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# Nematic Ordering in Semiflexible Polymer Chains

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ABSTRACT: The effect of anisotropic repulsive interactions on the isotropic–nematic phase transition of semiflexible polymers is studied by using the Onsager-type excluded-volume interaction. Exact, numerical solutions are obtained for the properties of the phase transition as functions of the flexibility of the polymers. The nematic ordering of different segments of the semiflexible polymers in the nematic state is also discussed.

## 1. Introduction

Low-molecular-weight liquid crystals are commonly modeled by rigid molecules interacting with each other through anisotropic interactions. It is now well-believed that the anisotropic repulsive interactions between molecules are responsible for the formation of the nematic state (i.e., directionally-ordered liquid) in liquid crystals. Simple theoretical models, such as hard rods and hard ellipsoids, have shown that first-order, isotropic–nematic phase transitions exist in these systems.[1–3] Polymer chains, however, have a certain finite *flexibility*, which in many cases are quite different from *rigid* molecules. The synthesis of new liquid-crystalline polymers has stimulated theoretical and experimental interests to search for the fundamental mechanism that leads to the nematic ordering in liquid-crystalline polymers.[4]

Khokhlov and Semenov (KS) have incorporated the Onsager-type repulsive interaction between segments of polymer chains with the continuum limit of the discrete freely-rotating-chain model.[5] In a freely-rotating chain, the bond lengths and bond angles have fixed values; the rotation about the adjacent bonds, however, is assumed to be free. Taking the limit of bond length of the discrete freely-rotating chain to zero, one obtains a continuous, so-called "wormlike" chain.[6,7] The stiffness of a wormlike chain is characterized by a persistence length. When the persistence length is much smaller than the total chain length, one has a completely flexible chain; when the persistence length is much larger than the total chain length, one has a rigid, rodlike chain. The partition function of a wormlike chain in the mean-field theory satisfies a diffusion-like equation in an external field. KS have deduced models for the asymptotic limits of rigid rods and flexible chains based on such an equation;[5] they have also obtained approximate results for the properties of the isotropic–nematic transition in these asymptotic limits using a variational method. For semiflexible chains, however, the model involves an integral–differential equation (see below) which cannot be solved easily. Using a clever argument, KS proposed approximate, interpolation expressions in order to study the properties of the phase transition of the semiflexible chains. They have found that only very stiff or very short chains behave like rigid rods near the phase transition, and that, at the transition, the orientational order parameter and the relative density difference have a minimum when the chains are approximately one-third of a persistence length long.

The functional integral formulation of a wormlike chain was introduced by Saito, Takahashi, and Yunoki (STY).[8] In this paper, I show that the STY formulation produces the same equations considered by KS. Exact solutions of the integral–differential equation for different persistence lengths, including the rigid-rod and flexible-chain limits, are obtained in numerical form. The results in this work show that the conclusions drawn by KS are qualitatively correct.[5]

The ordering of different segments of a semiflexible chain in the nematic state depends on the contour variable. This can be examined by taking averages with respect to a contour-dependent distribution function. These results are presented in section 3C.

## 2. Wormlike Chains

**2A. STY Approach.** The wormlike-chain model was introduced by Kratky and Porod to describe a single, semiflexible polymer chain.[7] STY formulated the problem using the functional integral approach, which results in a continuum version of the Kratky–Porod model.[8] STY describe a single semiflexible chain as a continuous space curve by specifying the tangent unit vector $\vec{n}(t)$, $0 \le t \le 1$, of the curve, where $t$ denotes the contour coordinate along the chain, and the points $t = 0$ and 1 are the two ends of the curve. The statistical probability $P[\vec{n}(t)]$ of such a chain configuration has a Gaussian form

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

where $\alpha$ is the flexibility of the chain defined as

$$\alpha = L/l \qquad (2.2)$$

with $L$ the total contour length and $l$ the persistence length, i.e., the length scale at which the polymer segment appears stiff. In eq 2.1, $D = 3$ is the dimensionality of space.

There are different ways to define a persistence length. Here, the persistence length is defined such that the mean-square end-to-end separation deduced from eq 2.1 satisfies the Kratky–Porod expression:[7]

$$\langle \vec{R}^2 \rangle = L^2\left[1 + \frac{1}{2\alpha}(\mathrm{e}^{-2\alpha} - 1)\right]/\alpha \qquad (2.3)$$

STY originally denoted the persistence length in eq 2.2 by a constant which represents the energy cost to bend the polymer chain. This bending elastic constant can be identified with the persistence length through eq 2.3. In this paper, an explicit $D - 1$ factor has been chosen in eq 2.1 in order to make the definition of the persistence length independent of the dimensionality of the system $D$.

The simplicity of the STY model is more advantageous than the much more complicated Harris–Hearst model,[9] including the revised versions,[10] and is particularly suitable to be used for describing directional ordering. Since the tangent vector is unit in the STY model, it simplifies the average procedure for the orientational distribution func-

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tion, which otherwise would also involve an average of the magnitude of the nonunit tangent vector in the Harris–Hearst model.

**2B. Free Energy.** In Appendix I, a mean-field theory is presented for a system of $N$ wormlike chains occupying a volume $V$, based on the functional integral approach.[6] One of the basic quantities is the orientational distribution function $f(\Omega)$ that measures the degree of orientational ordering of wormlike chains, where $\Omega$ is the solid angle in a three-dimensional space. It is convenient to define a dimensionless number density of the system:

$$\bar{C} \equiv NL^2D/V \qquad (2.4)$$

where $L$ and $D$ are the total contour length and diameter (i.e., thickness) of the polymer chains, respectively. The free energy per chain, in terms of the function $f(\Omega)$, can be written as

$$\frac{F}{Nk_BT} = \ln\left(\frac{4\pi\bar{C}}{Q}\right) - \int \mathrm{d}\Omega\, f(\Omega)\, w(\Omega) + \bar{C} \int\int \mathrm{d}\Omega\, \mathrm{d}\Omega' |\sin\gamma| f(\Omega)\, f(\Omega') \qquad (2.5)$$

The first two terms represent the entropy of a semiflexible chain. The mean field $w(\Omega)$ represents the averaged effect of the neighboring chains on the chain under consideration, and the quantity $Q$ is the total partition function of the chain. These terms prefer an isotropic orientational distribution in order to reach an entropy maximum. The third term represents the excluded-volume interaction, where $\gamma$ is the angle between two unit vectors pointing at $\Omega$ and $\Omega'$; this term prefers a parallel, i.e., nematic, ordering in order to minimize the energy due to the repulsive interaction. The isotropic–nematic phase transition is driven by the competition of these two opposite tendencies.

The self-consistent procedure to obtain the mean field $w(\Omega)$ is described as follows. A detailed derivation of these equations can be found in Appendix I. One needs to define the partition function $q(t,\Omega)$ of a partial chain of length $tL$ which has the final end pointing in a solid angle $\mathrm{d}\Omega$ around the orientation $\Omega$. The partition function $q(t,\Omega)$ of such a chain satisfies a diffusion equation in an external field $w(\Omega)$:

$$\frac{\partial q}{\partial t} = \left[\frac{2\alpha}{D-1}\nabla_{\hat{n}}^{\ 2} - w(\Omega)\right] q \qquad (2.6)$$

where the initial condition $q(t=0,\Omega) = 1$ is assumed. The derivative $\nabla_{\hat{n}}^2$ in eq 2.6 is understood to be taken in polar coordinates. The total partition function of a chain with length $L$, regardless of the orientations of both ends, is then equal to

$$Q = \int \mathrm{d}\Omega\, q(t=1,\Omega) \qquad (2.7)$$

One can then define a path-dependent distribution function

$$f(t,\Omega) \equiv q(t,\Omega)\, q(1-t,\Omega)/Q \qquad (2.8)$$

to characterize the probability of finding a segment with coordinate $t$ in the chain having orientation $\Omega$. Therefore different segments in the chain have different orientation probabilities. The chain-averaged distribution function $f(\Omega)$, used to describe the general orientation probability, is determined by

$$f(\Omega) = \int_0^1 \mathrm{d}t\, f(t,\Omega) \qquad (2.9)$$

**Table I. Rigid Rods: Properties at the Phase Transition**

| | $\bar{C}_i$ | $\bar{C}_n$ | $S_2$ |
|---|---|---|---|
| Onsager (trial function)[a] | 4.253 | 5.714 | 0.848 |
| Lasher[b] | 4.202 | 5.297 | 0.784 |
| Kayser and Ravechè[c] | 4.190 | 5.377 | |
| Lekkerkerker et al.,[d] Odijk[e] | 4.1895 | 5.3362 | 0.7922 |
| this work | 4.1895 | 5.3362 | 0.7922 |

[a] Reference 1. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 15.

In principle, solving eqs 2.6–2.9 yields a relationship between the mean field $w(\Omega)$ and the distribution function $f(\Omega)$. Considering the minimization condition $\mathrm{D}F/\mathrm{D}f(\Omega) = 0$ for eq 2.5

$$w(\Omega) = \lambda + 2\bar{C}\int \mathrm{d}\Omega' |\sin\gamma| f(\Omega') \qquad (2.10)$$

one obtains a self-consistent set of equations for solving $f(\Omega)$ and $w(\Omega)$. In eq 2.10, the constant $\lambda$ accounts for the Lagrange multiplier introduced when eq 2.5 is minimized subject to a normalization condition:

$$\int \mathrm{d}\Omega\, f(\Omega) = 1 \qquad (2.11)$$

Note that a trivial solution $f(\Omega) = 1/4\pi$ always exists for eqs 2.6–2.11, corresponding to an isotropic orientational distribution. The nematic states correspond to nontrivial solutions of $f(\Omega)$, for which a rotational symmetry about the nematic director can be assumed. The orientational distribution function $f(\Omega)$ becomes a function of the polar angle $\theta$ only, which is measured from the nematic director. Due to the symmetry of the kernel $|\sin\gamma|$, one can further take advantage of the symmetric properties $f(\theta) = f(\theta+\pi)$ and $f(\theta) = f(\pi-\theta)$, in calculating the integral in eq 2.10.

In practice, however, it is difficult and probably impossible to solve the coupled integral–differential equations (2.6)–(2.11) in analytic form. In the next section, a numerical procedure will be introduced in order to find a solution for this problem.

## 3. Phase Transition

In this section, the properties of the isotropic–nematic phase transition are studied by numerically solving the minimization condition in eq 2.10. The results for rigid rods, flexible chains, and semiflexible chains are presented in sections 3A–C, respectively.

**3A. Rigid Rods.** The relationship between the mean field and the distribution function becomes much simpler in the asymptotic limit of $\alpha = 0$ (the rigid-rod limit), for which eqs 2.6–2.9 have an analytic solution:

$$w(\Omega) = -\ln[Qf(\Omega)] \qquad (3.1)$$

The free energy in eq 2.5 can then be written as

$$\frac{F}{Nk_BT} = \ln(\bar{C}) + \int \mathrm{d}\Omega\, f(\Omega) \ln[4\pi f(\Omega)] + \bar{C}\int\int \mathrm{d}\Omega\, \mathrm{d}\Omega' |\sin\gamma| f(\Omega)\, f(\Omega') \qquad (3.2)$$

which was originally studied for rigid-rod molecules by Onsager.[1] The minimization condition becomes

$$-\ln f(\Omega) = \lambda + 2\bar{C}\int \mathrm{d}\Omega' |\sin\gamma|\, f(\Omega') \qquad (3.3)$$

Onsager used a variational method in order to minimize the free energy in eq 3.2. In this approach, the distribution function $f(\Omega)$ is assumed to have an artificially imposed anisotropic form:

$$f(\Omega)\ [\text{Onsager}] = \frac{\beta}{4\pi \operatorname{sh}\beta} \operatorname{ch}(\beta\cos\theta) \qquad (3.4)$$

The parameter $\beta$ is treated as a variational parameter whose value is determined by requiring $\mathrm{d}F/\mathrm{d}\beta = 0$. The results found by Onsager are summarized in Table I, where

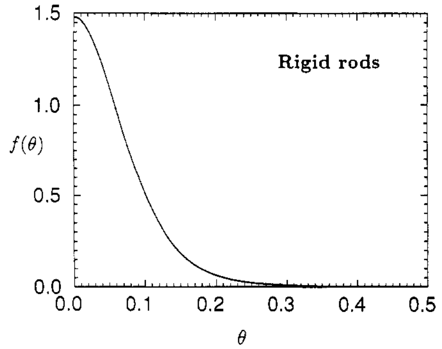

**Figure 1.** Distribution function vs the polar angle $\theta$ for rigid rods at the isotropic–nematic phase transition. The distribution function is strongly peaked at $\theta = 0$.

the values at the phase transition, of the number densities of the isotropic phase $\bar{C}_i$ and the nematic phase $\bar{C}_n$, and the orientational order parameter

$$S_2 = \langle P_2(\cos\theta) \rangle \tag{3.5}$$

are listed.

The second approach is to obtain an exact solution by solving the minimization condition of eq 3.3 numerically. The typical approaches have been to expand the distribution function and the kernel $|\sin\gamma|$ in terms of the Legendre polynomials.[11-13] In this work a numerical procedure is used to directly discretize eq 3.3 by replacing the integral with a finite sum, which is similar to the procedure studied by Herzfeld et al.[14] The interval $[0, \pi]$ for the variable $\theta$ is broken into $n_\theta = 400$ equal segments; at each of the $n_\theta + 1$ grid points, the value of $f(\theta)$ is specified. A Simpsons rule is used to approximate the integral in eq 3.3, so that the integral equation becomes $n_\theta + 1$ nonlinear equations with $n_\theta + 1$ unknown variables $f(\theta_i)$, ($i = 1, ..., n_\theta + 1$), which can be solved by implementing a Newton algorithm. The phase transition is determined by requiring the chemical potentials and osmotic pressures of the isotropic and nematic phases to be equal. The results obtained by this method are in good agreement with the numerical results obtained by Lekkerkerker et al.[13] and the more accurate results of Odijk,[15] which are computed using the same Lekkerkerker et al. algorithm (see Table I). The less accurate results of Lasher[11] and Kayser and Ravechė[12] are also listed in Table I for comparison. The distribution function vs the polar angle $\theta$ is plotted in Figure 1.

A generalization of the above-mentioned numerical procedure has been successfully used for a study of the Onsager problem of the isotropic–nematic interface in a rigid-rod system.[16]

**3B. Flexible Chains.** Another interesting asymptotic limit is the flexible-chain limit, $\alpha \gg 1$, for which the $\partial q/\partial t$ term in eq 2.6 can be neglected and the mean field can be expressed in terms of the distribution function:

$$w(\Omega) = \alpha\frac{\nabla^2 q}{q} = \alpha\frac{\nabla^2[f(\Omega)]^{1/2}}{[f(\Omega)]^{1/2}} \tag{3.6}$$

The free energy in eq 2.5 can be rewritten as

$$\frac{F}{\alpha N k_B T} = \frac{1}{4}\int d\Omega \frac{[\nabla f(\Omega)]^2}{f(\Omega)} + \frac{\bar{C}}{\alpha}\int\int d\Omega\, d\Omega' |\sin\gamma| f(\Omega)\, f(\Omega') \tag{3.7}$$

which was first derived by KS. In eq 3.7, only terms of order $\alpha^0$ are kept, and $\bar{C}$ is assumed to be of order $\alpha$ at the phase transition.

KS also used a variational treatment similar to that of Onsager's to minimize the free energy for flexible chains (eq 3.7). The same trial function (eq 3.4) is used, and their results were later improved by Odijk[15] (see Table II).

**Table II. Flexible Chains: Properties at the Phase Transition**

| | $\bar{C}_i/\alpha$ | $\bar{C}_n/\alpha$ | $S_2$ |
|---|---|---|---|
| Khokhlov and Semenov (trial function)[a] | 13.34 | 14.50 | 0.49 |
| Odijk (trial function)[b] | 13.774 | 15.781 | 0.610 |
| Vroege and Odijk[c] | 13.048 | 14.029 | 0.4617 |
| this work | 13.046 | 14.029 | 0.4618 |

[a] Reference 5. [b] Reference 15. [c] Reference 17.

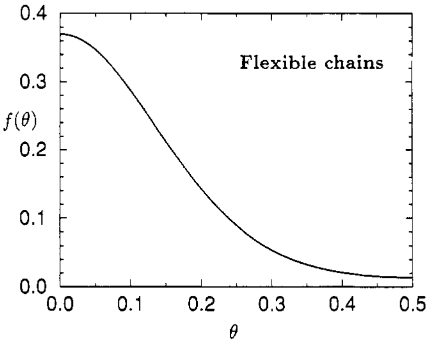

**Figure 2.** Distribution function vs the polar angle $\theta$ for flexible chains at the isotropic–nematic phase transition. The distribution function is less anisotropic compared to that of rigid rods in Figure 1.

Minimization of eq 3.7 yields

$$\frac{\nabla^2[f(\Omega)]^{1/2}}{[f(\Omega)]^{1/2}} = \lambda + 2\frac{\bar{C}}{\alpha}\int d\Omega' |\sin\gamma| f(\Omega') \tag{3.8}$$

This integrodifferential equation has been previously solved by Vroege and Odijk, who expanded both sides of eq 3.8 in Legendre polynomials.[17] The numerical procedure used here to solve eq 3.8 is similar to that for the rigid-rod case in section 3A. Taking finite differences for the derivative in eq 3.8 and replacing the integral with a Simpsons sum, one can again use a Newton algorithm to solve the nonlinear equation set. The results in Table II show that the results obtained this way are in excellent agreement with those due to Vroege and Odijk.[17] Compared to the distribution function of rigid rods, the distribution function at the phase transition is less anisotropic (Figure 2).

Except for the end segments, all segments of the flexible chain have the same orientational distribution. However, in the case of semiflexible chains, the degrees of orientational ordering are different at different segments of the chain. The diffusion-like equation (2.6) must be solved numerically. This is done in the next section.

**3C. Semiflexible Chains.** The numerical-iteration procedure used to solve the diffusion-like equation (2.6) and the minimization condition (2.10) proceeds as follows. For given $\alpha$ and $\bar{C}$, an initial approximation, which is usually taken from the solution for nearby $\alpha$ and $\bar{C}$, is assumed for the distribution function $f(\theta)$. The corresponding approximation for the mean field $w(\theta)$ is obtained from (2.10) by numerical integration, which is then used in eq 2.6. In solving eq 2.6 for the partition function $q(t,\theta)$, a Crank–Nicholson algorithm is implemented.[18] Through eqs 2.7 and 2.8, a new approximation for the distribution function $f(\theta)$ is obtained and is used in the next step of the numerical iteration. The numerical procedure finishes when the mean-square relative difference of the two successive new approximations for $f(\theta)$ is less than a small number $\epsilon$.

The order parameter, relative difference of the number densities of the isotropic and nematic phases $W \equiv \bar{C}_n/\bar{C}_i$

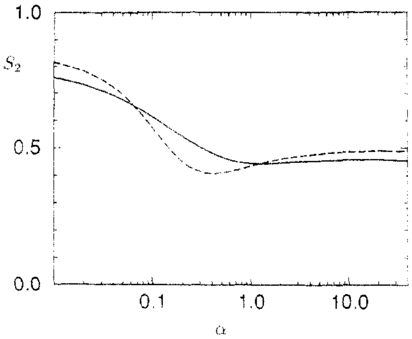

**Figure 3.** Order parameter $S_2$ at the phase transition vs the flexibility $\alpha$. The solid curve is the exact result produced by the current work, and the dashed curve is the approximation proposed by Khokhlov and Semenov.

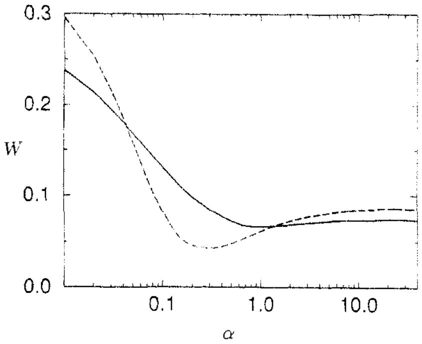

**Figure 4.** Number density difference $W$ at the phase transition vs the flexibility $\alpha$. The solid curve is the exact result produced by the current work, and the dashed curve is the approximation proposed by Khokhlov and Semenov.

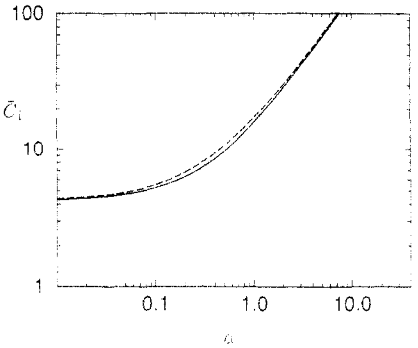

**Figure 5.** Isotropic number density at the phase transition $\bar{C}_i$ vs the flexibility $\alpha$. The solid curve is the exact result produced by the current work, and the dashed curve is the approximation proposed by Khokhlov and Semenov.

- 1, and number density of the isotropic phase, all at the phase transition, are shown as functions of the flexibility $\alpha$ in Figures 3–5 by solid curves. The dashed curves in Figures 3–5 represent the empirical expressions for these quantities introduced by KS, based on their variational solutions of the asymptotic limits ($\alpha \gg 1$ and $\alpha \ll 1$). It can be seen in Figures 3–5 that the basic features of the KS approximation are qualitatively correct. Indeed, as KS pointed out, there is a minimum in the order-parameter curve; however, the minimum occurs less dramatically and the location of the minimum is near $\alpha = 1$ instead of $\alpha = 0.3$. Similar observations can be made for the relative density difference $W$.

The solid curves in Figure 3–5 can be accurately represented by empirical equations

$$S_2 = \sum_{i=0}^{3} a_i\alpha^i/(1 + \sum_{i=1}^{3} b_i\alpha^i) \tag{3.9}$$

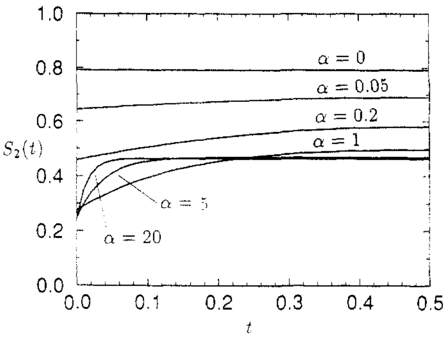

**Figure 6.** Contour-dependent order parameter at the phase transition $S_2(t)$ vs the contour variable $t$ for different chain flexibilities: $\alpha = 0$, $\alpha = 0.05$, $\alpha = 0.2$, $\alpha = 1$, $\alpha = 5$, and $\alpha = 20$.

**Table III. Constants in Equations 3.9–3.11**

| | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $b_1$ | $b_2$ | $b_3$ |
|---|---|---|---|---|---|---|---|
| $S_2$ | 0.7922 | 8.8479 | 11.8593 | 32.7591 | 15.6956 | 34.2650 | 70.9379 |
| $W$ | 0.2737 | 3.0357 | 3.0666 | 10.7859 | 26.8263 | 86.7892 | 143.145 |
| $C_i$ | 4.1895 | 26.1020 | 66.0026 | 117.846 | 3.4806 | 9.0331 | 0 |

$$W = \sum_{i=0}^{3} a_i\alpha^i/(1 + \sum_{i=1}^{3} b_i\alpha^i) \tag{3.10}$$

$$\bar{C}_i = \sum_{i=0}^{3} a_i\alpha^i/(1 + \sum_{i=1}^{2} b_i\alpha^i) \tag{3.11}$$

The coefficients $a_i$ and $b_i$, which are obtained by fitting eqs 3.9–3.11 to the above-obtained numerical results, are listed in Table III.

The ordering of different segments of a semiflexible chain in the nematic phase depends on the contour variable $t$. This can be examined by taking averages with respect to the $t$-dependent distribution function $f(t,\theta)$ in eq 2.8. Figure 6 shows the second-rank order parameter as a function of the contour variable $t$ for different $\alpha$. The ordering of the central parts ($t = {}^1/_2$) of the chain decreases monotonically when the chain flexibility increases. The ordering of the near-end parts of the chain behaves differently; when the flexibility is small, it decreases when the flexibility increases, similar to the behavior of the central parts; however, when the flexibility is large, the ordering increases when the flexibility increases. The shallow minimum in Figure 3. is caused by the effect of these near-end segments.

## 4. Summary

The effect of the repulsive interaction described by the Onsager-like interaction on the isotropic–nematic phase transition is studied for liquid-crystalline polymers. The exact results here confirm earlier qualitative predictions of KS.

The Onsager interaction term is based on a second virial coefficient. The approximation is valid as long as we are dealing with a dilute solution, and the diameter of the semiflexible polymer chain is much smaller than the total length. KS have also proposed approximations that go beyond the second virial coefficient for high-density systems, by modifying the function form of the excluded-volume interaction term, in order to include the effect of maximum packing.[19] Recently, Hentschke[20] and DuPré and Yang[21] have presented approximations for the equation of state of dense, liquid-crystalline polymer solutions, based on Lee's original rescaling concept for hard rods.[22] In a recent review, Vroege and Lekkerkerker have given an overview of other available theories for rigid, anisotropic-shaped molecules.[3]

Two-dimensional wormlike chains can be used to model polymer chains adsorbed on substrates or polymer films.

They exhibit a *second*-order, isotropic–nematic transition at a sufficiently high density. The critical density at which the transition takes place can be determined analytically by examining the instability of the free energy under the perturbation of a nematic state. These results are presented elsewhere.[23]

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## Appendix I. Functional-Integral Approach

The partition function for $N$ wormlike polymers, each labeled by $j$, is given by

$$Z = \frac{1}{N!}\int \prod_{j=1}^{N} D[\Omega_j(s)]\, P[\Omega_j(s)]\, \exp(-\beta W) \qquad \text{(I.1)}$$

where the wormlike chain is described by the statistical probability $P[\Omega_j(s)]$ in eq 2.1. Here, it is assumed that the tangent unit vector $\vec{n}(s)$ in eq 2.1 can be denoted by the solid angle $\Omega(s)$. The intermolecular potential can be written as

$$\beta W = \frac{1}{2V}\sum_{jj'} \int_0^1 \mathrm{d}s \int_0^1 \mathrm{d}s'\, v[\Omega_j(s),\Omega'_{j'}(s')] \qquad \text{(I.2)}$$

where $\mathrm{d}s\, \mathrm{d}s'\, v(\Omega,\Omega')$ is the excluded volume of two segments of lengths $L$ d$s$ and $L$ d$s'$ of orientations $\Omega$ and $\Omega'$

$$v(\Omega,\Omega') = 2L^2 D|\sin\gamma| \qquad \text{(I.3)}$$

In eq I.3, $L$ and $D$ are the total contour length and diameter of the polymer chains. Introducing the microscopic distribution density

$$\hat{f}(\Omega) = \frac{1}{N}\sum_{j=1}^{N} \int_0^1 \mathrm{d}t\, \delta[\Omega - \Omega_j(t)] \qquad \text{(I.4)}$$

one can write

$$\exp(-\beta W) = \int D[f(\Omega)]\, \delta[f(\Omega) - \hat{f}(\Omega)] \times \exp\left[-\frac{CN}{2}\int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, f(\Omega)\, v(\Omega,\Omega')\, f(\Omega')\right] \qquad \text{(I.5)}$$

where $C \equiv N/V$ is the number density of the system. One can now use the integral representation of the $\delta$ function

$$\delta[f(\Omega) - \hat{f}(\Omega)] \equiv \int D[w(\Omega)]\, \exp\{N\int \mathrm{d}\Omega\, w(\Omega)\, [f(\Omega) - \hat{f}(\Omega)]\} \qquad \text{(I.6)}$$

and rewrite the partition function in eq I.1:

$$Z = \frac{1}{N!}\int D[f(\Omega)]\, D[w(\Omega)]\, Q^N \exp\left\{N\left[\int \mathrm{d}\Omega\, w(\Omega)\, f(\Omega) - \frac{C}{2}\int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, f(\Omega)\, v(\Omega,\Omega')\, f(\Omega')\right]\right\} \qquad \text{(I.7)}$$

where

$$Q = \int D[\Omega(s)]\, P[\Omega(s)]\, \exp\{-\int_0^1 \mathrm{d}t\, w[\Omega(t)]\} \qquad \text{(I.8)}$$

is the partition function of a semiflexible chain in an external field $w$. Introducing the partition function $q(t,\Omega)$ of a chain of length $tL$ that has the final end pointing at orientation $\Omega$, one can write

$$Q = \int \mathrm{d}\Omega\, q(t{=}1,\Omega) \qquad \text{(I.9)}$$

It can be shown that $q(t,\Omega)$ satisfies a diffusion-like equation:[24]

$$\frac{\partial q}{\partial t} = \left[\frac{2\alpha}{D-1}\nabla_{\hat{n}}^{\,2} - w(\Omega)\right] q \qquad \text{(I.10)}$$

with an initial condition $q(t{=}0,\Omega) = 1$. Using the saddle-function treatment for eq I.7, one obtains a mean-field free energy:

$$\frac{F}{Nk_BT} = \ln\left(\frac{4\pi\tilde{C}}{Q}\right) - \int \mathrm{d}\Omega\, f(\Omega)\, w(\Omega) + \tilde{C}\int\int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, |\sin\gamma| f(\Omega)\, f(\Omega') \qquad \text{(I.11)}$$

Minimizing eq I.11 with respect to $w(\Omega)$ leads to

$$f(\Omega) = -\frac{1}{Q}\frac{\delta Q}{\delta w(\Omega)} = \frac{1}{Q}\int_0^1 \mathrm{d}s\, q(s,\Omega)\, q(1-s,\Omega) \qquad \text{(I.12)}$$

which gives eq 2.9.

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