Coil–Globule Type Transitions in Polymers. 2. Theory of Coil–Globule Transition in Linear Macromolecules

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ABSTRACT: The theory of the coil–globule transition is developed based on the Flory method and with the use of various distribution functions for the radius of gyration of the chain for the regions of chain swelling and contraction. The theory coincides with experimental data for polystyrene and with results of computer simulation for long chains.

Introduction

The theory of the random coil–globule transition has been developing for over 25 years. On the one hand, many authors, Stockmayer,[1] Ptitsyn and Eizner,[2] de Gennes,[3] Zimm and Post,[4] Sanchez,[5] DiMarzio,[6] and Muthukumar,[7] have investigated this problem on the basis of a simple Flory scheme.[8] On the other hand, in a larger series of papers by Lifshitz, Grosberg, and Khokhlov, a more rigorous and complex method has been developed (LGKh theory, see ref 9–11 and the literature cited there). Why is the present work also needed?

Analyzing refs 1–6, we were surprised to discover that these independent investigations carried out by authors well-known in polymer physics contain a common feature: the evaluation of the configurational entropy (and entropy force) is based on an expression inapplicable to the case considered but valid for the case of chain expansion. It is not improbable that the high scientific prestige of P. J. Flory induced the authors of refs 1–6 to extend the approximate expression used by Flory for the entropy of chain stretching beyond the range of its applicability. We believe that our paper is the first proper theory of the random coil–globule transition based on Flory's method.[8]

This theory turned out to be very productive. For the first time, it became possible to compare the results of a simple theory and the LGKh theory and to establish both quantitative agreement and the existence of fundamental divergencies. This is highly important; for until now the two lines of development of the coil–globule transition theory (the simple theory according to Flory's scheme and the LGH theory) ran parallel without being properly compared and discussed, though in some cases representatives of these trends exchanged brief critical remarks. Besides, the theory developed in the present paper makes it possible to interpret clearly the main features of the transition. It offers an algorithm for processing of experimental data and for the determination of several physical parameters. Some preliminary results of this work have been given.[12]

The Theory

Introductory Remarks. Generally, the relationships reported in this section are sufficiently evident. Moreover, some of them have already been widely used for the solution of similar problems. However, we consider it useful to analyze thoroughly and in detail all the initial concepts.

We will begin with the summary of Flory's scheme and will attempt to formulate it as rigorously as possible.

A linear chain consisting of n units will be considered. The unit is a symmetric chain element, the length of which is equal to the chain diameter taken as unit length. Let the chain exhibit a certain stiffness and p be the number of units in a Kuhn segment. The number of Kuhn's segments in the chain is $N = n/p$.

The chain size R is usually characterized either by the square of the end-to-end dimension h or by the square of the gyration radius S. It is often convenient to normalize the chain size to the average size of the unperturbed Gaussian chain $\langle h_0^2 \rangle = Np^2$ or $\langle S_0^2 \rangle = Np^2/6$ and to introduce the expansion factors

$$\alpha_h^2 = h^2/\langle h_0^2 \rangle$$

$$\alpha_S^2 = S^2/\langle S_0^2 \rangle \tag{1}$$

and the averaged values

$$\alpha_{av}^2 = \langle \alpha^2 \rangle$$

To avoid misunderstanding, it should be noted that in the literature the symbol α very often refers just to the averaged characteristic, which we call α_{av}, and we use the symbol α for the nonaveraged value in eq 1. The subscripts h and S at the expansion coefficients will be omitted if it is evident from the text which quantity is meant.

Free Energy of the Chain. In the spirit of Flory's scheme, we have

$$\Delta F = \Delta F_{el}(\alpha_{av}) + \Delta F_{int}(\alpha_{av}, N) \tag{2}$$

where $\Delta F_{el}(\alpha_{av})$ is the elastic free energy of Gaussian chain deformation from the unperturbed state with an average size $\alpha_{av} = 1$ and $\Delta F_{int}(\alpha_{av}, N)$ is the free energy of volume interaction between units distant from each other along the chain, depending on the chain size. (The interaction between units located close to each other along the chain effectively influences only the renormalization of chain stiffness and may not be taken into account in the framework of the method considered here.)

It should be emphasized that the parameter in eq 2 in the approximation used is an averaged chain size; i.e., the moment of chain size distribution (generally speaking, any even moment) and the choice of either the gyration radius or the end-to-end dimension as the chain size is due to the

necessity for an adequate description of chain conformations upon deformation.

The determination of the equilibrium value of α_{av} reduces to the minimization of free energy, ΔF (eq 2), for chain size, i.e., to finding the equilibrium conditions of forces:

$$f = \delta \Delta F / \delta \alpha_{av} \tag{3}$$

$$f_{el} = -f_{int} \tag{4}$$

The "forces" contained in eq 4 will be calculated separately (the marks "-" will be omitted). First, $f_{el}(\alpha_{av})$ will be considered.

Chain Deformation. Let us consider the most rigorous (from our viewpoint) approach to the calculation of elastic entropy or the corresponding elastic force connected with chain deformation. To our knowledge, this algorithm has not been previously used in the problems of chain deformation. In Flory's fundamental paper,[8] a physically equivalent but a more specific original approach has been used. In more recent papers,[5,6] the authors have not used rigorous reasoning, making, generally speaking, no distinction between the average and the most probable chain size.

Let us consider the partition function of a Gaussian chain subjected to the force $\tilde{f}$ conjugate to α_{av}^2. This partition function is related to the distribution function of chain size by the Laplace transformation.

$$G(\tilde{f}) = \int_0^\infty d\alpha^2 \exp(-\alpha^2 \tilde{f}) \, W(\alpha^2) \tag{5}$$

The average size of the deformed chain is given by

$$\alpha_{av}^2 = -d \ln G / d\tilde{f} \tag{6}$$

Actually, this equation determines the elastic force $\tilde{f}(\alpha_{av}^2)$ necessary for chain deformation to the average size α_{av}^2. The value of $f_{el}(\alpha_{av})$ in eq 3 in which we are interested is evidently determined by the equation

$$f_{el} = 2\alpha_{av}\tilde{f} \tag{7}$$

The free energy of Gaussian chain deformation (in kT units) is determined by the Legendre transformation from $\ln G(\tilde{f})$:

$$\Delta F_{el} = \ln [G(\tilde{f}(\alpha_{av}^2))] + \alpha_{av}^2 \tilde{f}(\alpha_{av}^2)$$

In order to carry out this procedure, it is necessary to choose an adequate characteristic of the chain size. This choice is the central point of this section and of this work in general.

The simplest characteristic of the chain size is the end-to-end dimension h. It is characterized by the Gaussian distribution function, which belongs to a broader class of functions of the form

$$W(\alpha_h^2) \, d\alpha_h^2 = k\alpha_h^{2x} \exp(-\gamma\alpha_h^2) \, d\alpha_h^2 \tag{8}$$

where k is the normalization factor.

Function 8 gives the correct value of $\langle \alpha_h^2 \rangle = 1$ at $x = \gamma - 1$; for the Gaussian distribution function $\gamma = 3/2$.

The application of function 8 and the scheme in eqs 5 and 6 permits the determination of the elastic force conjugate to the end-to-end dimension. Unfortunately, the end-to-end dimension is not a measure of the chain's volume. Thus, a chain closed in a ring retains an average volume $\sim N^{3/2}$, differing from that of a linear chain only in the numerical factor. However, it seems useful to find and analyze $f_{el}(\alpha_{av})$, applying eq 8 because, as already

mentioned, we have not found this rigorous approach in the literature, and the results will be useful in further discussion.

We obtain for $G(\tilde{f})$ from eq 5

$$G(\tilde{f}) = \frac{k\Gamma(x + 1)}{(\tilde{f} + \gamma)} \tag{9}$$

The desired elastic force is given by

$$f_{el} = 2\gamma\alpha_{av}\left(1 - \frac{x + 1}{\gamma}\alpha_{av}^{-2}\right) \tag{10}$$

As already mentioned, the value of $x = \gamma - 1$ ensures the correct average value $\alpha_{av} = 1$ for a free chain. In this case eq 10 leads to the natural result $f_{el}(\alpha_{av} = 1) = 0$.

For the evaluation of $\Delta F_{el}(\alpha)$ and $f_{el}(\alpha)$, the following expression is often used

$$\Delta F_{el}(\alpha) = -\ln [W(\alpha)] \tag{11}$$

Equations 8–11 show that this evaluation ensures the correct value for only the term with the highest power of α determined by the exponent in eq 8

$$\Delta F_{el}(\alpha) \sim \gamma\alpha^2$$

$$f_{el}(\alpha) \sim 2\gamma\alpha \tag{12}$$

The next term depending on the preexponential factor in eq 8 has the correct power of α but differs in the coefficient from that obtained by a rigorous method in eq 10.

Now the other chain characteristic, its radius of gyration, will be considered. It is precisely this characteristic that is a measure of the chain volume and a natural parameter for the theory of volume interactions. The distribution function of the gyration radius of a Gaussian chain is much more complex than the end-to-end distance. Its analytical form has not yet been obtained, but the function $G(\tilde{f})$ that we need, which is the Laplace transformation of $W(\alpha)$, has been estimated by Fixman[13] (see also ref 14)

$$G(\tilde{f}) = \left(\frac{\sin (4\tilde{f})^{1/2}}{2(\tilde{f})^{1/2}}\right)^{-3/2} \tag{13}$$

The value $\tilde{f} < 0$ corresponds to a contracted chain, and $\tilde{f} > 0$ corresponds to an expanded chain. (In refs 13 and 14, the Fourier transformation and not the Laplace transformation is reported, but the transition from one to the other is trivial.)

The equations of the elastic force are given by

$$\alpha_{av}^2 = \frac{3}{4}\left(\tilde{f}^{-1} - \frac{\cot 2(\tilde{f})^{1/2}}{(\tilde{f})^{1/2}}\right) \quad \tilde{f} > 0 \tag{14}$$

$$\alpha_{av}^2 = \frac{3}{4}\left(\tilde{f}^{-1} + \frac{\coth (2(-\tilde{f})^{1/2})}{(-\tilde{f})^{1/2}}\right) \quad \tilde{f} < 0 \tag{15}$$

They give $\alpha_{av}^2 = 1$ at $\tilde{f} = 0$.

Although it is impossible to solve these equations in explicit form for $\tilde{f}$, they make it possible to fine the numerical value of $f_{el} = 2\alpha_{av}\tilde{f}$ at any α_{av}; i.e., they give the solution of the problem (see Figure 1).

Carrying out the expansion of f_{el}, we find asymptotic dependences that are different for chain expansion and contraction:
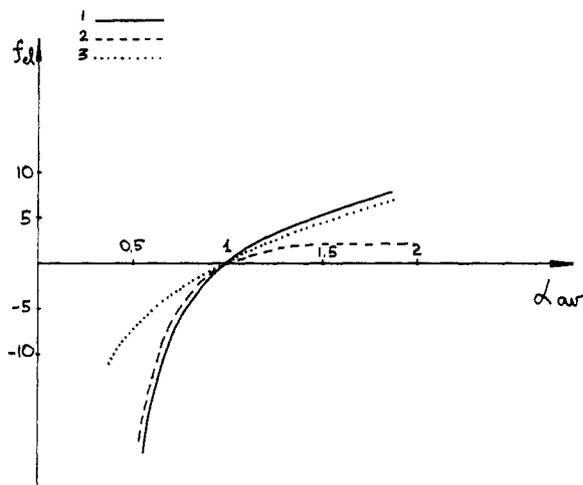
Figure 1. Force of elastic deformation of the Gaussian chain, f_{el}, vs mean-square radius of gyration of the deformed chain $\alpha_{av} = (\langle S^2 \rangle / \langle S_0^2 \rangle)^{1/2}$: curve 1, according to eqs 14 and 15; curve 2, according to eq 19; curve 3, according to eq 18.

$$f_{el} = \frac{\pi^2}{2}\alpha_{av}(1 - O(\alpha_{av}^{-2})) \qquad \alpha_{av} \gg 1 \qquad (16)$$

$$f_{el} = -\frac{9}{2}\alpha_{av}^{-3}(1 - O(\alpha_{av}^{2})) \qquad \alpha_{av} \ll 1 \qquad (17)$$

It is useful to have simple interpolating expressions, which not only would give the correct asymptotic forms but also would obey the condition $f_{el}(1) = 0$. Considering eqs 14–17, we conclude that these interpolating formulas should differ for the ranges $\alpha_{av} > 1$ and $\alpha_{av} < 1$. The simplest expressions of this type are the equations

$$f_{el} = \frac{\pi^2}{2}\alpha_{av}(1 - \alpha_{av}^{-2}) \qquad \alpha_{av} > 1 \qquad (18)$$

$$f_{el} = -\frac{9}{2}\alpha_{av}^{-3}(1 - \alpha_{av}^{2}) \qquad \alpha_{av} < 1 \qquad (19)$$

Figure 1 shows the comparison of the precise (eqs 14 and 15) and approximate (eqs 18 and 19) dependences $f_{el}(\alpha_{av})$.

The comparison of eqs 16 and 18 with eq 10 shows that the parametric dependence of the force on the average size in chain expansion is similar to that in its stretching at the ends. The main terms of the asymptotic forms coincide, with the exception of the coefficient. This fact makes it possible to use h as the parameter of chain expansion (with the exception of the coefficient at f) and leads to Flory's theory[8] for chain expansion.

A fundamentally different situation is observed in the case of chain contraction. It has already been mentioned that it is necessary to use the radius of gyration as the characteristic of chain volume. The decrease in the end-to-end dimension even to zero does not result in a considerable decrease in this volume. This is the reason for the great difference between eq 10 and eqs 17 and 19 at small α_{av} (see also Appendix).

Hence, it is possible to say that the authors of refs 1–4 and 6, who uncritically used the chain end-to-end dimension as the characteristic of the globule size (and the expressions of the type of eq 10 for the elastic force), without proper consideration, have underestimated the entropy of the chain contraction in collapse.

Sanchez[5] considered the radius of gyration as the chain size but used an expression of the type in eq 8 for its distribution function. Actually this expression was pro-

posed by Flory and Fisk[15] (see also ref 14) for the approximate description of the Gaussian chain distribution of the gyration radius yet only in the range of chain expansion (see Appendix). As a result, Sanchez obtained an expression for the elastic force of the type in eq 10 analogous to those in refs 1–4 and 6. This expression can hardly be qualified as correct in the range of chain contraction.

Finally, the conclusions made in ref 7 about the correctness of eq 10 for the elastic force in chain contraction should be considered. We suggest that this conclusion is based on the incorrect application of Edwards' considerations.[16] Edwards has shown that an asymptotic expression of the type in eq 10 can satisfy the first terms of the divergent series in the perturbation theory. These considerations cannot, however, lay claim to the solution of the opposite problem, i.e., the determination of the asymptotic relationship from the first members of this series as is done in ref 7 for the case of globularization.

It is interesting to note that the problem of entropy losses for the restriction of the size of an ideal chain is also raised in the well-known problem of the residence of an ideal chain in a pore. These losses, in contrast to analogous losses in compacting, have always been correctly evaluated by eq 17 by the authors of all papers (see, e.g., refs 17 and 18).

The main conclusion of this section is the fundamental difference between the parametric dependences of the elastic force in increase and decrease of the average chain size as compared to the unperturbed state.

Interaction between Segments. In order to determine $\Delta F_{int}(\alpha_{av})$, the commonly employed mean-field approximation will be used and it will be assumed that the change in the chain size is determined by a change in the interaction between units distant from each other along the chain. Only relatively loose globules will be considered, and virial expansion in the powers of the average segment density in the chain volume will be applied

$$\bar{c} = kN/S^3 = c_0/\alpha_{av}^3 \qquad (20)$$

where $c_0 \sim p^{-3}N^{-1/2}$ refers to the Gaussian chain and k is a numerical coefficient.

We obtain

$$\Delta F_{int} = N(\bar{c}v\tau + \bar{c}^2 w + ...) \qquad (21)$$

where $v\tau$ is the second virial coefficient of segment interaction and w is the third virial coefficient. The series may be ended at the first positive member (in a good solvent, only the first member is sufficient), and

$$\tau = (T - \Theta)/\Theta \qquad (22)$$

It is certainly possible to use a Flory lattice model[8] valid at any density for the calculation of $F_{int}(\alpha_{av})$ (see, e.g., ref 6) instead of a virial expansion. However, in the application to real systems, this does not give any advantage as compared to virial expansion because in actually observed globules the average density is very low, and the calculations made on the basis of this model are more complex.

On the whole, the expressions written in this section are standard and are widely used in practice in all variants of the theory of random coil–globule transition and in analogous problems.

According to eq 2, it is found that the force determined by the interaction between segments located far from each other along the chain is given by

$$f_{int} = \alpha_{av}^{-4}(N^{1/2}B\tau + C\alpha_{av}^{-3}) \qquad (23)$$
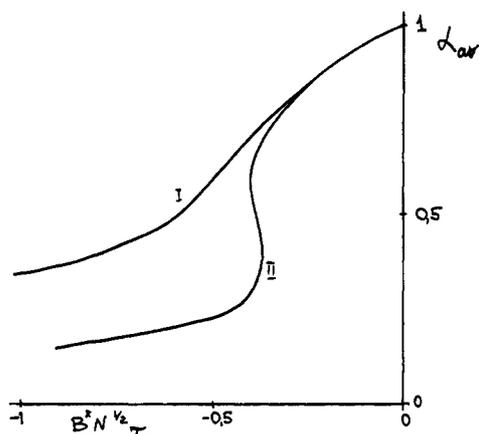
Figure 2. Average chain size, α_{av}, vs $N^{1/2}B^*$ obtained from eq 28 at the C^* values of 0.01 (curve I) and $C^* = 0.001$ (curve II) ($B^* = {}^2/_9B$, $C^* = {}^2/_9C$).

where

$$B = 3c_0N^{1/2}v \sim vp^{-3} \qquad C = 6c_0^2Nw \sim wp^{-6} \quad (24)$$

B and C are parameters that do not depend on N but depend on chain stiffness.

It can be seen that, for a nondeformed chain, i.e., at $\alpha_{av} = 1$, f_{int} becomes equal to zero at $\tau = -C/BN^{1/2}$. It is convenient to renormalize τ

$$\tau' = \tau - C/BN^{1/2} \quad (25)$$

so as to have $f_{int} = 0$ at $\alpha_{av} = 1$ and $\tau' = 0$. (In further discussion, the prime will be omitted.) This renormalization of τ takes into account the dependence of the observed Θ-temperature on the molecular weight of the chains. The force of steric interaction with these symbols is expressed by

$$f_{int} = -\alpha_{av}^{-4}(N^{1/2}B\tau + C(\alpha_{av}^{-3} - 1)) \quad (26)$$

Random Coil–Globule Transition. In order to calculate the equilibrium average chain size as a function of interaction parameters, eq 4 will be used. The rigorous solution may be obtained by substituting directly the force of volume interaction $\bar{f} = f/2\alpha_{av}$ (taking the sign into account) from eq 23 into eqs 14 and 15.

One can also use interpolation, eqs 18 and 19, which leads to the usual Flory type equation for the conditions of chain expansion

$$\alpha_{av}^5 - \alpha_{av}^3 = \frac{2}{\pi^2}BN^{1/2}\tau \qquad \tau > 0 \quad (27)$$

and to the new equation

$$\alpha_{av}^3 - \alpha_{av} = \frac{2}{9}(BN^{1/2}\tau + C(\alpha_{av}^{-3} - 1)) \qquad \tau < 0 \quad (28)$$

for globularization conditions.

Two characteristic types of dependence of α_{av} on τ exist in the region $\alpha_{av} < 1$ both for the precise solution and for eq 28. Over a wide range of C values exceeding a certain value, C_0, this dependence is monotonic, and at $C < C_0$ it has a loop characteristic of first-order phase transitions. Typical dependences of α_{av} on τ are shown in Figure 2.

Note that the erroneous evaluation of the entropy of chain contraction in refs 1–7 leads to the same qualitative dependences but with a higher C_0 value.

In the following paragraphs it will be assumed predominantly that $C > C_0$ and the transition proceeds smoothly. As will be shown below, this situation is characteristic of common flexible chain polymers. The

problem of the transition in stiff chains ($C < C_0$) will be outlined only briefly.

In order to avoid misunderstanding, it should be pointed out that our theory (as well as all other analytical theories of volume interactions in macromolecules) does not make it possible to calculate the change in the total free energy in the random coil–globule transition. It does not take into account the temperature-dependent contributions to the free energy proportional to N and related to the interaction between units located near each other along the chain. This is of no consequence, because the contributions depending on the chain size contain all the singular component of the free energy in the case of an infinite chain, and it is just these contributions that determine the transition order.

Transition in Finite Chains. Crossover between Regimes. Figure 2 shows that the temperature range of changes in α_{av} is inversely proportional to $N^{1/2}B$ and decreases with C. For convenience, the condition of chain equilibrium (eq 4) will be written in the form

$$-\phi_1(\alpha_{av}) = -\phi_2(N^{1/2}B\tau) + \phi_3(\alpha_{av},C) \quad (29)$$

where

$$\phi_1 = -\alpha_{av}^4f_{el}(\alpha_{av}), \quad \phi_2 = -N^{1/2}B\tau, \quad \phi_3 = C(\alpha_{av}^{-3} - 1) \quad (30)$$

$\phi_1 = \phi_2 = \phi_3 = 0$ at $\tau = 0$ and $\alpha_{av} = 1$ and ϕ_1, ϕ_2, and ϕ_3 > 0 at $\tau < 0$ and $\alpha_{av} < 1$.

The function ϕ_1 is related to entropy losses during chain globularization and ϕ_2 and ϕ_3 to the contributions of binary (attraction) and ternary (repulsion) interactions between units.

As $-\tau$ increases and α_{av} decreases, the functions ϕ_2 and ϕ_3 increase infinitely, and ϕ_1 passing through a maximum decreases to zero at $\alpha_{av} \rightarrow 0$. Hence, it may be concluded that two regimes with different ratios of the functions ϕ_1 and ϕ_3 can exist.

In regime I at $\tau > \tau_0$, we have $\phi_1 \simeq \phi_2 \gg \phi_3$; i.e., the pair interactions contracting the chain are mainly opposed by the entropy disadvantage of contraction. This regime is the continuation of the regime of coil expansion at $\tau > 0$, in which the pair repulsion is opposed by the entropy disadvantage of expansion.

In regime II at $\tau < \tau_0$ when ϕ_2 and $\phi_3 \gg \phi_1$, contraction is mainly opposed by the contributions of ternary interactions. The crossover point between regimes I and II is determined by the condition $\phi_1 = \phi_3$.

Now the power dependences of the system parameters will be considered (omitting the numerical coefficients).

Regime II corresponds to the globular structure in which $\phi_1 \ll \phi_3$. By application of the equality $\phi_2 = \phi_3$, the characteristics of this structure are found to be

$$\alpha_{av} = (C/|\tau|BN^{1/2})^{1/3} \quad (31)$$

$$\langle S^2 \rangle = (CN/B|\tau|)^{2/3} \quad (32)$$

From the condition $\phi_1 = \phi_3$ and eqs 31 and 32, the crossover characteristics, the chain size at the crossover point and the position of this point, are found:

$$\alpha(\tau_0) \sim C^{1/4} \sim \left(\frac{w}{p^6}\right)^{1/4} \quad (33)$$

$$\tau_0 \sim \frac{C^{1/4}}{N^{1/2}B} \sim \frac{p^{3/2}w^{1/4}}{N^{1/2}v} \quad (34)$$

It can be seen that the characteristics of the crossover are determined by two parameters: $BN^{1/2} \sim N^{1/2}v/p^3$

and $C \sim w/p^6$. The same parameters determine all the shape of the dependence $\alpha_{av}(\tau)$ and the globule characteristics in eqs 31 and 32.

In all cases the temperature τ appears only in the product $N^{1/2}B\tau \sim z$, where z is the usual parameter in the theory of volume interactions at $\tau > 0$. This determines the dependence of the transition characteristics on N and B $\sim v/p^3$. In particular, as can be seen from eqs 33 and 34, with increasing N the crossover point is displaced toward the Θ-point, and the transition becomes sharper. It should be emphasized that the value of $BN^{1/2}$ affects in a similar manner the chain behavior at both $\tau > 0$ and $\tau < 0$.

The parameter of ternary interactions $C \sim w/p^6$ that is not manifested in the range of $\tau > 0$ plays an important role in the transition. It can be seen from eqs 28–31 that at $C \sim 1$ the value of ϕ_3 is comparable to that of ϕ_1 even at $\alpha \sim 1$. With decreasing C, the limiting degree of contraction realized in regime I at $\phi_1 > \phi_3$ increases; i.e., $\alpha(\tau_0)$ decreases. As a result, the dependence $\alpha_{av}(\tau)$ becomes steeper, and the crossover point approaches the Θ-point ($\tau = 0$).

It has been shown in refs 1–7 and 9–12 that the random coil–globule transition in infinitely long chains ($N \to \infty$) is a second-order phase transition. In the case of finite chains, the choice of the position of the transition point is not unambiguous. In our theory, the position of the crossover point coincides with that of the point of the "phase transition in a finite system" in the LGKh theory. However, it should be noted that the point of maximum steepness of the dependence $\alpha_{av}(\tau)$ does not coincide with τ_0 and is closer to the Θ-point.

Comparison of the Theory with Experimental Data and Computer Simulation Data. In order to compare our theory with experimental data, eq 28 based on interpolation eq 19 will be used. Equation 28 will be rewritten to give

$$\frac{\alpha^3 - \alpha}{\alpha^{-3} - 1} = \frac{B^*N^{1/2}\tau}{\alpha^{-3} - 1} + C^* \qquad (35)$$

where $B^* = (2/9)B$ and $C^* = (2/9)C$.

Figure 3 shows the experimental data[21,22] and the data of computer simulation[24] for the random coil–globule transition in flexible-chain polymers referred to the system of coordinates $x = N^{1/2}\tau/(\alpha^{-3} - 1)$, $y = (\alpha^3 - \alpha)/(\alpha^{-3} - 1)$. It is clear that all the results adequately fit the linear dependence, in complete agreement with eq 35. Note that the linear dependence characterizes the conditions under which the entropy component in eq 35 is not small; i.e., $\tau_0 < \tau$ (regime I). The globular state at $\phi_1 \to 0$ corresponds to the intersection point with the abscissa.

Equation 35 shows that the slope of the straight lines is determined by the parameter B and the intercept on the ordinate is determined by the parameter C. Figure 3 permits certain conclusions to be drawn:

First, for all chains, both model and real, it follows from Figure 3 that the value of C is sufficiently small to ensure the sharpness of the observed random coil–globule transition but exceeds C_0 so that the transition is continuous.

Second, in computer simulation of the transition, the data for chains with different N values are described by a single dependence in Figure 3. On the other hand, for polystyrene (PS) in different solvents, the values of B differ by a factor of 3. These differences are hardly related to different N values of the samples because, according to the data of ref 26, the factor $N^{1/2}$ makes it possible to superpose the curves of the temperature dependence of size for PS with different N but in the same solvent. Unfortunately, the scale of the plot in ref 26 did not allow
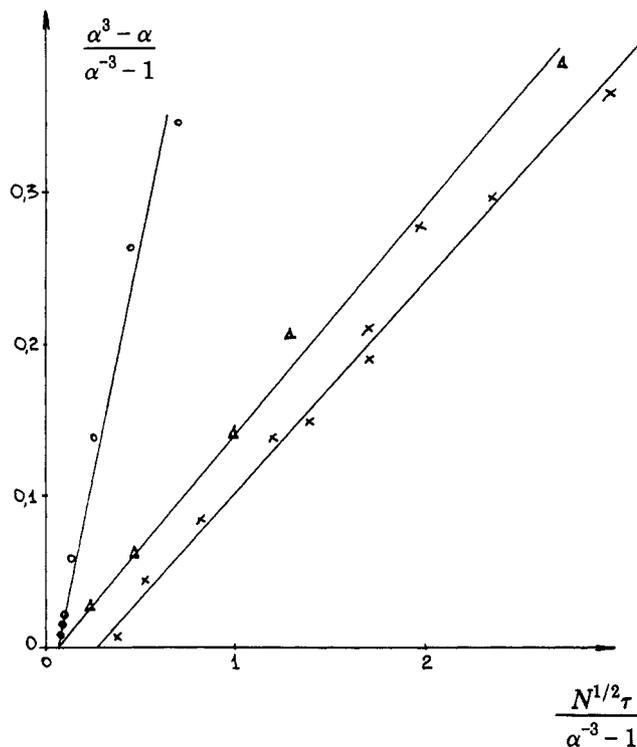
Figure 3. Experimental data for polystyrene (from refs 21 and 22) and results of computer simulation.[23,24] The values of α plotted in a system of coordinates $x = N^{1/2}\tau/(\alpha^{-3} - 1)$, $y = (\alpha^3 - \alpha)/(\alpha^{-3} - 1)$: (1) PS in cyclohexane, (2) PS in dioctyl phthalate, (3) five-choice cubic lattice chain (calculations by the Monte Carlo method). The values of $B^*/C^* \times 10^2$: (1) 0.56/3 (O); (2) 0.15/0.8 ($\triangle$); (3) 0.12/2 ($\times$).

us to refer their data to the coordinates in Figure 3. The observed differences are probably related to the effect of the finite size of solvent molecules on the second virial coefficient of unit interaction in solution (cf. ref 27). The sign of the observed effect agrees with this suggestion (the value of B for PS is smaller in dioctyl phthalate, a solvent with molecules of a larger size).

The value of C^* varies in the same direction to as that of B^* for PS in different solvents so that the B^*/C^* ratio $\simeq 18$ retains an approximately constant value.

Comparison with Other Theories and Dependence of the Character of the Transition on Chain Flexibility (Stiffness). As mentioned in the Introduction, up to now in papers by various authors investigating the random coil–globule transition on the basis of Flory's scheme, the configurational entropy of contraction has been underestimated, which led to an incorrect expression for $\phi_1(\alpha_{av})$.

Consequently, it is necessary to compare our results only with the series of LGKh papers[9–11] based on the more rigorous (and complex) Lifshitz method, which takes into account the density distribution of segments inside the globule. A good agreement is attained on many points. In both cases for flexible-chain polymers ($C > C_0$), the transition is similar to a second-order phase transition, with the possibility of a jumplike transition for very stiff polymers. Further, much attention has been devoted in the LGKh theory to finite chains for which the phase transition point has been determined. This point in the LGKh theory coincides with the crossover point of our theory.

However, there is still a considerable discrepancy between the results of our theory and those of the LGKh theory. On the one hand, the good agreement obtained between experiment for PS and our theory points to the

fact that the transition is continuous. Unlike our theory, the description of experiment for PS according to the LGKh theory[25] is based on the concept that the chain size changes by a jump from coil to globular state. It is interesting to note that nevertheless the results of the numerical calculation of $\alpha_{av}(\tau)$ (with the summation of contributions of the coil and globular states)[25] and our results are completely equivalent.[28] In particular, the results of the numerical calculation of $\alpha_{av}(\tau)$ fit the proposed linear dependence. Moreover, on the basis of the proposed theory, it has been possible[28] to investigate the fluctuations of the chain size in the range of the coil–globule transition. As to the data of computer simulation,[23,24] their processing was carried out for the first time because the degree of globularization attained was insufficient for comparison with the LGKh theory.

Now Figure 2 at $C < C_0$ will be considered. Generally speaking, the appearance of a loop indicates that a first-order transition takes place in a finite system. We suppose that the mean-field approximation used by us cannot be applied to the investigation of these transitions, particularly because neither experimentally nor in computer simulation has a random coil–structureless globule transition with an abrupt jump of sizes and a bimodal function of chain size distribution been observed. All jumplike coil–globule transitions have been accompanied by structurization in the globule, which led to this abrupt transition.[24,29,30] In this case the globule exhibits a liquid-crystalline type of structure. This problem probably requires further investigation.

Conclusion

In this work a new theory of volume interactions of a flexible polymer chain has been proposed. This theory, in the framework of the Flory type mean-field theory, describes the entire range of chain states from an expanded coil to a collapsed globule.

In the range of chain expansion, our theory is virtually equivalent to Flory's theory. In the range of globularization, a correct description was not given before.

In the framework of our theory, the interpolation crossover character of the LGKh theory can easily be revealed, and the suggestion of the authors of ref 25 about the abrupt character of the coil–globule transition in polystyrene is not confirmed.

In accordance with good agreement of eq 35 with experimental results, this dependence may be recommended for the processing of experimental data.

It is interesting that the introduction of the correct expression for the contraction entropy has been manifested to the greatest extent in the theoretical analysis of the compactization of a planar layer of grafted chains.

As has already been indicated above for an individual chain, the general features of the transitions are described by both the correct and the incorrect expression for the entropy. The difference is of a quantitative character. In contrast, for a planar layer of grafted chains, the use of the erroneous expression has led to ref 31 to a paradoxical result that a first-order phase transition can occur in a one-dimensional system. The use of the correct expression for entropy eliminates this paradox (see part 1[32] of this series for more details).

Appendix

As already mentioned, eq 11 is often used for the simple and clear evaluation of $F(\alpha_{av})$ and $f(\alpha_{av})$ dependences. Although the method proposed in this paper is more general and makes it possible to obtain both a rigorous

and an approximate solution, we will also consider the application of this more usual approach to the radius of gyration of the chain. It is known that a closed analytical form for the distribution function of the radius of gyration has not yet been determined. However, its asymptotic forms have been obtained and have been found to be different for $\alpha \gg 1$ and $\alpha \ll 1$[13,14]

$$W(\alpha^2)\, d\alpha^2 \simeq K_1 \exp\left(-\frac{\pi^2}{4}\alpha^2\right) d\alpha^2 \quad \alpha \to \infty \quad \text{(A1)}$$

$$W(\alpha^2)\, d\alpha^2 \simeq K_2 \exp\left(-\frac{9}{4}\alpha^{-2}\right) d\alpha^2 \quad \alpha \to 0 \quad \text{(A2)}$$

It follows at once from eqs A1, A2, and 11 that the functional dependences of the asymptotic relations for the free energy (and elastic force) are fundamentally different in the ranges of chain expansion and contraction. Moreover, it is easy to show that, for f_{el}, eqs 16 and 17 are obtained.

Neither of the asymptotic forms in eqs A1 and A2 describes the entire range of changes in α and, in particular, does not obey the evident requirement $\langle \alpha^2 \rangle = 1$. Hence, Flory and Fisk[15] considering the changes in the radius of gyration during chain expansion have plotted an empirical function $W(\alpha)$ requiring that this function should belong to the same class as the asymptotic form at $\alpha \gg 1$ but in contrast to it should give $\langle \alpha^2 \rangle = 1$. This function is evidently described by eq 8 with $x = \gamma - 1$. In order to obtain the values of the first even moments of the radius of gyration close to the precise values, in ref 15 the value of $\gamma = {}^7/_2$ was selected (instead of the coefficient $\pi^2/4$ in the precise asymptotic form).

The Flory–Fisk function provides an adequate functional dependence in the range of $\alpha > 1$ but does not give an approach to reality at $\alpha < 1$ because of the different structure of the asymptotic form in eq A2. Hence, its application to the problem of coil expansion is correct, but it is inapplicable to the globularization problem.

Note that the plotting of the empirical Flory–Fisk function in the form of eq 8 is equivalent to that of interpolation in eq 18 within the replacement of the coefficient $\pi^2/2$ by 7.

It should also be noted that interpolation eqs 18 and 19 in the range of low $\delta = 1 - \alpha^2$ give slightly different and not quite precise values of $f_{el} = (\pi^2/2)\delta$ and $f_{el} = {}^9/_2\delta$ at $\tau > 0$ and $\tau < 0$, respectively, whereas the precise value obtained according to eqs 14 and 15 is $f_{el} = {}^{15}/_4\delta$ and is independent of the sign at τ. The expression obtained according to Flory and Fisk gives $f_{el} = 7\delta$.

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