left(\frac{a^3}{Nv}\right)^{1/2} \tag{5.11}$$

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

The density in a globule at the transition point is

$$n_g = 3\left(\frac{\pi a^3}{2C^{3/2}N}\right)^{1/2} \sim \frac{1}{v}\left(\frac{a^3}{Nv}\right)^{1/2}, \tag{5.12}$$

i.e., because of dependence on N the density in a globule at the transition point falls to a value of the same order as the coil density. On the other hand, the parameter of volume binary interaction in the coil at the transition point is of order $Z = N^{1/2}B/a^3 \sim C^{1/4}a^{-3/2} \sim (v/a^3)^{1/2}$. Consequently, in the case under consideration, $v \ll a^3$ (see Footnote 12), the coil at the transition point can be considered as Gaussian and its density $n_c \sim 1/a^3 N^{1/2}$. The relative change in density during the transition is

$$\frac{n_g - n_c}{n_c} \sim \left(\frac{a^3}{v}\right)^{3/2}. \tag{5.13}$$

Thus the density at the transition point even when $N \rightarrow \infty$ increases only a finite number of times; the number of additionally formed contacts is relatively small (in comparison with the quantities $\sim N$). When the temperature is further lowered, the globule density increases gradually, tending to the maximum probable density $n \sim 1/v$ (at this density all the solvent molecules are displaced from the globule).

If $v \sim a^3$, then from (5.12) and from the extrapolation of the transition characteristics obtained earlier for the case $v \ll a^3$, it follows that in this case in the region around the θ point of width $\Delta T \sim \theta \cdot N^{-1/2}$ a gradual transition from the globular to the coil state occurs. It is natural to identify this transition with the second-order phase transition.

For the sake of comparison the approximate temperature dependence of the average density in the globule is shown in Fig. 13 for the two cases $v \ll a^3$ and $v \sim a^3$. The difference between the plots in Fig. 13 is due to the fact that when $v \ll a^3$ there exist in the transition region two minima in the configurational space with "pumping" of the distribution function of the system from one minimum to another during the transition. At the same time, when $v \sim a^3$ there exists only one minimum, continuously moving during the transition from the coil to the globular region.

Let us sum up the results of the consideration of the coil-globule phase transition in a long polymer chain.

(a) The case $v \ll a^3$ (stiff chains). Somewhat below the θ point [see Eq. (5.9)] there occurs a sharp first-order phase transition with the jump in density (5.13) and width

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[12] Such a formula for the free energy makes sense in this region only if $|F| \gg T$; if this is not the case the equations for globules are not applicable (see Sec. V.A). Thus this formula has a region of validity only if $a^3 \gg C^{1/2}$ or $v \ll a^3$. This will be implied unless otherwise indicated.

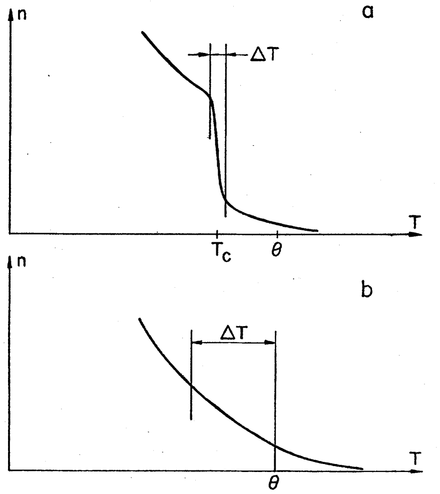

FIG. 13. The temperature dependence of the average density in a globule in the coil-globule transition region (a) $v \ll a^3$ (b) $v \sim a^3$.

(5.10). However, this transition has some features [for example, the heat of the transition (5.11)], which make it similar to a second-order phase transition.

(b) The case $v \sim a^3$ (flexible chains). A gradual second-order phase transition occurs over the width of the entire region.

Even in the case $v \ll a^3$, when there exists a significant jump in density, the heat of the transition is small. Hence this transition can be observed by means of the viscosimetric and light scattering methods more easily than by means of calorimetric methods.

In conclusion we note that the theory we developed is quite analogous to the classical van der Waals theory of surface tension at the critical point.

C. Conditions for the existence of globules in the solution

The main difficulty in experimentally observing the coil-globule transition in homopolymer solutions is the precipitation of the solution below the θ point. The precipitation leads to a gain in free energy due to the decrease in surface area contact between the globular phase and the pure solvent $\sim \sigma R_0^2$. However, in this case there is a loss in the free energy of the relative motion of globules $\sim T \ln(n_0/c)$, where c is the average concentration of monomers (since N/n_0 is the volume of a globule, and N/c is the volume per globule in the solution, n_0/c is the volume fraction of globules in the solution). Thus the solution does not precipitate if [see Eqs. (5.7) and (5.3)]

$$\left| \ln \frac{cv}{\tau} \right| \gtrsim N^{2/3} \left(\frac{a^3}{v} \right)^{1/3} \tau^{4/3} . \tag{5.14}$$

In particular, for the globule to remain in solution at the transition point, it is necessary [see Eq. (5.9)] that

$$\left| \ln c \left(\frac{C^{1/2}}{a^3} N \right)^{1/2} \right| \gtrsim \frac{a^3}{C^{1/2}} . \tag{5.15}$$

We see that the sharper the transition (or the larger the parameter v/a^3) the more dilute the solution must be in order to avoid precipitation at the transition point. Thus the main difficulty in experimental observation of the described transition is the weakness of effects from very dilute solutions.

If one replaces the sign $\gtrsim$ in (5.14) by $\sim$, one will obtain the equation for the precipitation curve at small concentrations, when chains exist in the solution in globular conformation. It was supposed by Daoud and Jannink (1976) that this curve is described (when $v \sim a^3$) by the scaling relation

$$\tau N^{1/2} = f(cN^{1/2}) . \tag{5.16}$$

Our result (5.14) is in accord with (5.10), and thus it gives explicitly the asymptotic form of the function f in (5.16) at the small values of the argument (i.e., at $c \ll c_{\mathrm{cr}}$):

$$f(x) \sim |\ln x|^{3/4} \quad \text{at } x \ll 1 . \tag{5.17}$$

D. Some other possible types of phase transitions in a globular macromolecule

(1) The function $\mu^*(n)$ can have several extrema at low temperatures. These extrema can be connected, in particular, with the existence of different phases in the gas of separate monomers.

In the presence of additional extrema Eq. (4.4), which determines the density n_0 in the globule, can have several solutions. These solutions correspond to globules with different densities in their cores and with different free energies $N\mu^*(n_0^{(1)})$ and $N\mu^*(n_0^{(2)})$. If owing to a change in temperature the difference of these free energies changes sign, then a first-order globule-globule phase transition occurs in which the core is rearranged. Graphically the transition point corresponds to the situation shown in Fig. 14.

(2) The situation when the plot $\mu^*(n)$ has the form shown in Fig. 15 is unlikely, but generally possible. In this case a coil-globule transition occurs, as may be seen from the figure, at $T_c > \theta$; the density in the globule re-

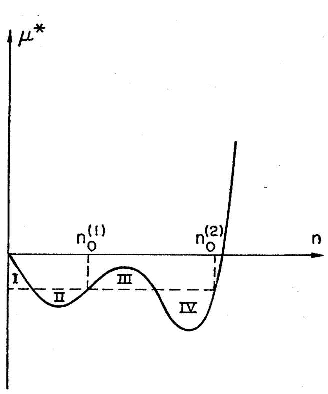

FIG. 14. Plot of $\mu^*(n)$ at the transition temperature between two globule states of density $n_0^{(1)}$ and $n_0^{(2)}$. Area I is equal to Area II; Area III is equal to Area IV.

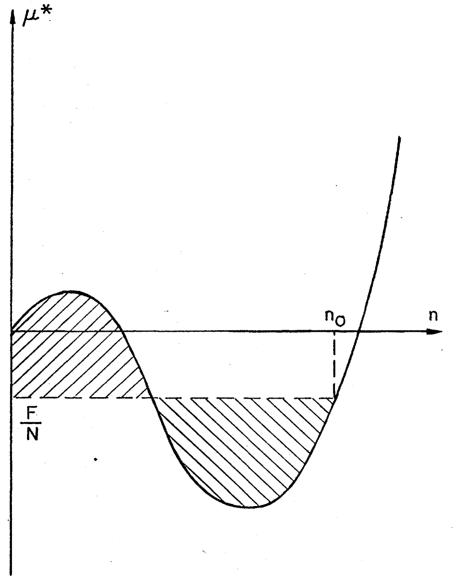

FIG. 15. An example of the dependence $\mu^*(n)$, at which the coil-globule transition is a first-order phase transition.

mains finite at the transition point even in the volume approximation. The transition itself is a first-order phase transition. Possibly this transition could be used as a model of the cooperative coil-globule transition in proteins.

(3) At sufficiently low temperatures, when the bound of density is formed at the surface of the globule, another type of phase transition is possible. The thermodynamic minimum could correspond not to a density distribution of the type shown in Fig. 5, but to the density distribution shown in Fig. 16. This is a first-order transition from a globule with fringe to a globule without fringe; it was considered by Lifshitz and Grosberg (1973).

(4) For a small globule (see Sec. IV.C) the temperature and the order of the coil–globule transition can also be found directly from the formulas of Sec. IV.C. Since in the small globule there exists a parameter a^3/v larger than N, the coil–globule transition in such a globule occurs in another way than that described above for the case of an extremely long chain; here we must search for intermediate asymptotic forms for the thermodynamic values.

From (4.24) it follows that the coil–globule transition occurs in this case at $P(\Lambda_0) = \ln\Lambda_0$ (see also Fig. 11).

Near the transition temperature we find with the help of Eqs. (4.22)–(4.24)

$$F = V_0(T - T_c)\, T_c\, \frac{\partial n_+}{\partial T_c}\, \frac{n_- - n_+}{n_+}\,.$$

Hence the transition is the usual first-order phase transition with a jump in density. The width (5.1) of this transition is $\sim 1/N$. It occurs below the critical temperature in the gas of separate monomers and, consequently, significantly below the θ point. When a small globule is formed, the density in the globule becomes at once equal to the value n_-, which correspond to a significant displacement of the solvent.

(5) If a polymer chain is stiff enough and if the attractive forces between the pieces of the chain are sufficiently strong, then orientational ordering, i.e., a transition to the liquid-crystalline state, becomes possible. The connection between the temperature of this transition and the other characteristic temperatures of the system is not yet known.

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

As has already been noted, there exists a great number of works devoted to determining coil–globule transition characteristics.

1. Theoretical approaches

The first attempt known to these authors to costruct a theory of the coil–globule transition was made by Ptitsyn and Eisner (1965). The theory was developed further by Eisner (1969). An analogous approach to this problem was formulated recently by de Gennes (1975). These works, in essence, modify Flory's method for the calculation of the expansion factor of a polymer chain α^2 (see Sec. II). If in the expression for the free energy of mixing F_{mix} not only the binary interaction, but also the three-body interaction of monomers is included, then Flory's equation (2.15) takes the form

$$\alpha^5 - \alpha^3 - c_2(y/\alpha^3) = c_1 Z\,, \tag{5.18}$$

where $y = C/a^6$, and c_2 is the numerical coefficient. Analysis of this equation shows that at small enough y the dependence $\alpha(Z)$ is not single-valued for some Z. At larger y the dependence $\alpha(Z)$ is always single-valued (see Fig. 17). This suggests (de Gennes, 1975) that when y (or v/a^3) is lowered a fairly sharp conformational transition can occur below the θ point, the sharpness

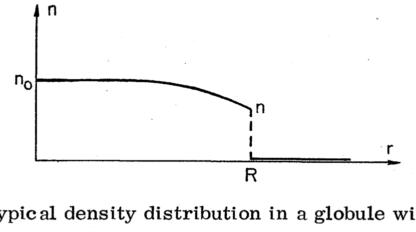

FIG. 16. Typical density distribution in a globule without fringe.

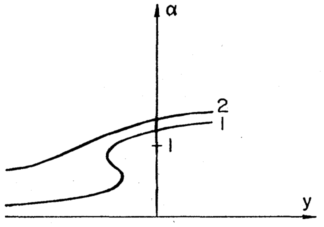

FIG. 17. The plot $\alpha(z)$ at (1) $y \ll 1$; (2) $y \sim 1$.

of the transition increasing with the decrease of y. This conclusion agrees with our considerations above. However, one cannot obtain more detailed information concerning the character of the transition on the basis of this approach.

Oono (1976) proved strictly that at any temperature $T < \theta\ R^2$ is always $\sim N^{2/3}$ at $N \to \infty$, where R is the mean square end-to-end distance. Saito and Inoue (1974) showed that $T_c \to \theta$ at $N \to \infty$. These conclusions can also be obtained from our theory.

Massih and Moore (1975) considered the exactly solvable lattice model of the self-interacting polymer chain, which is represented by walks on the lattice of the "Bethe cactus" type. It was shown that a second-order phase transition exists at some temperature for this model. However, this model describes a polymer chain not in the usual three-dimensional space, but rather in the space of infinite number of dimensions (Nagle, 1974); thus the obtained result bears no relation to the usual coil–globule transition.

An attempt to construct a theory of the coil–globule transition was made recently by Moore (1977). His approach is essentially analogous to that of Lifshitz, Grosberg, and Khokhlov (1976b) (Sec. V.B of this paper). However, the author, correctly noting from the beginning that the phase transition itself can occur only at infinite N, then refuses to consider and classify the conformational transitions occurring at finite N. Such an approach in application to polymers, in which the number of monomers is usually not great (10^4–10^5), does not seem to be convenient; for such a system our terminology (Sec. I.C) is physically more reasonable. In application to the problem of the coil–globule transition Moore's approach led to the incorrect conclusion that the coil–globule transition always (even at $v \ll a^3$) occurs as a second-order phase transition.[13]

2. Computer experiments

Let us pass now to the results obtained in the computer experiments. As a rule, in these experiments the chain is simulated by random self-avoiding walks on some spatial lattice, the attractive interaction energy being attributed to each two links of the chain separated by only one edge of the lattice.

The most complete analysis of the coil–globule transition in computer experiment was made in a series of articles Cron *et al.*, 1967; Elyashevich and Skvortzov, 1971; Birshtein, Elyashevich, and Morgenshtern, 1974. These articles differ from others in determing the influence of chain stiffness upon the characteriestics of the transition. The main conclusion of these works is the statement that the coil–globule transition occurs in stiff chains as a sharp first-order phase transition, and in flexible chains as a smoother transition which is not of the first-order. These facts agree with our theoretical considerations.

Domb (1974), basing his analysis on computer data, assumed that the coil–globule transition is always a first-order phase transition, occurring at some critical temperature $T_c < \theta$ (when $N \to \infty$). Apparently this conclusion is due to the incorrect extrapolation of computer data.

The conclusion that at some temperature T_c, which is significantly lower than θ, there exists a first-order phase transition was obtained by Finsy, Janssens, and Bellemans (1975) for the model chain on a cubic lattice. If after a more detailed analysis this conclusion should be confirmed, this will mean the existence for such a chain of the globule-globule transition described in Sec. V.D.

3. Experiments with real polymers

As to real experiments concerning the observation of the coil–globule transition, the main difficulty here, as has already mentioned, is in working with small concentrations of polymer in the solution. Polydispersity, presence of defects, branching of the chain, etc. also distort the picture; thus the polymers must be well-prepared. Studies of the conformations of such "pure" polymer chains below the θ point were initiated very recently (Mazur and McIntyre, 1975; Slagowski, Tsai, and McIntyre, 1976) on the well-known system of polystyrene in cyclohexane. In a note by Slagowski, Tsai, and McIntyre (1976) it is reported that when the temperature is lowered 1.5 degrees below the θ point the value of α^2 for the polymer chain ($N = 4.5 \cdot 10^5$) decreases 3 times. Further advances in the region below the θ point must allow us to observe the whole region of the coil–globule transition for a given polymer-solvent system.

In the literature there exist many reports on various conformational transitions in the vicinity of the θ point (for example, Eskin and Nesterov, 1965; Eskin and Serduk, 1969; Cuniberti and Bianchi, 1974; Mashimo *et al.*, 1975). Sometimes these transitions are called coil–globule transitions. However, for a coil–globule transition to occur, the intermolecular interaction must be weaker than the intramolecular one. In the indicated

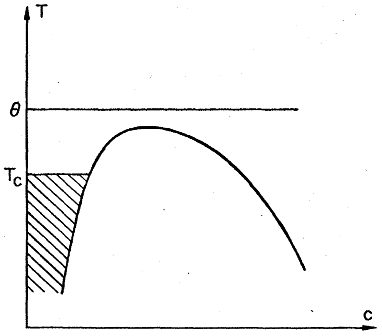

FIG. 18. The simplest phase diagram of a polymer solution. The shaded region corresponds to the region where isolated globules exist in the solution.

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[13] It should be noted that Moore's article (1977) also contains criticism of articles by Lifshitz (1968) and by Lifshitz and Grosberg (1973). This criticism is groundless for the same reason. The transitions at finite N, considered by Lifshitz (1968) and Lifshitz and Grosberg (1973), were classified as phase transitions in the sense indicated in the introduction.

works this is not always the case [for example, in the articles by Eskin and Nesterov (1965), Eskin and Serduk (1969]. The question whether in these works the coil–globule transition (and not some other transition) was actually observed, clearly requires additional experimental analysis.

The construction of a theory of the coil–globule transition completes the theory of globules, in the sense that this theory establishes the region of existence of homopolymer globules in the solution [see Eqs. (5.9) and (5.14)]. A phase diagram for polymer solutions with average monomer concentration c at variable temperatures T is given in Fig. 18. The shaded area corresponds to the region where globules exist in the solution.

VI. GLOBULAR STRUCTURES FORMED BY EXTERNAL FIELDS

A. Physical meaning of an effective attractive field

The equations which describe the structure of a chain without volume interaction in an external attractive field were obtained earlier [see (3.11) and (3.14)] in order to construct a general self-consistent theory of polymeric globules. However, in some cases, the problem of the behavior of a polymer chain in the external field has its own physical meaning. In these cases the attractive field is not necessarily a real physical field (electric, etc.); it may be some effective thermodynamic characteristic which reflects the spatial inhomogeneity of the solvent, the presence of the interphase surface, or macroparticles in the solvent, etc. The field φ is, in essence, determined by Eq. (3.7).

As it has already been noted in Sec. II, the spatial structure of a polymer chain in the presence of an external field depends essentially on whether the relevant equation [Eq. (3.11) in the absence of volume interactions, or Eq. (3.31) with the replacement of $\mu^*(n)$ by $\mu^*(n)+\varphi$ in the general case] has a discrete spectrum. Let T_c be the temperature at which the first discrete level splits off from the continuous spectrum. Then at $T>T_c$ the chain is not held by an attractive field,[14] i.e., field has no influence on its spatial structure. If $T<T_c$, then the chain is basically situated near the well (the chain is "captured" by the well) and forms a globule [see the definition of a globule and Eq. (3.18)]. It is natural to call T_c the temperature of capture. The capture of a polymer chain by the potential well, occurring when the temperature is lowered from $T>T_c$ to $T<T_c$, and the globular structure of the system after the capture (at $T<T_c$) were considered by Lifshitz (1968) for the chain without volume interaction and by Lifshitz, Grosberg, and Khokhlov (1976a) for the coil with excluded volume.

The most important physical case in which the polymer chain interacts with the potential well is the adsorption of the chain on the attracting surface. This phenomenon has been considered in a large number of theoretical works (see below).

B. Polymer chain without volume interactions in a potential well

1. Capture of a polymer by the well

Let us consider the solution of Eq. (3.11) at temperatures slightly below $T_c[\tau=(T_c-T)/T_c\ll 1]$. As we approach T_c we expect (this will be confirmed by the final result) that the globule will broaden until it becomes wider than the well. In this case the approximation $\hat{g}\to 1+a^2\Delta$ must be valid. This gives outside the well, where $\varphi=0$,

$$\psi|_{x\to\infty}\cong\frac{\text{const}}{x}\exp\left(-\frac{x}{a}(\Lambda-1)^{1/2}\right). \tag{6.1}$$

From (6.1) it is clear that the critical temperature corresponds to $\Lambda=1$ [in agreement with Eq. (3.31)]. Thus at the critical temperature

$$\psi|_{T_c,x\to\infty}\cong\frac{\text{const}}{x}. \tag{6.2}$$

Let us write Eq. (3.11) in the form

$$(\hat{g}-1)\psi=(\Lambda-1)\psi\exp(\varphi/T)+\psi\{\exp(\varphi/T)-1\} \tag{6.3}$$

and let us take into account in this equation that $\Lambda-1\ll 1,\ \tau\ll 1$

$$(\hat{g}-1)\psi-\psi\{\exp(\varphi/T_c)-1\}=\psi\exp(\varphi/T_c)\left\{(\Lambda-1)-\frac{\varphi}{T_c}\tau\right\}. \tag{6.4}$$

Since the function $\psi_c=\psi|_{T=T_c}$ is the solution of the homogeneous equation with the same left-hand side, the existence of a solution for (6.4) depends on the orthogonality of the right-hand side and on ψ_c having the appropriate weight:[15]

$$(\Lambda-1)\int\psi\psi_c\exp(\varphi/T_c)d^3x=-\frac{\tau}{T_c}\int\psi\psi_c\exp(\varphi/T_c)\varphi d^3x. \tag{6.5}$$

The integral in the left-hand side diverges when $\tau\to 0(\Lambda\to 1)$ at great distances due to the broadening of the globule. The character of this divergence can be found from (6.1) and (6.2). As a result we get from (6.5)

$$\Lambda=1+\tfrac{1}{2}A\tau^2. \tag{6.6}$$

After this from (3.13) we find

$$F=-\tfrac{1}{2}T_cNA\tau^2, \tag{6.7}$$

i.e., the capture has the character of a second-order phase transition—it occurs continuously, without a heat of transition, with the change in specific heat (NA) and with gradual broadening of the system from the dimensions of the well to the coil dimensions.[16]

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[14] In the future we shall use the term "potential well" or simply "well" instead of the term "attractive field."

[15] The weighting factor exp (ϕ/T) appears as a result of symmetrization when (3.11) is put into explicitly Hermitian form.

[16] The above consideration is valid only if Eq. (3.11) is valid, i.e., if the largest eigenvalue gives an overwhelming contribution to the partition function. Thus it is necessary (see Sec. V) that $|F|\gg T$, i.e., [see Eq. (6.7)] $\tau\gg N^{-1/2}$.

2. Globular structure of the ideal chain captured by the well

To analyze the globular structure of a chain captured by the well amounts to solving the linear equation (3.11) parallel with (3.14) and (3.15). If the characteristic dimension of the well R is much more than a, then the approximation $\hat{g} \to 1 + a^2\Delta$ is valid and (3.11) can be written in the form

$$\Delta\psi - \frac{\psi}{a^2}\left[\exp\left(\frac{\varphi - \lambda}{T}\right) - 1\right] = 0\,, \tag{6.8}$$

where $\exp(-\lambda/T) = \Lambda$. If in addition to this $\lambda - \varphi \ll T$ in the region of space where the majority of monomers is located, i.e., if the level is situated near the bottom of the well, then (6.8) becomes the Schrödinger equation with the potential φ/T

$$\Delta\psi + \frac{\lambda - \varphi}{a^2 T}\,\psi = 0\,. \tag{6.9}$$

The result (6.9) gives us a clear indication of the distribution of $\psi(x)$ in a given field.

For example, we can consider an infinitely deep spherical well of radius R. In this case

$$\psi(x) \sim \frac{\sin(\pi x/R)}{\pi x/R}\;;\quad \lambda = \left(\frac{\pi a}{R}\right)^2 T\,. \tag{6.10}$$

(Within the well $\varphi = 0$ and $\lambda \ll T$, i.e., Eq. (6.9) is applicable.) The pressure on the walls of the potential well is

$$p = -\frac{\partial F}{\partial V} = -N\frac{\partial \lambda}{\partial V} = \frac{N}{V}\cdot\frac{2}{3}\left(\frac{\pi a}{R}\right)^2 T \ll \frac{NT}{V}\,. \tag{6.11}$$

The fact that the pressure is significantly smaller than the pressure in the gas of separate monomers is the direct and trivial consequence of the linear memory. Roughly speaking, the longitudinal bonds take the main part of the pressure upon themselves.

A further manifestation of linear memory can be found if the distribution of pressure on the surface of a nonspherical well is considered (Grosberg, 1972). In this situation it turns out that the pressure is lowered in the remote narrow regions of the well and especially in the corner points ($\sim(a/R)^4$).

If the potential φ has a boundary surface (for example, in the case of the spherical well of finite depth), then it is necessary to formulate the boundary condtions on this surface. Since the function $\hat{g}\psi$ must be continuous and must have a continuous derivative on every boundary, it follows from (3.11) that the function

$$\ln\psi + \varphi/T \tag{6.12}$$

must also be continuous and must have a continuous derivative.

Taking into account this boundary condition a complete solution can be obtained for a large ($R \gg a$) spherical well of finite depth φ_0. The results are: the temperature of capture is

$$T_c = \varphi_0(2R/\pi a)^2\,, \tag{6.13}$$

the coefficient A [see Eq. (6.7); the change in the specific heat per monomer] is

$$A = \frac{\varphi_0}{T_c}\left[\left(\frac{\pi}{4}\right)^2 - \frac{1}{2}\right] \cong 0.12\varphi_0/T_c\,, \tag{6.14}$$

the pressure on the walls of the potential well (at small τ) is

$$p = p_\infty \tau\cdot\frac{3}{4}\left[\left(\frac{\pi}{4}\right)^2 - \frac{1}{2}\right] \approx 0.09 p_\infty \tau\,,$$

where p_∞ is the pressure (6.11) on the walls of an infinitely deep well of the same radius.

It should also be noted that in the appendix to Lifshitz, Grosberg, and Khokhlov (1976a) the capture temperature T_c was calculated as a function of the radius and the depth for a spherical well and for a well in the form of a round disk near the impenetrable surface (the latter well is used in the theory of polymer adsorption).

3. Adsorption

In the literature the subject of the most extensive studies is the case of a potential well of special form, in which the monomers feel the attraction only in the thin layer near the impenetrable surface. This form of the potential well is used for the description of polymer adsorption on attractive surfaces.

For this well all the above results are valid. In particular there exists a temperature T_c such that at $T > T_c$ the chain is not adsorbed by the well and remains in the solution, and at $T < T_c$ the adsorption (capture) occurs and there is an overwhelming probability (at large N) that the chain is situated near the surface. The transition at $T = T_c$ is a second-order phase transition.

The width of the adsorbed layer can be estimated from the one-dimensional analog of (6.1). This gives, taking into account (6.6)

$$D \sim \frac{a}{(\Lambda - 1)^{1/2}} \sim \frac{a}{\tau}\,.$$

Thus D does not depend on N. The asymptotic form for the density profile outside the well has the form

$$n|_{x\to\infty} = \psi^2|_{x\to\infty} \cong \text{const.}\,\exp\left(-\frac{(2A)^{1/2}}{a}\,\tau x\right)$$

etc. All these results were obtained long ago by means of somewhat different methods [see the references in de Gennes (1969, 1976)]. An approach analogous to that described above was developed for this specific case in a review by de Gennes (1972) and also in a recent paper by Wiegel (1977); in this last work the adsorption of a model polyelectrolyte without volume interactions is considered. (The introduction of electrostatic forces leads in this case only to the change of the form of potential well, but, as was noted above, the main results do not depend on the form of the well).

We should like to stress that the adsorption of the chain occurs as a second-order phase transition only if the attraction to the surface can be represented by a potential field. Skvortzov *et al.* (1976) considered the adsorption of macromolecules with nonalternating dipole moments on the charged surface. In this case the interaction of the polymer with the surface cannot be described in the form of a potential field and the adsorption occurs as a first-order phase transition (Skvortzov *et al.*, 1976).

Not taken into account by the above formalism (by the "bead" model) are the important effects connected with the influence of chain stiffness on adsorption. A substitution of the type (2.26), which allows us to study the equivalent bead model instead of the persistent model in the region $T>\theta$ and the coil-globule transition region, is no longer valid, because there is a characteristic dimension (the width of the well), which is comparable with the persistent length a. As a result a piece of a polymer chain of length $\sim a$ can not be considered as a whole, i.e., as an equivalent "bead."

A detailed study of the influence of chain stiffness on adsorption was undertaken by Skvortzov, Birshtein, and Julina (1976) and by Skrovtzov and Birshtein (1976) by means of Monte Carlo computer simulation of a polymer chain on the cubic lattice. It turned out that when chain stiffness increases, the phase transition becomes sharper (remaining a second-order phase transition) and the temperature T_c increases. Analogous results can be obtained by means of analytical methods (see, for example, Hoeve, DiMarzio, and Peyser, 1965; Murakami, 1976).

C. Polymer chain with volume interaction in a potential well

1. Capture of a polymer by the well

Let us consider now the capture of a polymeric coil with excluded volume. We shall show that a volume interaction of this type has no influence on the transition temperature T_c and on the type of transition: these features remain the same as for the chain without excluded volume in a given field φ. In essence this follows from the fact that for the ideal chain a second-order phase transition occurs. When the transition temperature is approached, the monomer density decreases and, thus, the perturbation due to volume interaction decreases also.

First of all it should be noted that when the external and the self-consistent fields are both present, the basic equations have the form

$$\hat{g}\psi=\Lambda\psi\exp\left\{\frac{\mu^*+\varphi}{T}\right\} \tag{6.15}$$

$$n=\psi^2\exp\left\{\frac{\mu^*+\varphi}{T}\right\}. \tag{6.16}$$

The free energy can be obtained, as usual, from Eq. (3.33).

Near the capture temperature the presence of excluded volume can be taken into account in the framework of perturbation theory (the condition of validity of the perturbation theory will be formulated below). When the transition point is approached, the monomer density becomes low and $\mu^*/T=2nB\ll 1$. Substituting this into Eqs. (6.15) and (6.16) and employing the usual perturbation theory, we find for the free energy

$$F=F_0+F_1\,;\quad F_1=TB\int n_0^2(\mathbf{x})d^3x, \tag{6.17}$$

where the index zero indicates the corresponding characteristics of the ideal chain in the same field.

It will be recalled [see Eqs. (6.7) and (6.14)] that in the large well

$$F_0\sim -N\varphi_0\tau^2\,. \tag{6.18}$$

Estimating the integral in (6.17) [with the help of Eqs. (6.1), (6.6), and (6.16)] we find

$$F_1\sim N\varphi_0\tau^2(NBR/a^4)\,. \tag{6.19}$$

Thus the perturbation theory is valid up to the transition point ($\tau=0$) if

$$NBR/a^4\ll 1\,. \tag{6.20}$$

If condition (6.20) is fulfilled, it can be seen from (6.19) that the type and the temperature of the transition are not altered when the excluded volume is introduced (but the jump in the specific heat is altered).

Although the condition (6.20) is very rigid and is never fulfilled for real polymers, the above conclusions (concerning the independence of T_c and the type of transition of v) are valid in the general case, because the problem under consideration does not contain any characteristic scale of B.

2. Globular structure of the chain captured by the well

It is natural that the structure of a chain captured by the well depends essentially on the excluded volume. A complete analysis of this structure can be performed in the hypothetical limiting case of a "small well"—the well whose dimensions $R\ll a$. As it often turns out, the study of this limiting case clears up the situation in the general case: the main qualitative features of the solution are valid for wells of arbitrary dimensions (see Lifshitz, Grosberg, and Khokhlov, 1976a).

It turns out that the free energy near T_c is equal to

$$F=-\frac{\varphi_0^2}{2T_c}\tau^2N\frac{1}{\alpha+J_1^2(1)/32\pi^2}\,, \tag{6.21}$$

where φ_0 is the depth of the well, $J_1(1)$ is a numerical constant which depends on the form of the operator $\hat{g}$ [see Eq. (4.24)], $\alpha=Nv/V$ is the characteristic dimensionless parameter of the problem, and V is the volume of the well. In accordance with the above consideration the temperature and the type of transition are not altered but the change in specific heat is altered when the excluded volume is varied. The behavior of the system differs qualitatively in the cases $\alpha\lesssim 1$ and $\alpha\gg 1$. [It should be noted, however, that $J_1^2(1)/32\pi^2\sim 10^{-2}$.]

When $\alpha\lesssim 1$ Eq. (6.21) gives $F\sim N$. It is easy to establish also that the number of links within the well $N_{\text{in}}\sim N$. The relative fluctuations of monomer density are, as in the usual thermodynamic system of N particles, $\sim N^{-1/2}$.

If $\alpha\gg 1$, then only a small fraction of the monomers can be located in the well. It turns out that in this case $N_{\text{in}}\sim V/v\ll N$ and $F\sim V/v$ (the free energy does not increase with the increase of N). It can be shown, moreover (Lifshitz, Grosberg, and Khokhlov, 1976a), that the relative density fluctuations are of order $\sim(V/v)^{-1/2}$. Although these fluctuations are small, they are much larger than the usual thermodynamic fluctuations, which are $\sim N^{-1/2}$. Thus at $\alpha\gg 1$ the polymer chain captured by the well is a sort of thermodynamic system in which the role of number of particles is played by V/v and not by N.

3. Adsorption

The results obtained above the wells of arbitrary dimensions can be applied also to a thin well located near the surface, a model which is used for the description of polymer adsorption. In this section we shall discuss some other approaches to the problem of adsorption of chains with volume interaction.

The majority of studies dealing with this problem are made with the help of a computer. In these studies the self-avoiding walks on several spatial lattices in the vicinity of the impenetrable surface and the attractive layer near this surface are simulated (see, for example, Lax, 1974, 1975), and the phase transition (at infinite N) is predicted at some temperature T_c. In the works by Lax (1974, 1975) it is shown that the temperatures T_c for random walks and self-avoiding walks coincide and that the transition itself has the features of a second-order phase transition.

As to theoretical approaches to this problem, the recent work by de Gennes must be mentioned. His Journal de Physique article (1976) contains not only a review and simple derivation of the self-consistent adsorption theory of the Flory type, but also a qualitative consideration of the scaling theory. [Scaling effects are to be taken into account due to fluctuations which develop in the adsorption layer in the case of "weak adsorptions"—see de Gennes (1976)].

In the above we have been mainly concerned with the adsorption of a coil with excluded volume. For biological applications it is interesting also to consider the adsorption of a polymer globule. This was done by Grosberg (1976b, 1977). In these articles an adsorption diagram with the variables T, φ_0, where φ_0 is the depth of the well, was constructed and various transitions in this system were described.

VII. CONCLUSION

Since "living matter is the most interesting subject of investigation for the living matter which is able to investigate" (Blumenfeld, 1973), we should like to make a few remarks here about natural biological globular molecules.

The most widespread examples of biological globules are the globular proteins—enzymes, immunoglobulines, etc. The dense conformation in these systems is due to the volume interactions of the links surrounded by the solvent (water).

Another interesting example of a biological globule is the double-helix molecule of DNA or RNA located in the head of the phage (Watson, 1965). In this system compression is made by the external field (the pressure of the walls of the head) and the volume interaction is basically repulsion. It should be noted that in our terminology this globule is neigher small nor large, because the persistent length of the double helix (~500 Å) coincides in order of magnitude with the dimensions of the head of the phage.

The main feature of biopolymers is the heterogeneity of their primary structure. Protein molecules have unique primary structures and show extremely high specificity in their biochemical activity. However at the present time it is unclear whether the thermodynamic properties of proteins under arbitrary conditions are sensitive to the details of the primary structure. (In the case of DNA the primary structure, apparently, does not play any role in the spatial structure, because the complementary pairs are situated in the interior of the double helix).

It is well known, for example, that the helix-coil transition has some features which do not depend on the correlation characteristics of the primary structure (Vedenov, Dykhne, Frank-Kamenetzkii, 1971), and some features which depend essentially on this structure (Lifshitz, 1973). Apparently the situation may be quite analogous for protein denaturation. It is natural to expect that the concepts developed in this work reflect qualitatively those protein properties which are not sensitive to the primary structure.

One example of this kind is the following: It is well known that in the usual conditions the hydrophobic monomers are located in the interior of the globule and the hydrophilic monomers are situated on its surface. Due to this fact the solution of protein globules does not precipitate. But according to the results of Sec. V, when the denatureation point is approached the globule must broaden, so the hydrophobic monomers must come out to the surface. This may lead to the precipitation of the solution of proteins. Similar effects in proteins are actually often observed (Joly, 1965).

Thus it is very important to determine the degree of influence of the primary structure on the thermodynamic properties of a globule.

It should be noted that if we analyze this problem with the proteins in mind, then only rather short chains are of interest. This is clear already from the experimentally observed property of self-organization in proteins, (i.e., the ability to form the "correct" ternary structure without the help of any external kinetic mechanism).[17]

Actually, it is evident that for self-organization to be safe and rapid, it must occur simultaneously in the different parts of the chain and, consequently, it must lead to a structure without knots. (Polymer chains with knotted conformations were studied by Vologodskii *et al.*, 1974). On the other hand elementary defects, for example the replacement of the neighbor particles, cannot exist in the globule, because the majority of these defects are connected with topological violations of the globule structure. Thus if the activation energy of such a defect is U_D, the requirement that the globule be stable with respect to these local defects is

$$T \ln N \ll U_D \qquad (7.1)$$

(for more detail see Lifshitz and Grosberg, 1973). Of course, Eq. (7.1) is not the strongest condition. But already this condition explains why the finiteness of the

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[17] It should be noted that the concept of "ternary structure" for biopolymers does not refer simply to the density distribution. This concept includes also the topological state of the chain. Self-organization of the ternary structure means that the equilibrium globule should have a definite topological structure (with "topological entropy" equal to zero), enabling one to call this structure crystal-like. These questions were discussed in detail by Lifshitz and Grosberg (1973).

chain must play an important role in the properties of proteins.

In conclusion we can say that the model theory developed in this article describes with qualitative accuracy the homopolymer chain in fairly simple situations and can, apparently, be used as a basis for further, more realistic approximations. As to biopolymers, this theory can stimulate the formulation of interesting problems.

APPENDIX A: LOCAL BOUNDARY CONDITIONS IN THE GLOBULE

Taking into account Eqs. (3.21), (3.22), and (3.25) we can write the function $F\{n\} - \lambda N$ in the form

$$F\{n\} - \lambda N = \int \{f(n) + Tn - 2n\lambda - 2Tn \ln \hat{g}\psi\} d^3x\,. \qquad (A.1)$$

Let us vary the globule boundary, changing the volume of the core by δv. It is the last term in Eq. (A.1) that requires the greatest amount of calculation. Even if the variation of ψ is located near the boundary, the variation of n is spread over a distance $\sim a$ due to the equality $\Lambda n = \psi \hat{g} \psi$. This fact somewhat lengthens the calculations, but does not make them more complex. The result has the form

$$\delta(F - \lambda N) = \int_{\delta v} [f - \lambda n - 2Tn \ln \hat{g}\psi] d^3x = 0 \qquad (A.2)$$

where the square brackets denote the jump in the value on the boundary. From (3.34) and (A.2) it follows that

$$[f - n\mu] = -[p] = 0\,; \quad p(n_-) = p(n_+)\,. \qquad (A.3)$$

The local pressure must be continuous. It will be recalled that this result is valid only if $v \ll a^3$ to within v/a^3.

APPENDIX B: LIMITS OF APPLICABILITY OF EQUATIONS (3.31) AND (3.32)

During the derivation of Eqs. (3.31) and (3.32) two important assumptions were made: (a) the steepest descent method (or the self-consistent field method) was used; (b) the functional $E\{n\}$ was written in the form (3.27). Let us consider each of these two assumptions.

(1) How far the self-consistent field theory may be applied to concentrated polymer solutions has been recently clarified (des Cloizeaux, 1975) with the help of the analogy between the magnet and the polymer (see Sec. II) and also with the help of the analogy between the θ point and the tricritical point (see Sec. II). As a result Daoud and Jannink (1976) attempted to determine the boundaries of the so-called tricritical region in which the self-consistent theory is applicable. It is essential for us that in the region of concentrated solutions at $T < \theta$ the self-consistent theory is valid, if

$$cv \gg (v/a^3)^2 \tau \qquad (B1)$$

[see the work by Daoud and Jannink (1976); in this work it is assumed that $v \sim a^3$, but the results can be easily reformulated for the general situation].

Now we note that each region of a globule can be considered in the local sense as a concentrated polymer solution. According to the results of Sec. 3 $cv \sim \tau$ in the globule. Comparing this with Eq. (B1) we find that if $v \ll a^3$, Eq. (B1) is fulfilled and thus the self-consistent approximation is valid. If $v \sim a^3$ then the density in globule lies just in the crossover region; thus the self-consistent theory gives only the order of magnitude.

(2) The functional $E\{n\}$ was written in the form (3.27) under the condition $v \ll a^3$ and $na^3 \gg 1$. Let us show that the fulfillment of the second condition is not obligatory.

Let $v \ll a^3$, but $na^3 \sim 1$. Then $nv \ll 1$, i.e., the density in the globule is low. Let us write the variational derivative $\delta E\{n\}/\delta n$ in the form

$$\delta E\{n\}/\delta n = 2B^* n + 3C^* n^2 + \cdots + \xi^2 \Delta(nB^* + \cdots) + (\text{terms with higher derivatives}). \qquad (B2)$$

Here B^* and C^* are for the present arbitrary and are not to be taken as the second and the third virial coefficients of monomer interaction.

It is natural to identify the value of ξ with the smallest possible smoothing radius. Since the smoothed density must be the thermodynamical value, ξ can be estimated from the condition that within the radius ξ the number of monomers which belong to neighboring and remote parts of the chain are of the same order; within a smaller radius the neighboring monomers would prevail and the density would fluctuate strongly. Let K and K' be the number of monomers within the radius ξ belonging, respectively, to the remote and neighboring parts of the chain. We have $\xi \sim a(K')^{1/2}$; $n\xi^3 \sim K$; $n \sim \tau/v$. Hence $K \sim K'$ when $\xi \sim v/\tau a^2$.

It was shown by Khokhlov (1977, see also Sec. II) that B^* is the renormalized second virial coefficient and that it differs from the true second virial coefficient B by the value $\sim v/a^3 B$. Thus, in the zeroth approximation with respect to v/a^3 we must take B^* in Eq. (5.20) to be equal to B. Analogously, it can be shown that $C^* = C$ in the zeroth approximation, etc. Collecting the terms in Eq. (B2) which do not include derivatives, we shall obtain in this approximation the function $\mu^*(n)$.

It remains for us to prove that one may neglect terms including the derivatives (at $v \ll a^3$). The most important among these, the terms for small n and smooth density profile, are written explicityly as one term in (B2). After expanding the exponential function in the right-hand side of Eq. (3.31) we shall have from this term an expression of the form $\xi^2 \psi \Delta(nB)$. This term is to be compared with the term with the analogous derivative in the left-hand side of the equation $a^2 \Delta\psi$. Assuming that $\Delta \sim 1/R^2$, we see that $\xi^2 \psi \Delta(nB)/a^2 \Delta\psi \sim (v/a^3)^2 \ll 1$ for $v \ll a^3$, which is what we set out to prove.

It can be concluded that Eqs. (3.31) and (3.32) are quantitatively correct descriptions of the globule structure at $v \ll a^3$ (to within v/a^3). At $v \sim a^3$ these equations may be used for qualitative purposes.

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