Polydisperse Semiflexible Polymer Chains at the Isotropic–Nematic Phase Equilibrium

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Received April 2, 1994
Revised Manuscript Received July 16, 1994

It can be demonstrated[1–8] that solutions of hard-rod molecules of various lengths, like their monodisperse counterparts,[9–16] exhibit a first-order phase transition from the isotropic (I) state to the nematic (N) state, due to repulsive interactions between rod molecules. Recent investigations[5,6,8] of solutions of bidisperse rod molecules have shown that a large polydispersity may have dramatic effects on the physical properties at the phase transition. For instance, the density range of the coexistence region of the two phases may be extensively enlarged; in a few special cases, a new nematic phase may become stable.[8] For weakly polydisperse rods, the change in the physical properties should not be as profound. However, it is important to understand these changes since polymer liquid crystalline molecules in most experimental systems are polydisperse. The perturbation treatment of weakly polydisperse rods is a powerful technique used to estimate these changes.[17,18] Our recent calculation[18] based on an extended Onsager model to account for polydispersity provides an accurate estimate of the correction terms to the leading behavior determined by a monodisperse model, for several important physical quantities.

Most liquid-crystalline polymers have a certain finite flexibility,[19,20] which can be described by the wormlike chain model of Saito, Takahashi, and Yunoki.[21–23] Solutions comprised of monodisperse semiflexible polymer chains interacting with each other through the excluded-volume interaction have been used as simple models to represent lyotropic liquid-crystalline molecules in real systems.[24–27] In these treatments, the effects of polydispersity, which exist in most real systems, are neglected. In this paper, we present a perturbation method to treat weakly polydisperse semiflexible polymers and obtain an estimate for the ratio $\bar{L}_I/\bar{L}_N$ between the averaged chain length in the isotropic phase and that in the nematic phase at the isotropic–nematic phase equilibrium. To lowest order in the fraction distribution width, this ratio can be determined from a balance between the translational entropy associated with the differences in lengths (the mixing entropy) and the changes in the orientational entropy, as is further demonstrated below.

Consider a system of volume V consisting of N semiflexible polymer chains. Among these N chains, a fraction $x(\kappa)$ of molecules has length $L(\kappa)$ where κ is a parameter specifying the type of the polymer chains. The fraction distribution function $x(\kappa)$ is considered here to be a continuous function of κ, satisfying

$$\int \mathrm{d}\kappa\, x(\kappa) = 1 \qquad (1)$$

For later convenience, we rescale $L(\kappa)$ using $\bar{L}_N$, the number average length of chains in the nematic phase, regardless of which phase is under consideration, so that $L(\kappa) = \kappa\bar{L}_N$. Let $f(\kappa,\Omega)$ be the orientational distribution function averaged with respect to different segments for polymer chains of length $L(\kappa)$. Based on the functional-integral approach, the free energy of the polydisperse system can be expressed in terms of the distributions $x(\kappa)$ and $f(\kappa,\Omega)$[24]

$$\frac{\beta F}{N} = \int \mathrm{d}\kappa\, x(\kappa) \ln \frac{4\pi\rho x(\kappa)}{Q(\kappa)} - \int \mathrm{d}\kappa\, x(\kappa) \int \mathrm{d}\Omega\, \omega(\kappa,\Omega)\, f(\kappa,\Omega) + \rho \int \mathrm{d}\kappa\, \mathrm{d}\kappa'\, \kappa\kappa' x(\kappa)\, x(\kappa') \int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, |\sin\gamma| f(\kappa,\Omega)\, f(\kappa',\Omega') \qquad (2)$$

where the last term represents Onsager's excluded-volume interaction.[9] In eq 2, the dimensionless number density $\rho = N\bar{L}_N{}^2 D/V$ is introduced, with D being the diameter of the wormlike cylindrical filaments. The angle between the two unit vectors pointing at angles specified by Ω and Ω' is denoted by γ.

For a monodisperse system, the flexibility of a polymer chain is characterized by $\alpha \equiv L/l$ where L is the total contour length of the chain and l is the Kuhn length. Similarly, in a polydisperse system, the ration $L(\kappa)/l$ is important to determine the conformation of a polymer chain of length $L(\kappa)$. We define the average flexibility α as $\alpha = \bar{L}_N/l$ so that the ratio $L(\kappa)/l$ can be written as $\alpha\kappa$. A continuous variable t ($0 \le t \le 1$) is used to specify the path coordinate of a polymer chain, regardless of the actual type. The total partition function $Q(\kappa)$ and the distribution function $f(\kappa,\Omega)$ can be written as[24–26]

$$Q(\kappa) = \int \mathrm{d}\Omega\, q(t{=}1,\kappa,\Omega) \qquad (3)$$

$$f(\kappa,\Omega) = \frac{1}{Q(\kappa)} \int_0^1 \mathrm{d}t\, q(t,\kappa,\Omega)\, q(1-t,\kappa,\Omega) \qquad (4)$$

where $q(t,\kappa,\Omega)$ satisfies

$$\frac{\partial q(t,\kappa,\Omega)}{\partial t} = [\alpha\kappa\nabla^2 - \omega(\kappa,\Omega)]q(t,\kappa,\Omega) \qquad (5)$$

The quantity $q(t,\kappa,\Omega)$ is the partition function of a type-κ chain that has length $tL(\kappa)$ and has the end (coordinate t) pointing at the direction specified by the solid angle Ω. Equation 5 must be considered with the initial condition $q(t = 0,\kappa,\Omega) = 1$. The mean field $w(\kappa,\Omega)$, representing the averaged effect of the neighboring chains on the chain under consideration, can be obtained self-consistently by minimizing the free energy with respect to the distribution function $f(\kappa,\Omega)$. This procedure leads to

$$\omega(\kappa,\Omega) = \lambda(\kappa) + 2\rho\kappa \int \mathrm{d}\kappa'\, x(\kappa') \int \mathrm{d}\Omega'\, |\sin\gamma| f(\kappa',\omega') \qquad (6)$$

where $\lambda(\kappa)$ corresponds to the Lagrange multiplier associated with the normalization condition

$$\int \mathrm{d}\Omega\, f(\kappa,\Omega) = 1 \qquad (7)$$

The set of coupled equations (1)–(7) must be solved self-consistently for each given flexibility α. Note that these equations reproduce the Khokhlov–Semenov free energy for *monodisperse* semiflexible liquid-crystalline polymer chains,[24,25] for which accurate numerical solutions exist.[26] For the hard-rod limit ($\alpha = 0$) of a *polydisperse* system, these equations can be simplified by a single free energy expression, which was first considered by Sluckin[17] and recently by one of us.[18]

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0024-9297/94/2227-5930$04.50/0

The isotropic–nematic phase equilibrium is determined by the condition that the osmotic pressure P and the chemical potentials $\mu(\kappa)$ for species κ are equal in both phases

$$P_{\mathrm{I}}(\rho_{\mathrm{I}}) = P_{\mathrm{N}}(\rho_{\mathrm{N}}) \tag{8a}$$

$$\mu_{\mathrm{I}}(\kappa,\rho_{\mathrm{I}}) = \mu_{\mathrm{N}}(\kappa,\rho_{\mathrm{N}}) \tag{8b}$$

Bearing in mind that, in general, the fraction distribution functions for the isotropic and nematic phases, $x_{\mathrm{I}}(\kappa)$ and $x_{\mathrm{N}}(\kappa)$, are not the same at the phase equilibrium, we can write P_{I}, μ_{I}, P_{N}, and μ_{N} separately, using the free energy in eq 2. For the isotropic phase,

$$\beta \bar{L}_{\mathrm{N}}{}^{2}\, DP_{\mathrm{I}}(\rho) = \rho + \frac{\pi}{4}\rho^{2}\Big[\int \mathrm{d}\kappa\, \kappa x_{\mathrm{I}}(\kappa)\Big]^{2} \tag{9a}$$

$$\beta\mu_{\mathrm{I}}(\kappa,\rho) = 1 + \ln x_{\mathrm{I}}(\kappa)\,\rho + \frac{\pi}{2}\rho\kappa \tag{9b}$$

and for the nematic phase,

$$\beta \bar{L}_{\mathrm{N}}\, DP_{\mathrm{N}}(\rho) = \rho + \rho^{2}\int \mathrm{d}\kappa\, \mathrm{d}\kappa'\, \kappa\kappa' x_{\mathrm{N}}(\kappa)\, x_{\mathrm{N}}(\kappa') \int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, |\sin\gamma| f(\kappa,\Omega)\, f(\kappa',\omega') \tag{10a}$$

$$\beta\mu_{\mathrm{N}}(\kappa,\rho) = 1 + \ln\frac{4\pi\rho x_{\mathrm{N}}(\kappa)}{Q(\kappa)} - \lambda(\kappa) \tag{10b}$$

According to Gibbs' phase law for a multicomponent system, one of the fraction distribution functions must be specified. When this is done, solving eq 8 determines the phase transition boundary of polydisperse semiflexible chains.

For a weakly polydisperse system, we note that the degree of polydispersity can be measured by a single parameter σ, where $\sigma^2 = \bar{L}_{\mathrm{W}}/\bar{L}_{\mathrm{N}} - 1$ and $\bar{L}_{\mathrm{W}}$ is the weight-average length. It is sufficient to examine the influence on the system of a small σ for weak polydispersity. In particular, the first and second moments of $x_{\mathrm{N}}(\kappa)$ can be written as

$$\bar{\kappa}_{\mathrm{N}} = \int \mathrm{d}\kappa\, \kappa x_{\mathrm{N}}(\kappa) = 1, \quad \overline{\kappa_{\mathrm{N}}^{2}} = \int \mathrm{d}\kappa\, \kappa^{2} x_{\mathrm{N}}(\kappa) = 1 + \sigma^{2} \tag{11}$$

where σ also describes the width of the distribution of length about the mean $\bar{L}_{\mathrm{N}}$. Since the number fraction distribution is assumed relatively narrow, we can use σ only to specify the distribution for the nematic phase and neglect the effects due to higher moments of the distribution. The fraction distribution $x_{\mathrm{I}}(\kappa)$ is then calculated by applying the phase equilibrium conditions. In this preliminary note we report the calculation of eqs 9 and 10 up to first order in the perturbation parameter σ.

The fraction distribution $x_{\mathrm{I}}(\kappa)$ is treated perturbatively, i.e., is considered to be not too different from $x_{\mathrm{N}}(\kappa)$. It can be shown[18] that the expansion of $x_{\mathrm{I}}(\kappa)$ can be written as

$$x_{\mathrm{I}}(\kappa) = x_{\mathrm{N}}(\kappa)\,[1 + A(\kappa - 1) + B\sigma^{2} - B(\kappa - 1)^{2} + C\sigma(\kappa - 1) + \mathcal{O}(\sigma^{3})] \tag{12}$$

Here, terms of order $(\kappa - 1)^3$ or higher will produce moments of order σ^3 or higher, and therefore are neglected. In eq 12, the parameter A represents the deviation of the number-average length of chains in the isotropic phase from that in the nematic phase,

$$\frac{\bar{L}_{\mathrm{I}}}{\bar{L}_{\mathrm{N}}} = \int \mathrm{d}\kappa\, \kappa x_{\mathrm{I}}(\kappa) = 1 + A\sigma^{2} + \mathcal{O}(\sigma^{4}) \tag{13}$$

The coefficients B and C represent other characteristics of $x_{\mathrm{I}}(\kappa)$, which are not considered here.[18] By writing down the series expansion in eq 12, we have implicitly assumed that the nth-order moments of the distribution function $x_{\mathrm{N}}(\kappa)$ are of order σ^n. For most frequently used $x_{\mathrm{N}}(\kappa)$,[28] the conditions imposed here are satisfied. This assumption, however, may become invalid when $x(\kappa)$ has a tail decaying slower than the rate indicated by the moments with orders specified above. Also, in general, $x(\kappa)$ may have several peaks rather than a single maximum considered in this paper. For instance, a binary mixture of molecules with lengths L_1 and L_2 is described by a two-peak fraction distribution function. These complications are not important for *weak* dispersity.

Accurate to first order in $\kappa - 1$, the partition function resulting from solving eq 5 is

$$q(t,\kappa,\Omega) = q_{0}(t,\Omega) + t\left[\frac{\partial q_{0}(t,\Omega)}{\partial t} - q_{0}(t,\Omega)\frac{\partial\lambda(\kappa)}{\partial\kappa}\right](\kappa - 1) \tag{14}$$

and from eq 3

$$Q(\kappa) = Q_{0} - \left[\int \mathrm{d}\Omega\, \omega_{0}(\Omega)\, q_{0}(t{=}1,\Omega) + Q_{0}\frac{\partial\lambda(\kappa)}{\partial\kappa}\right](\kappa - 1) \tag{15}$$

In the above equations and hereafter the subcript 0 denotes the corresponding unperturbed quantities of the monodisperse semiflexible polymer system with the flexibility α. The minimization condition for the free energy (eq 6) and the expression for the osmotic pressure (eq 8a) have the same form as that of the monodisperse model.[26] Using eqs 6 and 8a, one can further show that quantities such as $f(\kappa{=}1,\Omega)$, $\lambda(\kappa{=}1)$, ρ_{I}, and ρ_{N} are also unchanged up to this order. The chemical potential for the isotropic phase is

$$\beta\mu_{\mathrm{I}}(\kappa,\rho_{\mathrm{I}}) = \beta\mu_{\mathrm{I}0}(\rho_{\mathrm{I}0}) + \ln x_{\mathrm{N}}(\kappa) + A(\kappa - 1) + \frac{\pi}{2}\rho_{\mathrm{I}0}(\kappa - 1) \tag{16}$$

and for the nematic phase is

$$\beta\mu_{\mathrm{N}}(\kappa,\rho_{\mathrm{N}}) = \beta\mu_{\mathrm{N}0}(\rho_{\mathrm{N}0}) + \ln x_{\mathrm{N}}(\kappa) + Q_{1}(\kappa - 1) \tag{17}$$

with

$$Q_{1} = \frac{1}{Q_{0}}\int \mathrm{d}\Omega\, (\omega_{0}(\Omega) - \lambda_{0})\, q_{0}(t{=}1,\Omega) \tag{18}$$

Using eqs 15–17 we can show from the equilibrium condition that

$$A = Q_{1} - \frac{\pi}{2}\rho_{\mathrm{I}0} \tag{19}$$

For the rigid-rod limit ($\alpha = 0$) we have the analytic solution[24–26]

$$q_{0}(t{=}1,\Omega) = \exp(-\omega_{0}(\Omega)) = Q_{0} f_{0}(\Omega) \tag{20}$$

Substitution eq 20 into eq 18, we have

$$Q_{1} = \int \mathrm{d}\Omega\, (\omega_{0}(\Omega) - \lambda_{0}) f_{0}(\Omega) = 2\rho_{\mathrm{N}}\int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, |\sin\gamma| f_{0}(\Omega)\, f_{0}(\Omega') \tag{21}$$

and then recover from eqs 21 and 18 the result

$$A(\alpha{=}0) = -1.844 \qquad (22)$$

determined previously.[18] This is larger than Sluckin's estimation ($A = -5.8$[17]); he used a similar perturbation treatment, but the fraction distributions are restricted to the Gaussian distribution.

Another interesting asymptotic limit is the flexible-chain limit ($\alpha \gg 1$), for which

$$q_0(t,\Omega) = [Q_0 f_0(\Omega)]^{1/2} \qquad (23)$$

and

$$\omega_0(\Omega) = \nabla^2 q_0/q_0 \qquad (24)$$

Substitution of eq 24 into eq 18 yields $Q_1 = -\lambda_0$. Then

$$A(\alpha{\gg}1) = -\lambda_0 - \frac{\pi}{2}\rho_{I0} \qquad (25)$$

Note that both λ_0 and ρ_{I0} are of order α for large α; to order α, the two terms in eq 25 cancel each other. However, to order α^0, the coefficient A is nonzero after the equilibrium condition for the unperturbed chemical potential is taken into account. We then have

$$A(\alpha{\gg}1) = -\ln[4\pi\rho_{N0}/(Q_0\rho_{I0})] \qquad (26)$$

where $Q_0 = [\int d\Omega f_0^{1/2}(\Omega)]^2$. Using the numerical result for $f_0(\Omega)$ calculated earlier,[26] we obtain

$$A(\alpha{\gg}1) = -0.3326 \qquad (27)$$

within a relative error less than 1%.

For an arbitrary α, a numerical procedure has been developed to solve the self-consistent equations of the monodisperse system in ref 26. Using the previous numerical results[26] for ω_0 and λ_0, we obtain the numerical solution for $A(\alpha)$, which is shown in Figure 1 as a function of α at the isotropic–nematic phase equilibrium. As illustrated, A(α) monototically increases from $A(\alpha{=}0)$ to $A(\alpha{\gg}1)$ and is a negative quantity. It can therefore be concluded that the shorter chains prefer to remain in the isotropic phase, while the longer chains prefer to go to the nematic phase, as observed in previous studies of similar problems for rigid rods.[1-8,17,18]

The crossover from rigid-rod to flexible-chain behavior occurs near $\alpha \simeq 0.1$, consistent with the observation of other physical quantities.[26,27] The curve in Figure 1 can be accurately represented by the empirical equation

$$A(\alpha) = -\frac{1.844 + 24.995\alpha + 28.982\alpha^2 + 31.983\alpha^3}{1 + 26.326\alpha + 100.345\alpha^2 + 96.162\alpha^3} \qquad (28)$$

from a fitting of the numerical solution for $0.01 \le \alpha \le 10$; the two asymptotic limits of $A(\alpha)$ at $\alpha = 0$ and $\alpha \gg 1$ are fixed by the solutions in eqs 22 and 27.

Our choice of starting from the nematic distribution $x_N(\kappa)$ and attempting to predict the isotropic distribution $x_I(\kappa)$ is only for convenience in the calculation. Doing so, we write

$$x_I(\kappa) = x_N(\kappa)\,[1 + A(\alpha)\,(\kappa - 1) + \ldots]$$

and

$$\bar{L}_I(\kappa) = \bar{L}_N(\kappa)\,[1 + A(\alpha)\,\sigma^2 + \ldots]$$

We can show that one may perform the same analysis by choosing a fixed $x_I(\kappa)$ to predict $x_N(\kappa)$. Then, the result can be written as

$$x_N(\kappa) = x_I(\kappa)\,[1 - A(\alpha)\,(\kappa - 1) + \ldots] \qquad (29)$$

and

$$\bar{L}_N(\kappa) = \bar{L}_I(\kappa)\,[1 - A(\alpha)\,\sigma^2 + \ldots] \qquad (30)$$

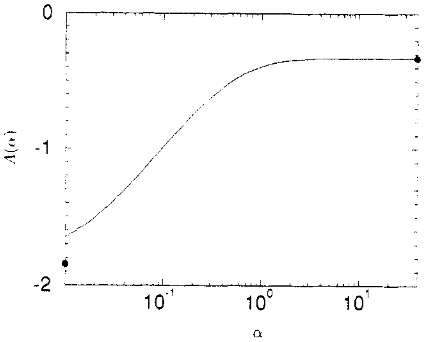

Figure 1. Deviation parameter $A(\alpha)$ of the number-average length of chains in the isotropic phase from that in the nematic phase at the isotropic–nematic phase transition as a function of the average flexibility constant α. The average flexibility is defined as $\alpha = \bar{L}_N/l$ where $\bar{L}_N$ is the number-average length of chains in the nematic phase and l is the Kuhn length. The asymptotic limits of $A(\alpha)$ are indicated by the filled circles.

where $A(\alpha)$ is given in eq 28. In eqs 29 and 30, one can replace the definiiton $\alpha = \bar{L}_N/l$ by $\alpha = \bar{L}_I/l$ and regard σ as the width of the distribution function $x_I(\kappa)$ about $\bar{L}_I$. These two approaches are equivalent. Equations 29 and 30 are probably the more convenient forms for an experimentalist who generally starts with $x_I(\kappa)$ and would like to know how $x_N(\kappa)$ ends up.

In conclusion, we have generalized the mean-field theory of the isotropic–nematic phase transition for monodisperse semiflexible chains to polydisperse semiflexible chains and calculated the ratio of the average chain lengths in the isotropic and nematic phases, at the isotropic–nematic phase equilibrium. The perturbation theory is valid for weak polydispersity. Utilizing the second-order perturbation expansion for the chemical potential and osmotic pressure will enable us to perform calculations of the correction terms to the isotropic and nematic densities and orientational order parameter at the isotropic–nematic phase transition,[18] these calculations are currently in progress.

Acknowledgment. This work was supported by the National Science and Engineering Research Council of Canada. The authors acknowledge O. Akcakir for his help in proofreading the manuscript.

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