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Conformational Transitions of Polymers in Critical Binary Fluids

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ABSTRACT: A mean-field theory for the coil to globule transition of polymers in critical binary fluids is presented. We show using the uniform expansion method how the density fluctuations of the solvents can bring about the collapse transition close to the critical temperature. When the size of the polymer is comparable to the correlation length of the solvent density fluctuations, we find that a polymer undergoes a partial collapse in a mixture of good solvents of slightly different quality. We calculate the blob size of a partially collapsed chain, which depends on the preferential adsorption of better solvent onto the polymer. On length scales smaller than the blob size, the chain is self-avoiding; on length scales larger than the blob size it is collapsed with $R \approx N^{1/3}$. Close to the critical temperature, the blob size of the polymer is found to depend on the nonclassical critical exponent η .

I. Introduction

Polymers in a critical binary mixture of good solvents show rich conformational behavior. The size of the polymer is determined by the proximity to the critical point of the bicomponent solvents. In particular, far away from the critical point, the polymer is swollen, $R \sim N^{3/5}$; as it approaches the critical point of a mixture, it collapses to a globular state, $R \sim N^{1/3}$; and at the critical point, it reexpands, $R \sim N^{3/5}$. The onset of the coil to globular transition is mainly determined by the proximity to the critical point, which in turn depends on the correlation length of the solvent density fluctuations. The fact that the solvent density fluctuations can induce a partial chain collapse even in a mixture of good solvents has raised much interest in the past.^{1–11}

When a polymer is dissolved in a mixture of two good solvents of slightly different solvent qualities, the better solvent is preferentially absorbed onto the polymer. This means that away from the critical point, the polymer is immersed in a good solvent, and the excluded-volume repulsive interactions between different parts of the chain dominates the overall size. As the mixture of solvents approaches its critical point, the solvent density fluctuations become more and more correlated resulting in fluctuation induced attractive interactions between chain segments, the range of which depends on the proximity to the critical point. Therefore, the interplay between the excluded-volume induced repulsive interactions and fluctuation induced attractive interactions determines the size of the polymer on approach toward criticality. Close to the critical point, when the correlation length of the solvent density fluctuations is of the size of the polymer, the solvent density fluctuations completely shield the excluded-volume interactions, and the chain collapses to a globular state. At the critical point, however, when the solvent density fluctuation act on a much longer length scale compared to the polymer size, the chain regains its original size. These effects first predicted by Brochard and de Gennes¹ using simple scaling arguments were later confirmed by the simulations of Magda et al.² and Vasilevskaya et al.³ The collapse transition is not limited to a binary mixture of good solvents. Recent simulations of polymers in a single solvent close to the lower critical solution temperature (LCST) show similar effects.⁴

Dynamic light scattering measurements in solutions of poly-(acrylic acid) in water and 2,6-lutidine show evidence of partial chain collapse close to the critical point of the solvents.⁷ However, these studies do not give clear evidence of the reexpansion of the chain at the critical point. Recent experiments in the same system using fluorescence correlation spectroscopy have confirmed chain reexpansion at the critical point.⁸

On the theoretical side, the scaling predictions of Brochard and de Gennes have been re-formulated in the field theoretic description by Vilgis et al.⁹ However, the latter theory ultimately relies on a simplified version of Flory theory, which only accounts for the longest length scale fluctuations ($k = 0$) in the problem. As a result, the proximity to the critical point is not well-defined. In a mean-field treatment by Dua et al.,¹¹ the size of a polymer close to the critical point has been calculated using the uniform expansion method of Edwards and Singh.¹⁶ However, the neglect of the three-body interaction term in their description leads to an incorrect prediction of the chain size close to the collapse transition. We have recently included the three-body interaction term in the uniform expansion method, which leads to a nonuniform contraction of the chain size and allows us to estimate the blob size of the collapsed chain.¹⁸ In this paper we present a rigorous analysis of this problem using the uniform expansion method. In particular, we calculate the size of the polymer as a function of proximity to the critical point.

II. Model

The Hamiltonian of a polymer dissolved in a binary mixture of good solvents is given by

$$\mathcal{H} = \mathcal{H}_p + \mathcal{H}_{pf} + \mathcal{H}_f \quad (1)$$

where \mathcal{H}_p is the polymer Hamiltonian given by

$$\mathcal{H}_p = \frac{3}{2b^2} \int_0^N ds \left(\frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 + \frac{v_{mm}}{2} \int_0^N ds \int_0^N ds' \delta[\mathbf{r}(s) - \mathbf{r}(s')] + \frac{w}{6} \int_0^N ds \int_0^N ds' \int_0^N ds'' \delta[\mathbf{r}(s) - \mathbf{r}(s')] \delta[\mathbf{r}(s') - \mathbf{r}(s'')] \quad (2)$$

where the polymer conformation is described by the radius vector $\mathbf{r}(s)$ at distance s from one end of the chain; b is the Kuhn length;

N is the number of monomers; v_{mm} and w measure the strength of the two-body and three-body interactions respectively. The first term in the above Hamiltonian describes the entropic elasticity of the chain. The second term accounts for the repulsive interaction due to excluded volume effects and the last term takes into account the three body interactions. The fluid, on the other hand, is described by a collection of n point particles whose positions in space is represented by the vectors q_i , $i = 1, \dots, n$. Therefore, the fluid Hamiltonian \mathcal{H}_f is given by

$$\mathcal{H}_f = \sum_{\sigma, \tau} \sum_{ij} V^{\sigma, \tau}(\mathbf{q}_i^\sigma - \mathbf{q}_j^\tau) \quad (3)$$

where i, j label the solvent molecules of two different types given by $\sigma, \tau = 1, 2$. The interaction between the polymer and the fluid is given by

$$\mathcal{H}_{pf} = \sum_{\sigma=1,2} \sum_i v_{m\sigma} \int_0^N ds \delta(\mathbf{r}(s) - \mathbf{q}_i^\sigma) \quad (4)$$

where $v_{m\sigma}$ is the short range interaction between the monomers and the different species of the fluid. It is essential that the solvent quality is slightly different, that is, $v_{m1} \neq v_{m2}$. This amounts to the preferential adsorption of the first solvent onto the polymer when $v_{m1} < v_{m2}$.

The problem is simplified if one introduces a collective density field for the fluid given by

$$\rho^\sigma(\mathbf{q}) = \sum_i \delta(\mathbf{q} - \mathbf{q}_i^\sigma) \quad (5)$$

which satisfies the incompressibility constraint $\rho^1(\mathbf{q}) + \rho^2(\mathbf{q}) = \rho_0$, where $\rho^1(\mathbf{q})$, $\rho^2(\mathbf{q})$ and ρ_0 represent the density of the first solvent, the second solvent and the mean density respectively. The incompressibility condition, as defined above, is not complete since the effects due to the presence of the polymer are not accounted for. If included, they lead to a shift in the critical temperature, which depends of the volume fraction of the polymer, ϕ_p . Since in a dilute solution ϕ_p is very small, we neglect these effects.^{1,12} Using eq 5 and the incompressibility constraint in eq 4, one recovers

$$\mathcal{H}_{pf} = (v_{m1} - v_{m2}) \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k} \cdot \mathbf{r}(s)} \rho(\mathbf{k}) \quad (6)$$

where $\rho(\mathbf{k}) = \int d\mathbf{q} e^{i\mathbf{k} \cdot \mathbf{q}} \rho(\mathbf{q})$. The Hamiltonian for the incompressible fluid, in terms of the density field $\rho(\mathbf{q})$ is given by

$$\mathcal{H}_f[\rho(\mathbf{q})] = \int d^3\mathbf{q} \left\{ \frac{1}{2} (|\nabla \rho(\mathbf{q})|^2 + \tau \rho^2(\mathbf{q})) + \frac{\lambda}{4!} r^4(\mathbf{q}) \right\} \quad (7)$$

where $\tau = \chi_s - \chi$; χ is the Flory Huggins interaction parameter of the fluid given by $2\chi = 2v_{12} - (v_{11} + v_{22})$. χ_s is the mean field spinodal defined as $\chi_s = 1/(\phi_1\phi_2)$, where ϕ_1 and ϕ_2 are the volume fractions of solvents 1 and 2 respectively; λ is a phenomenological parameter. It is to be noted that the above equation can be obtained from eq 3 by introducing the density field given by eq 5 and accounting for the entropy of the fluid.¹³

The average over the solvent degrees of freedom can be carried out using the above Hamiltonian, \mathcal{H}_f . However, the presence of the quartic term in the fluid Hamiltonian presents difficulties.¹⁴ Away from the critical point, $\chi_s \gg \chi$, it is sufficient to account for the Gaussian fluctuations. This amounts to ignoring the quartic term in the above Hamiltonian. Within this approximation, the average over the density field can easily be carried out to give the following effective Hamiltonian:

$$\begin{aligned} \mathcal{H}_{eff} = & \frac{3}{2b^2} \int_0^N ds \left(\frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 + \frac{1}{2} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \int_0^N ds \int_0^N ds' \times \\ & \tilde{v}(\mathbf{k}) e^{i\mathbf{k} \cdot |\mathbf{r}(s) - \mathbf{r}(s')|} + \frac{w}{6} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \int \frac{d^3\mathbf{q}}{(2\pi)^3} \times \\ & \int_0^N ds \int_0^N ds' \int_0^N ds'' e^{i\mathbf{k} \cdot |\mathbf{r}(s) - \mathbf{r}(s')|} e^{i\mathbf{q} \cdot |\mathbf{r}(s') - \mathbf{r}(s'')|} \quad (8) \end{aligned}$$

where

$$\tilde{v}(\mathbf{k}) = v_{mm} - \frac{(v_{m1} - v_{m2})^2}{b^2(k^2 + \xi^{-2})} \quad (9)$$

where $(v_{m1} - v_{m2})^2$ measures the strength of the attractive interactions due to the density fluctuation and ξ is the correlation length of density fluctuations. In writing the above equation we have used¹⁴

$$\langle \rho(\mathbf{k}) \rho(-\mathbf{k}) \rangle = \frac{1}{b^2(k^2 + \xi^{-2})} \quad (10)$$

Equation 8 can be represented as

$$\mathcal{H}_{eff} = \mathcal{H}_0 + \mathcal{H}_2 + \mathcal{H}_3 + \mathcal{H}_4 \quad (11)$$

where the first term represents the entropic interaction, the second and the fourth term represents the two body and three body interactions respectively. The third term represents the interaction term due to critical fluctuations, which is attractive in nature. In the next section, we will use the uniform expansion method to calculate the size of the polymer in a binary critical fluid.

III. The Size of the Polymer

The uniform expansion method of Edwards and Singh is a well-known self-consistent variational approach to study the size and the probability distribution of the end-to-end distance of a chain in a good solvent.^{15,16} The method is based on the uniform expansion of a chain in terms of the expansion in an unknown step length b_1 such that the size of the self-avoiding chain consisting of N segments is governed by Gaussian statistics, $R = N^{1/2}b_1$. The variational parameter b_1 is then determined self-consistently by a perturbative calculation, usually truncated at first order. The details of the method are provided in Appendix A. The governing variational equation can be obtained by writing eq A15 in the following dimensionless form:

$$1 - \alpha^2 + \frac{v_{mm}N^{1/2}}{b^3\alpha^3} - \frac{(\Delta v)N^{3/2}F(\beta)}{b^3\alpha\beta^{5/2}} + \frac{1}{\alpha^6} = 0 \quad (12)$$

where $\alpha = R/R_0$ is the expansion factor; $R_0 = N^{1/2}b$ is the size of the unperturbed chain; $\Delta v = (v_{m1} - v_{m2})^2$; and $\beta = \langle R^2 \rangle / 6\xi^2$ is the dimensionless ratio of the size of the polymer and the correlation length of the density fluctuations of the solvent. It characterizes the proximity to the critical point. In writing eq 12, we have used $w = b^6$. $F(\beta)$ is given by

$$F(\beta) = e^\beta [1 - \phi(\sqrt{\beta})] (1 - 2\beta/3 + \beta^2/6) + 2\sqrt{\beta/\pi} - \beta/3 - 1 \quad (13)$$

where ϕ is the probability integral. The first two terms in eq 12 account for the entropy of the polymer; the third term is due to the excluded volume interactions between the chain segments; the fourth term accounts for the attractive interactions due to the solvent density fluctuations; the last term represents the

three-body interactions. For convenience, we have ignored all the numerical coefficients.

In what follows, we will consider the solution of eq 12 in three different regimes: first, $\beta \gg 1$, representing temperatures far away from the critical temperature T_c , corresponding to the region of weak critical fluctuations; second, $\beta \sim 1$, corresponding to temperatures where the size of the critical fluctuations is comparable to the size of the polymer; third, $\beta \ll 1$, representing temperatures close to the critical temperature T_c .

Far away from the critical point $\xi \rightarrow 0$ and $\beta \gg 1$. In this limit $F(\beta) \rightarrow \beta^{3/2}$ and the above equation is given by

$$1 - \alpha^2 + \frac{\tilde{v}_{\text{mm}} N^{1/2}}{b^3 \alpha^3} - \frac{\Delta \tilde{v} N^{3/2}}{b^3 \alpha \beta} + \frac{1}{\alpha^6} = 0 \quad (14)$$

Since in this limit the fourth term is very small, it can be ignored. The excluded volume effect, as described by the third term, is a perturbation ($\alpha \sim 1$) as long as $\tilde{v} = v_{\text{mm}} N^{1/2} / b^3 < 1$.^{16,17} The perturbation theory breaks down when $\tilde{v} \sim 1$. This happens when N reaches the thermal blob size given by $N_T \sim b^6 / v_{\text{mm}}^2$. For large \tilde{v} , it is expected that $\alpha > 1$. Therefore, the comparison of the second and the third term yields $\alpha = v_{\text{mm}}^{1/5} N^{1/10} b^{-3/5}$ and $R \sim v_{\text{mm}}^{1/5} N^{3/5} b^{2/5}$. So the chain is swollen.

As the temperature of a binary solvent approaches the critical temperature, the solvent density fluctuations grow in size. When the correlation length of the solvent density fluctuation is comparable to the size of the polymer, $\beta \sim 1$, eq 12 is given by

$$1 - \alpha^2 + \frac{v_{\text{mm}} N^{1/2}}{b^3 \alpha^3} - \frac{\Delta v N^{3/2} F(1)}{b^3 \alpha} + \frac{1}{\alpha^6} = 0 \quad (15)$$

where $F(1) = 3\pi e[1 - \phi(1)] + 12\sqrt{\pi} - 8\pi$. In this limit, the size of the polymer is determined by the balance between the repulsive interactions due to excluded volume and the attractive interactions due to critical fluctuations. Since the range of the attractive and repulsive interactions is different, one expects a partial collapse. The latter implies that on length scales smaller than the blob size, R_1 , the chain is unaffected by the attractive interaction due to the critical fluctuations, and retains the self-avoiding statistics of a good solvent. On scales larger than the blob size, the chain begins to feel the attractive interactions due to the critical fluctuations, and the blobs are space filling, that is, $\rho R_1^3 \sim 1$ implying $R \sim (N/N_1)^{1/3} R_1$, where N_1 is the number of monomers in a blob, ρ being the chain density. As discussed above, in a good solvent $\alpha = v_{\text{mm}}^{1/5} N^{1/10} b^{-3/5}$ as long as $\Delta v N^{3/2} / b^3 \alpha < 1$. As $\Delta v N^{3/2} / b^3 \alpha \sim 1$, $\alpha \approx \Delta \tilde{v} N^{3/2} / b^3$. The comparison of the with the latter with the former gives $N_1 \approx \tilde{v}^{1/7} \Delta \tilde{v}^{-5/7} b^{12/7}$ such that for $N \leq N_1$ the chain is a self-avoiding walk of size $R_1 \approx \tilde{v}^{1/5} N_1^{3/5} b^{2/5}$ implying $R_1 \approx \tilde{v}^{2/7} \Delta \tilde{v}^{-3/7} b^{10/7}$. For $N > N_1$, on the other hand, the chain is collapsed and is given by $R \approx (N/N_1)^{1/3} R_1$, where N_1 is the number of monomers in a self-avoiding blob of size R_1 . The substitution of N_1 and R_1 in R gives $R \approx N^{1/3} \tilde{v}^{5/21} \Delta \tilde{v}^{-4/21} b^{6/7}$.

Close to the critical point, $\xi \rightarrow \infty$, implying $\beta \ll 1$. In this regime the Gaussian approximation is not sufficient to account for the density fluctuations close to the critical temperature T_c , and the quartic term in eq 7 needs to be included. However, in the presence of the quartic term the density field, $\rho(q)$, cannot be integrated out. Therefore, at the simplest level of approximation, one can replace the density correlation as given by eq 10 with the one that provides a correct scaling at the critical point.

$$\langle \rho(\mathbf{r}) \rho(0) \rangle = \frac{A}{r^{d-2+\eta}} \quad (16)$$

where A is the amplitude and η is the critical exponent, which is zero in the classical Gaussian theory. The above form of the correlation function when substituted into eq 11 gives the following equation for \mathcal{H}_c :

$$\frac{A \Delta v}{2} \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \int_0^N ds \int_0^N ds' \frac{e^{i\mathbf{k} \cdot (\mathbf{r}(s) - \mathbf{r}(s'))}}{|\mathbf{k}|^{2-\eta}} \quad (17)$$

The above equation when substituted into eqs A1, A2, and A5 gives the following variational equation:

$$1 - \alpha^2 + \frac{v_{\text{mm}} N^{1/2}}{b^3 \alpha^3} - \frac{A \Delta v N^{3/2-\eta/2}}{b^3 \alpha^{1+\eta}} + \frac{1}{\alpha^6} = 0 \quad (18)$$

The relevant blob size close to the critical temperature can be found by comparing the third and the fourth term corresponding to the repulsive and attractive interactions respectively. This gives the critical number of monomers

$$N_2 \approx \left(\frac{v_{\text{mm}}}{A \Delta v} \right)^{2/(2-\eta)} \quad (19)$$

These monomers are present in a Gaussian blob of size $R_2 \approx (v_{\text{mm}} / A \Delta v)^{1/(2-\eta)} b$. The size of the blob and its dependence on the critical exponent η is consistent with the scaling predictions of Brochard and de Gennes¹ and Vilgis et al.⁹

IV. Conclusions

We interpret our results to suggest that the interplay between two length scales—the size of the polymer and the critical length of the solvent density fluctuations—determine the proximity to the critical temperature. Our results provide a clear evidence of a collapse transition when $\langle R^2 \rangle \sim \xi^2$. Since, in this limit, the range of attractive and repulsive interactions is different, the collapse is partial. These results are consistent with experiments^{5–8} and simulations.^{2–4} At the critical temperature, the blob size depends on the non-classical critical exponent η .

The experimental and numerical results show difference in the point. This, however, cannot be captured by the present method since far above the critical point the chain finds itself in a well mixed good solvent. Far below the critical point, on the other hand, the chain lowers its free energy by preferentially adsorbing the solvent whose solvent quality is slightly better than the other.

The recent experiment by Grabowski and Mukhopadhyay provides the first experimental evidence of chain collapse and reexpansion on approach to the critical point of a binary solvent.⁸ On approaching very close to the critical point, they observe a dramatic increase in the size of the polymer to a value which is much higher than the size far away from the critical point. The mean field theory presented in this paper cannot predict such a dramatic increase in the size of the polymer since it only accounts for the Gaussian fluctuations very close to the critical point. A more rigorous treatment accounting for the quartic term in the density field of the solvent is required to explore the region very close to the critical point, and capture some of the effects seen in the experiment.

Appendix A: Uniform Expansion Method

Let us first review some of the main results of the uniform expansion method, which is essentially based on defining a new step length, $b_1 \gg b$, such that the mean square end-to-end

distance of the chain in presence of the excluded volume is Gaussian and is governed by $\langle \mathbf{R}^2 \rangle = Nb_1^2$. This condition amounts to replacing the original Hamiltonian $\mathcal{H}_0 = 3/2b^2 \int_0^N ds \dot{\mathbf{r}}(s)^2$ with the reference Hamiltonian $\mathcal{H}_1 = 3/2b_1^2 \int_0^N ds \dot{\mathbf{r}}(s)^2$. This step can easily be carried out by adding and subtracting \mathcal{H}_1 from \mathcal{H}_0 to give the following expression for the mean square end-to-end distance:

$$\langle \mathbf{R}^2 \rangle = \frac{\int \mathcal{D}[\mathbf{r}(s)] \mathbf{R}^2 \exp[-(\mathcal{H}_1 + (\mathcal{H}_0 - \mathcal{H}_1) + \mathcal{H}_2 - \mathcal{H}_c + \mathcal{H}_3)]}{\int \mathcal{D}[\mathbf{r}(s)] \exp[-(\mathcal{H}_1 + (\mathcal{H}_0 - \mathcal{H}_1) + \mathcal{H}_2 - \mathcal{H}_c + \mathcal{H}_3)]} \quad (\text{A1})$$

where \mathcal{H}_2 and \mathcal{H}_3 are the two and three-body interaction terms respectively and \mathcal{H}_c represents the critical term as defined in eq 8. The idea is to expand $\langle \mathbf{R}^2 \rangle$ in a perturbative series about the reference Hamiltonian \mathcal{H}_1 such that to the first order correction in v_{mm} , $(v_{\text{m1}} - v_{\text{m2}})^2$ and w one obtains the following variational equation for the unknown parameter b_1 :

$$\langle \mathbf{R}^2 \rangle_1 (\mathcal{H}_0 - \mathcal{H}_1 + \mathcal{H}_2 - \mathcal{H}_c + \mathcal{H}_3)_1 - \langle \mathbf{R}^2 (\mathcal{H}_0 - \mathcal{H}_1 + \mathcal{H}_2 - \mathcal{H}_c + \mathcal{H}_3) \rangle_1 = 0 \quad (\text{A2})$$

where $\langle \dots \rangle_1$ denotes the average with respect to the probability distribution

$$\mathcal{A}[\mathbf{r}(s)] \propto \exp \left[-\frac{3}{2b_1^2} \int_0^N ds \dot{\mathbf{r}}(s)^2 \right]$$

The Gaussian nature of the probability distribution makes the evaluation of the above averages simple. The details of the uniform expansion method are well-known.¹⁵ The detailed calculations of the terms containing the entropic interaction, $\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_0 - \mathcal{H}_1 \rangle_1 - \langle \mathbf{R}^2 (\mathcal{H}_0 - \mathcal{H}_1) \rangle_1$ and the two-body interaction, $\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_2 - \mathcal{H}_c \rangle_1 - \langle \mathbf{R}^2 (\mathcal{H}_2 - \mathcal{H}_c) \rangle_1$, are fairly standard and can be found in refs 15 and 16

$$\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_0 - \mathcal{H}_1 \rangle_1 - \langle \mathbf{R}^2 (\mathcal{H}_0 - \mathcal{H}_1) \rangle_1 = Nb_1^4 \left(\frac{1}{b_1^2} - \frac{1}{b^2} \right) \quad (\text{A3})$$

$$\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_2 \rangle_1 - \langle \mathbf{R}^2 (\mathcal{H}_2) \rangle_1 = \frac{2v_{\text{mm}}b_1^4}{9(2\pi)^2} \int_0^\infty dk \int_0^N ds \int_0^s ds' \times (s-s')^2 k^4 e^{-k^2 b_1^2 (s-s')/6} \quad (\text{A4})$$

$$\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_c \rangle_1 - \langle \mathbf{R}^2 (\mathcal{H}_c) \rangle_1 = -\frac{2\Delta v b_1^4}{9(2\pi)^2 b^2} \int_0^\infty dk \int_0^N ds \times \int_0^s ds' (s-s')^2 \frac{k^4}{(k^2 + \xi^{-2})} e^{-k^2 b_1^2 (s-s')/6} \quad (\text{A5})$$

where $\Delta v = (v_{\text{m1}} - v_{\text{m2}})^2$. The uniform expansion method of Edwards and Singh does not include the three body interaction term. In what follows, we present the detailed calculation of the three body interaction term, $\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_3 \rangle_1 - \langle \mathbf{R}^2 (\mathcal{H}_3) \rangle_1$, the calculation of which is very similar to that of the two-body interaction term. Let us first calculate $\langle \mathbf{R}^2 \mathcal{H}_3 \rangle_1$,

$$\langle \mathbf{R}^2 \mathcal{H}_3 \rangle_1 = \frac{w}{6} \int_0^N ds \int_0^N ds' \int_0^N ds'' \langle \mathbf{R}^2 \delta[\mathbf{r}(s) - \mathbf{r}(s')] \delta[\mathbf{r}(s') - \mathbf{r}(s'')] \rangle \quad (\text{A6})$$

The above equation, in terms of the wave vectors \mathbf{k} and \mathbf{q} , can be written as

$$\frac{w}{6} \int_{-\infty}^\infty \frac{d^3 \mathbf{k}}{(2\pi)^3} \int_{-\infty}^\infty \frac{d^3 \mathbf{q}}{(2\pi)^3} \int_0^N ds \int_0^N ds' \int_0^N ds'' \langle \mathbf{R}^2 e^{i\mathbf{k} \cdot [\mathbf{r}(s) - \mathbf{r}(s')] + i\mathbf{q} \cdot [\mathbf{r}(s') - \mathbf{r}(s'')]} \rangle \quad (\text{A7})$$

The average with respect to the probability distribution can be explicitly written as

$$\langle \mathbf{R}^2 \mathcal{H}_3 \rangle_1 = \mathcal{N} \int \mathcal{D}[\mathbf{r}(s_1)] \int_{-\infty}^\infty \frac{d^3 \mathbf{k}}{(2\pi)^3} \int_{-\infty}^\infty \frac{d^3 \mathbf{q}}{(2\pi)^3} \int_0^N ds \times \int_0^s ds' \int_0^{s'} ds'' [(N-s) - \mathbf{r}(s) + (\mathbf{r}(s) - \mathbf{r}(s')) + (\mathbf{r}(s') - \mathbf{r}(s'')) + (\mathbf{r}(s'') - \mathbf{r}(0))]^2 e^{i\mathbf{k} \cdot [\mathbf{r}(s) - \mathbf{r}(s')] + i\mathbf{q} \cdot [\mathbf{r}(s') - \mathbf{r}(s'')]} \times e^{-3/2b_1^2 \left[\int_0^{s''} ds_1 |\dot{\mathbf{r}}(s_1)|^2 + \int_{s''}^{s'} ds_1 |\dot{\mathbf{r}}(s_1)|^2 + \int_{s'}^s ds_1 |\dot{\mathbf{r}}(s_1)|^2 + \int_s^N ds_1 |\dot{\mathbf{r}}(s_1)|^2 \right]} \quad (\text{A8})$$

where

$$\mathcal{N} = \left[\int \mathcal{D}[\mathbf{r}(s)] e^{-3/2b_1^2 \int_0^N ds_1 |\dot{\mathbf{r}}(s_1)|^2} \right]^{-1}$$

In writing the above equation, we have expanded the mean square end-to-end distance and the probability distribution in terms of the internal coordinates. Since the probability distribution is Gaussian, it can easily be seen that all odd powered terms in $\mathbf{r}(s)$ will vanish. The above equation can, therefore, be written in a more compact form as

$$\langle \mathbf{R}^2 \mathcal{H}_3 \rangle_1 = w \int_{-\infty}^\infty \frac{d^3 \mathbf{k}}{(2\pi)^3} \int_{-\infty}^\infty \frac{d^3 \mathbf{q}}{(2\pi)^3} \int_0^N ds \int_0^s ds' \int_0^{s'} ds'' \times \left\langle \left[(\mathbf{r}(N) - \mathbf{r}(s))^2 - \frac{1}{k^2} \frac{\partial^2}{\partial \lambda_1^2} - \frac{1}{q^2} \frac{\partial^2}{\partial \lambda_2^2} + (\mathbf{r}(s'') - \mathbf{r}(0))^2 \right] e^{i\mathbf{k} \cdot [\mathbf{r}(s) - \mathbf{r}(s')] + i\mathbf{q} \cdot [\mathbf{r}(s') - \mathbf{r}(s'')]} \right\rangle_{\lambda_1, \lambda_2=1} \quad (\text{A9})$$

where we have written $(\mathbf{r}(s) - \mathbf{r}(s'))^2 = -1/k^2 \partial^2/\partial \lambda_1^2 e^{i\mathbf{k} \cdot \mathbf{r} \int_{s'}^s ds_1 |\dot{\mathbf{r}}(s_1)|} |_{\lambda_1=1}$ and $(\mathbf{r}(s') - \mathbf{r}(s''))^2 = -1/q^2 \partial^2/\partial \lambda_2^2 e^{i\mathbf{q} \cdot \mathbf{r} \int_{s''}^{s'} ds_1 |\dot{\mathbf{r}}(s_1)|} |_{\lambda_2=1}$. Since all the averages in the above equation are Gaussian, one can easily carry them out using the well-known results of Gaussian averages with zero mean: $\langle (\mathbf{r}(s) - \mathbf{r}(s'))^2 \rangle = |s - s'|b_1^2$ and $\langle e^{-ikx} \rangle = e^{-k^2 \langle x^2 \rangle / 2}$, where x is a Gaussian variable. The resulting equation is

$$\langle \mathbf{R}^2 \mathcal{H}_3 \rangle_1 = w \int_{-\infty}^\infty \frac{d^3 \mathbf{k}}{(2\pi)^3} \int_{-\infty}^\infty \frac{d^3 \mathbf{q}}{(2\pi)^3} \int_0^N ds \int_0^s ds' \times \int_0^{s'} ds'' \left[(N-s)b_1^2 - \frac{1}{k^2} \frac{\partial^2}{\partial \lambda_1^2} - \frac{1}{q^2} \frac{\partial^2}{\partial \lambda_2^2} + s''b_1^2 \right] \times e^{-k^2 \lambda_1^2 (s-s')b_1^2/6} e^{-q^2 \lambda_2^2 (s'-s'')b_1^2/6} |_{\lambda_1, \lambda_2=1} \quad (\text{A10})$$

After simplification, the above equation reduces to

$$\langle \mathbf{R}^2 \mathcal{H}_3 \rangle_1 = w \int_{-\infty}^\infty \frac{d^3 \mathbf{k}}{(2\pi)^3} \int_{-\infty}^\infty \frac{d^3 \mathbf{q}}{(2\pi)^3} \int_0^N ds \int_0^s ds' \times \int_0^{s'} ds'' \left[Nb_1^2 - \frac{(s-s')^2 k^2 b_1^4}{9} - \frac{(s'-s'')^2 q^2 b_1^4}{9} \right] \times e^{-k^2 (s-s')b_1^2/6} e^{-q^2 (s'-s'')b_1^2/6} \quad (\text{A11})$$

Following the same procedure, one can calculate $\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_3 \rangle_1$, which is given by

$$\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_3 \rangle_1 = w \int_{-\infty}^{\infty} \frac{d^3 \mathbf{k}}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{d^3 \mathbf{q}}{(2\pi)^3} \int_0^N ds \int_0^s ds' \times \int_0^{s'} ds'' N b_1^2 e^{-\mathbf{k}^2(s-s')b_1^2/6} e^{-\mathbf{q}^2(s'-s'')b_1^2/6} \quad (\text{A12})$$

which implies that

$$\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_3 \rangle_1 - \langle \mathbf{R}^2 \mathcal{H}_3 \rangle_1 = w \int_{-\infty}^{\infty} \frac{d^3 \mathbf{k}}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{d^3 \mathbf{q}}{(2\pi)^3} \times \int_0^N ds \int_0^s ds' \int_0^{s'} ds'' \left[\frac{(s-s')^2 \mathbf{k}^2 b_1^4}{9} + \frac{(s'-s'')^2 \mathbf{q}^2 b_1^4}{9} \right] \times e^{-\mathbf{k}^2(s-s')b_1^2/6} e^{-\mathbf{q}^2(s'-s'')b_1^2/6} \quad (\text{A13})$$

In the scalar form, the above equation can be rewritten as

$$\langle \mathbf{R}^2 \rangle_1 \langle \mathcal{H}_3 \rangle_1 - \langle \mathbf{R}^2 \mathcal{H}_3 \rangle_1 = \frac{4w b_1^4}{9(2\pi)^4} \int_0^{\infty} dk \int_0^{\infty} dq \times \int_0^N ds \int_0^s ds' \int_0^{s'} ds'' [(s-s')^2 k^4 q^2 + (s'-s'')^2 k^2 q^4] e^{-k^2 b_1^2(s-s')/6} e^{-q^2 b_1^2(s'-s'')/6} \quad (\text{A14})$$

The integration of the last integral is tricky as it diverges as $q \rightarrow \infty$. However, within the mean-field description the divergence can be removed by introducing an upper cutoff for the wave number q . This leads to a nonuniform contraction of a chain, the details of which are discussed in ref 18. The integrations in eqs A4, A5 and A14 can easily be carried out, the results when substituted in eq A2 gives the following variational equation:

$$N b_1^2 \left(1 - \frac{b_1^2}{b^2} \right) + \frac{6^{1/2} v_{\text{mmr}} N^{3/2}}{\pi^{3/2} b_1} - \frac{6^{1/2} (\Delta v) N^{5/2} b_1 F(\beta)}{\pi b^2 \beta^{5/2}} + \left(\frac{3}{\pi} \right)^3 \left[\left(\frac{2}{3} \right)^{3/2} - \frac{\pi^{1/2}}{4} \right] \frac{w N}{b_1^4} = 0 \quad (\text{A15})$$

where $F(\beta) = e^{\beta} [1 - \phi(\sqrt{\beta})] (1 - 2\beta/3 + \beta^2/6) + 2\sqrt{\beta/\pi} - \beta/3 - 1$; ϕ is the probability integral; $\beta = N b_1^2/6\xi^2$ and ξ is the correlation length. The above equation can be written in a dimensionless form by dividing it by $N b_1^2$ and defining $\alpha = b_1/b$. The final form of this variational equation is given by eq 12.

References and Notes

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