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Quantitative Theory of the Globule-to-Coil Transition. 1. Link Density Distribution in a Globule and Its Radius of Gyration

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ABSTRACT: In this series of papers new results and a brief review of the current state of mean-field theories of the condensed globular state and of the globule-to-coil transition in the Θ-region for a linear, homogeneous, noncharged macromolecule are presented. As a basis of our consideration, we use both Lifshitz's theory and interpolation Flory-type theory. Complete quantitative theoretical results are obtained and compared with experimental data. In this first paper of the series the unary characteristics of a polymer chain are considered. It is shown that the density distribution of monomers inside a globule depends on parameters of a polymer–solvent system in the combination $t \equiv N^{1/2}BC^{-1/4}(a^2/6)^{-3/4} \sim N^{1/2}(T - \Theta)/\Theta$ only (a stands for the distance between neighboring links along the chain, N is the total number of links in the chain, T stands for temperature, and B and C are the second and third virial coefficients of quasimonomer interactions, respectively). The form of the t-dependence (or of the $(T - \Theta)N^{1/2}$-dependence) of a macromolecule expansion factor is determined by the polymer rigidity parameter $\sqrt{C}/a^3$. The question of the bimodality of macromolecular states in the transition region is discussed.

1. Introduction

1.1. Overview of Problems under Consideration.

The coil and globular states of a polymer chain suspended in dilute solution and the coil-to-globule transition represent a well-known simple basic model for a lot of phenomena (see review in ref 1). They have a special interest in applications such as, for example, heteropolymer and protein folding, native DNA packing, polymer network collapse, interpolymer complexes, etc.

The opinion is that this basic model is now well understood due to classical investigations of Flory, Lifshitz, and many others. Actually, a decrease in the polymer coil radius in a poor solvent was observed repeatedly in experiments[2–21] and in computer simulations[22–33] as well. Theory also predicts polymer chain compression below the Θ-point.[1,34] Therefore, qualitative agreement between theory and experiment is obvious.

However, the theory describes not only the simple decreasing of chain dimensions but also dramatic reconstruction of the chain spatial structure as a whole—the coil-to-globule phase transition. It is important because just this concept of the special globular phase state of a polymer chain is exploited actively in all the abovementioned applications.

The main problem arising due to this fact is whether the existing experimental data confirm the peculiar globular state concept as a whole (including static, hydrodynamic, and fluctuational properties) or the slight chain compression only. It would be desirable also to find out, in particular, (i) whether the mixture used in experiments on the coil–globule transition is a stable one-phase solution without aggregation or whether it is only a metastable solution in the course of an initial state of precipitation; (ii) whether it is inevitable to use extremely dilute solutions, where suspended globules can exist without aggregation, or whether it is possible to observe equilibrium globules in an unstable ("metastable") solution; (iii) whether there is equilibrium knotting in observable collapsed chains; and (iv) whether an observable collapsed chain is under nondraining conditions.

Since available experimental data deal mainly with the measurements of chain dimensions, then the unique possibility lies in the detailed quantitative comparison of these data with theoretical results. We emphasize from the very beginning that it is absolutely insufficient to restrict the comparison to the simplest scaling-like theoretical prediction $R \sim \tau^{-1/3}$ only (R is the globule radius, $\tau \equiv (T - \Theta)/\Theta$ stands for reduced temperature); this simplified approach was used in some papers, but we will explain that it leads to some essential misunderstandings. Therefore, for a real comparison it is necessary first of all to obtain theoretical results in the complete quantitative numerical form.

Let us remind everyone that the coil–globule transition theory was discussed numerously in the literature. The main ideas are those of Flory[35] and Lifshitz;[36] the theory has been described in books and review articles[1,34,37–39] (see also ref 40). All versions of the theory can be classified into two groups; they differ with the choice of the order parameter. In the first group of so-called Flory-type theories[39–49] the simple scalar value of the chain dimension or expansion factor plays this role; of course, for the collapsed globular state the term "contraction factor" seems to be more preferable than "expansion factor"; however, we follow tradition and use just the latter term. In the second group of Lifshitz-type theories (see reviews in refs 1, 34, and 37 and books in refs 38 and 39) the more complex order parameter of spatial density distribution provides a more detailed description.

Historically, the first work on the subject was done in 1965 by Ptitsyn and Eizner[41] in the framework of Flory's approach. This approach was developed by a number of authors[42–50] and brought to the most correct form in refs 40 and 49. An alternative approach was found in 1968 by Lifshitz[36] in the course of some fundamental biophysical problems discussions,[51] and it was developed in refs 1, 34, 37, and 52.

Flory-type and Lifshitz-type theories are well developed at present. Nevertheless, some important problems remain unsolved in spite of the fact that these very problems ought to be solved before sensible comparison with experiments. For example:

(i) Among all experimentally observable characteristics of chain dimensions only the radius of gyration (which can be measured using the elastic light scattering technique) was the subject of theoretical calculations; other ones, such as mean-square fluctuations of the gyration radius and hydrodynamic radius (which can be measured

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in viscosimetric or in nonelastic light scattering experiments), have not been considered theoretically.

(ii) In experiments on the globular state the main difficulty deals with the strong tendency toward macroscopic precipitation of a solution below the Θ-point. In the meantime, interchain interactions, binodal and spinodal decomposition, and other similar problems have not been analyzed theoretically in sufficient detail (see, however, ref 34).

Furthermore, we can expect also some essential obstacles in the comparison of theory and experiments.

(i) The theory is based on the concept of Θ-point (including monomer-to-quasimonomer renormalizations); it is unclear whether this concept's accuracy is sufficient for quantitative theory.

(ii) The theory in question is a mean-field type. Since Θ is the tricritical point,[44] mean-field-type theory would be valid to some logarithmic corrections.[53] However, it is difficult to estimate these corrections numerically; therefore, quantitative applicability of the theory is unclear.

(iii) We do not know a priori the concrete value of the stiffness parameter, the so-called v/a^3 parameter,[34] for different polymers. The theory implies that the whole picture of the coil-to-globule transition and, moreover, the whole adequate terminology for its description depend strongly on the v/a^3 value:[1,34] a two-phase system with a bimodal distribution and heterophase fluctuations for the case $v/a^3 \ll 1$ does not cause smooth enlargement, while the unimodal distribution does for the opposite case $v/a^3 \sim 1$.

There exist some qualitative reasons for the expectation that the v/a^3 value is comparatively small in the 3D case, but it is unclear as to how small it is in reality. This question is important not only for the coil-to-globule transition theory but also for polymer physics as a whole:[38] the v/a^3 value defines the range of fluctuational regions in the temperature–concentration diagrams of polymer solutions, grafted macromolecular systems, etc.

(iv) Polymer chain immersion into a poor solvent media does not lead necessarily to equilibrium globule formation. For example, fast compression of the single chain leads to another, so-called, crumpled globule state.[54,55] (The crumpled globule differs from the equilibrium one first of all with respect to chain knotting.) On the other hand, during a sufficiently long time globularlike interchain aggregates can come into being. Practically, under real conditions we cannot know a priori whether there is enough time for equilibrium chain knotting or whether the aggregation process has started.

1.2. Aim and Plan of the Series of Papers. In accordance with the discussion above, our problems are (i) quantitative version development of the globular state mean-field theory including calculation of (a) the density distribution inside the globule and density–density correlation function, (b) the radius of gyration, its mean-square fluctuations, and the hydrodynamic radius, (c) the globule–globule interaction free energy and its corresponding virial coefficient, and (d) coexistence and spinodal curves of a polymer solution in the globular range and (ii) detailed comparison of the theoretical results with experimental data.

Some particular results we have published in Russian earlier.[52,56,57] Here, those as well as some new results are presented in systematic form.

In this series of papers, the outline is as follows. In the first paper we give the quantitative version of both Lifshitz-type and Flory-type theories; i.e., we calculate the intraglobular density distribution and, as a conclusion, the temperature (or solvent quality) dependence of the globule radius of gyration. We discuss also in this paper some delicate questions concerning the interrelation of these two types of theories. The second paper deals with the intraglobular density–density correlation function, the globule hydrodynamic radius, and gyration radius fluctuations. In the third paper we investigate interchain interaction; i.e., we calculate corresponding virial coefficients and analyze coexistence and spinodal curves for a polymer solution in the globular range of temperature. Finally, the fourth paper is devoted to the comparison of these theoretical results with experimental data.

At last, we give the outline of this paper in more detail. We start with a brief description of the well-known basic notations of the globule state concept (section 2). In section 3 we formulate the quantitative version of Lifshitz's theory. To do so, we analyze numerically the corresponding nonlinear Schroedinger-type equation in complete 3D form (unlike the 1D approximation in previous investigations[34]). Since this result's applicability is restricted to the poor solvent region only, in sections 4 and 5 we use them with the perturbation theory for the Θ-region. We formulate this last theory in section 4 for concordance with the globule theory using renormalized parameters of quasimonomer interactions[58,59] instead of the initial monomer's virial coefficients in common perturbative calculations.[60] In section 5 we sew our globular and perturbative results using a two-level (coil and globule) system approximation for a rigid chain and a trivial interpolation for a flexible chain. Finally, section 6 is devoted to Flory-type theory, which we consider as another possibility for the interpolation description of the whole region from a poor solvent to a Θ-solvent; to determine the imminent phenomenological parameter of this theory (the ratio of the globule's volume to the gyration radius cube), we use the result of previous Liftshitz theory.

1.3. On the Paper's Structure. Taking into account the large volume of our work, we have written it in the form of a series of four papers.

In obtaining our quantitative results, we dealt with some tedious calculations. In order to liberate, nevertheless, the text, we have carried out all the complex formulas and placed them in appendices. This is why our papers have an extremely large number of appendices, and their total volume equals approximately to one-third of the papers' volume. Papers can be read directly on the qualitative level, but all the mathematics are placed in the appendices.

2. Globular State: Basic Notions

The main property of a globule, in contrast to a coil, is the following: a small volume within a globule contains a number of uncorrelated parts of the chain and, in this sense, resembles a solution or a melt of independent chains. Therefore, the equilibrium globular size R or intraglobular density $n_0 \sim N/R^3$ (N is the number of monomers per chain) is balanced when the polymer osmotic pressure inside the globule becomes equal to the external pressure, i.e., to zero:

$$p^*(n_0) = 0 \tag{1}$$

(Let us remind everyone that, in the coil, according to Flory,[35] the polymer osmotic pressure compensates with a polymer entropic elastic tension.) Moreover, this pressure would be equal to zero within all intraglobular volume elements; so a dense globule has a core with uniform density n_0.

Using eq 1 and an ordinary virial approximation with binary ($\sim B$ = second virial coefficient) and tertiary ($\sim C$

= third virial coefficient) quasimonomer collisions, i.e.

$$p^*(n_0) \cong TBn_0^2 + 2TCn_0^3 \qquad (1a)$$

it is easy to determine the globule density

$$n_0 = -B/2C \qquad (2)$$

its radius

$$R_0 = \left[\frac{3N}{4\pi n_0}\right]^{1/3} = \left[\frac{3NC}{2\pi(-B)}\right]^{1/3} \qquad (3)$$

and also its free energy

$$F_0 = N\mu^*(n_0) = -TNB^2/4C \qquad (4)$$

where

$$\mu^*(n_0) \cong 2TBn_0 + 3TCn_0^2 \qquad (5)$$

is the link chemical potential in the system of long chains.

Near the Θ-point

$$B(T) \sim \tau \equiv (T - \Theta)/\Theta, \quad C(T) \simeq \text{const} \qquad (6)$$

and eqs 3 and 4 signify scaling dependences $R_0 \sim |\tau|^{-1/3}N^{1/3}$ and $F_0 \sim -\tau^2 N$. For the first time these results were obtained in ref 5. They represent the manifestation of the most basic properties of the globular state.

However, when a polymer–solvent system approaches the Θ-point ($\tau \rightarrow 0$), the globular size R_0 and its surface $\sim R_0^2$ increase; moreover, the globular surface energy (in Lifshitz's terminology) or its polymer elastic energy (in Flory's terminology) grows progressively. At the same time, estimations above are based on the neglecting of these facts, i.e., on the so-called volume approximation. Therefore, to describe a globule near the transition region, it is necessary to take into account these additional terms of free energy. Lifshitz- and Flory-type theories realize it in different ways, and we will discuss these possibilities.

3. Quantitative Version of Lifshitz's Theory

3.1. Density Profile inside a Polymer Globule. As we have already mentioned above, Lifshitz's theory uses the most detailed (in the framework of the mean-field approximation) description in terms of smoothed spatial density distribution $n(\mathbf{X})$. The coupled equations for equilibrium $n(\mathbf{X})$, presented in Appendix A, were constructed in ref 34. Using dimensionless variables, these equations can be reduced (see Appendix A and ref 52) to a nonlinear Schroedinger-type equation

$$\Delta\chi = \varkappa(2 - 3\varkappa)\chi(\mathbf{r}) - 2\varkappa\chi^3(\mathbf{r}) + 3\varkappa^2\chi^5(\mathbf{r}) \qquad (7)$$

with the normalizing condition

$$\varkappa\int\chi^2(\mathbf{r})\,\mathrm{d}^3r = t^2 \qquad (8)$$

and additional conditions of regularity of the $\chi(\mathbf{r})$ function at a globule center and its exponential tendency to zero at infinity. Here $\varkappa$ is an analog of the eigenvalue, $\mathbf{r}$ and $\chi(\mathbf{r})$ are dimensionless radius-vector

$$\mathbf{r} = \mathbf{X}\frac{|B|}{C^{1/2}(a^2/6)^{1/2}} \sim \frac{\mathbf{X}}{h} \qquad (9)$$

(h is a thickness of globule surface layer) and function

$$\chi(\mathbf{r}) = \left[\frac{n(\mathbf{X})}{2\varkappa n_0}\right]^{1/2} = \left[\frac{n(\mathbf{X})C}{\varkappa|B|}\right]^{1/2} \qquad (10)$$

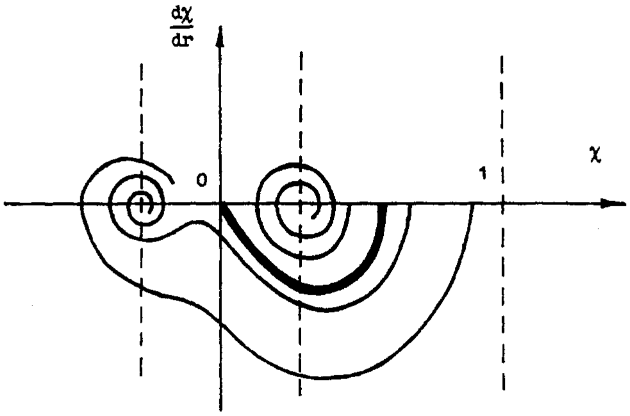

Figure 1. Phase portrait of eq 7 for the range of physical interest $^1/_2 < \varkappa < {}^2/_3$. The solution determining the globule structure corresponds to the separatrix shown by the thick line.

and the t parameter is the reduced temperature

$$t = \frac{N^{1/2}B}{C^{1/4}(a^2/6)^{3/4}} \sim \tau N^{1/2} \qquad (11)$$

In eq 7 the negative term $\sim\chi^3$ corresponds to attractive pair interactions, while the positive one $\sim\chi^5$ corresponds to repulsive ternary collisions; the linear terms both describe the chain "linear memory",[34] or, in other words, polymer elastic energy. The phase portrait of eq 7, taking into account the spherical symmetry of a globule in a self-consistent field ($\chi(\mathbf{r}) = \chi(r)$, where $r \equiv |\mathbf{r}|$ is a distance with respect to the globule center), for the range of physical interest $^1/_2 < \varkappa < {}^2/_3$ is shown in Figure 1. The solution determining the structure of a globule corresponds to the separatrix, which is marked by the thick line. Let us note that the density profile inside a globule depends on the chain's parameters N, a, B, and C through the single combination for t (eq 11) only.

Qualitative analysis of the equation for the density distribution $n(\mathbf{X})$ is given in ref 34. It has been demonstrated that when $T \ll \Theta$ (or $\tau \rightarrow -1$), this distribution in accordance with the evaluations of eqs 2 and 3 represents a constant density n_0 inside a sphere with radius R_0. But with a decrease of $|\tau|$ not only radius R_0 but also the thickness of the surface layer h increase and h/R_0 increases too, so that $h/R_0 \sim (-t)^{-2/3}$.

We obtained a quantitative solution of eqs 7 and 8 in ref 52. Here we will give a short summary of the results. The radial distribution of the monomer density in a globule varies from "a sharp step", when $t \rightarrow -\infty$, to a progressively dim profile, when t increases up to values corresponding to the globule–coil transition region. These density distributions can be presented as functions χ^2 vs $|\mathbf{X}|$ (Figure 2) or $y \equiv (n/N)S_{\text{id}}^3(\sqrt{C}/a^3)^{3/2}$ vs $x \equiv (|\mathbf{X}|/S_{\text{id}})(\sqrt{C}/a^3)^{-1/2}$ (Figure 3) at various t, where $S_{\text{id}}^2 = Na^2/6$ is the Gaussian coil mean-square radius of gyration.

3.2. Globule Free Energy. If the solution of eqs 7 and 8 is found, i.e., the t-dependences of $\varkappa$ and of function $\chi(\mathbf{r})$ are calculated, then the globule free energy can be calculated using the expression

$$F = -\frac{a^3}{C^{1/2}}T\tilde{F}(t) \qquad (12)$$

where

$$\tilde{F}(t) = 6^{-3/2}\varkappa\{(2 - 3\varkappa)t^2 - \varkappa\int[\chi^4(\mathbf{r}) - 2\varkappa\chi^6(\mathbf{r})]\,\mathrm{d}^3r\}$$

Parameter $\sqrt{C}/a^3$ characterizes a value of the polymer

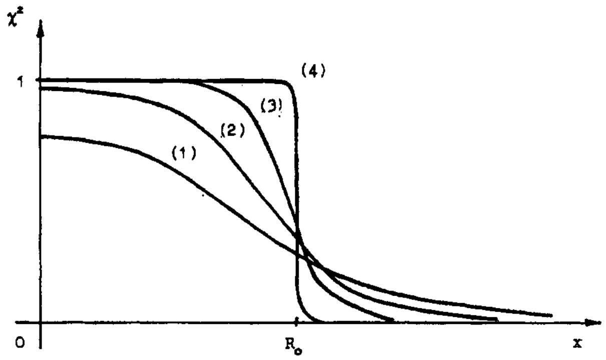

Figure 2. Radial density distribution in a globule, $\chi^2 \sim n/\tau$. Curves 1–4 correspond to $t = t_{tr} \simeq -10.2$ and $t = -20, -50$, and -1500, respectively.

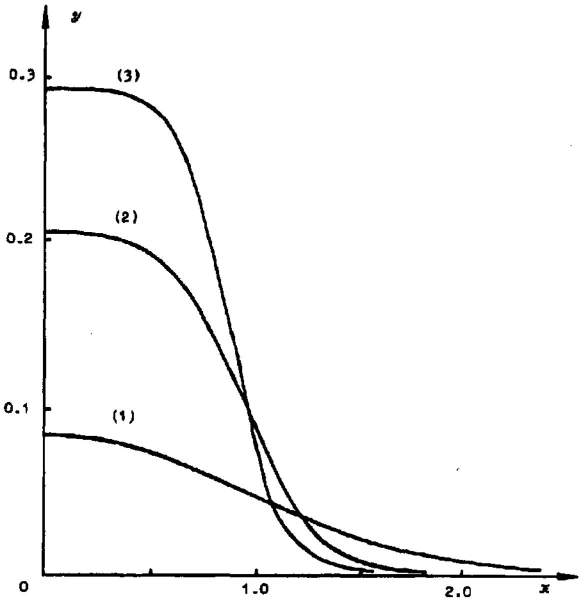

Figure 3. Radial density distribution in a globule presented in T-independent form (the dependence on temperature is determined by parameter t only). Curves 1–3 correspond to $t = -10$, -20, and -30, respectively.

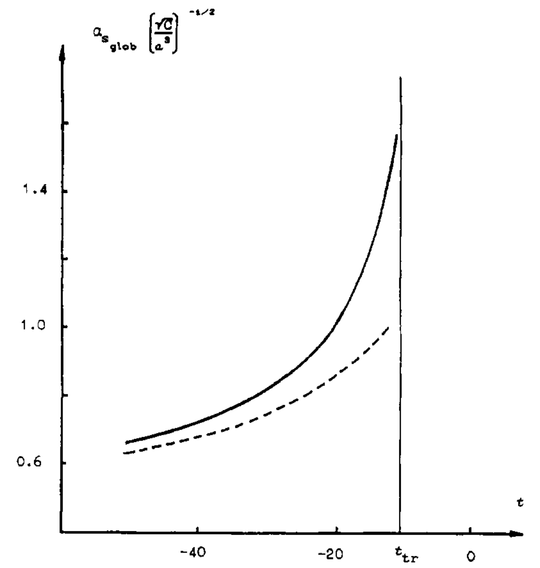

Figure 4. Expansion factor of a globule radius of gyration $\alpha_{S_{glob}}$ multiplied by the polymer rigidity scale $(\sqrt{C}/a^3)^{-1/2}$ vs t.

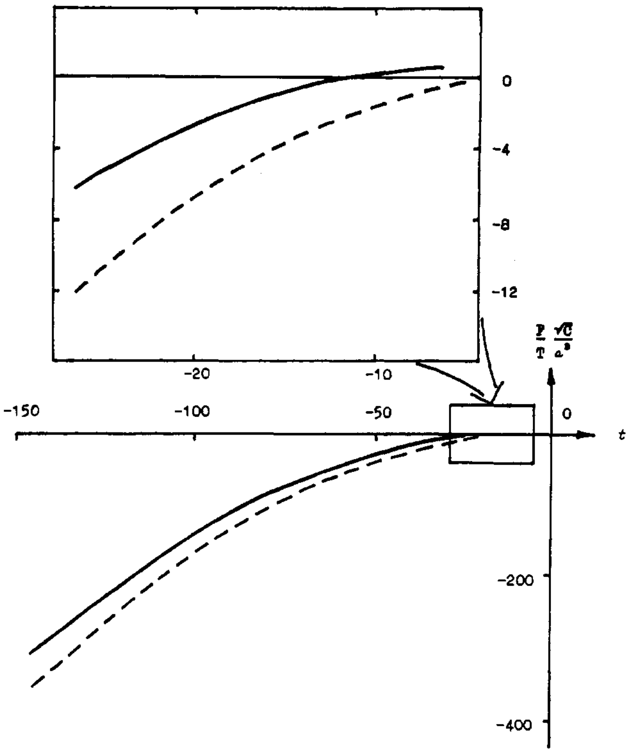

Figure 5. Free energy F of a globule multiplied by $\sqrt{C}/a^3$ as a function of t shown by the solid line. Relatively far from the transition point the system exhibits a behavior which agrees qualitatively with the predictions of the volume approximation (the dashed line).

rigidity (see Appendix A; Figure 4). For the zero point in eq 12 we have used the ideal Gaussian coil free energy. The free energy (eq 12) is negative; i.e., the polymer chain is globulized under the condition $t < t_{tr} \simeq -10.2$.

Figure 5 shows the connection between the free energy F of a globule and the t parameter in the volume approximation (eq 4) and with account of surface energy (eq 12). When $t = t_{tr} \simeq -10.2$, the value $F(t)$ turns into zero, while its derivative with respect to t is positive

$$\left.\frac{F}{T}\frac{\sqrt{C}}{a^3}\right|_{t \simeq t_{tr}} \simeq -0.7\left[\left(\frac{t}{t_{tr}}\right)^2 - 1\right] = -0.7\left[\left(\frac{\tau}{\tau_{tr}}\right)^2 - 1\right]$$

so the derivative of the resulting free energy has a jump at the transition point $t = t_{tr}$.

3.3. Globule Radius of Gyration. When the density distribution is known, the mean-square globule radius of gyration can be calculated. It is determined by the expression

$$\langle S_{glob}^{\ 2}\rangle = \frac{1}{N}\int n(\mathbf{X})\, x^2\, \mathrm{d}^3x = 4\pi 6^{3/2} S_{id}^{\ 2} \varkappa t^{-4} \frac{\sqrt{C}}{a^3}\int_0^\infty \chi^2(r)\, r^4\, \mathrm{d}r \quad (13)$$

The corresponding expansion factor of radius of gyration equals to

$$\alpha_{S_{glob}} \equiv \left[\frac{\langle S_{glob}^{\ 2}\rangle}{S_{id}^{\ 2}}\right]^{1/2} = \left(\frac{\sqrt{C}}{a^3}\right)^{1/2} \tilde{\alpha}(t) \qquad (14)$$

where $\tilde{\alpha}(t)$ is the calculated function of the single parameter t. When $t \to -\infty$, in the volume approximation

$$\tilde{\alpha}^2(t) = 6^{3/2}\frac{3}{5}\left[\frac{3}{2\pi(-t)}\right]^{2/3} \simeq (-0.08t)^{-2/3} \qquad (15)$$

In the general case, $\tilde{\alpha}(t)$ dependence is presented in Figure 4 and in Table I.

Table I
Numerically Calculated Results of t-Dependences of the Following Values: $\varkappa$-Parameter, Dimensionless Density χ^2 at the Globule Center, Globule Mean-Square Expansion Factor Divided by the $\sqrt{C}/a^3$ Value ($\alpha_{S_{glob}}{}^2 \equiv \tilde{\alpha}^2\sqrt{C}/a^3$), and Globule Free Energy with the Analogous Scale Factor[a]

$\varkappa$	t	$1-\chi(0)$	$\tilde{\alpha}^2$	$(F/T)(\sqrt{C}/a^3)$
0.63	−10.0	1.7×10^{-1}	3.44	1.9×10^{-2}
0.62	−11.1	1.1×10^{-1}	2.61	-1.0×10^{-1}
0.61	−12.5	6.9×10^{-2}	2.03	-3.2×10^{-1}
0.60	−14.4	4.1×10^{-2}	1.59	-7.0×10^{-1}
0.59	−16.8	2.2×10^{-2}	1.26	−1.4
0.58	−20.2	1.1×10^{-2}	1.01	−2.6
0.57	−24.9	4.4×10^{-3}	0.80	−4.9
0.56	−31.7	1.4×10^{-3}	0.63	−9.4
0.55	−42.2	2.8×10^{-4}	0.49	-1.9×10^{1}
0.54	−59.7	2.6×10^{-5}	0.37	-4.4×10^{1}
0.53	−93.4	4.8×10^{-7}	0.27	-1.2×10^{2}
0.52	−174.0	1.6×10^{-10}	0.17	-4.5×10^{2}
0.51	−501.0	4.1×10^{-21}	0.08	-4.0×10^{3}

[a] For practical calculations we have used the $\varkappa$-parameter as an independent parameter; that is more convenient.

4. Polymer Chain State near the Θ-Point: Perturbation Theory and Monomer-to-Quasimonomer Renormalizations

The results, discussed above, describe a macromolecule below the point of a globule-to-coil transition. For polymer chains of real length there is a considerable gap between the transition point and the Θ-point. To analyze the Θ-region theoretically, it is natural to use the ordinary classical perturbation theory.[60]

We remind everyone that application of the perturbation theory is usually based on the notion of the dominating role of binary interactions.[60] Correspondingly, the results of this theory are represented by the expansion in powers of parameter

$$Z_0 = \left(\frac{3}{2\pi a^2}\right)^{3/2} 2B_0 N^{1/2}$$

where B_0 is the second virial coefficient of the links interaction.

Below the Θ-temperature the chain shrinks and binary collisions are no longer dominating. To compare with the globular regime theory, discussed in the previous section, it is necessary to take into account three-body collisions in the perturbation theory. It is well-known[58,59] that this fact is connected with monomer-to-quasimonomer renormalizations. In the explicit form the quasimonomer renormalizations are presented in refs 61–64 and in the simplest form in Appendix B. There it is shown that in the first order of the perturbation theory the square expansion factor of the radius of gyration in our designations equals

$$\alpha_{S_{coil}}{}^2 \simeq 1 + \frac{134}{105}Z - \frac{13}{16}\left(\frac{9}{\pi}\right)^2 \frac{C}{a^6} \tag{16}$$

where

$$Z = \left(\frac{3}{2\pi a^2}\right)^{3/2} 2BN^{1/2} = \left(\frac{3}{8\pi^2}\right)^{3/4} 2t\left(\frac{\sqrt{C}}{a^3}\right)^{1/2} \tag{17}$$

B, which is not equal to B_0, and C are the second and third virial coefficients of quasimonomer interactions, respectively; just these coefficients were used above in the globule theory.

We note that the result in eq 16 agrees with qualitative conclusions of ref 58: in the Θ-point, where $B = 0$, the expansion factor is smaller than unity, and this deviation increases with macromolecular flexibility.

It would be helpful to present the perturbation theory result in terms of parameters t and $\sqrt{C}/a^3$:

$$\alpha_{S_{coil}}{}^2 \simeq 1 + 0.2197t\left(\frac{\sqrt{C}}{a^3}\right)^{1/2} - 0.06168t^2\frac{\sqrt{C}}{a^3} - 6.668\left(\frac{\sqrt{C}}{a^3}\right)^2 \tag{18}$$

Here we have taken into account not only the first-order result in eq 16 but also the second-order data from ref 60.

5. On the Region of a Globule-to-Coil Transition

We have already described the behavior of a macromolecule both above and below the globule-to-coil transition region. Now we will try to sew these results.

It is simple for the case of a rigid chain with a small $\sqrt{C}/a^3$ value. Really, our quantitative results presented above provide the following qualitative description, given earlier in ref 34. Comparatively far from the transition point our system behavior is typical for the second-order phase transition region, because free energy is proportional to $F \sim -\tau^2$ (within 10% when $t < -200$) and the globule size expands approximately according to a power law ($\alpha \sim |\tau|^{-1/3}$ with the same accuracy when $t \lesssim -30$). On the contrary, in the nearest neighborhood of the transition

$$\frac{F}{T} \simeq -1.4\frac{a^3}{\sqrt{C}}\left(\frac{t}{-10.2} - 1\right)$$

and at the transition point the derivative of free energy with respect to temperature has a jump, which is proportional to $(a^3/\sqrt{C})N^{1/2}$. This jump is the latent heat; in the usual thermodynamics it is a manifestation of the bimodal distribution in phase space—this is the case, for example, in the first-order phase transition. In our case the jump value is proportional to $N^{1/2}$, contrary to N in the first-order phase transition. Nevertheless, this value as well as other characteristics of transition sharpness (see also the second paper in this series), increases when chain rigidity parameter $\sqrt{C}/a^3$ decreases. It is quite natural to suppose therefore that a rigid chain with a small $\sqrt{C}/a^3$ value can be treated as a two-level system in the transition region. Then the respective population ratio on globule and coil levels equals $\exp(-F/T)$. The mean-square expansion factor in this case is

$$\alpha_S{}^2 = [\exp(F/T) + 1]^{-1}\alpha_{S_{glob}}{}^2 + [\exp(-F/T) + 1]^{-1}\alpha_{S_{coil}}{}^2 \tag{19}$$

where $\alpha_{S_{glob}}$ and $\alpha_{S_{coil}}$ are presented by the expressions in eqs 14 and 18. It is noteworthy that just this average is measured in the elastic light scattering experiments.

The correctness of this two-level averaging (eq 19) for rigid chains is confirmed also by the fact that with a decrease of $\sqrt{C}/a^3$ the value of perturbation parameter Z (eq 17) at the point of a globule-to-coil transition decreases also:

$$Z|_{t=t_{tr}} = -1.79(\sqrt{C}/a^3)^{1/2}$$

According to the expressions in eqs 12, 14, 18, and 19 the α parameter depends on t and $\sqrt{C}/a^3$ values only. In Figure 6 calculated plots of α vs t are reported for the cases $\sqrt{C}/a^3 = 0.05$, 0.01, and 0.001. Figure 7 presents analogous dependences using the logarithmic scale; here the globular part of the curves is of the universal form, independent of the $\sqrt{C}/a^3$ value.

For flexible chains the two-level approximation (eq 19) is incorrect and the question of effective interpolation

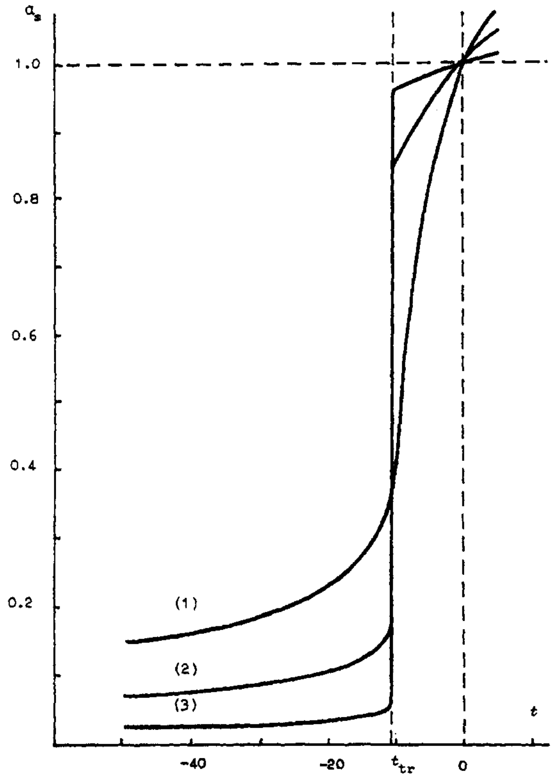

Figure 6. Expansion factor of a macromolecule α_S plotted vs t. Curves 1–3 correspond to $\sqrt{C}/a^3$ = 0.05, 0.01, and 0.001, respectively. Cases 2 and especially 3 correspond to a very rigid macromolecule, while case 1 approximately corresponds to the smallest chain rigidity, which can be described in the two-level approximation.

between the expressions in eqs 14 and 18 still stands. Analysis of the accuracy of formulas 14 and 18 shows, however (see Appendix C), that the question of their interpolation for chains of real finite length is not interesting enough (see Figure 8). It is noteworthy that the accuracy of the theoretical results, shown in Figure 8, is sufficient for interpretation of real experiments (see part 4 of this series of papers).

6. Quantitative Version of Flory-Type Theory

Now we will consider another simpler Flory-type approach to the problem. As we have mentioned above, this approach describes the chain in terms of a single scalar order parameter—expansion factor α of the radius of gyration. (The radius of gyration characterizes macromolecular size in the collapsed globular state more adequately[40,49] than the mean-square end-to-end distance, which is used in the original Flory-type theory.[35] The difference between these two characteristics becomes most essential in the region of collapse.)

Polymer free energy in this approach can be written[40] as

$$F(\alpha) = F_{el}(\alpha) + F_{int}(\alpha) \qquad (20)$$

where F_{el} is a deviation of the conformational entropy from the ideal chain level and F_{int} is a contribution of the intramolecular interactions to the free energy, calculated in the mean-field approximation with virial expansion:

$$F_{int}/T = N^2B/V + N^3C/V^2 + ... \qquad (21)$$

$V = \lambda\langle S^2\rangle^{3/2}$ is a conditional volume occupied by a macromolecule. ($\langle S^2\rangle$ is the chain mean-square radius of gyration; λ = const.) It was shown in ref 40 that in terms

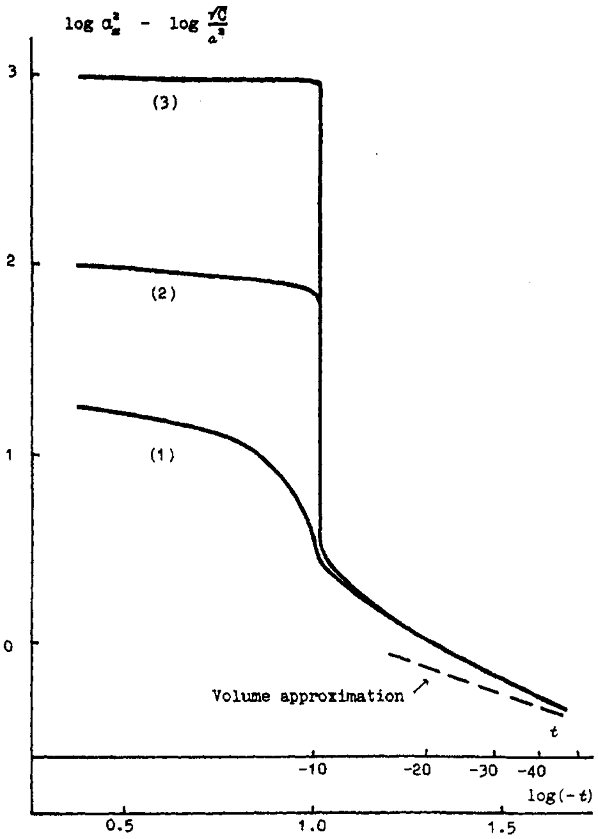

Figure 7. log–log plot of the squared expansion factor of a macromolecule multiplied by $(\sqrt{C}/a^3)^{-1}$ as a function of t. Curves 1–3 correspond to $\sqrt{C}/a^3$ = 0.05, 0.01, and 0.001, respectively. The globular parts of the curves do not depend practically on $\sqrt{C}/a^3$.

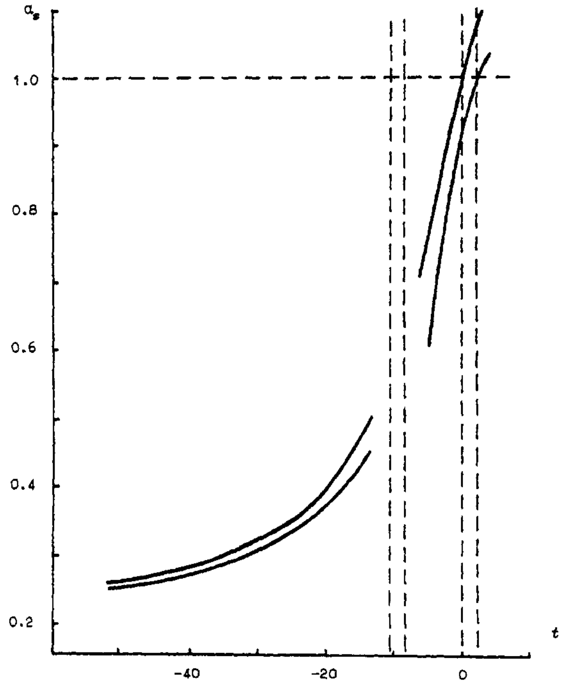

Figure 8. Expansion factor of a flexible macromolecule ($\sqrt{C}/a^3$ = 0.15) plotted vs t. This dependence is presented in the form of a "corridor" characterizing both experimental and theoretical errors that were connected with the definition of the Θ-point (see Appendix C).

of $\alpha^2 \equiv \langle S\rangle^2/(Na^2/6)$ we can write

$$F_{el}/T = \gamma[\alpha^{-2} + 2 \ln \alpha], \quad \gamma = \text{const} \qquad (22)$$

instead of $F_{el} \sim T\alpha^2$ in the original Flory-type theory, α

being the expansion factor of the mean-square end-to-end distance.

Let us clarify in a few words the origin of the leading term $F_{el} \sim T\alpha^{-2}$ in eq 22. To obtain it, let us consider the ideal chain embedded into the hole of the radius ρ. Any part of the chain with the number of monomers less than $g \sim (\rho/a)^2$ behaves as an ideal chain without constraints. Therefore, the free energy of chain confinement is of order T per each g monomer. It gives $F_{el} \sim TN/g \sim TNa^2/\rho^2 \sim T\alpha^{-2}$ (see also ref 38).

The interpolation expression of the type

$$F_{el}/T = \gamma[\alpha^{-2} + \alpha^2]$$

can also be used with the same success[38] as eq 22. The advantage of this last form of the interpolation is its validity for all the regimes from the strongly collapsed chain (leading term is α^{-2}) through the Gaussian chain (free energy has a minimum at $\alpha = 1$) and up to the swollen coil regime (leading term is α^2). Following the work in ref 40, we will use the interpolation in eq 22.

Due to the second term $\sim \ln\alpha$, the first derivative of $F_{el}(\alpha)$ (eq 22) vanishes at $\alpha = 1$; the constant value of F_{el} itself at $\alpha = 1$ is not of physical importance.

The expression in eq 20 for free energy can be rewritten using eqs 21 and 22. To fit the result to the a priori requirement that for $t = 0$ the first derivative of $F(\alpha)$ vanishes at $\alpha = 1$, the phenomenological shift of the Θ-point was proposed in ref 40. When such a shift Δt is introduced formally, the free energy should be expressed as

$$\frac{F(\alpha)}{T\gamma} = \alpha^{-2} + 2\ln(\alpha) + \frac{2u(t + \Delta t)}{3\alpha^3} + \frac{w}{3\alpha^6} \tag{23}$$

where

$$u \equiv \frac{9}{6^{1/4}\gamma\lambda}(\sqrt{C}/a^3)^{1/2}, \quad w \equiv \frac{648}{\gamma\lambda^2}(\sqrt{C}/a^3)^2$$

The equilibrium value of α obeys the rather simple equation

$$\alpha^3 - \alpha = u(t + \Delta t) + w\alpha^{-3} \tag{24}$$

This equation is the main result of Flory-type theory in the most consistent form of ref 40. It gives α on t dependence for any fixed u, w, and Δt values. In accordance with the above results, this dependence is comparatively smooth when $\sqrt{C}/a^3 \sim 1$ (flexible chains), becomes sharper when the $\sqrt{C}/a^3$ value decreases, and turns into a discontinuous one for $\sqrt{C}/a^3 < (\gamma/2)^{1/2}\lambda/243$ (rigid chains). Equation 24 can also be presented as a linear dependence of $\alpha^4(\alpha^2 - 1)$ on $\alpha^3(t + \Delta t)$, which makes it quite simple.

A minimization procedure for the free energy expression (eq 23) with respect to α, which resulted in eq 24, means, in fact, that in the exact expression

$$\alpha \equiv \langle\alpha^2\rangle^{1/2} = \left(\frac{\int_0^\infty \alpha^2 e^{-F/T}\,d\alpha}{\int_0^\infty e^{-F/T}\,d\alpha}\right)^{1/2}$$

the integrals are taken by the saddle-point approximation. This method would be correct for a sharply defined minimum of free energy $F(\alpha)$. It is true for the globular state and, generally speaking, is incorrect for the coil state and for the region of transition. Thus for the transition and coil regions eq 24 presents a rather qualitative description.

Equation 24 has, of course, an essentially simpler form than the results of the above-described Lifshitz-type theory. However, in order to use it, one must preliminarily choose the concrete values of the γ, λ, and Δt parameters. Since we are free to choose these *three* values, it is desirable to satisfy the following *four* physical requirements:

(i) In the case of an extremely poor solvent eq 24 would lead to the same result as the volume approximation, because this last approximation is the exact one for the well-formed globule with a steplike density distribution. In this limit ($t \to -\infty$ and $\alpha \to 0$) eq 24 leads to $\alpha^3 \simeq 2(6^{9/4}/\lambda(-t))(\sqrt{C}/a^3)^{3/2} = 6^{3/2}(2/\lambda)(-C/N^{1/2}Ba^3)$ whereas the volume approximation result has the form of eq 2 within the macromolecule volume $V = N/n_0$; i.e., $\alpha^3 \simeq (3/2\pi)(18/5)^{3/2}(-C/N^{1/2}Ba^3)$. Therefore, we obtain $\lambda = (4\pi/3)(5/3)^{3/2}$.

(ii) As to the origin of the γ parameter, it is the coefficient in the expression of the polymer elastic energy for a strongly compressed chain; i.e., $F_{el} \simeq T\gamma\alpha^{-2}$ ($\alpha \ll 1$). This coefficient has been calculated in ref 65 in the framework of standard Gaussian bead models, and it was shown that $\gamma = {}^9/_4$.

Other γ values can be obtained for several concrete polymer models. For example, for a wormlike persistent chain[38] the confinement energy equals $F_{el} \simeq (3/2)T\alpha^{-2}$, i.e., $\gamma = {}^3/_2$, when the globule radius R is essentially smaller than the effective segment l ($R \ll l$). However, these other γ values characterize some nonuniversal features of the limited length chains. This is why we will use the $\gamma = {}^9/_4$ value.

Using $\gamma = {}^9/_4$ and $\lambda = (4\pi/3)(5/3)^{3/2}$ values, we obtain

$$u = 0.2836(\sqrt{C}/a^3)^{1/2}, \quad w = 3.5454(\sqrt{C}/a^3)^2$$

(iii) Near the Θ-point ($t = 0$) the results of eq 24 would coincide with perturbation ones (eq 18).

(iv) The coil–globule transition point would be $t_{tr} \simeq -10.2$ (see section 3.2) at least at the limit when the $\sqrt{C}/a^3$ parameter tends to zero ($\sqrt{C}/a^3 \to 0$).

In fact, however, it is *impossible* to satisfy *all* these requirements simultaneously. We consider this fact as a confirmation of the principal inconsistency of the Flory-type approach for the globular state description, even in the best form of ref 40. Nevertheless, the Flory-type result (eq 24) provides a good interpolation for the whole region from the Θ-coil to the well-formed globule both for Lifshitz-type theory results and for experimental data (see the fourth paper of this series). Of course, the Flory-type theory is nevertheless very attractive due to its simplicity, in spite of the many limitations of its applicability.

7. On the Order of Globule-to-Coil Transition

Summing up the results, presented in this paper, we can say that two different theoretical approaches yield the following general conclusions. The globule-to-coil transition starts with a pretransitional swelling resembling an approach to the second-order phase transition point. However, for rigid polymer chains the globule-to-coil transition itself looks like a first-order phase transition, including the effects of two-minima free energy and the bimodal state distribution (this regime takes place when $\sqrt{C}/a^3 \lesssim 0.05$); for flexible chains ($\sqrt{C}/a^3 \gtrsim 0.05$) the transition is comparatively smooth and looks like a second-order phase transition; the question on the number of free-energy minima loses physical contents in this case, because of the chain finiteness.

Appendix A: Equations for the Density of a Polymer Globule

The well-known fact is that the globule-to-coil transition region is universal. This means that macroscopic properties of the polymer chain in this region are independent of the details of its microscopic structure (see refs 34 and 38). This is why the theory is a three-parametric one; it includes a one-dimensional value Na^2 and two dimensionless parameters t and $\sqrt{C}/a^3$. The universality of the Gaussian coil is in connection with the universal properties of a continuous Brownian trajectory. Correspondingly, the theory of a coil-to-globule transition can also be formulated from the very beginning in terms of this continuous Brownian model of the chain (see ref 38). However, in this case the method of introduction of the characteristics of chain stiffness and of volume interactions, in our mind, is not very obvious physically. From this point of view the "beads on a string" model and the wormlike persistent model seem to be preferable. The known fact of universality means that the macroscopic properties of these models must converge to the model-independent results in the continuous limit, when all the sizes in the system, such as the globule's radius or surface layer thickness, become larger than the distance between neighboring beads or than the persistent length. We start with the beads on a string model and, taking the continuous limit, obtain the universal results.

The globule free energy expression, including volume and surface parts and with the zero point in the ideal Gaussian coil state, can be written down[34] as

$$F = -TN\ln(\Lambda) - \int p^*(n(\mathbf{X}))\,\mathrm{d}\mathbf{X} \qquad \text{(A1)}$$

The intraglobular smoothed density distribution $n(\mathbf{X})$ and eigenvalue Λ are defined by the following coupled equations:[34]

$$\begin{aligned} \hat{g}\psi(\mathbf{X}) &= \Lambda\psi(\mathbf{X})\exp[\mu^*(n(\mathbf{X}))/T] \\ n(\mathbf{X}) &= \psi^2(\mathbf{X})\exp[\mu^*(n(\mathbf{X}))/T] \\ N &= \int n(\mathbf{X})\,\mathrm{d}\mathbf{X} \qquad \text{(A2)} \end{aligned}$$

Here $\hat{g}$ stands for the integral operator; it describes the linear memory of the chain[36] or the properties of the string connecting the beads in the beads on a string model:

$$\hat{g}\psi(\mathbf{X}) = \int g(\mathbf{X}-\mathbf{X}')\,\psi(\mathbf{X}')\,\mathrm{d}\mathbf{X}' \qquad \text{(A3)}$$

$g(\mathbf{X}-\mathbf{X}')$ is the conditional probability to find the next chain link at $\mathbf{X}$, when the previous one is fixed at $\mathbf{X}'$; $\psi(\mathbf{X})$ can be considered as the eigenfunction.

In our situation the characteristic spatial scale of changing density is much more than the mean spatial distance a between adjacent monomers and that is why the operator $\hat{g}$ can be presented[34] as $1 + (a^2/6)\Delta$, where Δ is the Laplacian operator. This representation of the $\hat{g}$ operator corresponds to the replacement of the discrete beads on a string model by the continuous Brownian model. Further, in the globule–coil transition region the polymer link density is small and it allows us to use the virial expansion (eqs 1a and 5) for the $p^*(n)$ and $\mu^*(n)$ functions. In order to analyze quantitatively the basic equations in eq A2, it is convenient to introduce instead of Λ the special numerical parameter $\varkappa$ using the following implicit definition:

$$\Lambda = \exp\left[-\frac{\mu^*(n_1)}{T}\right], \quad n_1 \equiv 2\varkappa n_0 = -\varkappa B/C \qquad \text{(A4)}$$

After the transformations and introduction of dimensionless quantities $\mathbf{r}$ (eq 9) and $\chi(\mathbf{r})$ (eq 10), eq A2 becomes transformed into eqs 7 and 8, and the expression in eq A1 for the free energy looks like eq 12.

The scale factor $(\sqrt{C}/a^3)^{-1}$ in eq 12 characterizes a value of the polymer rigidity. This fact can be clearly explained in terms of the persistent, or wormlike, model. If the thickness and the effective segment of a polymer in this model are d and l, respectively, then $B \sim l^2 d\tau$ and $C \sim l^3 d^3$, while the rigidity is characterized by parameter $p = l/d$. In the bead model the average distance between adjacent links in a chain $a \sim l$ and the rigidity is determined therefore by parameter $C^{1/2}/a^3 \sim (d/l)^{3/2} = p^{-3/2}$. A detailed comparison of these two models in a description of the polymer globule properties can be found in ref 56.

Appendix B: Perturbation Theory and Renormalization of the Second Virial Coefficient

As in Appendix A, we start with the discrete beads on a string model and then obtain the universal results by means of the corresponding limit transition to the continuous model.

Let us begin our consideration of quasimonomer renormalizations with a simple example of the calculation of the mean-square end-to-end distance

$$\langle R^2\rangle = \frac{\int R^2 Z\left(\begin{smallmatrix}0\\0\end{smallmatrix}\middle|\begin{smallmatrix}N\\R\end{smallmatrix}\right)\mathrm{d}R}{\int Z\left(\begin{smallmatrix}0\\0\end{smallmatrix}\middle|\begin{smallmatrix}N\\R\end{smallmatrix}\right)\mathrm{d}R}$$

in the framework of the perturbation theory. Here

$$Z\left(\begin{matrix}0\\0\end{matrix}\middle|\begin{matrix}N\\R\end{matrix}\right) = \int \delta(\mathbf{X}_0)\,\delta(\mathbf{X}_N-R)\exp\left[-\frac{\epsilon(\Gamma)}{T}\right]\prod_{j=1}^{N} g(\mathbf{X}_j-\mathbf{X}_{j-1})\,\mathrm{d}\Gamma$$

is the partition function of the chain whose ends are fixed at the zero point and at the R point.

$$g(\mathbf{X}_j-\mathbf{X}_i) = \left[\frac{3}{2\pi(j-i)a^2}\right]^{3/2}\exp\left[-\frac{3(\mathbf{X}_j-\mathbf{X}_i)^2}{2(j-i)a^2}\right]$$

$\Gamma \equiv \{\mathbf{X}_0, \mathbf{X}_1, ..., \mathbf{X}_N\}$ is a point in the chain configurational space and $\epsilon(\Gamma)$ is the microscopic energy of volume interactions in the Γ configuration.

In the absence of volume interactions, when $\epsilon(\Gamma) = 0$, we have, naturally, $\langle R^2\rangle = Na^2$. In the presence of volume interactions in the framework of the first-order perturbation theory, but taking into account triple interactions as well as pair ones, we can write down the following expression for the expansion factor:

$$\alpha_R{}^2 \equiv \frac{\langle R^2\rangle}{Na^2} \simeq 1 + \frac{2B_0}{N}\sum_{0\leqslant i<j\leqslant N}\left[\frac{3}{2\pi(j-i)a^2}\right]^{3/2}(j-i) + \frac{6C_0}{N}\sum_{0\leqslant i<j<k\leqslant N}\left[\frac{3}{2\pi(j-i)a^2}\right]^{3/2}\left[\frac{3}{2\pi(k-j)a^2}\right]^{3/2}(k-i) \qquad \text{(B1)}$$

To explain ongoing consideration, we note that pair interactions correspond to the diagram shown in Figure

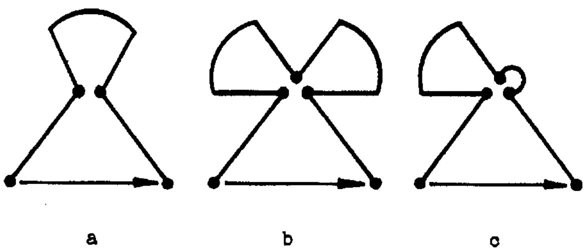

Figure 9. Diagrams that explained the renormalization of the second virial coefficient.

9a; meanwhile, the diagram for triple interactions looks like that in Figure 9b. It is obvious from these diagrams that triple interactions, where two participants are comparatively close to each other along the chain (Figure 9c), can be considered in a quite natural way as an interference of a third partner in pair interaction. Interactions of higher orders would be considered in a similar way. This is a representation of the physical nature of the renormalizations under consideration. Using these ideas it is convenient to rewrite eq B1 as

$$\alpha_R^{\;2} = 1 + \left(\frac{3}{2\pi a^2}\right)^{3/2} \frac{2}{N} \sum_{0 \leqslant i < j \leqslant N} \Bigg\{ (j-i)^{-1/2} \Bigg[B_0 + \left(\frac{3}{2\pi}\right)^{3/2} \frac{3C_0}{a^3} \Big(\sum_{0 < m \leqslant N-j} m^{-3/2} + \sum_{0 < m \leqslant i} m^{-3/2} \Big) \Bigg] \Bigg\} \qquad \text{(B2)}$$

If $N \to \infty$, the expression in the square brackets would represent the effective second virial coefficient of quasimonomer interactions

$$B = B_0 + \left(\frac{3}{2\pi}\right)^{3/2} \frac{6C_0}{a^3} \sum_{0 < m < \infty} m^{-3/2} \simeq B_0 + \frac{C_0}{a^3}\left(\frac{3}{2\pi}\right)^{3/2} \frac{12}{\delta^{1/2}} \qquad \text{(B3)}$$

where δ is the formally introduced cutoff parameter, which establishes the lower bound of the integration, when the sum over m is replaced by the integral. Of course, the transformation of the sum into the integral corresponds to the replacement of the discrete "beads" model of the chain by the continuous Brownian model.

The divergence of B in the small cutoff limit $\delta \to 0$ ("the ultraviolet catastrophe") means that the main contribution for the monomer renormalization is done by their near neighbors in the chain. Here the situation is quite similar to the one found in electrodynamics: the nonrenormalized value B_0 and the δ parameter are not of great significance (in any case, their meaning strongly depends on the polymer chain microstructure). What has really a physical sense is the only observable combination B (eq B3).

It must be specified that here we do not discuss the analogous renormalization of the third virial coefficient at the expense of the fourth and subsequent ones and the next contributions into the second virial coefficient B, because their consideration would be an excess of precision in comparison with the above globule theory.

In the finite length polymer the different links are really under different conditions depending on their position in the chain. In eq B2 the second virial coefficient looks as "not quite renormalized" because of the absence of infinite ends, though the near link environment, which makes the main contribution to renormalization, remains constant for almost all the links along the whole chain. In terms of correctly renormalized (eq B3) virial coefficient B, the expression in eq B2 can be rewritten as

$$\alpha_R^{\;2} = 1 + \left(\frac{3}{2\pi a^2}\right)^{3/2} \frac{2}{N} \sum_{0 \leqslant i < j \leqslant \mathrm{N}} \Bigg\{ (j-i)^{-1/2} \Bigg[B - \left(\frac{3}{2\pi}\right)^{3/2} \frac{3C}{a^3} \Big(\sum_{N-j < m < \infty} m^{-3/2} + \sum_{i < m < \infty} m^{-3/2} \Big) \Bigg] \Bigg\}$$

These sums can be replaced by integrals, and it means physically that the consideration of the chain in terms of the continuous Brownian model is possible using the renormalized virial coefficients. Taking the sums, we obtain finally

$$\alpha_R^{\;2} = 1 + \frac{4}{3}\left(\frac{3}{2\pi a^2}\right)^{3/2} N^{1/2}(2B) - \frac{81}{\pi^2}\frac{C}{a^6} \qquad \text{(B4)}$$

It is important that α_R in eq B4 depends on observable quantities B and C only and does not depend on δ.

The result in eq B4 agrees with the qualitative conclusion of ref 58 that at the Θ-point ($B = 0$) the expansion factor must be less than unity due to the triple interactions. The more macromolecular flexibility there is, the more the deviation from unity.

Similarly we can consider the value of the polymer mean-square radius of gyration:

$$\langle S^2 \rangle = \frac{1}{N^2} \sum_{m<n} \langle R_{mn}^{\;2} \rangle = \frac{1}{N^2} \sum_{m<n} \frac{\int R^2 Z\left(\begin{matrix} m \\ 0 \end{matrix} \middle| \begin{matrix} n \\ R \end{matrix}\right) \mathrm{d}R}{\int Z\left(\begin{matrix} m \\ 0 \end{matrix} \middle| \begin{matrix} n \\ R \end{matrix}\right) \mathrm{d}R}$$

Here $\langle R_{mn}^{\;2} \rangle$ is the mean-square distance between the polymer links with numbers m and n

$$Z\left(\begin{matrix} m \\ 0 \end{matrix} \middle| \begin{matrix} n \\ R \end{matrix}\right) = \int \delta(\mathbf{X}_m)\, \delta(\mathbf{X}_n - R) \exp\left[-\frac{\epsilon(\Gamma)}{T}\right] \prod_{j-1}^{N} g(\mathbf{X}_j - \mathbf{X}_{j-1})\, \mathrm{d}\Gamma$$

is the partition function of the chain with m links at the zero point and n links at the R point. Omitting rather cumbersome calculations, we write down the final result for the expansion factor.

$$\alpha_S^{\;2} \equiv \frac{6\langle S^2 \rangle}{Na^2} = 1 + \frac{134}{105}\left(\frac{3}{2\pi a^2}\right)^{3/2} N^{1/2}(2B) - \frac{13}{16}\frac{81}{\pi^2}\frac{C}{a^6} \qquad \text{(B5)}$$

Here, as in the case of α_R, the value of α_S is less than unity when $B = 0$, but the deviation from unity is somewhat smaller.

It is important that the different types of expansion factors turn into unity, or, otherwise, they take the unperturbed values, in different points, corresponding to different nonzero values of the second virial coefficient B of quasimonomer interactions. Naturally, with an increase of N all these apparent Θ-points come closer to each other, and when $N \to \infty$, they tend to the true Θ-point, where $B = 0$.

The quasimonomer concept was introduced by Khokhlov.[58] The perturbation theory including the three-body interactions was proposed in refs 61 and 62; the results for the real three-dimensional case were supposed to be dependent on the cutoff parameter δ (see eq B3). These results were criticized by Duplantier,[63] who has obtained also for the first time the physical results independent of

δ, which are quite similar to eqs B4 and B5.

Appendix C: Analysis of the Precision of the Theory

As has been noted above, there exists a certain difference between the apparent Θ-points, in which some polymer dimensions equal to the ideal ones, and the real Θ-point, in which the effective renormalized second virial coefficient of quasimonomer interactions becomes equal to zero. This distinction, being the result of the polymer length finiteness, is essential mainly for flexible macromolecules. We will consider here experimental and theoretical errors that can arise from this distinction of Θ-point determinations. In accordance with the expression in eq 18 for the expansion factor of the radius of gyration, the distance between the real and the apparent Θ-points can be characterized by the value $\Delta t \simeq 30.4(\sqrt{C}/a^3)^{3/2}$ or $\Delta\Theta \simeq 7.92\Theta C/N^{1/2}ba^3$ ($b \equiv B/\tau$). Moving the theoretical curve $\alpha_S(t)$ along the t axis at a Δt distance, we can construct a certain corridor, which just characterizes the errors for the coil region. This corridor is represented in Figure 8 for the case $\sqrt{C}/a^3 = 0.15$. (In the coil region it is sufficient to construct the upper bound of the corridor in the first order of the perturbation theory.)

The precision of the globule theory is considered here in more detail. Besides the mean-field approximation, the potential source of errors in this theory is the fact that the contribution of volume interactions into globule thermodynamic functions was written in terms of the disconnected link system, i.e., quasimonomers. It means that B, C, ..., in the formulas of the globule theory are renormalized virial coefficients. But strictly speaking these values characterize the infinite chain only. It is quite natural to assume that for the finite chain the exact equations of the globule theory can be obtained by changing $B \rightarrow B + \Delta B$, where ΔB is the value of order of "non quite renormalization" (see Appendix B) because of the chain finiteness ($\Delta B \rightarrow 0$, when $N \rightarrow \infty$). Hence, the indicated error of the globular theory can be effectively turned to the redefining of the Θ-point, and thereby it can be characterized by the width of the same corridor in Figure 8. When the polymer rigidity increases, i.e., $\sqrt{C}/a^3$ value decreases, the distance between the borders of this corridor decreases, and these borders are practically fused into one line for a rigid macromolecule (see Figure 6).

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