Configuration of Semiflexible Polymer Chains in the Nematic Phase

Zheng Yu Chen

Guelph–Waterloo Program for Graduate Work in Physics and Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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ABSTRACT: The mean square projections of the end-to-end separation and radius of gyration along and perpendicular to the nematic director are determined for semiflexible polymer chains at the isotropic–nematic transition. The polymer chains are assumed to obey the Saito–Takahashi–Yunoki distribution for wormlike chains, interacting with each other through an Onsager-type excluded volume interaction, accurate to the second virial approximation.

1. Introduction

Semiflexible polymer chains are usually treated in a wormlike chain model, which is a limiting case of a freely-rotating chain model[1,2] when the bond lengths are taken to zero, or in the continuum Saito–Takahashi–Yunoki (STY) model,[3] in which a functional formulation of the chain configuration is introduced. Both models introduce a persistence length for semiflexible polymer chains; the spatial configuration of such chains depends on the total chain length and the persistence length. It is customary to use the mean-square end-to-end separation, $\langle R^2 \rangle$, and radius of gyration, $\langle R_g^2 \rangle$, to measure the geometrical size of a polymer chain.[4] The Kratky–Porod results,[5] $\langle R^2 \rangle_{KP}$ and $\langle R_g^2 \rangle_{KP}$, deduced from the above-mentioned models, give a useful interpolation between the asymptotic rigid-rod and flexible-chain behavior of those quantities.

The existence of a repulsive interaction between two segments of the polymer chains produces interesting physical phenomena. The effects of the repulsive interaction can be best described by a simple approximation, called the excluded volume interaction, which does not allow two segments to occupy the same volume.[6] Numerical simulations performed for systems that consist of rigid, anisotropic-shaped molecules clearly demonstrate that an isotropic–nematic phase transition exists at a sufficiently high density or interaction strength, the latter phase being an orientationally ordered state of molecules.[7–13] Mean-field theories, which incorporate the Onsager-type interaction with statistical models for semiflexible polymer chains, have shown that semiflexible polymer chains exhibit a similar phase transition.[14–17] These studies have provided us with a basis for further generalization of the Onsager theory to include more realistic features, in order to understand the characteristics of polymer liquid crystals.

The configuration of a polymer chain in a nematic phase is an interesting problem. Since an orientational order is developed, the overall shape of a nematic polymer chain is elongated along the nematic director, which in this paper is chosen to be the z-direction. Different configuration measures, $\langle R_\parallel^2 \rangle$, $\langle R_\perp^2 \rangle$, $\langle R_{g\parallel}^2 \rangle$, and $\langle R_{g\perp}^2 \rangle$, must be introduced to characterize the extension of the polymer chain along the nematic director and the size of the projection of the polymer chain on the plane perpendicular to the nematic director.

A particular important problem is to calculate these configuration measures for a polymer chain in the nematic state *at* the isotropic–nematic phase transition. The phase transition boundary is a relatively well studied reference point where theoretical results on many other physical properties, such as the scaled transition density and order parameter, are available;[14–16] therefore it is desirable to study the configuration measures at the same phase transition boundary. In addition, obtaining a good estimate of the radius of gyration is useful for locating the transition in light scattering experiments. Khokhlov and Semenov were the first to estimate $\langle R_\parallel^2 \rangle$ for flexible chains.[18] Later, Vroege and Odijk determined $\langle R_\parallel^2 \rangle$ for the same limit much more accurately.[15] In this paper, all four quantities mentioned above are determined at the isotropic–nematic transition for polymers of arbitrary flexibility. The current work is an extension of the previous one on the determination of the isotropic–nematic transition point.[16,17]

There are a number of other complications that are not considered here. When the orientational order is further deepened at high densities, the overall shape of a polymer chain crossed over from weakly anisotropic to highly anisotropic.[18] Also, it would be of more practical value to study physical quantities including the configuration measures for a more realistic model that goes beyond the second virial coefficient approximation.[19–21] The model studied in this paper is valid as long as the persistence length is much greater than the diameter (or thickness) of a polymer chain.

The mean-field theory presented in ref 16 gives a detailed angular dependence of the nematic mean field; this nematic mean field represents the mean effect created by the neighboring chains on the chain under consideration in the nematic phase. The question is to find the quantities $\langle R_\parallel^2 \rangle$ and $\langle R_\perp^2 \rangle$ of a STY chain in the presence of a nematic mean field. Determining the statistical properties of a polymer chain usually requires calculating the end-to-end Green function, which can become a difficult task to perform because of the complexity of the algebra involved.[3] However, for the mean square end-to-end separation, one can use the fluctuation–dissipation theorem by invoking an external perturbation field; this method, first introduced by Khokhlov and Semenov[18] and later by Vroege and Odijk[15] simplifies the procedure of finding $\langle R_\parallel^2 \rangle$ and $\langle R_\perp^2 \rangle$. A complete derivation based on this method is given in Appendices I and II.

This paper is organized as follows. In section 2, the basic formalism is introduced. The function–integral model for semiflexible polymer chains can be transformed into an equivalent form of a partial differential equation in an external field. We see that the resulting equation

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must be solved numerically to determine the configuration measures. In section 3, we deduce the Kratky–Porod results for polymers in the isotropic phase as a useful verification of the procedure used in this paper. The results for polymers in the nematic phase are presented in section 4.

2. Basic Formalism

In this paper, the statistical probability of the semiflexible polymer chains is assumed to obey[16,22]

$$P[\vec{n}(t)] \propto \exp\left\{-\frac{D-1}{8\alpha}\int_0^1\left[\frac{\mathrm{d}\vec{n}(t)}{\mathrm{d}t}\right]^2 \mathrm{d}t - \int_0^1 w[\vec{n}(t)]\,\mathrm{d}t\right\} \tag{2.1}$$

where the polymer chain is described as a continuous space curve specified by the tangent unit vector $\vec{n}(t)$, $0 \le t \le 1$, of the curve. The contour variable t specifies the contour coordinate along the chain. As in the previous paper, a flexibility constant,

$$\alpha = L/l \tag{2.2}$$

is used here, where L denotes the total contour length and l the persistence length. In eq 2.1, $D = 3$ is the dimensionality of the system. The information on the influence of other chains in the system is contained in the mean field $w(\vec{n})$, which has already been determined earlier.[16] Furthermore, the unit vector $\vec{n}(t)$ can be alternatively specified by the solid angle $\Omega(t)$; in this paper, these two notations, $\Omega(t)$ and $\vec{n}(t)$, are used interchangeably.

The relationship between the end-to-end separation and the tangent unit vector $\vec{n}(t)$ is given by

$$\vec{R} = L\int_0^1 \mathrm{d}t\, \vec{n}(t) \tag{2.3}$$

To characterize the measure of the size of a polymer chain along the direction of the nematic director $\hat{z}$, we define the mean square of the projection of the end-to-end separation to the z-axis to be

$$\langle R_\parallel^2\rangle = L^2\int_0^1 \mathrm{d}t_1\int_0^1 \mathrm{d}t_2\, \langle n_z(t_1)\, n_z(t_2)\rangle \tag{2.4}$$

Similarly, to characterize the size of the chain perpendicular to the nematic director, we define

$$\langle R_\perp^2\rangle = L^2\int_0^1 \mathrm{d}t_1\int_0^1 \mathrm{d}t_2\, \langle n_x(t_1)\, n_x(t_2) + n_y(t_1) n_y(t_2)\rangle \tag{2.5}$$

As discussed in Appendix I, the fluctuation–dissipation theorem states that these averages can be expressed in terms of susceptibilities associated with the external orientational fields along the z- and x-directions, $\epsilon_\parallel$ and $\epsilon_\perp$, respectively:

$$\langle R_\parallel^2\rangle = L^2 \frac{\partial S_\parallel'}{\partial \epsilon_\parallel}\bigg|_{\epsilon_\parallel=0} \tag{2.6}$$

and

$$\langle R_\perp^2\rangle = 2L^2 \frac{\partial S_\perp'}{\partial \epsilon_\perp}\bigg|_{\epsilon_\perp=0} \tag{2.7}$$

where $S_\parallel'$ and $S_\perp'$ are the averages

$$S_\parallel' = \langle \cos\theta\rangle' \tag{2.8}$$

$$S_\perp' = \langle \sin\theta\cos\phi\rangle' \tag{2.9}$$

The prime superscripts in these expressions represent the statistical average with respect to the probability of the form

$$P'[\Omega(t)] = P[\Omega(t)]\exp\{\epsilon\int_0^1 g[\Omega(t)]\,\mathrm{d}t\} \tag{2.10}$$

which includes the effect of the external orientational field ϵ in addition to $w[\Omega(t)]$. Here, $g(\Omega) = \cos\theta$, $\epsilon = \epsilon_\parallel$, and $g(\Omega) = \sin\theta\cos\phi$, $\epsilon = \epsilon_\perp$, for eqs 2.6 and 2.7, respectively. This rather elegant calculation scheme of avoiding a direct treatment of the end-to-end Green function, which would be very difficult to realize even numerically, was mentioned by Khokhlov and Semenov in the past.[18] Vroege and Odijk gave a complete derivation.[15]

Therefore, the task of finding the averages $\langle R_\parallel^2\rangle$ and $\langle R_\perp^2\rangle$ becomes that of calculating the expectation values $S_\parallel$ and $S_\perp$ to the first order in ϵ, which can be done perturbatively as discussed in Appendix II. The procedure can be summarized as follows. The susceptibilities are obtained by

$$\frac{\partial S_\parallel'}{\partial \epsilon_\parallel}\bigg|_{\epsilon_\parallel=0} = \int \cos\theta\, f_1(\Omega)\,\mathrm{d}\Omega \tag{2.11}$$

and

$$\frac{\partial S_\perp'}{\partial \epsilon_\perp}\bigg|_{\epsilon_\perp=0} = \int \sin\theta\cos\phi\, f_1(\Omega)\,\mathrm{d}\Omega \tag{2.12}$$

The function $f_1(\Omega)$ is the first-order correction to the distribution function, $f'(\Omega) = f(\Omega) + \epsilon f_1(\Omega)$, which can be determined by

$$f_1 = \frac{2}{Q}\int_0^1 \mathrm{d}t\, q_1(t,\Omega)\, q(1-t,\theta) \tag{2.13}$$

with q_1 satisfying

$$\frac{\partial q_1}{\partial t} = [\alpha\nabla_\Omega^2 - w(\theta)]q_1 + g(\Omega)\, q(t,\theta) \tag{2.14}$$

Note that in these equations the mean field $w(\theta)$, partition functions $q(t,\theta)$, and Q are the unperturbed quantities associated with the probability given in eq 2.1, which can be calculated through the method described in ref 16.

Equation 2.14 has two special analytic solutions, corresponding to the cases of a system in an isotropic state (see section 3) and a system consisting of rodlike molecules (see section 4A). Otherwise this equation must be solved numerically.

Before we go any further into details, we note a technical point that is used in the calculation. For the existence of an external field in the nematic direction [i.e., when $\epsilon = \epsilon_\parallel$ and $g(\Omega) = \cos\theta$], one can show that the symmetry property

$$q_1(t,\theta) = -q_1(t,\pi-\theta) \tag{2.15}$$

holds. Equation 2.14 can be written as

$$\frac{\partial q_1}{\partial t} - [\alpha\nabla_\parallel^2 - w(\theta)]q_1 = \cos\theta\, q(t,\theta) \tag{2.16}$$

where

$$\nabla_{\parallel}^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \qquad (2.17)$$

For the existence of an external field in the $\hat{x}$-direction [i.e., when $\epsilon = \epsilon_\perp$ and $g(\Omega) = \sin\theta\cos\phi$], one can show that function $\tilde{q}_1(t,\theta) \equiv q_1(t,\Omega)/(\sin\theta\cos\phi)$ depends on θ only and obeys the symmetry property

$$\tilde{q}_1(t,\theta) = \tilde{q}_1(t,\pi-\theta) \qquad (2.18)$$

The quantity $\tilde{q}_1(t,\theta)$ satisfies

$$\frac{\partial\tilde{q}_1}{\partial t} - [\alpha\nabla_\perp^2 - w(\theta)]\tilde{q}_1 = q(t,\theta) \qquad (2.19)$$

where

$$\nabla_\perp^2 = \frac{3\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} - 2 \qquad (2.20)$$

It is equations 2.16 and 2.19 that are solved numerically in sections 4B and 4C of this paper. The symmetry properties in eqs 2.15 and 2.18 can be taken advantage of, so that $q_1(t,\theta)$ and $\tilde{q}_1(t,\theta)$ are calculated in the range $\theta = [0,\pi/2]$ only.

So far, we have discussed the basic formalism for calculating the mean square end-to-end separation. The mean square radius of gyration can be written as[4]

$$\langle R_g^2\rangle = \int_0^1 \mathrm{d}t_1 \int_0^1 \mathrm{d}t_2\, \langle(\vec{R}(t_1) - \vec{R}(t_2))^2\rangle \qquad (2.21)$$

where $\langle(\vec{R}(t_1) - \vec{R}(t_2))^2\rangle$ is the mean square end-to-end separation of two points with path coordinates, t_1 and t_2 of the polymer chain, which is a function of $t_1 - t_2$ (the length of that segment) only. Introducing a new variable $s = t_1 - t_2$ and interchanging the order of integration, we can rewrite eq 2.21 as[1]

$$\langle R_g^2\rangle = \int_0^1 \mathrm{d}s\,(1-s)\langle R^2\rangle|_{L\to Ls} \qquad (2.22)$$

Here, the variable L must be replaced by Ls in the last part of eq 2.22. We shall use eq 2.22 to evaluate $\langle R_g^2\rangle$.

3. Kratky-Porod Result

The procedure described above should produce a mean square end-to-end separation in agreement with the Kratky–Porod result in the absence of a nematic mean field $w(\Omega)$. This expectation is discussed in this section. Note for an unperturbed isotropic phase, $q(t,\Omega) = 1$ and $Q = 4\pi$.

Let us first consider the case of $\langle R_\parallel^2\rangle$. Equation 2.14 becomes

$$\frac{\partial q_1}{\partial t} = \alpha\nabla^2 q_1 + \cos\theta \qquad (3.1)$$

with an initial condition $q_1(t = 0,\Omega) = 0$. The solution to eq 3.1 can be easily found,

$$q_1(t,\theta) = \frac{1}{2\alpha}[1 - \exp(-2\alpha t)]\, P_1(\cos\theta) \qquad (3.2)$$

where $P_1(x)$ is the first-rank Legendre polynomial. Using this solution in eqs 2.13 and 2.11 gives rise to

$$\left.\frac{\partial S_\parallel}{\partial\epsilon_\parallel}\right|_{\epsilon_\parallel=0} = \frac{1}{3\alpha}\left[1 + \frac{1}{2\alpha}(\mathrm{e}^{-2\alpha} - 1)\right] \qquad (3.3)$$

Since for an isotropic phase, $2\langle R_\parallel^2\rangle = \langle R_\perp^2\rangle$, it can then be concluded that

$$\langle R^2\rangle_{\mathrm{KP}} = 3\langle R_\parallel^2\rangle = \frac{L^2}{\alpha}\left[1 + \frac{1}{2\alpha}(\mathrm{e}^{-2\alpha} - 1)\right] \qquad (3.4)$$

which is the Kratky–Porod result for the end-to-end separation of a wormlike chain.[5] STY obtained the same result using the method of finding the end-to-end Green function.[3] It is worth mentioning that eq 3.4 gives the valid limiting behavior $\langle R^2\rangle_{\mathrm{KP}}(\alpha = 0) = L^2$ and $\langle R^2\rangle_{\mathrm{KP}}(\alpha\gg 1) = L^2/\alpha$

Equation 3.4 can also be obtained through the evaluation of $\langle R_\perp^2\rangle$, as prescribed in eq 2.7. One needs to solve

$$\frac{\partial q_1}{\partial t} = \alpha\nabla^2 q_1 + \sin\theta\cos\phi \qquad (3.5)$$

with an initial condition $q_1(t = 0,\Omega) = 0$. The solution to eq 3.5 is

$$q_1(t,\Omega) = \frac{1}{2\alpha}[1 - \exp(-2\alpha t)]\sin\theta\cos\phi \qquad (3.6)$$

We can then show that the Kratky–Porod expression in eq 3.4 is recovered, using eqs 2.13 and 2.12.

The Kratky–Porod result for the mean square radius of gyration can be simply evaluated through eq 2.22. Consequently,[1,23]

$$\langle R_g^2\rangle_{\mathrm{KP}} = \frac{L^2}{\alpha}\left[\frac{1}{6} - \frac{1}{4\alpha} + \frac{1}{4\alpha^2} + \frac{1}{8\alpha^3}(\mathrm{e}^{-2\alpha} - 1)\right] \qquad (3.7)$$

Equation 2.23 has the limiting behavior $\langle R_g^2\rangle_{\mathrm{KP}} = L^2/12$ for $\alpha = 0$ and $\langle R_g^2\rangle_{\mathrm{KP}} = L^2/6\alpha$ for $\alpha \gg 1$.

4. Nematic State at the Isotropic–Nematic Transition

A. Rigid Rods. Onsager studied the isotropic–nematic transition of a system of rigid rods using a trial-function approach.[6] Subsequent studies have shown that at the isotropic–nematic transition, the orientational order parameter $S_2 \equiv \langle P_2(\cos\theta)\rangle = 0.7922 \pm 0.0001$.[16,24–26] It is straightforward to show from the basic definition of the end-to-end separation that

$$\langle R_\parallel^2\rangle = \langle L^2\cos^2\theta\rangle = L^2\frac{2S_2 + 1}{3} \qquad (4.1a)$$

and

$$\langle R_\perp^2\rangle = \langle L^2\sin^2\theta\cos^2\phi\rangle = 2L^2\frac{1 - S_2}{3} \qquad (4.1b)$$

Also, we have

$$\langle R_{g\parallel}^2\rangle = \left\langle\frac{L^2}{12}\cos^2\theta\right\rangle = L^2\frac{2S_2 + 1}{36} \qquad (4.2a)$$

and

$$\langle R_{g\perp}^2\rangle = \left\langle\frac{L^2}{6}\sin^2\theta\cos^2\phi\right\rangle = L^2\frac{1 - S_2}{18} \qquad (4.2b)$$

These results should be recovered from the procedure of finding susceptibilities described above. In the limit of rigid rods ($\alpha = 0$), eq II.2 can be solved exactly

$$q'(t,\Omega) = \mathrm{e}^{-[w(\theta) - \epsilon g(\Omega)]t} \qquad (4.3)$$

Expanding eq 4.3 to the first order in ϵ enables us to identify

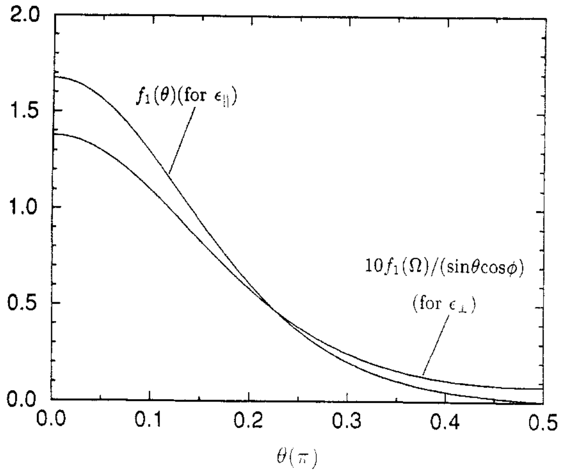

Figure 1. Correction to the distribution function vs the polar angle θ for flexible chains ($\alpha \gg 1$) at the isotropic–nematic transition. For $\epsilon = \epsilon_\parallel$, we note that $f_1(\theta)$ satisfies the symmetry property $f_1(\theta) = -f_1(\pi-\theta)$; for $\epsilon = \epsilon_\perp$, we plot here $\bar{f}_1(\theta) \equiv f_1(\Omega)/(\sin\theta\cos\phi)$, which satisfies the symmetry property $\bar{f}_1(\theta) = \bar{f}_1(\pi-\theta)$. The scale for $\bar{f}_1$ is enlarged 10 times in the figure.

q_1:

$$q'(t,\Omega) = q(t,\theta)[1 + \epsilon t g(\Omega)] + \mathcal{O}(\epsilon^2) \qquad (4.4)$$

Substituting $q_1(t,\theta) = tq(t,\theta)\ g(\Omega)$ into eq 2.13 and integrating over t, we have

$$f_1(\Omega) = f(\theta)\, g(\Omega) \qquad (4.5)$$

Here, $q(t,\theta)$ and $f(\theta)$ are the unperturbed quantities related to each other by $q(t,\theta) = [Qf(\theta)]^t$.[16] We then obtain from eqs 2.11 and 2.12 the same results for $\langle R_\perp^2\rangle$ and $\langle R_\perp^2\rangle$ in eqs 4.1 and 4.2.

B. Flexible Chains. Another interesting asymptotic limit is the flexible-chain limit, i.e., $\alpha \gg 1$. In contrast to that of the rigid-rod molecules, the $\partial q_1/\partial t$ term in eqs 2.16 and 2.19 can be dropped[15,16] because all segments in the polymer chain are equally weighted. Denoting $q_1(t,\Omega)$ by $q_1^\infty(\Omega)/\alpha$ and $q(t,\theta)$ by $q^\infty(\theta)$, which are now functions of Ω only, we need to solve eqs 2.16 and 2.19 for $q_1^\infty(\Omega)$ numerically. In our previous work,[16] we have developed a numerical procedure that can be used to determine $w(\theta)/\alpha$ and $q^\infty(\theta)$ at discretized points θ_j, where $\theta_j (j=1,2,...,N_\theta)$ are equally spaced points between $\theta = 0$ and $\theta = \pi/2$. Taking the same method of discretizing the variables and writing the derivative in eq 4.6 in the form of a finite difference, we can represent the operator $-[\nabla_k^2 - w(\theta)/\alpha]$ on the left-hand side of eqs 2.16 and 2.19 by an $N_\theta \times N_\theta$ matrix, where $k = \parallel$ and $\perp$ for eqs 2.16 and 2.19, respectively. Inverting this matrix gives the desirable partition function $q_1^\infty(\Omega)$ for $\alpha \gg 1$. Figure 1 illustrates two curves for the correction to the distribution function, $f_1(\Omega)$, as functions of θ, corresponding to the situations when $\epsilon_\parallel$ and $\epsilon_\perp$ are present separately. Owing to the symmetry properties in eqs. 2.15 and 2.18, here we plot these functions in the region $[0,\pi/2]$ only. Note that for the case of $\epsilon = \epsilon_\perp$, we plot the rescaled $\bar{f}_1 = f_1/(\sin\theta\cos\phi)$.

Having determined $f_1(\Omega)$, we can use eqs 2.11–2.13 to find

$$\langle R_\parallel^2\rangle = L^2(3.255 \pm 0.002)/\alpha \qquad (4.6)$$

$$\langle R_\perp^2\rangle = L^2(0.1630 \pm 0.0001)/\alpha \qquad (4.7)$$

Here, we have adopted $N_\theta = 400$. The errors in eq 4.6 are estimated by comparing with the results from another run when $N_\theta = 200$ is used. Equation 4.6 can be compared with the values $\langle R_\parallel^2\rangle \approx 4L^2/\alpha$ estimated by Khokhlov and Semenov[18] and $\langle R_\parallel^2\rangle = 3.253L^2/\alpha$ calculated by Vroege and Odijk.[15]

Through eq 2.23, we further obtain

$$\langle R_{g\parallel}^2\rangle = L^2(0.5425 \pm 0.0004)/\alpha \qquad (4.8)$$

$$\langle R_{g\perp}^2\rangle = L^2(0.02717 \pm 0.00002)/\alpha \qquad (4.9)$$

C. Semiflexible Chains. Most liquid-crystalline polymers have a certain finite flexibility. They cannot be described by rigid rods or flexible chains. Therefore it is desirable to study the system for an arbitrary α. Since we expect that the partition function $q_1(t,\Omega)$ depends on the segmental length tL in general, eq 2.14 must be solved for q_1 at an arbitrary α. In ref 16, a numerical analysis was presented to solve the nonlinear integrodifferential equation for $q(t,\theta)$; in order to implement a Crank–Nicholson algorithm, we discretized the interval [0,1] for variable t into $n_t = 400$ equally spaced segments and the interval $[0,\pi]$ for variable θ into $n_\theta = 200$ equally spaced segments; at each of the $(n_t + 1) \times (n_\theta + 1)$ grid points, the value of $q(t,\theta)$ is found. We use here the same way of discretizing the variable space and again use the Crank–Nicholson algorithm to determine $q_1(t,\theta)$ and $\bar{q}_1(t,\theta)$ in eqs 2.16 and 2.17. The results are used to calculate $\langle R_\perp^2\rangle$ and $\langle R_\perp^2\rangle$.

We use eq 2.22 to calculate the mean square radius of gyration from the numerical results obtained here. The integration in eq 2.22 is carried out by implementing a Simpsons algorithm.

D. Discussion. Figures 2a and 3a illustrate nematic $\langle R_\parallel^2\rangle$, $\langle R_\perp^2\rangle$, $\langle R_{g\parallel}^2\rangle$ and $\langle R_{g\perp}^2\rangle$ as functions of α at the isotropic–nematic phase transition. Also the corresponding Kratky–Porod functions, which represent the behavior of an isotropic polymer chain with the same flexibility, are plotted for comparison. Near the asymptotic $\alpha = 0$ limit, the polymer chains obey a rodlike behavior, which is indicated by the slowly decreasing $\langle R_\parallel^2\rangle_{\mathrm{KP}}$ and $\langle R_{g\parallel}^2\rangle_{\mathrm{KP}}$. When α starts to increase, the polymer chains become weakly flexible, which results in a decreasing order parameter S_2 as discussed in ref 15. Correspondingly, $\langle R_\parallel^2\rangle$ and $\langle R_{g\parallel}^2\rangle$ decrease and $\langle R_\perp^2\rangle$ and $\langle R_{g\perp}^2\rangle$ increase, as can be roughly estimated by using eqs 4.1 and 4.2. Note that compared to the Kratky–Porod curve, the rate of decreasing for $\langle R_\parallel^2\rangle$ is somewhat faster, which indicates that the decreasing in $\langle R_\parallel^2\rangle$ is caused mainly by the softening of the anisotropy.

For an isotropic polymer chain, the ratios $\langle R_\parallel^2\rangle/\langle R_\perp^2\rangle$ and $\langle R_{g\parallel}^2\rangle/\langle R_{g\perp}^2\rangle$ should have a value of $^2/_3$. We also plot these ratios in Figures 2b and 3b for the nematic polymer chains at the phase transition. These figures can also be used to explain the behavior near $\alpha = 0$ discussed above.

Near the flexible limit $\alpha \gg 1$, an increasing α would require a higher phase transition density. By studying the properties of the phase transition boundary, we can show that the orientational order increases weakly when α increases near this limit. This behavior is characterized through a weakly increasing S_2 (see ref 15) and $\langle R_{g\parallel}^2\rangle/\langle R_{g\perp}^2\rangle$ in Figure 3b.

The minima in $\langle R_\parallel^2\rangle/\langle R_\perp^2\rangle$ and $\langle R_{g\parallel}^2\rangle/\langle R_{g\perp}^2\rangle$ and the maxima in $\langle R_\perp^2\rangle$ and $\langle R_{g\perp}^2\rangle$ signal the crossover of the polymer chains from rodlike to flexible-like behavior. These extremes occurs close to the value of α where the order parameter shows a minimum.[16]

The numerical results in Figure 2 can be represented to a good accuracy by an empirical equation

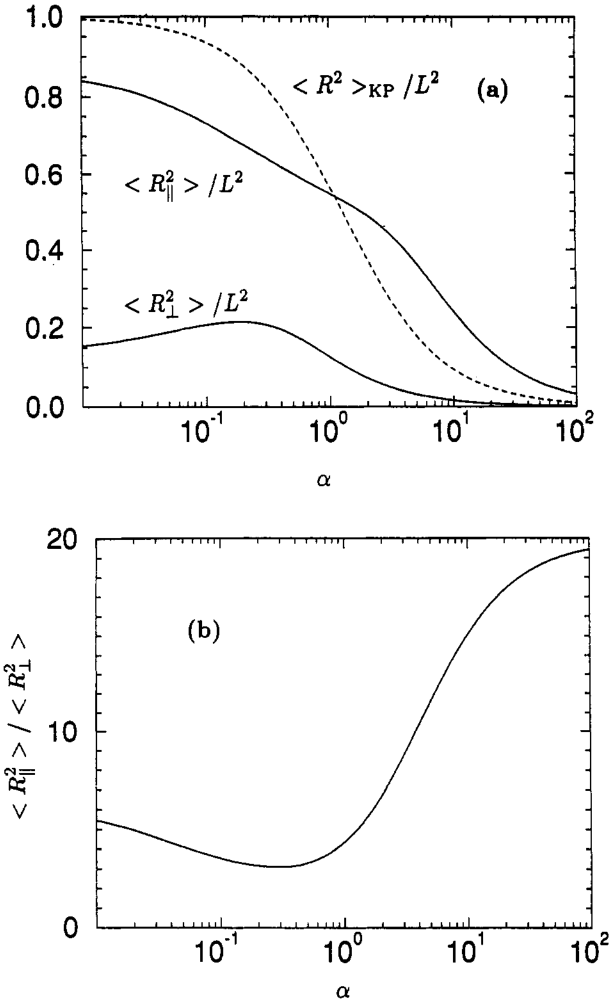

Figure 2. (a) Mean square of the projection of the end-to-end separation along and perpendicular to the nematic director, $\langle R_\parallel^2\rangle$ and $\langle R_\perp^2\rangle$, as a function of the flexibility of polymer chains, α, in the nematic phase at the isotropic–nematic phase transition. Also we plot here the Kratky–Porod function for an isotropic polymer chain. The asymptotic limits are $\langle R_\parallel^2\rangle(\alpha=0) = 0.8615L^2$, $\langle R_\parallel^2\rangle(\alpha\gg1) = 3.255L^2/\alpha$, $\langle R_\perp^2\rangle(\alpha=0) = 0.1385L^2$, and $\langle R_\perp^2\rangle(\alpha\gg1) = 0.163L^2/\alpha$. (b) Ratio $\langle R_\parallel^2\rangle/\langle R_\perp^2\rangle$ vs α at the isotropic–nematic phase transition. This ratio represents the anisotropy of the overall shape of a nematic polymer chain.

$$\langle R_k^2\rangle/\langle R^2\rangle_{KP} = \sum_{i=0}^{3} a_i\alpha^i/(1 + \sum_{i=1}^{3} b_i\alpha^i) \qquad (4.10)$$

The values for coefficients a_i and b_i, specified in Table 1, are obtained by fitting the above equation to numerical results, subject to the $\alpha = 0$ and $\alpha = \infty$ limiting behavior determined in sections 4A and 4B.

5. Summary

This paper, together with other recent publications, is devoted to understanding the effects of repulsive interactions between liquid-crystalline polymers on the properties of the isotropic–nematic phase transition. Using a statistical model that incorporates the STY description for semiflexible polymers with the Onsager-type excluded volume interaction, we are able to determine the orientational distribution of the nematic phase, phase transition density,[16,17] interfacial profile of the isotropic–nematic interface of a rigid-rod system,[27,28] and mean square end-to-end separation of polymer chains in the nematic phase.

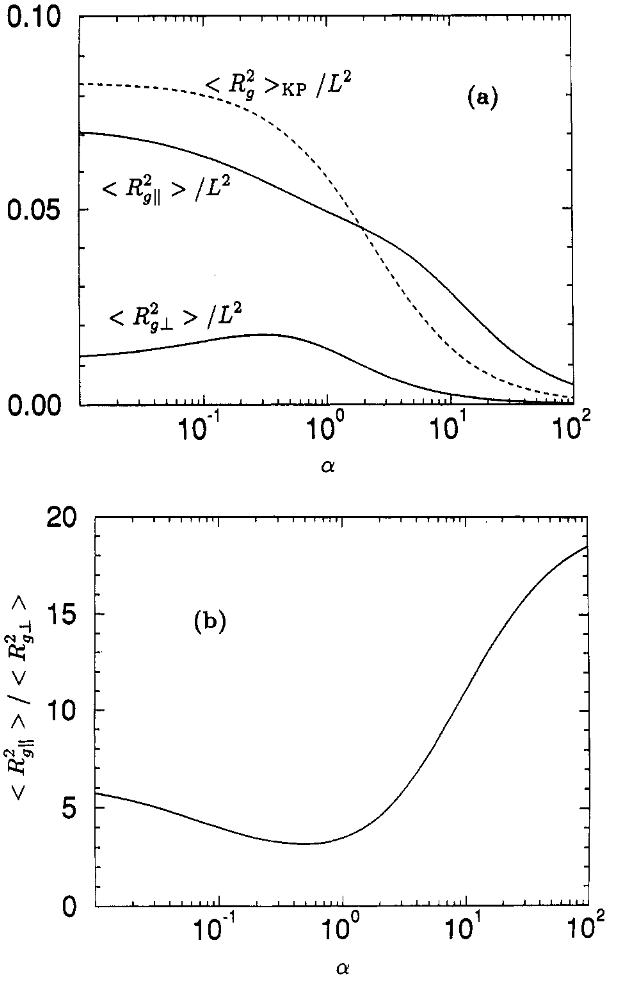

Figure 3. (a) Mean square of the projection of the radius of gyration along and perpendicular to the nematic director, $\langle R_{g\parallel}^2\rangle$ and $\langle R_{g\perp}^2\rangle$, as a function of the flexibility of polymer chains, α, in the nematic phase at the isotropic–nematic phase transition. Also we plot here the Kratky–Porod function for an isotropic polymer chain. The asymptotic limits are $\langle R_{g\parallel}^2\rangle(\alpha=0) = 0.07179L^2$, $\langle R_{g\parallel}^2\rangle(\alpha\gg1) = 0.5425L^2/\alpha$, $\langle R_{g\perp}^2\rangle(\alpha=0) = 0.01154L^2$, and $\langle R_{g\perp}^2\rangle(\alpha\gg1) = 0.02717L^2/\alpha$. (b) Ratio $\langle R_{g\parallel}^2\rangle/\langle R_{g\perp}^2\rangle$ vs α at the isotropic–nematic phase transition. This ratio represents the anisotropy of the overall shape of a nematic polymer chain.

Table 1. Constants in Equation 4.10

k	a_0	a_1	a_2	a_3	b_1	b_2	b_3
$\parallel$	0.86147	6.9388	4.0988	2.7817	10.090	3.2581	0.8546
$\perp$	0.13853	3.8258	3.2220	5.7011	14.143	7.8810	34.976

The current work is based on an approximation which is valid to the accuracy of the second virial coefficient only. The equation of state can be improved by introducing various approximations for liquid-crystalline polymers at higher concentrations.[19-21] Since in those models, orientational and translational degrees of freedom are decoupled, it is obscure how these approximations can be generalized to determine the interfacial properties. A generalization of the current calculation of the mean square end-to-end separation to deal with more realistic systems also needs more study.

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Appendix I. Fluctuation–Dissipation Theorem

In this appendix, a derivation of the fluctuation–dissipation theorem that leads to eqs 2.6–2.9 is outlined.[15,18] To do so, a statistical probability

$$P'[\Omega(t)] = P[\Omega(t)] \exp\{\epsilon \int_0^1 g[\Omega(t)]\, \mathrm{d}t\} \qquad \text{(I.1)}$$

can be introduced, where $g(\Omega)$ is the physical quantity for which the desirable correlation property is considered. The partition function of (I.1) is thereby denoted as

$$Q' = \int D[\Omega(t)]\, P'[\Omega(t)] \qquad \text{(I.2)}$$

In eq I.2, as in the rest of this appendix, a prime superscript denotes the statistical average under probability (I.1). The mean value of $g(\Omega)$ can be written as

$$\langle g(\Omega)\rangle' = \int_0^1 \mathrm{d}s\, \langle g[\Omega(s)]\rangle' = \frac{\partial \ln Q'}{\partial \epsilon} \qquad \text{(I.3)}$$

An alternative method is to use the notion of the chain-averaged distribution function $f'(\Omega)$ for the average in (I.3):

$$\langle g(\Omega)\rangle' = \int \mathrm{d}\Omega\, g(\Omega)\, f'(\Omega) \qquad \text{(I.4)}$$

From (I.3), one can write the susceptibility due to an external field ϵ as

$$\left.\frac{\partial\langle g(\Omega)\rangle'}{\partial \epsilon}\right|_{\epsilon=0} = \left.\frac{\partial^2 \ln Q'}{\partial \epsilon^2}\right|_{\epsilon=0} = \int_0^1 \mathrm{d}s_1\, \mathrm{d}s_2\, \langle g[\Omega(s_1)]\, g[\Omega(s_2)]\rangle - \langle g(\Omega)\rangle^2 \qquad \text{(I.5)}$$

Letting $g(\Omega) = u_z = \cos\theta$ and $\epsilon = \epsilon_\parallel$ yields

$$\left.\frac{\partial\langle \cos\theta\rangle'}{\partial \epsilon_\parallel}\right|_{\epsilon_\parallel=0} = \int_0^1 \mathrm{d}s_1\, \mathrm{d}s_2\, \langle u_z(s_1)\, u_z(s_2)\rangle \qquad \text{(I.6)}$$

The right-hand side of eq I.6 can be identified with $\langle R_\parallel{}^2\rangle/L^2$ in eq 2.4, which gives eq 2.6 in section 2.

Letting $g(\Omega) = u_x = \sin\theta\cos\phi$ and $\epsilon = \epsilon_\perp$ yields

$$\left.\frac{\partial\langle \sin\theta\cos\phi\rangle'}{\partial \epsilon_\perp}\right|_{\epsilon_\perp=0} = \int_0^1 \mathrm{d}s_1\, \mathrm{d}s_2\, \langle u_x(s_1)\, u_x(s_2)\rangle \qquad \text{(I.7)}$$

The right-hand side of eq I.7 can be identified with $\langle R_\perp{}^2\rangle/2L^2$ in eq 2.5, which gives eq 2.7 in section 2. Here, a rotational symmetry of the distribution function around the nematic director is assumed.

Appendix II. Perturbation Theory

In this section, a first-order perturbation theory is developed to calculate the desired average $\partial\langle g(\Omega)\rangle'/\partial\epsilon|_{\epsilon=0}$ in eq I.5, where, as in Appendix I, a prime superscript denotes a statistical average using probability (I.1). Let $q'(t,\Omega)$ be the partition function of a partial chain of length tL which has one end pointing at a solid angle $\mathrm{d}\Omega$ around the orientation Ω while the other end is left free. It is convenient to introduce a chain-averaged orientational distribution function $f'(\Omega)$ which can be written in terms of $q'(t,\Omega)$,

$$f(\Omega) = \int_0^1 \mathrm{d}t\, q'(t,\Omega)\, q'(1-t,\Omega)/Q' \qquad \text{(II.1)}$$

The total partition function Q' is defined in (I.2). It is shown that the partition function $q'(t,\Omega)$ satisfies a diffusion-like partial differential equation in external fields:[15,16]

$$\frac{\partial q'}{\partial t} = [\alpha\nabla_\Omega^2 - w(\Omega) + \epsilon g(\Omega)]q' \qquad \text{(II.2)}$$

For the purpose of calculating S_1, it is sufficient to solve eq II.2 to the accuracy of the first order in ϵ. Hence, eq II.2 can be rewritten as

$$\frac{\partial q_1(t,\Omega)}{\partial t} = [\alpha\nabla_\Omega^2 - w(\Omega)]q_1(t,\Omega) + g(\Omega)\, q(t,\Omega) + \mathcal{O}(\epsilon) \qquad \text{(II.3)}$$

where the quantity q_1 has been approximated by

$$q'(t,\Omega) = q(t,\theta) + \epsilon q_1(t,\Omega) + \mathcal{O}(\epsilon^2) \qquad \text{(II.4)}$$

The remaining term, $\mathcal{O}(\epsilon^2)$, represents higher order contributions in ϵ, which are of no interest to us here. On introducing $f_1(\Omega)$ as the first derivative of the distribution function with respect to ϵ

$$f_1 \equiv \left.\frac{\partial f'(\Omega)}{\partial \epsilon}\right|_{\epsilon=0} = \frac{2}{Q}\int_0^1 \mathrm{d}t\, q_1(t,\Omega)\, q(1-t,\theta) \qquad \text{(II.5)}$$

eq I.4 becomes

$$\left.\frac{\partial\langle g(\Omega)\rangle'}{\partial \epsilon}\right|_{\epsilon=0} = \int \mathrm{d}\Omega\, g(\Omega)\, f_1(\Omega) \qquad \text{(II.6)}$$

In arriving at eq II.6, it is assumed that the average of $g(\Omega)$ with respect to the unperturbed probability in eq 2.1 is zero $[\langle g(\Omega)\rangle = 0]$.

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