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Quantitative Theory of the Globule-to-Coil Transition. 2. Density–Density Correlation in a Globule and the Hydrodynamic Radius of a Macromolecule

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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 paper (the second in this series) the macromolecule properties determined by the pair density–density correlation function are considered. This function for a polymer globule is calculated in the framework of mean-field Lifshitz's theory. Using the correlation function, the hydrodynamic radius of a macromolecule is found in the Kirkwood approximation. The value of fluctuations of the macromolecule radius of gyration is calculated in the region of the globule-to-coil transition, which is connected with a sharp change in the fluctuational regime. The existence of a maximum of fluctuations in the transition region is shown.

1. Introduction

In the previous paper[1] we discussed the intraglobular density distribution and corresponding experimentally observable macromolecule characteristics, such as, first of all, its radius of gyration. In the meantime, a lot of important macromolecule properties depend also on binary density–density correlations. These are, in particular, the fluctuation magnitude of the radius of gyration and the hydrodynamic radius, which is often measured in inelastic light scattering experiments.

An additional interest in the chain fluctuational properties in the globular state is to account for the main difference between the globular and coil phases—this difference is just connected with the fluctuational regime (see refs 2 and 3 for more details).

2. Intraglobular Density–Density Correlation Function

As is well-known and as was mentioned in our previous paper,[1] the central core of a large enough globule looks like a solution of independent chains with the same density n_0. Therefore, the correlation function of density fluctuations in the large globule should be of the standard Ornstein–Zernike type:

$$\Phi(\mathbf{X}_1,\mathbf{X}_2) \sim \text{const} + |\mathbf{X}_1 - \mathbf{X}_2|^{-1} \exp\left[-\frac{|\mathbf{X}_1 - \mathbf{X}_2|}{\zeta}\right] \quad (1)$$

Here the correlation radius ζ is independent of the globule size and coincides with the correlation length of the polymer solution with n_0 concentration; i.e., $\zeta^2 \cong (a^2/6)(C/B^2)$ (see refs 4 and 5 and Appendices B and C). As usual, a stands for the link's size, and B and C are the second and third quasimonomer virial coefficients.

The expression in eq 1 is valid for a large globule core only but not for a globule surface layer. Therefore, its applicability breaks down in the globule-to-coil transition region. For the globule at an arbitrary temperature, including the globule-to-coil transition point, the intraglobular correlator can be obtained as the static response function using the following general statistical theorem:[2]

$$\Phi(\mathbf{X}_1,\mathbf{X}_2) \equiv \langle \delta n(\mathbf{X}_1)\, \delta n(\mathbf{X}_2) \rangle = -T\frac{\delta^2 F}{\delta\varphi(\mathbf{X}_1)\, \delta\varphi(\mathbf{X}_2)} = -T\frac{\delta n(\mathbf{X}_1)}{\delta\varphi(\mathbf{X}_2)} = -T\frac{\delta n(\mathbf{X}_2)}{\delta\varphi(\mathbf{X}_1)} \quad (2)$$

Here $\delta n(\mathbf{X}) \equiv n_\Gamma(\mathbf{X}) - n(\mathbf{X})$, $n_\Gamma(\mathbf{X})$ is an instant value of the polymer link density in the **X** point, the smoothed link density $n(\mathbf{X}) \equiv \langle n_\Gamma(\mathbf{X})\rangle = \delta F/\delta\varphi$, and the broken brackets mean an average over the thermodynamical ensemble of chains. $\varphi(\mathbf{X})$ stands for the effective potential, which is a conjugate to the density $n(\mathbf{X})$. Since the free energy functional $F\{\varphi\}$ of the globular chain under the action of an external field $\varphi(\mathbf{X})$ is just the key construction of Lifshitz-type globule theory,[2] one may derive the equation for the correlation function using this Lifshitz-type approach. The derivation is performed in Appendix A; however, the resulting eq A9 is rather tedious. Its analysis in the volume approximation (Appendix B) yields eq 1. Some simplifications can be reached using dimensionless variables (Appendix C). We discuss separately the results which can be obtained for different values of physical interest: the fluctuation magnitude of the macromolecule radius of gyration (section 3) and the hydrodynamic radius (section 4).

3. Magnitude of the Fluctuations of the Macromolecule Radius of Gyration

3.1. Lifshitz-Type Approach for Globule Fluctuations. We characterize fluctuations of the globule gyration radius with the value $[\langle S_\Gamma{}^4\rangle - \langle S_\Gamma{}^2\rangle^2]/\langle S_\Gamma{}^2\rangle^2$, where the instantaneous radius of gyration equals $S_\Gamma = [(1/N)\int n_\Gamma(\mathbf{X})\, x^2\, d\mathbf{X}]^{1/2}$, where **X** is the radius-vector from the globule's center and $N = \int n_\Gamma(\mathbf{X})\, d\mathbf{X}$ is the total number of monomers per chain. Since

$$\langle S_\Gamma{}^2\rangle^2 = \left\langle \frac{1}{N}\int n_\Gamma(\mathbf{X})\, x^2\, d\mathbf{X} \right\rangle^2 = N^{-2}\int \langle n_\Gamma(\mathbf{X}_1)\rangle x_1{}^2 \langle n_\Gamma(\mathbf{X}_2)\rangle x_2{}^2\, d\mathbf{X}_1\, d\mathbf{X}_2 \quad (3a)$$

and

$$\langle S_\Gamma{}^4\rangle \equiv \langle (S_\Gamma{}^2)^2\rangle = \left\langle \left[\frac{1}{N}\int n_\Gamma(\mathbf{X})\, x^2\, d\mathbf{X}\right]^2\right\rangle = N^{-2}\int \langle n_\Gamma(\mathbf{X}_1)\, n_\Gamma(\mathbf{X}_2)\rangle x_1{}^2 x_2{}^2\, d\mathbf{X}_1\, d\mathbf{X}_2 \quad (3b)$$

the difference between these two values is expressed through the pair correlation function $\Phi(\mathbf{X}_1,\mathbf{X}_2)$ (eq 2):

$$\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2} = \frac{\int\int \Phi(\mathbf{X}_1,\mathbf{X}_2)\, x_1{}^2 x_2{}^2\, d\mathbf{X}_1\, d\mathbf{X}_2}{[\int n(\mathbf{X})\, x^2\, d\mathbf{X}]^2} \quad (4)$$

where the smoothed density spatial distribution $n(\mathbf{X}) \equiv \langle n_\Gamma(\mathbf{X})\rangle$ has been calculated in the previous paper.[1]

Analysis of the expression in eq 4 is essentially simpler than that of the correlation function Φ itself. Nevertheless, this analysis is also rather complex; we put it into Appendix D. Here we formulate the following main results:

(i) The dimensionless version of eq 4 can be written in the form

$$\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2} = \frac{\sqrt{C}}{a^3}s(t) \quad (5)$$

where the ratio $\sqrt{C}/a^3$ is a characteristic of the polymer chain rigidity.[1] $s(t)$ is the complex integral expression (see Appendix D), but it depends on the single value of the reduced temperature only:

$$t = \frac{N^{1/2}B}{C^{1/4}(a^2/6)^{3/4}} \sim \frac{T-\Theta}{\Theta}N^{1/2} \quad (6)$$

(T stands for temperature). The expression in eq 5 proves, in particular, the fact that the globule fluctuation magnitude decreases with an increase in the polymer rigidity (i.e., with a decrease of the $\sqrt{C}/a^3$ parameter). On the qualitative level this fact was formulated in refs 2 and 3.

(ii) The poor solvent asymptotic behavior when $-t \gg 1$ is $s(t) \simeq 5.6t^{-2}$.

(iii) We have calculated numerically $s(t)$ function behavior in the range of smaller $-t$ near the transition point; the result is shown in Figure 1.

As was expected, the $s(t)$ function grows sharply, when the reduced temperature approaches the transition point, and in this very point it reaches the value $s(t_{tr}) \simeq 3.5$, so that

$$\left.\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2}\right|_{t=t_{tr}} \simeq 3.5\sqrt{C}/a^3 \quad (7)$$

At the same time in the ideal Gaussian coil, according to ref 7

$$\left(\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2}\right)_{\rm id} = 4/15 \simeq 0.27 \quad (8)$$

Therefore, the fluctuation magnitude in the transition point is greater than that in the Gaussian state for the chain with $\sqrt{C}/a^3 > 0.08$. This is the case for many flexible polymers. For example, according to our estimations[8] and to those expressed in refs 9 and 10, for polystyrene $\sqrt{C}/a^3$ parameter equals approximately 0.1 ÷ 0.2.

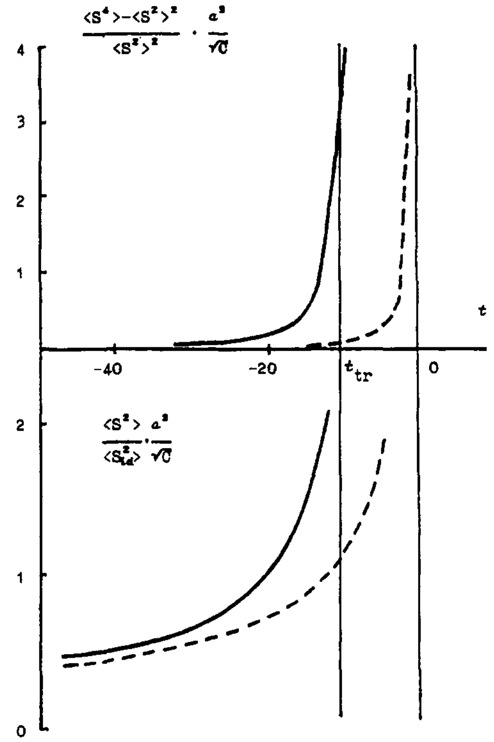

Figure 1. Fluctuation values of the radius of gyration of a polymer globule scaled by $(\sqrt{C}/a^3)^{-1}$ vs the t parameter of reduced temperature ($t \sim N^{1/2}(T-\theta/\theta)$ near the transition point to the coil state. The corresponding value of the expansion factor is shown at the bottom of this figure. The dashed lines are the results of volume approximation.

3.2. Chain Fluctuations in the Transition Region. Our approach based on Lifshitz's globule theory cannot be applied to the coil state and cannot describe by itself, without modifications, the whole transition area. In ref 1 we have shown that for rigid chains a two-level system approximation is valid for calculation of the mean-square gyration radius $\langle S^2\rangle$. Using this approximation, we have found the simple interpolation expression for $\langle S^2\rangle$. The same approximation leads to an analogous expression for $\langle S^4\rangle$, and as a result we have the following formula for fluctuations:

$$\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2} = \frac{e^{-F/T}}{(e^{-F/T}\beta^2+1)^2}\left[\frac{\langle S_{\rm glob}{}^4\rangle - \langle S_{\rm glob}{}^2\rangle^2}{\langle S_{\rm glob}{}^2\rangle^2}(e^{-F/T} + 1)\beta^4 + \frac{\langle S_{\rm coil}{}^4\rangle - \langle S_{\rm coil}{}^2\rangle^2}{\langle S_{\rm coil}{}^2\rangle^2}(e^{F/T}+1) + (\beta^2-1)^2\right] \quad (9)$$

where $\beta^2 \equiv \langle S_{\rm glob}{}^2\rangle/\langle S_{\rm coil}{}^2\rangle$; $\langle S_{\rm glob}{}^2\rangle$ and $\langle S_{\rm coil}{}^2\rangle$ are macromolecular mean-square radii of gyration in globular and coil states, respectively. The difference between free energies of the globule and the coil F was calculated in ref 1. The last term in the righthand side of this expression corresponds to macromolecular fluctuations between different states (levels), globular and coil, and it is this very term which leads to the appearance of a maximum of fluctuations in the transition region.

The interpolation expression in eq 9 is valid for rigid chains only, because just for that case we expect the bimodal distribution in the transition region,[1] and this very form of the distribution is the basis of the two-level approximation.

3.3. Flory-Type Interpolation Theory for Chain Fluctuations. To analyze the fluctuations of the macromolecular radius of gyration in the region of the globule–coil transition, we can also use the Flory-type interpolation approach, developed in ref 10 and already discussed in the previous paper.[1] We reiterate that this approach is based on treating the free energy of a polymer–solvent system as a whole interpolation expression of one variable only—the expansion factor α of the gyration radius S (eq

23 in ref 1):

$$\frac{F(\alpha)}{T\gamma} = \alpha^{-2} + \ln(\alpha^2) + \frac{2ut_{\mathrm{eff}}}{3\alpha^3} + \frac{w}{3\alpha^6} \quad (\gamma \simeq 9/4) \quad (10)$$

where in accordance with the discussion in ref 1 the parameters are chosen as follows:

$$u \cong 0.2836(\sqrt{C}/a^3)^{1/2}, \quad w \cong 3.5454(\sqrt{C}/a^3)^2 \quad (11)$$

The mean values of the expansion factor can be calculated from the definition

$$\langle \alpha^k \rangle^{1/k} = \left[\frac{\int_0^\infty \alpha^k e^{-F/T}\,\mathrm{d}\alpha}{\int_0^\infty e^{-F/T}\,\mathrm{d}\alpha} \right]^{1/k}$$

Using the saddle-point approximation, i.e., the Taylor expansion of the $F(\alpha)$ function near its minimum point, one can obtain the following simple result:

$$\frac{\langle S^4 \rangle - \langle S^2 \rangle^2}{\langle S^2 \rangle^2} = \frac{\langle (\alpha^2 - \langle \alpha^2 \rangle)^2 \rangle}{\langle \alpha^2 \rangle^2} \simeq \left(\frac{\alpha^2}{4T} \frac{\mathrm{d}^2 F}{\mathrm{d}\alpha^2} \right)^{-1} \Bigg|_{\alpha=\alpha_0} = \frac{8}{9}(3 - \alpha_0^{-2} + 3w\alpha_0^{-6})^{-1} \quad (12)$$

Here the "saddle-point" value α_0 is defined from the condition of the free energy minimum

$$\alpha_0^{\;3} - \alpha_0 = ut_{\mathrm{eff}} + w\alpha_0^{\;-3}$$

and it is, of course, just the equilibrium value of α (eq 24 in ref 1).

The result of eq 12 is valid, at least qualitatively, for a flexible enough chain only, namely, for the case where $w > {}^4/_{729}$ or $\sqrt{C}/a^3 > 0.04$. The righthand side of eq 12 has a nonphysical singularity in the opposite case, when the globule-to-coil transition looks like the first-order phase transition and when the Flory-type approach predicts the discontinuous dependence of the α_0 value on reduced temperature t_{eff}.

For flexible macromolecules with $\sqrt{C}/a^3 < 0.04$ the expression in eq 12 predicts the maximum of fluctuations at the reduced temperature point $t_{\mathrm{max\ fluct}}$ which can be determined from the equation

$$\alpha_0(t_{\mathrm{max\ fluct}}) = (9w)^{1/4} \simeq 2.377(\sqrt{C}/a^3)^{1/2}$$

The result is illustrated in Figure 2, where the dependence of eq 12 and the corresponding dependence of α_0 on t_{eff} are shown for $\sqrt{C}/a^3 = 0.1$.

3.4. Discussion. Thus, we have arrived at two interpolation formulas for the description of the fluctuation magnitude of the radius of gyration in the whole region of the globule–coil transition: the expression in eq 9 is correct for rigid polymer chains (approximately $\sqrt{C}/a^3 \leqslant 0.04$), and the expression in eq 12 is valid for flexible chains ($\sqrt{C}/a^3 \geqslant 0.04$).

The difference between forms of these two equations reflects the difference in the physical picture of the transition:[1] the bimodal distribution function and the corresponding idea of a two-level system are inherent for rigid chains; the more smooth type of transition with the monomodal distribution is the case for flexible chains. The great fluctuations in the rigid chains correspond physically to the spontaneous jumps between the globular and coil states; it is just the typical mechanism of the so-called heterophase fluctuations. On the other hand, great fluctuations in a flexible polymer are caused by a growth in the width of the single peak of the monomodal distribution; this mechanism is analogous to the one for the fluctuations near the critical point or the second-order phase transition. In spite of that essential difference in the physical picture, the qualitative behavior of the fluctuation magnitude is practically the same in both these cases.

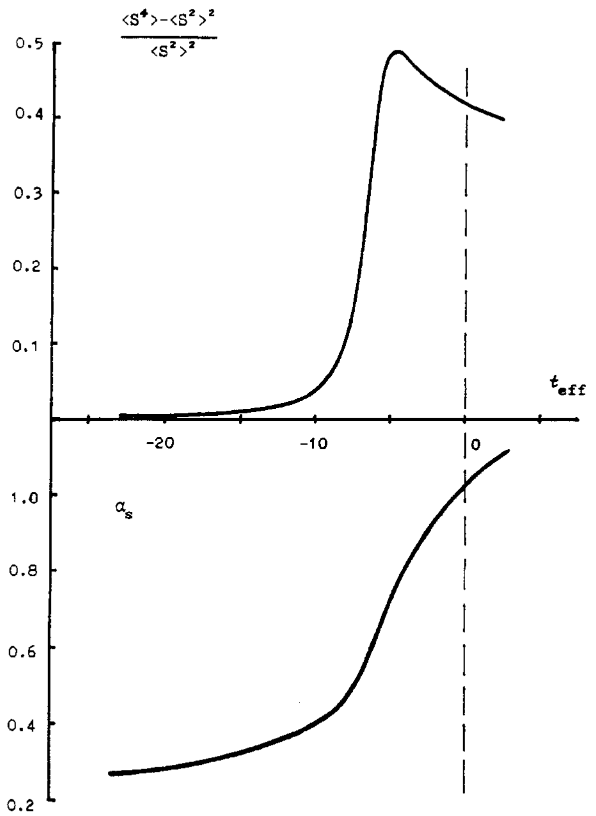

Figure 2. Dependences of fluctuation values of the macromolecule radius of gyration and its corresponding expansion factor vs the t_{eff} parameter of the effective reduced temperature in the globule-to-coil transition region. These results were calculated using the Flory-type theory when $\sqrt{C}/a^3 = 0.1$.

As is seen in Figures 1 and 2, both approaches yield quite close results for the fluctuation magnitude in the globular region and predict the presence of a maximum of fluctuations in the transition region. Of course, the existence of this maximum could be expected: whatever the true mechanism (order) of this transition might be, the function of the system distribution in phase space expands near it; i.e., fluctuations get access to states of rather different sizes (close to the coil and globular states, respectively), and the magnitude of the fluctuations reaches its maximum. Such a maximum was observed in a real experiment[11] and in computer simulation.[12]

4. Hydrodynamic Radius of a Macromolecule

In experiments with isolated macromolecules suspended in dilute solution, not only the radius of gyration but also another parameter of expansion—the so-called hydrodynamic radius R_{H}—are usually measured. R_{H} can be measured in viscosimetric and in inelastic scattering experiments because the very size of the macromolecule characterizes its friction when it moves through the medium of a liquid solvent. If the diffusion coefficient of the macromolecule equals D and, correspondingly, its friction coefficient is $f = T/D$, then its hydrodynamic radius can be defined via the relation

$$D = (T/6\pi\eta)\langle R_{\mathrm{H}}^{\;-1} \rangle \quad (13)$$

where η stands for the solvent viscosity. Due to the well-known phenomenon of hydrodynamic interactions, the friction of the chain monomers is nonadditive; i.e., the value of $f = T/D \sim R_H$ is not proportional to the chain length N. For the polymer coil the hydrodynamic radius R_H scales as the gyration radius; i.e., it is proportional to $N^{1/2}$ for the Gaussian coil and to N^{ν} for the swollen coil.[13] These facts are usually described by the Kirkwood–Riseman theory,[13] which leads for R_H to a relation of the type

$$\langle R_H^{-1}\rangle \simeq N^{-2}\sum_{m\neq n}\langle|\mathbf{X}_n-\mathbf{X}_m|^{-1}\rangle \simeq N^{-2}\int\int\frac{\langle n_\Gamma(\mathbf{X}_1)\,n_\Gamma(\mathbf{X}_2)\rangle}{|\mathbf{X}_1-\mathbf{X}_2|}\,\mathrm{d}\mathbf{X}_1\,\mathrm{d}\mathbf{X}_2 \quad (14)$$

This expression is often considered to be the exact definition of the hydrodynamic radius. However, when the physical definition (eq 13) is used, then the Kirkwood–Riseman formula in eq 14 becomes rough and its accuracy is on the order of a slowly changing constant numerical coefficient.[14]

The Kirkwood–Riseman theory is based on the supposition that all monomers are equally bathed by the solvent. Naturally, it is not the case for a non-free-draining chain, especially for a dense globular chain. For example, if the density $n_\Gamma(\mathbf{X})$ is uniformly distributed in a sphere of radius R and it does not fluctuate, then the Kirkwood–Riseman expression gives $R_H = (5/6)R$ instead of the correct result for a solid sphere, $R_H = R$. This coefficient $^5/_6 \neq 1$ characterizes the accuracy of the Kirkwood–Riseman theory. Nevertheless, we use this theory and the expression in eq 14—because we simply do not know what would be better. At the same time we are ready beforehand to get an accuracy on the order of $1 - {}^5/_6 \simeq {}^1/_6$ or 17%.

4.1. Hydrodynamic Radius of a Slightly Compressed Coil. For the Gaussian coil the Kirkwood–Riseman expression gives, as is well-known (see, for example, ref 15)

$$\langle R_H^{-1}\rangle_{\mathrm{id}} = N^{-2}\sum_{i=0}^{N}\sum_{j=0}^{N}\left(\frac{2}{3}\pi a^2|i-j|\right)^{-3/2}\times \int\rho^{-1}\exp\left[-\frac{3\rho^2}{2|i-j|a^2}\right]\mathrm{d}^3\rho = \frac{8}{3}\left(\frac{6}{\pi N a^2}\right)^{1/2} \quad (\rho = |\mathbf{X}_i-\mathbf{X}_j|) \quad (15)$$

For a slightly perturbed coil the value of the hydrodynamic radius was originally calculated in ref 16. Here for our purposes it is of importance to formulate the results using renormalized virial coefficients of quasimonomers (just as has been done for the radius of gyration in the previous paper of this series[1]). To do so, it is convenient to rewrite eq 14 in the form

$$\langle R_H^{-1}\rangle = N^{-2}\sum^{m,n}\langle R_{mn}^{-1}\rangle = N^{-2}\sum^{m,n} = \frac{\int R^{-1}Z\left(\begin{matrix}m\\0\end{matrix}\middle|\begin{matrix}n\\R\end{matrix}\right)\mathrm{d}^3R}{\int Z\left(\begin{matrix}m\\0\end{matrix}\middle|\begin{matrix}n\\R\end{matrix}\right)\mathrm{d}^3R}$$

where R_{mn} is a distance between the chain links of a polymer with numbers m and n.

$$Z\left(\begin{matrix}m\\0\end{matrix}\middle|\begin{matrix}n\\R\end{matrix}\right)$$

is a partition function of the chain which has a link with number m in the zero point and a link with number n in the R point. Omitting some simple but cumbersome computations (for a detailed discussion on the method of this kind of calculations, see Appendix B of the previous paper in this series[1]), we give the final result for the expansion factor, obtained in the first order of the perturbation theory:

$$\alpha_{H_{\mathrm{coil}}}^{-1} \equiv \frac{\langle R_H^{-1}\rangle}{\langle R_H^{-1}\rangle_{\mathrm{id}}} = 1 + \left(\frac{3}{2\pi a^2}\right)^{3/2}2BN^{1/2}\times\left[\frac{3\pi}{2}\left(\frac{9}{8}-\ln\frac{3}{2}\right)-4\right] \simeq 1 - 0.1049t\left(\frac{\sqrt{C}}{a^3}\right)^{1/2} \quad (16)$$

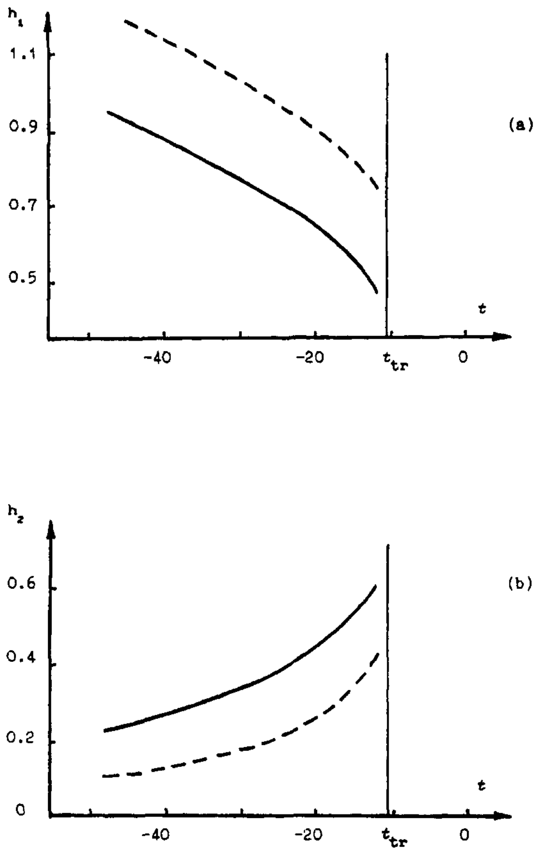

Figure 3. Functions $h_1(t)$ and $h_2(t)$ determining the expansion factor of the polymer globule hydrodynamic radius (eq 16). The h_1 function was calculated using the smoothed density distribution, while the h_2 function was calculated using the density pair correlation function. When $\sqrt{C}/a^3 \ll 1$, the h_1 function makes the main contribution to the expansion factor. The dashed lines correspond to the volume approximation.

4.2. Hydrodynamic Radius of a Globule. For globule theory it is convenient to divide the expression in eq 14 into two terms, because

$$\langle n_\Gamma(\mathbf{X}_1)\,n_\Gamma(\mathbf{X}_2)\rangle = n(\mathbf{X}_1)\,n(\mathbf{X}_2) + \Phi(\mathbf{X}_1,\mathbf{X}_2) \quad (17)$$

in accordance with the correlator Φ definition (eq 2). The first term is defined by the smoothed density distribution $n(\mathbf{X})$; it has been calculated in the previous paper of this series[1]; the second term depends on the correlation function $\Phi(\mathbf{X}_1,\mathbf{X}_2)$. The results of the present work lead to the following expression for the expansion factor of the macromolecule hydrodynamic radius (see Appendix E):

$$\alpha_{H_{\mathrm{glob}}}^{-1} \equiv \frac{\langle R_H^{-1}\rangle}{\langle R_H^{-1}\rangle_{\mathrm{id}}} = \left(\frac{\sqrt{C}}{a^3}\right)^{-1/2}\left[h_1(t) + \frac{\sqrt{C}}{a^3}h_2(t)\right] \quad (18)$$

Here both $h_1(t)$ and $h_2(t)$ are functions of one dimensionless parameter t only, introduced by eq 6. These dependences are reported in Figure 3.

4.3. Hydrodynamic Radius of a Macromolecule in the Globule-to-Coil Transition Region. Omitting the

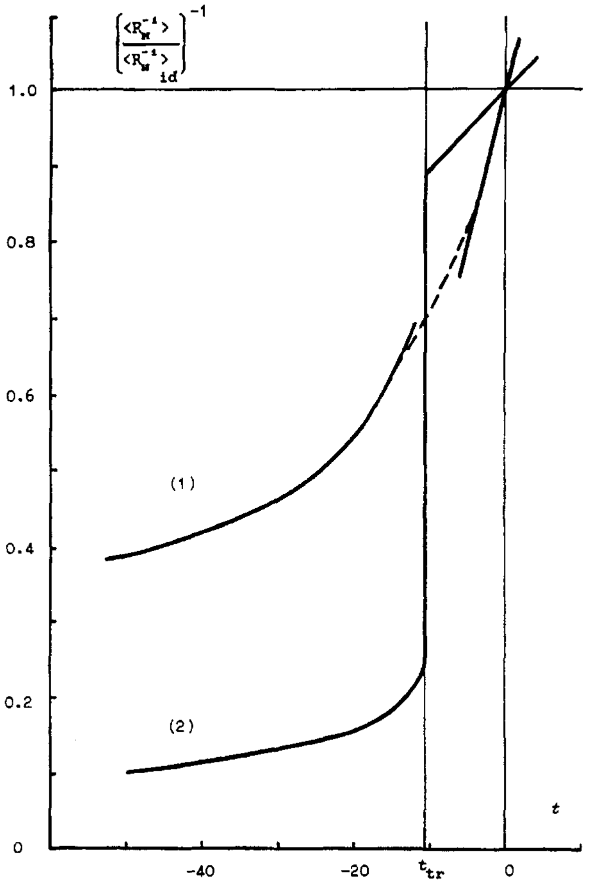

Figure 4. Expansion factor of the macromolecule hydrodynamic radius vs the t parameter of the reduced temperature for a flexible chain, when $\sqrt{C}/a^3 = 0.15$ (curve 1), and for a rigid chain, when $\sqrt{C}/a^3 = 0.01$ (curve 2).

reasoning from the previous paper in this series[1] we reiterate that for rigid macromolecules the polymer–solvent system in the region of the globule–coil transition can be treated as a two-level system, where the ratio of the populations on the coil and globular levels is $\exp(F/T)$. The difference in the free energies of the globule and the coil F, which is a function of t and α_H is

$$\alpha_H^{-1} = [\exp(F/T) + 1]^{-1}\alpha_{H_{glob}}^{-1} + [\exp(-F/T) + 1]^{-1}\alpha_{H_{coil}}^{-1} \quad (19)$$

For more flexible macromolecules this kind of interpolation is incorrect and the notion of transition order is not generally adequate. But in reality in this case eqs 16 and 18 present a sufficiently complete (in the limits of accessible accuracy) idea of $\alpha_H(t)$ dependence in the whole transition region, and there is no need to introduce any special interpolation expressions for this dependence.

In Figure 4 calculated plots of α_H vs t for various values of $\sqrt{C}/a^3$, i.e., for both rigid and flexible polymer chains, are reported. To make it more obvious, the results, corresponding to the globular and coil states of one flexible macromolecule, are connected by a broken line.

Appendix A: Equation for the Pair Density–Density Correlation Function of a Globule

In this appendix the equation for the correlation function is derived in the standard way[17] in the framework of a self-consistent-field approximation. In this approximation the density distribution inside a polymer globule can be described by Liftshitz's equations.[2] For our purposes it is convenient to suppose the existence of external field $\varphi(\mathbf{X})$, which acts on the monomers of a polymer chain together with self-consistent field $\mu^*(n)$. If so, then Lifshitz's coupled equations can be written in the following form:

$$\hat{g}\psi = \psi \exp\left(\frac{\mu^* + \varphi - \lambda}{T}\right) \quad (A1)$$

$$n = N\frac{\psi^2 \exp(\mu^* + \varphi)}{\int \psi^2 \exp\left(\frac{\mu^* + \varphi}{T}\right) \mathrm{d}\mathbf{X}} \quad (A2)$$

Here the normalizing condition $\int n(\mathbf{X})\, \mathrm{d}\mathbf{X} = N$ for the smoothed density $n(\mathbf{X})$ is realized automatically, function $\psi(\mathbf{X})$ can be considered as an eigenfunction, the value of the λ parameter is determined by the solution of these equations, and T stands for temperature. $\hat{g}$ is the integral operator, characterizing the "linear memory" of the chain:

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

$g(\mathbf{X}-\mathbf{X}')$ stands for the probability of two neighboring link positions at the spatial distance $|\mathbf{X} - \mathbf{X}'|$ from each other.

In accordance with eq 2, a change in the link density distribution is the response to a change in the external field:

$$\delta n(\mathbf{X}) = -\frac{1}{T}\int \Phi(\mathbf{X},\mathbf{X}')\, \delta\varphi(\mathbf{X}')\, \mathrm{d}\mathbf{X}' \quad (A3)$$

The form of expression in eq A3 clarifies the following standard calculation procedure for the correlation function on the basis of eqs A1 and A2. A certain small addition $\delta\varphi(\mathbf{X})$ is made to an external field $\varphi(\mathbf{X})$, and then perturbation of the whole system caused by the addition is considered. Assuming that the $\delta\varphi(\mathbf{X})$ value is small in each point of the system, we make all calculations in the first order with respect to the perturbation. In this case eq A1 transforms into

$$\hat{L}(\delta\psi) = \psi \exp\left(\frac{\mu^* + \varphi - \lambda}{T}\right)\frac{\delta\mu^* + \delta\varphi - \delta\lambda}{T} \quad (A4)$$

where linear operator L equals

$$\hat{L} \equiv \hat{g} - \exp\left(\frac{\mu^* + \varphi - \lambda}{T}\right)$$

so that $\hat{L}\psi = 0$ is in accordance with eq A1.

The choice of the $\delta\lambda$ value must ensure the existence of a solution of eq A4. Since $\hat{L}$ stands for the Hermitian operator and the corresponding equation $\hat{L}\psi = 0$ has the nontrivial solution $\psi(\mathbf{X})$ (just this solution describes the globule density distribution and has been presented in the previous paper in this series[1]), then in accordance with Fredholm's theorem, eq A4 is solvable if and only if the right member of this equation is orthogonal to $\psi(\mathbf{X})$. This condition with account of the formula in eq A2 means that

$$\delta\lambda = \frac{1}{N}\int (\delta\mu^* + \delta\varphi) n\, \mathrm{d}\mathbf{X} \quad (A5)$$

We introduce the functions $\Psi(\mathbf{X}_1,\mathbf{X}_2)$ and $\Omega(\mathbf{X})$ by analogy with eq A3:

$$\delta\psi(\mathbf{X}) = \int \Psi(\mathbf{X},\mathbf{X}')\, \delta\varphi(\mathbf{X}')\, \mathrm{d}\mathbf{X}'$$

$$\delta\lambda = \int \Omega(\mathbf{X}')\, \delta\varphi(\mathbf{X}')\, \mathrm{d}\mathbf{X}'$$

Since eqs A4 and A5 are valid for an arbitrary small perturbation $\delta\varphi(\mathbf{X})$, then they can be transformed to

$$\hat{L}_1\Psi(\mathbf{X}_1,\mathbf{X}_2) = \frac{\psi_1}{T}\exp\left(\frac{\mu_1{}^* + \varphi_1 - \lambda}{T}\right)\left[\delta(\mathbf{X}_1-\mathbf{X}_2) - \frac{1}{T}\frac{\partial\mu_1{}^*}{\partial n_1}\Phi(\mathbf{X}_1,\mathbf{X}_2) - \Omega_2\right] \quad \text{(A6)}$$

$$\Omega(\mathbf{X}_2) = \frac{n_2}{N} - \frac{1}{NT}\int n\frac{\partial\mu^*}{\partial n}\Phi(\mathbf{X}_1,\mathbf{X}_2)\,\mathrm{d}\mathbf{X} \quad \text{(A7)}$$

Here and from now on the subscripts 1 and 2 mean that the function under analysis should be considered in points $\mathbf{X}_1$ and $\mathbf{X}_2$, respectively, while $\hat{L}_1$ operates on the function of the first variable, $\mathbf{X}_1$.

Similar transformations will make eq A2 look like

$$\Phi(\mathbf{X}_1,\mathbf{X}_2) = \hat{K}_1\left\{n_1\left[\frac{1}{T}\frac{\partial\mu_1{}^*}{\partial n_1}\Phi(\mathbf{X}_1,\mathbf{X}_2) - \delta(\mathbf{X}_1-\mathbf{X}_2) - \frac{2T}{\psi_1}\Psi(\mathbf{X}_1,\mathbf{X}_2)\right]\right\} \quad \text{(A8)}$$

where operator $\hat{K}$ for the arbitrary function $\xi(\mathbf{X}_1,\mathbf{X}_2)$ is

$$\hat{K}_1\xi(\mathbf{X}_1,\mathbf{X}_2) \equiv \xi(\mathbf{X}_1,\mathbf{X}_2) - \frac{n_1}{N}\int\xi(\mathbf{X}_1,\mathbf{X}_2)\,\mathrm{d}\mathbf{X}_1$$

It must be noted that $Kn(\mathbf{X}_1) = 0$.

We can obtain an equation for the correlation function $\Phi(\mathbf{X}_1,\mathbf{X}_2)$ of the monomer density, excluding from eqs A6 and A8 the function $\Psi(\mathbf{X}_1,\mathbf{X}_2)$. In this equation it is already possible to omit the auxiliary external field $\varphi(\mathbf{X}) = 0$:

$$\hat{L}_1\left[\frac{\psi_1}{n_1}\left(1 - \frac{n_1}{T}\frac{\partial\mu_1{}^*}{\partial n_1}\right)\Phi(\mathbf{X}_1,\mathbf{X}_2)\right] = 2\psi_1\exp\left(\frac{\mu_1{}^* - \lambda}{T}\right)\left[\frac{1}{T}\frac{\partial\mu_1{}^*}{\partial n_1}\Phi(\mathbf{X}_1,\mathbf{X}_2) + \Omega(\mathbf{X}_2) - \delta(\mathbf{X}_1-\mathbf{X}_2)\right] - \psi_2\hat{L}_1\delta(\mathbf{X}_1-\mathbf{X}_2) \quad \text{(A9)}$$

Here $n(\mathbf{X})$, $\psi(\mathbf{X})$, and λ are the results of the solution of coupled equations A1 divided by A2, considered in ref 1. Function $\Omega(\mathbf{X})$ is determined from the condition in eq A7. We note that the correlation function $\Phi(\mathbf{X}_1,\mathbf{X}_2)$ is obviously of a symmetrical type

$$\Phi(\mathbf{X}_1,\mathbf{X}_2) = \Phi(\mathbf{X}_2,\mathbf{X}_1) \quad \text{(A10)}$$

and it is under the condition of conservation of the total link number in the macromolecule:

$$\int\Phi(\mathbf{X}_1,\mathbf{X}_2)\,\mathrm{d}\mathbf{X}_1 = 0 \quad \text{(A11)}$$

Appendix B: Correlation Function of the Density in the Volume Approximation

In the limits of volume approximation functions n, ψ, and μ^* are constant inside a globule and equal to zero outside a globule. In this approximation $\exp((\mu^* - \lambda)/T) = 1$, $\hat{L} = \hat{g} - 1$, $\Omega(\mathbf{X}) = n/N$, and eq A9 takes the form

$$\frac{1-\epsilon}{2n}(\hat{g}_1 - 1)\Phi(\mathbf{X}_1,\mathbf{X}_2) = \frac{\epsilon}{n}\Phi(\mathbf{X}_1,\mathbf{X}_2) + \frac{n}{N} - \frac{1}{2}(\hat{g}_1 + 1)\delta(\mathbf{X}_1-\mathbf{X}_2) \quad \text{(B1)}$$

where $\epsilon \equiv (n/T)(\partial\mu^*/\partial n)$.

We remind everyone that in the beads model, which is used in the present case (the region of the globule–coil transition is the region of universality, i.e., independence of the macroscopic polymer properties from a choice of the concrete model), it is supposed that in a chain the neighboring beads are connected to each other by a long and absolutely flexible string. This means that the operator $\hat{g}$ has a Gaussian nucleus:

$$\hat{g}_1\Phi(\mathbf{X}_1,\mathbf{X}_2) = \left(\frac{2}{3}\pi a^2\right)^{-3/2}\int\exp\left[-\frac{3|\mathbf{X}_1 - \mathbf{X}_0|^2}{2a^2}\right]\times\Phi(\mathbf{X}_0,\mathbf{X}_2)\,\mathrm{d}\mathbf{X}_0 \quad \text{(B2)}$$

The solution of eq B1 can be presented in the following form:

$$\Phi(\mathbf{X}_1,\mathbf{X}_2) = -\frac{n^2}{N\epsilon} - \frac{n}{1-\epsilon}\delta(\mathbf{X}_1-\mathbf{X}_2) - \frac{2n}{(2\pi)^3(1-\epsilon)^2}\int\frac{e^{-ik(\mathbf{X}_2-\mathbf{X}_1)}\,\mathrm{d}k}{e^{-k^2a^2/6} - \left(1 + \frac{2\epsilon}{1-\epsilon}\right)} \quad \text{(B3)}$$

The integral in the right-hand side of this expression can be presented in the form of infinite series

$$\Phi(\mathbf{X}_1,\mathbf{X}_2) = -\frac{n^2}{N\epsilon} + \frac{n}{1+\epsilon}\delta(\mathbf{X}_1-\mathbf{X}_2) + \frac{3n}{\pi a^2|\mathbf{X}_2 - \mathbf{X}_1|(1-\epsilon^2)}\sum_{i=0}^{\infty}\left\{\cos\left[\frac{|\mathbf{X}_2 - \mathbf{X}_1|}{\sqrt{2}\zeta}\left(\left(1 + \frac{4\pi^2 i^2}{\ln^2\left(\frac{1+\epsilon}{1-\epsilon}\right)}\right)^{1/2} - 1\right)^{1/2}\right]\exp\left[-\frac{|\mathbf{X}_2 - \mathbf{X}_1|}{\sqrt{2}\zeta}\left(\left(1 + \frac{4\pi^2 i^2}{\ln^2\left(\frac{1+\epsilon}{1-\epsilon}\right)}\right)^{1/2} + 1\right)^{1/2}\right]\right\} \quad \text{(B4)}$$

where

$$\zeta = \left(6\ln\frac{1+\epsilon}{1-\epsilon}\right)^{-1/2}a$$

When $|\mathbf{X}_2 - \mathbf{X}_1| \gtrsim a$ in the infinite series of eq B4, only the term with $i = 0$ plays the main role. In this case the correlation function of the density has the following standard Ornstein–Zernike-type asymptotic form:

$$\Phi(\mathbf{X}_1,\mathbf{X}_2) = -\frac{n}{\frac{N}{T}\frac{\partial\mu^*}{\partial n}} + \frac{3n}{\pi a^2|\mathbf{X}_2 - \mathbf{X}_1|\left[1 - \left(\frac{n}{T}\frac{\partial\mu^*}{\partial n}\right)^2\right]}\times\exp\left[-\frac{|\mathbf{X}_2 - \mathbf{X}_1|}{\zeta}\right] \quad \text{(B5)}$$

Appendix C: Equation for the Correlation Function of the Density in Dimensionless Quantities

The equation for the correlation function $\Phi(\mathbf{X}_1,\mathbf{X}_2)$ of the monomer density can be simplified by virial expansion, due to the smallness of the globule density. As was done for calculation of the smoothed density,[1] we limit ourselves by accounting the most essential pair and triple interactions of quasimonomers only and in addition we neglect higher-order terms of powers of $B^2/C \sim \tau^2$ ($\tau \equiv (T-\Theta)/\Theta$). Besides, it is convenient to use dimensionless quantities, introduced in ref 1:

(i) radius-vector

$$\mathbf{r} = \mathbf{X}\frac{(-B)}{C^{1/2}(a/\sqrt{6})} \qquad \text{(C1)}$$

(ii) reduced temperature

$$t = \frac{N^{1/2}B}{C^{1/4}(a/\sqrt{6})^{3/2}} \qquad \text{(C2)}$$

(iii) parameter $\varkappa$ so that $\lambda \equiv \mu^*(\tilde{n})$, where $\tilde{n} = -\varkappa B/C$

(iv) density

$$\chi^2(\mathbf{r}) = n(\mathbf{r})/\tilde{n} \qquad \text{(C3)}$$

(Here B and C stand for the second and third virial coefficients of the interaction between quasimonomers, and a is the root-mean-square spatial distance between adjacent monomers.) In these notations the virial expansion for the self-consistent field μ^* acquires the form

$$\mu^*/T = 2nB + 3n^2C = -(B^2/C)\varkappa\chi^2(2 - 3\varkappa\chi^2)$$

and hence $\lambda/T = -(B^2/C)\varkappa(2 - 3\varkappa)$ and $(1/T)(\partial\mu^*/\partial n) = 2B(1 - 3\varkappa\chi^2)$.

We introduce also the dimensionless functions $\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2)$ and $\Omega_{\mathrm{d}}(\mathbf{r})$ as

$$\Phi(\mathbf{X}_1,\mathbf{X}_2) = \frac{2\varkappa^2t^2}{NC}\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2) = (2)(6^{3/2})\frac{\sqrt{C}}{a^3}\left[\frac{\varkappa(-B)}{C}\right]^2\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2) \qquad \text{(C4)}$$

$$\Omega(\mathbf{X}) = \frac{\varkappa t^2(-B)}{NC}\Omega_{\mathrm{d}}(\mathbf{r}) \qquad \text{(C5)}$$

Taking into account the form (eq B2) of the $\hat{g}$ operator and $\delta(\mathbf{X}_1-\mathbf{X}_2) = \delta(\mathbf{r}_1-\mathbf{r}_2)t^2(-B)/NC$, eq A9 is transformed as

$$\frac{C}{B^2}\left\{\left(\frac{4\pi B^2}{C}\right)^{-3/2}\int\exp\left[-\frac{|\mathbf{r}_1-\mathbf{r}|^2}{4B^2/C}\right]\frac{\Phi_{\mathrm{d}}(\mathbf{r},\mathbf{r}_2)}{\chi(\mathbf{r})}\,\mathrm{d}\mathbf{r} - \frac{\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2)}{\chi(\mathbf{r}_1)}\right\} - f(\mathbf{r}_1)\frac{\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2)}{\chi(\mathbf{r}_1)} = \chi(\mathbf{r}_1)\,\Omega_{\mathrm{d}}(\mathbf{r}_2) - \frac{\chi(\mathbf{r}_2)}{2\varkappa}\delta(\mathbf{r}_1-\mathbf{r}_2) - \frac{\chi(\mathbf{r}_2)}{2\varkappa}\left(\frac{4\pi B^2}{C}\right)^{-3/2}\exp\left[-\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{4B^2/C}\right] \qquad \text{(C6)}$$

where

$$f(\mathbf{r}) \equiv \varkappa(2 - 3\varkappa - 6\chi^2 + 15\varkappa\chi^4) \qquad \text{(C7)}$$

It is easy to see that in accordance with the condition in eq A7 the solution of this equation for Φ_{d} exists only if $\Omega_{\mathrm{d}}(\mathbf{r}_2)$ equals

$$\Omega_{\mathrm{d}}(\mathbf{r}_2) = \frac{4\varkappa^2}{t^2}\int\chi^3(\mathbf{r})[1 - 3\varkappa\chi^2(\mathbf{r})]\frac{\Phi_{\mathrm{d}}(\mathbf{r},\mathbf{r}_2)}{\chi(\mathbf{r})}\,\mathrm{d}\mathbf{r} + \frac{\chi^2(\mathbf{r}_2)}{t^2} \qquad \text{(C8)}$$

It is noteworthy that the correlation function $\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2)$ is included in eq C6 only in the combination form

$$\frac{\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2)}{\chi(\mathbf{r}_1)} \equiv \xi(\mathbf{r}_1,\mathbf{r}_2)$$

Hence, for function

$$\xi^{(0)}(\mathbf{r}_1,\mathbf{r}_2) \equiv \xi(\mathbf{r}_1,\mathbf{r}_2) + \frac{B^2}{C}\frac{\chi(\mathbf{r}_2)}{2\varkappa}\delta(\mathbf{r}_1-\mathbf{r}_2)$$

the equation will take the following form:

$$\frac{C}{B^2}\left\{\left(\frac{4\pi B^2}{C}\right)^{-3/2}\int\exp\left[-\frac{|\mathbf{r}_1-\mathbf{r}_0|^2}{4B^2/C}\right]\xi^{(0)}_{0,2}\,\mathrm{d}\mathbf{r}_0 - \xi^{(0)}_{1,2}\right\} - f_1\xi^{(0)}_{1,2} = \chi_1\Omega_{\mathrm{d}_2} - \frac{\chi_2}{\varkappa}\delta(\mathbf{r}_1-\mathbf{r}_2) \qquad \text{(C9)}$$

As has been said, in our designations the subscripts correspond to the point numbers where the function is put under our consideration.

The presence of a delta function in the right-hand members of eqs C6 and C9 leads to a loss of smoothness for the correlation function and for the function $\xi^{(0)}_{1,2}$ at the point $\mathbf{r}_1 = \mathbf{r}_2$. If $\xi^{(0)}_{1,2}$ did not show singularity in this point, then the expression in braces in eq C9 with a precision of smaller terms of powers of B^2/C would have the form $(B^2/C)\Delta_1\xi^{(0)}_{1,2}$ (Δ_1 stands for a Laplacian operator with respect to $\mathbf{r}_1$). However, it turns out that such a transformation is correct for a more common case as well. For the function $\xi^{(0)}_{1,2}$ with the exception of a very small neighborhood of the point $\mathbf{r}_1 = \mathbf{r}_2$, we can write the following:

$$\Delta_1\xi^{(0)}_{1,2} - f_1\xi^{(0)}_{1,2} = \chi_1\Omega_{\mathrm{d}_2} - (\chi_2/\varkappa)\delta(\mathbf{r}_1-\mathbf{r}_2) \qquad \text{(C10)}$$

Below we estimate the area in the neighborhood of the point $\mathbf{r}_1 = \mathbf{r}_2$ where eq C9 cannot be transformed into eq C10. Let us assume (and the ensuing manipulations will confirm the correctness of our assumption) that the area of the neighborhood is very small indeed. Then with a precision of much smaller terms of powers of B^2/C it can be considered that in this neighborhood $\chi(\mathbf{r}_1) = \chi(\mathbf{r}_2)$ and consequently $f(\mathbf{r}_1) = f(\mathbf{r}_2)$. Using Fourier transformation, the solution of eq C9 can be presented in the following form:

$$\xi^{(0)}_{1,2} = (2\pi)^{-3/2}\Omega_{\mathrm{d}_2}\frac{B^2}{C}\int\frac{\chi_k e^{ik\mathbf{r}_1}\,\mathrm{d}k}{\exp(-k^2B^2/C) - (1 + (B^2/C)f_2)} - (2\pi)^{-3}\frac{\chi_2B^2}{\varkappa C}\int\frac{e^{-ik(\mathbf{r}_2-\mathbf{r}_1)}\,\mathrm{d}k}{\exp(-k^2B^2/C) - (1 + (B^2/C)f_2)} \qquad \text{(C11)}$$

Here χ_k is the Fourier transform of $\chi(\mathbf{r})$. This expression could transform to a solution for eq C10 by changing

$$\exp(-k^2B^2/C) \rightarrow 1 - k^2B^2/C$$

in eq C11. Therefore, we need to ascertain a condition under which this change is possible. For this purpose it is convenient to present the integral in eq C11 as the infinite series like in eq B3. So we write

$$\frac{1}{e^{-k^2B^2/C} - (1 + (B^2/C)f_2)} = (1 + (B^2/C)f_2)^{-1}\left[\frac{1}{1 - (1 + (B^2/C)f_2)e^{k^2B^2/C}} - 1\right]$$

and

$$\int \frac{e^{-ik(\mathbf{r}_2-\mathbf{r}_1)}\,\mathrm{d}k}{1-(1+(B^2/C)f_2)e^{k^2B^2/C}} = -(B^2/C)^{-1}\frac{2\pi^2}{|\mathbf{r}_2-\mathbf{r}_1|}\sum_{i=0}^{\infty}\{\cos\,[|\mathbf{r}_2-\mathbf{r}_1|(f_2/2)^{1/2}\times ((1+4i^2\pi^2(B^2/C)^{-2}f_2^{-2})^{1/2}-1)^{1/2}]\,\exp[-|\mathbf{r}_2-\mathbf{r}_1|(f_2/2)^{1/2}\times ((1+4i^2\pi^2(B^2/C)^{-2}f_2^{-2})^{1/2}+1)^{1/2}]\}$$

The change presented above is correct when here only the term with $i = 0$ becomes essential. Indeed, under the condition

$$|\mathbf{r}_2-\mathbf{r}_1| \gtrsim -B/\sqrt{C} \sim -\tau \quad (|\tau| \ll 1) \qquad \text{(C12)}$$

all higher terms of the sum with $i \geqslant 1$ are exponentially small.

Thus, under the condition in eq C12, eq C9 can be presented in simplified form, as given in eq C10. Under the same condition

$$\xi^{(0)}(\mathbf{r}_1,\mathbf{r}_2) = \xi(\mathbf{r}_1,\mathbf{r}_2) = \Phi_\mathrm{d}(\mathbf{r}_1,\mathbf{r}_2)/\chi(\mathbf{r}_1)$$

and the equation for the correlation function is directly presented by the expression

$$[\Delta_1 - f(\mathbf{r}_1)]\frac{\Phi_\mathrm{d}(\mathbf{r}_1,\mathbf{r}_2)}{\chi(\mathbf{r}_1)} = \chi(\mathbf{r}_1)\,\Phi_\mathrm{d}(\mathbf{r}_2) - \frac{\chi(\mathbf{r}_2)}{\varkappa}\delta(\mathbf{r}_1-\mathbf{r}_2) \qquad \text{(C13)}$$

The range of inapplicability of this equation is very small in the region of the globule-to-coil transition, where $|\tau| \equiv |T-\Theta|/\Theta \ll 1$. The expression in eq C13 should be supplemented for a globule by the natural condition that the correlation function decrease exponentially at infinity ($|\mathbf{r}_1|$ or $|\mathbf{r}_2| \to \infty$).

Appendix D: Calculation of the Fluctuation Value of the Radius of Gyration of a Polymer Globule

Here we will use the dimensionless quantities in eqs C1–C5 of Appendix C and introduce a new dimensionless function

$$\tilde{\chi}(\mathbf{r}) \equiv \int \frac{\Phi_\mathrm{d}(\mathbf{r},\mathbf{r}_2)}{\chi(\mathbf{r})} r_2^{\,2}\,\mathrm{d}\mathbf{r}_2 \qquad \text{(D1)}$$

Taking into consideration these designations, we can present eq 4 in the form

$$\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2} = \frac{6^{3/2}}{2\pi}\frac{\sqrt{C}}{a^3}\frac{\int_0^\infty \chi(r)\,\tilde{\chi}(r)\,r^4\,\mathrm{d}r}{[\int_0^\infty \chi^2(r)\,r^4\,\mathrm{d}r]^2} \qquad \text{(D2)}$$

We used the condition of spherical symmetry of a globule, which means, particularly, that both the $\chi(\mathbf{r})$ function and the newly introduced $\tilde{\chi}(\mathbf{r})$ function depend on the distance $r \equiv |\mathbf{r}|$ between the point $\mathbf{r}$ and the center of the globule only.

To determine the function $\tilde{\chi}(r)$, there is not a special necessity to solve eq C6 for the correlation function $\Phi_\mathrm{d}(\mathbf{r}_1,\mathbf{r}_2)$. Having multiplied every member of this equation by r_2^2 and integrated by variable $\mathbf{r}_2$, we have

$$\frac{C}{B^2}\left\{\left(\frac{4\pi B^2}{C}\right)^{-3/2}\int \exp\left[-\frac{|\mathbf{r}-\mathbf{r}_0|^2}{4B^2/C}\right]\tilde{\chi}(r_0)\,\mathrm{d}\mathbf{r}_0 - \tilde{\chi}(r)\right\} - f(r)\,\tilde{\chi}(r) = \chi(r)\,(\tilde{w} - r^2/\varkappa) + O(B^2/C) \qquad \text{(D3)}$$

where

$$\tilde{w} \equiv \int \Phi_\mathrm{d}(\mathbf{r})\,r^2\,\mathrm{d}\mathbf{r} = t^{-2}\int \chi^2(r)\,r^2\,\mathrm{d}\mathbf{r} + 4\varkappa^2 t^{-2}\int \chi^3(r)\,[1-3\varkappa\chi^2(r)]\tilde{\chi}(r)\,\mathrm{d}\mathbf{r} \qquad \text{(D4)}$$

It is noteworthy that the function $\tilde{\chi}(r)$ is smooth, because the singularity of the correlation function $\Phi_\mathrm{d}(\mathbf{r}_1,\mathbf{r}_2)$ in the $\mathbf{r}_1 = \mathbf{r}_2$ point disappears when we integrate this correlation function (eq D1). Taking into account only the leading terms with respect to $B^2/C \ll 1$, we can immediately represent the expression in the braces of eq D3 as $(B^2/C)\Delta\tilde{\chi}(r)$ (for the linear memory operator, it corresponds to $\hat{g} \simeq 1 + (B^2/C)\Delta_r$; see previous appendixes):

$$[\Delta - f(r)]\tilde{\chi}(r) = \chi(r)\,(\tilde{w} - r^2/\varkappa) \qquad \text{(D5)}$$

We remind everyone that the function $f(r)$ is determined by eq C7, while $\tilde{w}$ is in fact an eigenvalue determined by the condition of the existence of the solution of eq D5, i.e., by eq D4.

To complete the problem, it is necessary to formulate boundary conditions proper to a globule. Taking into account eq D1, we can write conditions of the following type:

$$\frac{\mathrm{d}}{\mathrm{d}r}(\chi\tilde{\chi})|_{r=0} = 0, \quad (\chi\tilde{\chi})|_{r\to\infty} \to 0 \qquad \text{(D6)}$$

At the same time the density function $\chi(\mathbf{r})$ is under the conditions[1]

$$\text{at } r = 0: \qquad \mathrm{d}\chi/\mathrm{d}r = 0, \quad \chi \neq 0$$

$$\text{at } r \to \infty: \qquad \chi \simeq \frac{k(t)}{r}\exp(-\eta^{1/2}r) \to 0 \qquad \text{(D7)}$$

where $\eta \equiv \varkappa(2-3\varkappa)$. The value $k(t)$ was determined in the framework of numerical calculations of ref 1 using the following control condition of asymptotic behavior:

$$\left(\frac{1}{\chi}\frac{\mathrm{d}\chi}{\mathrm{d}r}\right)\bigg|_{r\to\infty} \simeq -\eta^{1/2} - r^{-1}$$

In view of these facts, boundary conditions in eq D6 acquire the following form:

$$\frac{\mathrm{d}\tilde{\chi}}{\mathrm{d}r}\bigg|_{r=0} = 0, \quad \left[\tilde{\chi}\frac{k(t)}{r}e^{-\eta^{1/2}r}\right]\bigg|_{r\to\infty} \to 0 \qquad \text{(D8)}$$

It is noteworthy that the property of the $\tilde{\chi}(r)$ function, resulting from the condition in eq A11 of conservation of the total number of monomers in a chain, is

$$\int \chi(r)\,\tilde{\chi}(r)\,\mathrm{d}\mathbf{r} = 0 \qquad \text{(D9)}$$

At the beginning we consider fluctuations of macromolecular size in the simplest volume approximation. We remind everyone that in this approximation inside the globule, i.e., when $x \leqslant R_0 \equiv (3N/4\pi n_0)^{1/3}$ ($n_0 = -B/2C$), or, using dimensionless quantities, when $r \leqslant R_{0_\mathrm{d}} = (3t^2/2\pi)^{1/3}$, we have $\chi(r) = 1$, $\varkappa = 0.5$, and so $f(r) = 1$. Outside the globule, when $r > R_{0_\mathrm{d}}$, we have $\chi(r) = 0$ and $\tilde{\chi}(r) = 0$. Taking into account eqs D4 and D9, we see that $\tilde{w} = (4\pi/5t^2)R_{0_\mathrm{d}}^{\,5} = (6/5)R_{0_\mathrm{d}}^{\,2}$. Thus we can write eq D5 in the new form

$$[\Delta - 1]\tilde{\chi}(r) = (6/5)R_{0_\mathrm{d}}^{\,2} - 2r^2$$

The solution of this equation outside the small neighborhood of the $r = 0$ point is the following:

$$\tilde{\chi}(r) = 2r^2 + 12 - (6/5)R_{0_\mathrm{d}}^{\,2} - 16\pi R_{0_\mathrm{d}}^{\,3}e^{-r}/r \qquad \text{(D10)}$$

This solution corresponds to the conservation condition in eq D9. Substituting the $\tilde{\chi}(r)$ function from eq D10 into eq D2 for the fluctuation values of the polymer radius of gyration in the volume approximation ($|t| \gg 1$), we have

$$\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2} = 6^{3/2}\frac{8}{21}t^{-2}\frac{\sqrt{C}}{a^3} \simeq 5.6t^{-2}\frac{\sqrt{C}}{a^3} \qquad \text{(D11)}$$

However, as will become clear, if we use the volume approximation (i.e., neglect all the globule surface energy) for the calculation of the fluctuation values of the polymer size in the neighborhood of the globule–coil transition point, then we get a result that is considerably smaller than the true one. Therefore, here we must calculate the $\tilde{\chi}(r)$ dependence directly from eq D5 with the boundary conditions in eq D8.

Taking into account eq D4, we can rewrite eq D5 in the following form:

$$[\Delta - f(r)]\tilde{\chi}(r) = \frac{16\pi\varkappa^2}{t^2}\chi(r)\int_0^\infty \chi^3(r_0)[1 - 3\varkappa\chi^2(r_0)]\tilde{\chi}(r_0) \times r_0^{\,2}\,\mathrm{d}r_0 + \left[\frac{4\pi}{t^2}\int_0^\infty \chi^2(r_0)\, r_0^{\,4}\,\mathrm{d}r_0 - \frac{r^2}{\varkappa}\right]\chi(r) \qquad \text{(D12)}$$

It is convenient here to introduce the $\tilde{\beta}$ parameter as follows:

$$\tilde{\beta} \equiv \int_0^\infty \chi^3(r_0)\,[1 - 3\varkappa\chi^2(r_0)]\tilde{\chi}(r_0)\, r_0^{\,2}\,\mathrm{d}r_0 \qquad \text{(D13a)}$$

Then the solution of eq D12 can be written in the form

$$\tilde{\chi}(r) = \tilde{\beta}\tilde{\chi}^{(1)}(r) + \tilde{\chi}^{(2)}(r) \qquad \text{(D13b)}$$

where functions $\tilde{\chi}^{(1)}(r)$ and $\tilde{\chi}^{(2)}(r)$ are the solutions of the following equations:

$$[\Delta - f(r)]\tilde{\chi}^{(1)}(r) = \frac{16\pi\varkappa^2}{t^2}\chi(r) \qquad \text{(D14)}$$

$$[\Delta - f(r)]\tilde{\chi}^{(2)}(r) = \left[\frac{4\pi}{t^2}\int_0^\infty \chi^2(r_0)\, r_0^{\,4}\,\mathrm{d}r_0 - \frac{r^2}{\varkappa}\right]\chi(r) \qquad \text{(D15)}$$

The value of $\tilde{\beta}$ can be calculated after $\tilde{\chi}^{(1)}(r)$ and $\tilde{\chi}^{(2)}(r)$ determinations:

$$\tilde{\beta} = \frac{\int_0^\infty \chi^3(r)\,[1 - 3\varkappa\chi^2(r)]\tilde{\chi}^{(2)}(r)\, r^2\,\mathrm{d}r}{1 - \int_0^\infty \chi^3(r)[1 - 3\varkappa\chi^2(r)]\tilde{\chi}^{(1)}(r)\, r^2\,\mathrm{d}r} \qquad \text{(D16)}$$

Boundary conditions in eq D8 take the form

$$\left.\frac{\mathrm{d}\tilde{\chi}^{(1)}(r)}{\mathrm{d}r}\right|_{r=0} = 0, \quad \left.\tilde{\chi}^{(1)}(r)\right|_{r\to\infty} \simeq \left[\frac{\text{const}}{r} - \frac{8\pi\varkappa^2 k(t)}{t^2\eta^{1/2}}\right]e^{-\eta^{1/2}r}$$

$$\left.\frac{\mathrm{d}\tilde{\chi}^{(2)}(r)}{\mathrm{d}r}\right|_{r=0} = 0, \quad \left.\tilde{\chi}^{(2)}(r)\right|_{r\to\infty} \simeq \left[\frac{\text{const}}{r} - \frac{2\pi k(t)}{t^2\eta^{1/2}} \times \int_0^\infty \chi^2(r_0)\, r_0^{\,4}\,\mathrm{d}r_0 + \frac{k(t)}{6\varkappa\eta^{1/2}}\left(\frac{3}{2\eta} + \frac{3r}{2\eta^{1/2}} + r^2\right)\right]e^{-\eta^{1/2}r} \qquad \text{(D17)}$$

We obtain now the problem which is accessible for a numerical solution. The result of its numerical solution is presented in Figure 1.

Appendix E: Calculation of a Globule Hydrodynamic Radius

For a hydrodynamic radius using the dimensionless variables of eqs C1–C5 and taking into consideration eq 17, we can rewrite the above-discussed Kirkwood–Riseman expression (eq 14) as

$$\langle R_{\mathrm{H}}^{-1}\rangle = \frac{\varkappa^2}{6^{1/4}N^{1/2}a|t|^3}\left(\frac{\sqrt{C}}{a^3}\right)^{-1/2} \times \left[\int\!\!\int \frac{\chi^2(r_1)\,\chi^2(r_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 + (2)(6^{3/2})\frac{\sqrt{C}}{a^3}\int\!\!\int \frac{\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\right] \qquad \text{(E1)}$$

The first term in square brackets of this expression can be obtained from the results of the numerical calculations of the previous paper in this series.[1] The second term, which is determined by the correlation function, becomes insignificant for highly rigid chains ($\sqrt{C}/a^3 \ll 1$). In the general case, however, it is necessary to calculate the value

$$E(t) \equiv \int\!\!\int \frac{\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \qquad \text{(E2)}$$

where the dimensionless correlation function $\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2)$ is determined by eq C13 (with the exception of a very small area bounded by the condition in eq C12).

As has already been done, here we consider the previous globule hydrodynamic radius in the volume approximation. In this approximation eq B4 leads to the result

$$\Phi_{\mathrm{d}}(\mathbf{r}_1,\mathbf{r}_2) = \frac{e^{-|\mathbf{r}_1-\mathbf{r}_2|}}{2\pi|\mathbf{r}_1 - \mathbf{r}_2|} - t^{-2} \qquad \text{(E3)}$$

inside the globule. This result is valid under the condition in eq C12, i.e., when $|\mathbf{r}_1 - \mathbf{r}_2| \gtrsim -\tau$. However, when $-\tau \ll 1$, the area $|\mathbf{r}_1 - \mathbf{r}_2| < -\tau$ gives a negligible contribution to the integral $E(t)$; therefore

$$E(t) \simeq \int\!\!\int_{|\mathbf{r}_1|,|\mathbf{r}_2|<R_{0_{\mathrm{d}}}} \left[\frac{e^{-|\mathbf{r}_1-\mathbf{r}_2|}}{2\pi|\mathbf{r}_1 - \mathbf{r}_2|} - t^{-2}\right]\frac{\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

The dimensionless radius of the globule in the volume approximation is $R_{0_{\mathrm{d}}} = (3t^2/2\pi)^{1/3}$. Since this approximation is valid when $-t \gg 1$, then $R_{0_{\mathrm{d}}}$ should be considered as a greater parameter. Therefore, the leading term of $E(t)$ is

$$E(t) \simeq 4t^2$$

Besides

$$\int\!\!\int \frac{\chi^2(r_1)\,\chi^2(r_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 = \int\!\!\int_{|\mathbf{r}_1|,|\mathbf{r}_2|<R_{0_{\mathrm{d}}}} \frac{\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{32}{15}\pi^2 R_{0_{\mathrm{d}}}^{\;5} = \frac{8}{5}(18\pi t^{10})^{1/3}$$

Finally, in the volume approximation we have

$$\langle R_{\mathrm{H}}^{-1}\rangle = 2(6^{1/4}N^{1/2}a)^{-1}\left(\frac{\sqrt{C}}{a^3}\right)^{-1/2}\left[\frac{1}{5}(18\pi|t|)^{1/3} + 6^{3/2}\frac{\sqrt{C}}{a^3}|t|^{-1}\right]$$

while expansion factor α_{H}, taking into account eq 15, equals

$$\alpha_{\mathrm{H}} \equiv \frac{\langle R_{\mathrm{H}}^{-1}\rangle_{\mathrm{id}}}{\langle R_{\mathrm{H}}^{-1}\rangle} = \frac{40}{6^{1/4}18^{1/3}\pi^{5/6}}|t|^{-1/3}\left(\frac{\sqrt{C}}{a^3}\right)^{1/2} \simeq 3.76|t|^{-1/3}\left(\frac{\sqrt{C}}{a^3}\right)^{1/2} \qquad \text{(E4)}$$

Near the globule-to-coil transition point the volume approximation becomes ineffective. Besides, it is not already possible to use the same simplification of eq C13 for the correlation function when we calculate $E(t)$ (eq E2), as has been done in the calculation of the fluctuation values of the radius of gyration. We should remind everyone here that, to determine the value of the fluctuations, it was sufficient to know the function of the form $\int \Phi_d(\mathbf{r}_1,\mathbf{r}_2)\, r_2^2\, d\mathbf{r}_2$ only. We have derived the equation for this function by integration of all terms of eq C13. This integration led to a considerable simplification of the equation in question. In the present case it is necessary to calculate the function $\Phi_d(\mathbf{r}_1,\mathbf{r}_2)$ directly (or the function $\xi(\mathbf{r}_1,\mathbf{r}_2) \equiv \Phi_d(\mathbf{r}_1,\mathbf{r}_2)/\chi(\mathbf{r}_1)$). According to eq C13, $\xi(\mathbf{r}_1,\mathbf{r}_2)$ has the following form:

$$\Delta_1\xi(\mathbf{r}_1,\mathbf{r}_2) - f(r_1)\, \xi(\mathbf{r}_1,\mathbf{r}_2) = \chi(r_1)\, \Omega_d(r_2) - [\chi(r_2)/\varkappa]\delta(\mathbf{r}_1-\mathbf{r}_2) \tag{E5}$$

Here $f(r)$ is determined by eq C7, while eq C8 is correct for $\Omega_d(r)$. This equation should necessarily be supplemented by the natural condition of the exponential decreasing of $\xi(\mathbf{r}_1,\mathbf{r}_2)$ when $r_1 \rightarrow \infty$ or $r_2 \rightarrow \infty$. We look for the solution in a form like eq D13b

$$\xi(\mathbf{r}_1,\mathbf{r}_2) = \Omega_d(r_2)\, \xi^{(1)}(r_1) + \xi^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$$

where the function $\xi^{(1)}(r)$ obeys the equation

$$\frac{d^2\xi^{(1)}}{dr^2} + \frac{2}{r}\frac{d\xi^{(1)}}{dr} - f(r)\, \xi^{(1)}(r) = \chi(r) \tag{E6}$$

The value of $\Omega_d(r_2)$ can be defined after calculation of the functions $\xi^{(1)}(r)$ and $\xi^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$:

$$\Omega_d(r_2) = \frac{\chi^2(r_2) + 4\varkappa^2\int \chi^3(r)[1 - 3\varkappa\chi^2(r)]\xi^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\, d\mathbf{r}}{t^2 - 4\varkappa^2\int \chi^3(r)[1 - 3\varkappa\chi^2(r)]\xi^{(1)}(r)\, d\mathbf{r}}$$

Since the globule has spherical symmetry, the function $\xi^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ depends on three scalar arguments only (instead of two vectorial ones): $r \equiv |\mathbf{r}_2|$, $\rho \equiv |\mathbf{r}_1 - \mathbf{r}_2|$, and γ—cosine of the angle between vectors $\mathbf{r}_2$ and $\mathbf{r}_1 - \mathbf{r}_2$. Therefore, the equation for $\xi^{(2)}(r,\rho,\gamma)$ can be written in the form (if $\rho \neq 0$)

$$\frac{\partial^2\xi^{(2)}}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial\xi^{(2)}}{\partial\rho} + \frac{1}{\rho^2}\left[(1-\gamma^2)\frac{\partial^2\xi^{(2)}}{\partial\gamma^2} - 2\gamma\frac{\partial\xi^{(2)}}{\partial\gamma}\right] - f(r_1)\xi^{(2)} = 0 \tag{E7}$$

where $r_1 = (\mathbf{r}^2 + \rho^2 + 2r\rho\gamma)^{1/2}$.

Let us consider now additional conditions for eqs E6 and E7. As for the $\xi^{(1)}(r)$ function, it is natural to assume its regularity at the $r = 0$ point and an exponential decrease when $r \rightarrow \infty$. With respect to eq E6, this means that

$$\xi^{(1)}(r)|_{r\rightarrow 0} = a_0 + \left[a_0 + \frac{\chi(0)}{f(0)}\right]\left[\frac{f(0)}{6}r^2 + O(r^4)\right] + \frac{b_0}{r}\left[1 + \frac{f(0)}{2}r^2 + O(r^4)\right] \tag{E8}$$

where a_0 and b_0 are constants. The condition of regularity, when $r \rightarrow 0$, makes it necessary to choose the solution with $b_0 = 0$. Besides

$$\xi^{(1)}(r)|_{r\rightarrow\infty} = \exp(-\eta^{1/2}r)\left[\frac{a_\infty}{r} - \frac{k(t)}{2\eta^{1/2}}\right] \tag{E9}$$

where $\eta \equiv \varkappa(2 - 3\varkappa)$, and $k(t)$ is determined according to eq D7, while the a_∞ constant should be chosen in such a way that it could satisfy the condition $b_0 = 0$. The solution $\xi^{(1)}(r)$ of eq E6 with all presented additional conditions can easily be found numerically.

Equation E7 should be supplemented by the conditions of the exponential decreasing of $\xi^{(2)}(r,\rho,\gamma)$, when both $r \rightarrow \infty$ and $\rho \rightarrow \infty$. It follows from eq E5 that in the $\rho = 0$ point this function has the singularity

$$\xi^{(2)}(r,\rho,\gamma)|_{\rho\rightarrow 0} \simeq \frac{\chi(r)\, e^{-\rho(f(r))1/2}}{4\pi\varkappa\rho} \tag{E10}$$

We may solve eq E7 independently for every value of $r \geqslant 0$. Taking into account the spherical symmetry of a globule, it is sufficient to solve the problem on a half-plane, which lies on one side of the diametric line, which goes through the globule center and the $\mathbf{r} \equiv \mathbf{r}_2$ point. This line consists of two parts in different directions from the $\mathbf{r}$ point, where $\gamma = \pm 1$. The form of eq E7 and the properties of function $\xi^{(2)}$ allow us to calculate at first this function along the diametric line in question, taking into account the additional condition

$$\xi^{(2)}\Big|_{\substack{\gamma=\pm 1\\ \rho\rightarrow\infty}} = (a_\infty^{(2)}/\rho)\exp(-\eta^{1/2}\rho)$$

where constant $a_\infty^{(2)}$ is chosen from its correspondence to eq E10. This choice can be demonstrated in more detail.

Using the expansion in a power series of ρ at $\rho \rightarrow 0$

$$f(|r\pm\rho|)|_{\rho\rightarrow 0} = f(r) \pm \rho f'(r) + (\rho^2/2)f''(r) \pm \ldots$$

for the function $\xi^{(2)}$, we can write that

$$\xi^{(2)}\Big|_{\substack{\gamma=\pm 1\\ \rho\rightarrow 0}} = a_0^{(2)}\left[1 + \frac{f(r)}{6}\rho^2 \pm \frac{f'(r)}{12}\rho^3 + O(\rho^4)\right] + \frac{b_0^{(2)}}{\rho}\left[1 + \frac{f(r)}{2}\rho^2 \pm \frac{f'(r)}{6}\rho^3 + O(\rho^4)\right]$$

Here $a_0^{(2)}$ and $b_0^{(2)}$ are constants. The value of $a_\infty^{(2)}$ should be chosen in such a way that

$$b_0^{(2)} = \chi(r)/4\pi\varkappa$$

which corresponds to eq E10 for $\xi^{(2)}$ function.

The remaining part of the problem according to the determination of the $\xi^{(2)}$ function can be presented as eq E7 with four boundary conditions. Two of them (at $\gamma = \pm 1$) are numerical solutions of the problem mentioned above. In the limit $\rho \rightarrow 0$ $\xi^{(2)}$ does not depend on γ, and those values of the function $\xi^{(2)}$, which was calculated at the minimum deviation from the $\rho = 0$ point at $\gamma = \pm 1$, cover an arbitrary γ value as well. This forms the third boundary condition, while the fourth one is the exponential decrease at $\rho \rightarrow \infty$.

The correctness of the obtained results after all numerical calculations can be controlled by the condition in eq A11 of conservation of the total number of monomers, which in this case looks like

$$2\Omega_d(r_2)\int_0^\infty \chi(r_1)\, \xi^{(1)}(r_1)\, r_1^2\, dr_1 + \int_0^\infty \int_{-1}^1 \chi[(r_2^2 + \rho^2 + 2r_2\rho\gamma)]^{1/2}\xi^{(2)}(r_2,\rho,\gamma)\, \rho^2\, d\rho\, d\gamma = 0$$

This very formula can be used for the calculation of $\Omega_d(r_2)$ instead of eq C8.

Now the determined function $\xi(\mathbf{r}_1,\mathbf{r}_2)$ can be used for the $E(t)$ value calculation in accordance with eq E2, which can be presented as

$$E(t) = 8\pi^2\int_0^\infty [\Omega_d(r_2)\int_0^\infty \int_{-1}^1 \chi(r_1)\, \xi^{(1)}(r_1)\, \rho\, d\rho\, d\gamma + \int_0^\infty \int_{-1}^1 \chi(r_1)\, \xi^{(2)}(r_2,\rho,\gamma)\, \rho\, d\rho\, d\gamma]\, r_2^2\, dr_2$$

where $r_1 = (r_2^2 + \rho^2 + 2r_2\rho\gamma)^{1/2}$. This means that here we have all the necessary information to calculate the globule hydrodynamic radius R_{H} according the expression in eq E1. Taking into account eq 15, we can write the expansion factor α_{H} of the hydrodynamic radius with respect to the Gaussian coil size

$$\alpha_{\mathrm{H}}^{-1} \equiv \frac{\langle R_{\mathrm{H}}^{-1}\rangle}{\langle R_{\mathrm{H}}^{-1}\rangle_{\mathrm{id}}} = \left(\frac{\sqrt{C}}{a^3}\right)^{-1/2}\left[h_1(t) + \frac{\sqrt{C}}{a^3}h_2(t)\right]$$

Here $h_1(t)$ and $h_2(t)$ are the functions of one dimensionless parameter of the reduced temperature t (eq 6) only:

$$h_1(t) = \frac{3\pi^{1/2}\varkappa^2}{(6^{3/4})(8|t|^3)}\int\int\frac{\chi^2(r_1)\,\chi^2(r_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$$

$$h_2(t) = \frac{(6^{3/4})(3\pi^{1/2}\varkappa^2)}{4|t|^3}E(t)$$

The dependences of $h_1(t)$ and $h_2(t)$, which were obtained in the present work, are shown in Figure 3.

References and Notes

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