Effect of polydispersity on the isotropic-nematic phase transition of rigid rods

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The effect of polydispersity on the isotropic-nematic phase transition of rigid rods is analyzed in terms of a second-order perturbation theory, in which the width σ of an arbitrary number fraction is used as a perturbation parameter. These results show that the isotropic-nematic phase transition takes place at the isotropic density n_I, where $n_I \bar{L}_N^2 D = 4.189(1+2.128\sigma^2)$, and the nematic density n_N, where $n_N \bar{L}_N^2 D = 5.336(1+1.655\sigma^2)$, with D and $\bar{L}_N$ being the diameter and the number-averaged length of rods in the nematic phase. At the transition density, the weight- and number-averaged orientation order parameters have the values $S_W = 0.7922 + 1.1333\sigma^2$ and $S_L = 0.7922 + 0.816\sigma^2$; the ratio between the number-averaged length of rods in the isotropic phase, $\bar{L}_I$, and that in the nematic phase, $\bar{L}_N$, is $\bar{L}_I / \bar{L}_N = 1 - 1.844\sigma^2$. These perturbation results are compared with the numerical solution of the equilibrium conditions for the isotropic-nematic transition of rods obeying two modeled number fraction distributions.

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I. INTRODUCTION

The thermodynamic properties of dilute solutions of long rigid rods were first treated by Onsager, who concluded that such solutions exhibit a first-order phase transition between an isotropic phase with no particular orientational order to a nematic phase with the nematic order [1]. Owing to the recent interests in rigid and semiflexible liquid crystalline polymers, theories have been developed to refine the original Onsager model, producing a much clearer physical picture of the isotropic-nematic transition in these systems [2–14].

In most of these studies, rod molecules are treated as monodisperse ones. However, the majority of synthesized polymer chains have a certain distribution of lengths, whose detailed form varies according to the process and nature of the polymerization [15,16]. A typical number fraction distribution can be characterized by various statistical moments of the distribution, among them the most important ones being the number averaged length $\bar{L}$ (the first moment) and the weight-averaged length $\bar{L}_W$ (the ratio between the second and first moments) [15–17]. It is often considered to be sufficient to represent a weakly polydisperse system by experimentally measuring these two quantities only, regardless of the explicit form of the fraction distribution. The degree of polydispersity can be measured in terms of the ratio of the weight-averaged length to the number-averaged length, $\bar{L}_W / \bar{L} \equiv 1 + \sigma^2$, where σ describes the width of the distribution about the mean $\bar{L}$.

The effect of length bidispersity on the isotropic-nematic transition of rigid rods has been examined numerically by Lekkerkerker *et al.* [18] and Birshtein, Kolegov, and Pryamitsyn [19] for length ratios $L_2/L_1 = 2$ and $L_2/L_1 = 5$. Among other interesting features, they demonstrated that when the isotropic-nematic phase equilibrium is achieved, longer rods prefer

to stay in the nematic phase rather than in the isotropic phase, and that the biphasic gap (i.e., the difference between the isotropic and nematic densities) is widened. As in other studies of similar systems, they also found a stronger orientational order of longer rods in the nematic phase. Some of these numerical observations were analyzed by Odijk and Lekkerkerker [10]. Odijk [3] also presented a general discussion on the polydispersity effect based on the approximate technique of using Gaussian trial functions to represent the orientational distributions. This treatment is useful for a qualitative analysis, but not for a quantitative calculation. McMullen, Gelbart, and Ben-Shaul considered the system of polydisperse micellar rods [21], whose lengths are determined by the chemical potential equilibrium condition rather than being fixed by the system, at the isotropic-nematic transition. This system bears many similarities to the system studied in this paper. In an approach similar to that used in this paper, Sluckin [22] used a perturbation theory to evaluate the properties at the transition, using a Gaussian distribution for the number fraction. The Odijk Gaussian ansatz for the orientational distributions is used. It should be mentioned that the effect of polydispersity on the isotropic-nematic transition was first considered by Flory and coworkers within Flory's lattice treatment of rigid rods [23–26]. The mathematical representation and, therefore, physical results are different from the Onsager model, and the results are restricted to a number of special models for the fraction distribution; nevertheless, these theories provided quite an important insight for the further study of similar problems.

In this paper, we use a perturbation method to solve the phase equilibrium and free-energy-minimization conditions of the Onsager model for polydisperse rods. The number fraction distribution is assumed to be relatively narrow so that the relative mean square deviation $\sigma^2 \equiv \langle (L - \bar{L})^2 \rangle / \bar{L}^2 = \bar{L}_W / \bar{L} - 1$ from the number-averaged length $\bar{L}$ can be used as a perturbation parame-

ter, where $\bar{L}_W \equiv \overline{L^2}/\bar{L}$ is the weight-averaged length. The explicit form of the number fraction distribution is not required in this treatment. Sluckin [22] used a similar quantity as the perturbation parameter, but his approach is restricted to the Gaussian fraction distribution. The perturbation theory determines the correction terms to physical quantities at the phase transition due to the polydisperse effect.

Most practical examples to which the Onsager theory may be applied are lyotropic liquid crystal systems consisting of polymers or colloidal particles. Reference [2] gives an extensive review of these systems. The calculation in this paper can be extended to study the effect of polydispersity on semiflexible polymer systems, in which the molecules are characterized by a flexibility coefficient. This calculation will be reported elsewhere [27].

This paper is organized as follows. In Sec. II, the numerical solution to the Onsager problem for monodisperse rods is reviewed; a generalized free energy based on the Onsager model for a polydisperse rod system is proposed. In Sec. III, perturbation expansions for the chemical potentials and osmotic pressure for both the isotropic and nematic phases, and the minimization condition of the free energy for the nematic state, are calculated. The main results are discussed in Sec. IV.

II. BASIC FORMALISM

A. Onsager problem for monodisperse rods

The solution to the Onsager problem is used as the zeroth order approximation in the perturbation treatment. The main results are summarized in this section.

Consider the system of volume V, consisting of N rigid rod molecules of length L and diameter D. Let $f_0(\Omega)$ be the orientational distribution function of finding a rigid rod pointing at the direction specified by the solid angle Ω, and $n \equiv N/V$ the average number density of rigid particles in the system. The free energy per particle, accurate to the second order in the virial expansion, can be written as [1]

$$F^{\text{Onsager}}/NkT = \ln\rho + \int f_0(\Omega)\ln[4\pi f_0(\Omega)]d\Omega$$
$$+ \rho \int d\Omega\, d\Omega'|\sin\gamma|f_0(\Omega')f_0(\Omega) ,$$

$$\tag{2.1}$$

where γ is the angle between the two unit vectors pointing at the directions specified by Ω and Ω', and $\rho = nL^2/D$ is the dimensionless density.

Minimizing the free energy with respect to the distribution function $f_0(\Omega)$ leads to a nonlinear integral equation for $f_0(\Omega)$:

$$\ln[4\pi f_0(\Omega)] = \lambda_0 - 2\rho \int d\Omega'|\sin\gamma|f_0(\Omega') , \tag{2.2}$$

where λ_0 accounts for the Lagrange multiplier introduced when the free energy is the minimized subject to the normalization condition

$$\int f_0(\Omega)d\Omega = 1 . \tag{2.3}$$

For the isotropic (I) phase, the dimensionless chemical potential $\tilde{\mu}_0^I \equiv \mu_0^I/(kT)$ can be written as

$$\tilde{\mu}_0^I(\rho) = 1 + \ln\rho + \frac{\pi}{2}\rho \tag{2.4}$$

and the dimensionless osmotic pressure $\tilde{P}_0^I \equiv L^2 DP_0^I/(kT)$,

$$\tilde{P}_0^I(\rho) = \rho + \frac{\pi}{4}\rho^2 . \tag{2.5}$$

For the nematic (N) phase, the dimensionless chemical potential and osmotic pressure can be expressed in terms of the distribution function $f_0(\Omega)$:

$$\tilde{\mu}_0^N(\rho) = 1 + \ln\rho + \lambda_0(\rho) , \tag{2.6}$$

$$\tilde{P}_0^N(\rho) = \rho + \rho^2 \int d\Omega\, d\Omega' f_0(\Omega) f_0(\Omega')|\sin\gamma| . \tag{2.7}$$

The isotropic-nematic phase equilibrium is determined by the coexistence conditions

$$\tilde{\mu}(\rho_0^I) = \tilde{\mu}_0^N(\rho_0^N) \tag{2.8}$$

$$\tilde{P}_0^I(\rho_0^I) = \tilde{P}_0^N(\rho_0^N) . \tag{2.9}$$

Numerical calculations to solve the coupled Eqs. (2.2), (2.3), (2.8), and (2.9) have shown that at the isotropic-nematic phase transition, the coexisting number densities have the values [3,12,18,28,29]

$$\rho_0^I = 4.189 , \tag{2.10}$$

$$\rho_0^N = 5.336 . \tag{2.11}$$

The solution of $f_0(\Omega)$ to Eq. (2.2), corresponding to ρ_0^N, is presented in Fig. 1. As a measure of the degree of orientational order, it is customary to define the orientational order parameter

$$S_0 = \langle P_2(\cos\theta) \rangle = 0.7922 . \tag{2.12}$$

For later use, the values of the constants p_1 and p_2 at the transition, defined below, can be calculated

$$p_1 = \int f_0(\Omega)\ln[4\pi f_0(\Omega)] = 1.6021 , \tag{2.13}$$

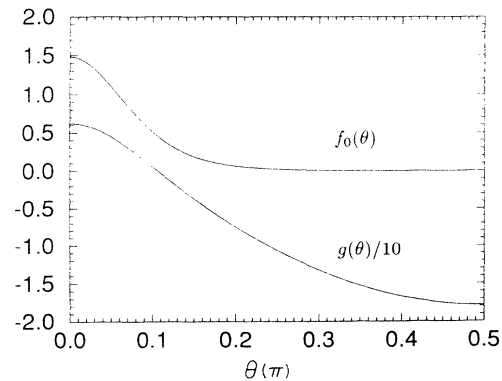$$p_2 = \int f_0(\Omega)\ln^2[4\pi f_0(\Omega)] = 4.2499 . \tag{2.14}$$

FIG. 1. Monodisperse distribution function $f_0(\theta)$ and the correction to the distribution function $g(\theta)$. The expansion of the distribution function $f(\theta)$ is given by $f_0(\theta)[1 + g(\theta)\sigma^2 + \cdots]$. Note that the scale for $g(\theta)$ is reduced ten times here.

Note that p_1 is the orientational entropic contribution to the free energy of a nematic state.

B. Free energy for polydisperse systems

Next, consider the system of volume V consisting of N polydisperse particles at the isotropic-nematic transition; among these N particles, a fraction of $x(\kappa)$ molecules has

length $L = \kappa \bar{L}_N$ where $\bar{L}_N$ is the number averaged length of rods in the nematic phase. Instead of $\bar{L}_N$, we could choose the number-averaged length of rods in the isotropic phase, $\bar{L}_I$, as our basic length scale, but the above choice greatly simplifies the calculation in this paper. The orientational distribution function $f(\kappa, \Omega)$ is now a function of the rod type κ.

A generalization of the Onsager model to include the polydispersity yields [3,22]

$$F/NkT = \ln\rho + \int d\kappa\, x(\kappa)\ln x(\kappa) + \int d\kappa\, x(\kappa) \int f(\kappa,\Omega)\ln[4\pi f(\kappa,\Omega)]d\Omega$$
$$+ \rho \int d\kappa\, x(\kappa)\kappa \int d\kappa'\, x(\kappa')\kappa' \int d\Omega\, d\Omega'|\sin\gamma|f(\kappa,\Omega)f(\kappa',\Omega')\,, \tag{2.15}$$

where the dimensionless number density is defined by

$$\rho \equiv \frac{N}{V}\bar{L}_N^2 D \,. \tag{2.16}$$

The distribution functions $x(\kappa)$ and $f(\kappa,\Omega)$ satisfy the normalization conditions,

$$\int x(\kappa)d\kappa = 1 \,, \tag{2.17}$$

$$\int f(\kappa,\Omega)d\Omega = 1 \,. \tag{2.18}$$

Note that for the asymptotic limit of monodisperse systems, $x(\kappa)=\delta(\kappa-1)$, the free energy (2.15) becomes that of the Onsager model, up to an unimportant constant.

III. PERTURBATION THEORY

A. Number fraction distribution

Since we are dealing with a multicomponent system, the number fraction distributions $x_I(\kappa)$ and $x_N(\kappa)$ are different in general, when the isotropic-nematic phase equilibrium is reached. From Gibbs's phase law, one of the $x(\kappa)$ functions must be specified; here in this paper, $x_N(\kappa)$ is chosen to be the specified one, for convenience. The fraction distribution $x_I(\kappa)$ will be determined by the phase equilibrium condition. In particular, $x_N(\kappa)$ is assumed to have the first and second moments

$$\bar{\kappa}_N \equiv \int d\kappa\, \kappa x_N(\kappa) = 1 \tag{3.1}$$

$$\langle \kappa_N^2 \rangle \equiv \int d\kappa\, \kappa^2 x_N(\kappa) = 1 + \sigma^2 \,. \tag{3.2}$$

It may seem that in order to determine the phase equilibrium boundary, the explicit functional form of $x_N(\kappa)$ must be given [22]; close inspection of the phase equilibrium conditions indicates that only the first and second moments of $x_N(\kappa)$ are involved for a relatively sharp fraction distribution.

For monodisperse molecules, the distribution function $x_I(\kappa)$ is identical to $x_N(\kappa)$, and both should be a δ function centered at $\kappa=1$. For weakly polydisperse molecules, the difference between the former and the latter

must be small. Thus, we can represent the ratio $x_N(\kappa)/x_I(\kappa)$ by a Taylor expansion of the parameters characterizing the weakness of the polydispersity. In general, this ratio depends on two parameters, σ and κ. For a smooth distribution sharply peaked at $\kappa=1$, we expect $\langle(\kappa-1)^m\rangle = O(\sigma^m)$. Therefore, we may expand $x_N(\kappa)/x_I(\kappa)$ in the vicinity of $\kappa=1$ and $\sigma=0$:

$$x_I(\kappa)=x_N(\kappa)[1+a_1\sigma+a_2(\kappa-1)+a_3\sigma^2+a_4(\kappa-1)^2$$
$$+a_5(\kappa-1)\sigma+\cdots]\,.$$

All terms of order σ^3, $\sigma^2(\kappa-1),\sigma(\kappa-1)^2$, and $(\kappa-1)^3$ or higher are not important; these terms either have order higher than σ^2, or indirectly produce them when the average over the number fraction distribution is considered. In a second-order perturbation theory, these terms can be discarded in the perturbation expansion.

Using the normalization condition (2.17), one can show that $a_1=0$ and $a_3=-a_4$. Redefining the constants leads to

$$x_I(\kappa)=x_N(\kappa)[1+\alpha(\kappa-1)+\beta\sigma^2$$
$$-\beta(\kappa-1)^2+\eta(\kappa-1)\sigma+\cdots]\,, \tag{3.3}$$

where α, β and η will be determined below. The parameter α represents the deviation of the number averaged length of rods from $\bar{L}_N$ in the isotropic state,

$$\bar{L}_I/\bar{L}_N \equiv \bar{\kappa}_I = \int d\kappa\, x_I(\kappa)\kappa = 1 + \alpha\sigma^2 \,. \tag{3.4}$$

The parameter β represents the deviation of $x_I(\kappa)$ from $x_N(\kappa)$ at $\kappa=1$:

$$x_I(1)=x_N(1)(1+\beta\sigma^2)\,. \tag{3.5}$$

B. Nematic orientational distribution function

From the energy minimization condition of the distribution function $f(\kappa,\Omega)$,

$$\ln[4\pi f(\kappa,\Omega)]=\lambda(\kappa)-2\rho\kappa\int d\kappa' x(\kappa')\kappa'$$
$$\times \int d\Omega'|\sin\gamma|f(\kappa',\Omega')\,,$$

it can be shown in general that [3]

$$f(\kappa,\Omega) \propto [f(1,\Omega)]^\kappa , \qquad (3.6)$$

where $f(1,\Omega)$ is the distribution function for $\kappa=1$ satisfying

$$\ln[4\pi f(1,\Omega)] = \lambda - 2\rho \int d\kappa' x(\kappa')\kappa'$$
$$\times \int d\Omega' |\sin\gamma| f(\kappa',\Omega') . \qquad (3.7)$$

Here we have simplified the notation by denoting $\lambda(1)=\lambda$. The Lagrange multiplier $\lambda(\kappa)$ can be related to λ by considering the normalization condition for $f(\kappa,\Omega)$, which depend on $f(1,\Omega)$ via Eq. (3.6). We then have

$$\lambda(\kappa) = \kappa\lambda - (\kappa-1)p_1 - (p_2-p_1^2)(\kappa-1)^2/2 + \cdots .$$

Thus, $f(\kappa,\Omega)$ can be written perturbatively as

$$f(\kappa,\Omega) = f(1,\Omega)[1+(\kappa-1)\Delta f_1(\Omega)$$
$$+(\kappa-1)^2\Delta f_2(\Omega)+ \cdots] , \qquad (3.8)$$

where

$$\Delta f_1(\Omega) = \ln[4\pi f_0(\Omega)] - p_1 , \qquad (3.9)$$

and

$$\Delta f_2(\Omega) = \{\ln^2[4\pi f_0(\Omega)] - p_2\}/2 - p_1\Delta f_1 \qquad (3.10)$$

are known functions of Ω. Again, terms of order $(\kappa-1)^3$ or higher are not important and thus neglected. Finally, equation (3.7) gives

$$\ln[4\pi f(1,\Omega)]$$
$$= \lambda - 2\rho \int d\Omega' |\sin\gamma| [1+(\Delta f_1+\Delta f_2)\sigma^2] f(1,\Omega') .$$
$$(3.11)$$

Note that Eq. (3.11) recovers the minimization condition for a monodisperse system at $\sigma^2=0$.

C. First-order perturbation

To first order in σ, the minimization condition (3.11) has the same form as that of the Onsager model [Eq. (2.2)]. The expression for the osmotic pressure is also unchanged up to this order. The chemical potential for species κ can be obtained from the derivative of the free energy with respect to the number of rods of length $\kappa\bar{L}_N$. It follows that for the isotropic phase,

$$\tilde{\mu}_\kappa^I(\rho) = \tilde{\mu}_0^I(\rho) + \ln x_N(\kappa) + \alpha(\kappa-1) + \frac{\pi}{2}\rho(\kappa-1) + \cdots ,$$
$$(3.12)$$

and for the nematic phase,

$$\tilde{\mu}_\kappa^N(\rho) = \tilde{\mu}_0^N(\rho) + \ln x_N(\kappa) + (\lambda - p_1)(\kappa-1) + \cdots . \qquad (3.13)$$

The coexistence equation for the isotropic and nematic chemical potentials, $\tilde{\mu}_\kappa^I(\rho^I) = \tilde{\mu}_\kappa^N(\rho^N)$, implies

$$\alpha = \lambda_0 - p_1 - \frac{\pi}{2}\rho_0^I = -1.845 . \qquad (3.14)$$

Using the minimization condition for the free energy and the equilibrium condition for the pressure, we can also show that,

$$\lambda = \lambda_0 + O(\sigma^2) , \qquad (3.15)$$

$$f(1,\Omega) = f_0(\Omega) + O(\sigma^2) , \qquad (3.16)$$

$$\rho^I = \rho_0^I + O(\sigma^2) , \qquad (3.17)$$

and,

$$\rho^N = \rho_0^N + O(\sigma^2) . \qquad (3.18)$$

Therefore, we need to perform a second-order perturbation analysis in order to obtain the leading correction terms to ρ^I, ρ^N, and $f(1,\Omega)$.

D. Second-order perturbation

As shown above, we can draw the conclusion that the deviation of the distribution function $f(1,\Omega)$ from $f_0(\Omega)$ is of order σ^2. Expressed in terms of the second order expansion in σ,

$$f(1,\Omega) = f_0(\Omega)[1+g(\Omega)\sigma^2+ \cdots] , \qquad (3.19)$$

$$\lambda = \lambda_0 + \lambda_1\sigma^2 , \qquad (3.20)$$

$$\rho^I = \rho_0^I(1+\rho_1^I\sigma^2) , \qquad (3.21)$$

and

$$\rho^N = \rho_0^N(1+\rho_1^N\sigma^2) . \qquad (3.22)$$

Equation (3.11) for the unknown function $g(\Omega)$ can be rewritten in the form of a linear integral equation

$$g(\Omega) = \lambda_1 - 2\rho_0^N\rho_1^N \int d\Omega' |\sin\gamma| f_0(\Omega')$$
$$- 2\rho_0^N \int d\Omega' |\sin\gamma| f_0(\Omega')$$
$$\times [\Delta f_1(\Omega') + \Delta f_2(\Omega') + g(\Omega')] , \qquad (3.23)$$

where Δf_1 and Δf_2 are those functions in Eqs. (3.9) and (3.10). The above equation must be solved in conjunction with the condition

$$\int f_0(\Omega)g(\Omega) = 0 , \qquad (3.24)$$

which resulted from the normalization condition (2.18). The constants ρ_1^I, ρ_1^N, and λ_1 are the coefficients of the correction terms to the isotropic and nematic densities and the Lagrange multiplier, that must be determined under the phase equilibrium conditions.

For the isotropic phase, the chemical potential of the species κ is given by

$$\tilde{\mu}_\kappa^I(\rho^I) = \tilde{\mu}_0^I(\rho_0^I) + \ln x_N(\kappa) + (\lambda_0 - p_1)(\kappa-1)$$
$$+ \sigma^2(p_3\rho_1^I + p_4 + \beta) - \beta(\kappa-1)^2 + \eta\sigma(k-1)$$
$$- \alpha^2(\kappa-1)^2/2 . \qquad (3.25)$$

The pressure can be written as

$$\tilde{P}^I(\rho^I) = \tilde{P}_0^I(\rho_0^I) + \sigma^2[p_3\rho_1^I + p_4]\rho_0^I , \qquad (3.26)$$

where $\tilde{P}_0^I$ and $\tilde{\mu}_0^I$ are those defined in Eqs. (2.4) and (2.5),

and the constants p_3 and p_4 are defined in Table I.

For the nematic phase, the expression for the chemical potential can be simplified when the minimization condition of the free energy is used. Hence,

$$\bar{\mu}_\kappa^N(\rho^N) = \bar{\mu}_0^N(\rho_0^N) + \ln x_N(\kappa) + (\lambda_0 - p_1)(\kappa - 1)$$

$$+ (p_1^2 - p_2)(\kappa - 1)^2/2 + (\rho_1^N + \lambda_1)\sigma^2 . \quad (3.27)$$

The expression for the pressure up to order σ^2 is rather simple,

$$\tilde{P}^N(\rho^N) = \tilde{P}_0^N(\rho_0^N) + \rho_0^N(\rho_1^N + \lambda_1)\sigma^2 , \quad (3.28)$$

where $\tilde{P}_0^N$ and $\bar{\mu}_0^N$ are those in Eqs. (2.6) and (2.7).

Equating the chemical potentials in Eq. (3.25) with Eq. (3.27) at order σ^2 yields the results for the constants β and η:

$$\beta = (p_2 - p_1^2)/2 - \alpha^2/2 = -0.8588 , \quad (3.29)$$

$$\eta = 0 . \quad (3.30)$$

In addition, it also produces a linear equation for the variables ρ_1^I, ρ_1^N, and λ_1,

$$p_3\rho_1^I - \rho_1^N - \lambda_1 = -p_4 - \beta . \quad (3.31)$$

Another linear equation involving the above variables comes from the equilibrium condition of the osmotic pressure,

$$p_3\rho_0^I\rho_1^I - \rho_0^N(\rho_1^N + \lambda_1) = -p_4\rho_0^I . \quad (3.32)$$

Elimination of the factor $(p_1^N + \lambda_1)$ by combining Eq. (3.31) with Eq. (3.32) gives,

$$\rho_1^I = \frac{\rho_0^N\beta}{(\rho_0^I - \rho_0^N)p_3} - \frac{p_4}{p_3} = 2.128 . \quad (3.33)$$

Using Eq. (3.32), we can calculate for $\rho_1^N + \lambda_1$,

$$\rho_1^N + \lambda_1 = \frac{\rho_0^N\beta}{\rho_0^I - \rho_0^N} . \quad (3.34)$$

Substituting λ_1 by ρ_1^N using Eq. (3.34), we obtain a set of linear integral equations, Eqs. (3.23) and (3.24), for the

TABLE I. Properties of the Onsager model at the isotropic-nematic phase transition. In this table, ρ_0^I and ρ_0^N are the isotropic and nematic densities at the transition; S_0 is the orientational order parameter; $p_l (l = 1, \ldots, 4)$ are the constants used in the paper.

	Value	Definition
ρ_0^I	4.1895	
ρ_0^N	5.3362	
S_0	0.7922	$\int f_0(\Omega)P_2(\cos\theta)d\Omega$
p_1	1.6026	$\int f_f(\Omega)\ln[4\pi f_0(\Omega)]d\Omega$
p_2	4.2499	$\int f_0(\Omega)\ln^2[4\pi f_0(\Omega)]d\Omega$
p_3	7.5808	$1 + \frac{\pi}{2}\rho_0^I$
p_4	-12.142	$\pi\alpha\rho_0^I/2$
λ_0	6.3389	See Eq. (2.2)

TABLE II. Expansion of physical quantities in σ at the phase transition. In this table, ρ^I and ρ^N are the isotropic and nematic number densities at the phase transition; α, β, and η appear in the expression for the ratio between the isotropic and nematic number fractions, Eq. (3.4); see Table I for the values of ρ_0^I and ρ_0^N.

	Value	Definition
ρ_1^I	2.128	$\rho^I = \rho_0^I(1 + \rho_1^I\sigma^2 + \cdots)$
ρ_1^N	1.655	$\rho^N = \rho_0^N(1 + \rho_1^N\sigma^2 + \cdots)$
α	-1.844	$\bar{L}_I/\bar{L}_N = 1 + \alpha\sigma^2 + \cdots$
β	-0.8588	
η	0	
λ_1	1.4824	$\lambda = \lambda_0 + \lambda_1\sigma^2 + \cdots$
s_1	0.317	$\int f_0(\Omega)\Delta f_1(\Omega)P_2(\cos\theta)d\Omega$
s_2	-0.391	$\int f_0(\Omega)\Delta f_2(\Omega)P_2(\cos\theta)d\Omega$
s_3	1.207	$\int f_0(\Omega)g(\Omega)P_2(\cos\theta)d\Omega$

unknown function $g(\Omega)$ and variable ρ_1^N; these equations must be solved numerically. Using the previous numerical results for the distribution function $f_0(\Omega)$, we obtain the numerical solution for $g(\Omega)$ as plotted in Fig. 1. The numerically determined ρ_1^N has the value

$$\rho_1^N = 1.655 . \quad (3.35)$$

Table II summarizes the results of our calculation.

IV. DISCUSSION

Equation (3.4) represents the ratio between the number-averaged length of rods in the isotropic phase and that in the nematic phase. Since $\alpha = -1.844$ is negative, we can conclude that the shorter rods prefer to remain in the isotropic phase, while the longer rods prefer to go to the nematic phase, as has been observed in previous studies of similar problems. The constant $\alpha = -1.844$ can be compared with Sluckin's estimation [22] of -5.8. Shorter rods possess higher orientational entropy, thus can be more easily fitted in the isotropic liquid. [18-25].

Equations (3.21) and (3.22) represent the isotropic and nematic densities at the phase transition, including the leading correction terms due to the polydispersity effect. The constants in Eqs. (3.21) and (3.22) are $\rho_0^I = 4.189$, $\rho_0^N = 5.336$, $\rho_1^I = 2.128$, and $\rho_1^N = 1.655$. These results can be compared with Sluckin's $\rho^I = 4.393(1 + 2.4\sigma^2)$ and $\rho^N = 6.52(1 - 2.2\sigma^2)$, where we have rescaled these quantities using the convention in this paper [22]. Note that the latter contains a negative correction term, while our solution indicates the opposite. The biphasic difference scaled by $\bar{L}_N^2 D$ can be written as,

$$(n_N - n_I)\bar{L}_N^2 D = 1.147(1 - 0.072\sigma^2 + \cdots) . \quad (4.1)$$

Contrary to the observation made by other authors [18-25], the biphasic difference narrows when the system becomes weakly polydisperse. The rather small slope

associated with the correction term in Eq. (4.1) indicates that the narrowing effect can be quite weak. Since we are dealing with a perturbation series of the biphasic difference for small σ, we are not able to predict whether or not the broadening effect actually exists for a stronger polydisperse system.

The nematic orientational order can be measured by defining an order parameter for species κ,

$$S(\kappa)=\int d\Omega\, f(\kappa,\Omega)P_2(\cos\theta)$$

$$=S_0+s_1(\kappa-1)+s_2(\kappa-1)^2+s_3\sigma^2+\cdots, \quad (4.2)$$

where s_1, s_2, and s_3 are the coefficients of the correction terms, defined in Table II. The number- and weight-averaged order parameters, S_L and S_W, can be determined by using Eq. (4.2)

$$S_L\equiv\int d\kappa\, S(\kappa)=S_0+(s_2+s_3)\sigma^2+\cdots$$

$$=0.7922+0.816\sigma^2+\cdots, \quad (4.3)$$

$$S_W\equiv\int d\kappa\,\kappa S(\kappa)=S_0+(s_1+s_2+s_3)\sigma^2+\cdots$$

$$=0.7922+1.133\sigma^2+\cdots. \quad (4.4)$$

Equation (4.2) is valid only for $|\kappa-1|\ll1$; however, it can already be deduced from Eq. (4.2) that the longer rods in the nematic phase are ordered more strongly, while the shorter rods more weakly. Inspection of the distribution function in Eq. (3.6) supports this conclusion [3].

In order to evaluate the accuracy of the perturbation theory, we also have conducted a numerical study of the isotropic-nematic phase transition when $x_N(\kappa)$ follows two modeled number fraction functions [16],

$$x_N(\kappa)\big|_{\text{Gauss}}=\frac{1}{\sigma(2\pi)^{1/2}}\exp\left[-\frac{(\kappa-1)^2}{2\sigma^2}\right], \quad (4.5)$$
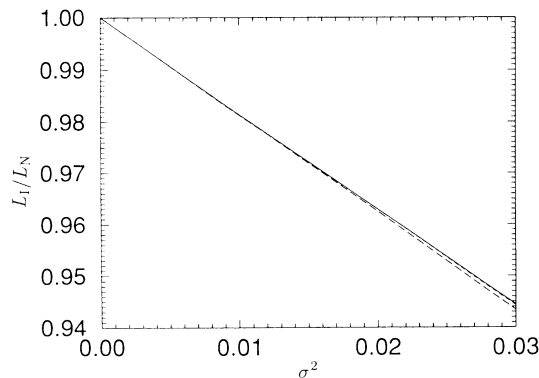
and

FIG. 2. Ratio between the mean length of rods in the isotropic phase and that in the nematic phase. The solid line is predicted by the perturbation theory (see Table II); the short-dashed and the long-dashed curves are the numerical results from solving the phase equilibrium condition for the two modeled nematic number fractions, in Eqs. (4.5) and (4.6).
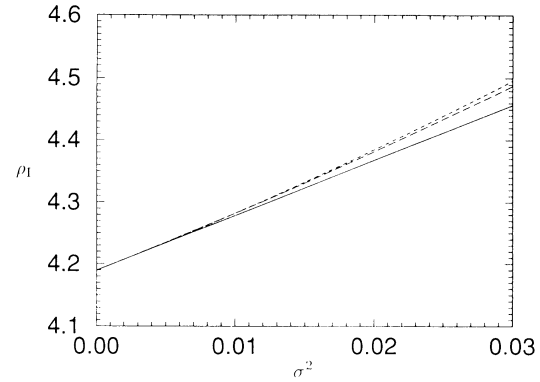

FIG. 3. Isotropic density at the phase transition. The solid line is predicted by the perturbation theory (see Table II); the short-dashed and the long-dashed curves are the numerical results from solving the phase equilibrium condition for the two modeled nematic number fractions in Eqs. (4.5) and (4.6).

$$x_N(\kappa)\big|_{\text{LK}}=\frac{1}{\sigma(2\pi)^{1/2}\kappa}\exp\left[-\frac{[\ln(\kappa/\kappa_m)]^2}{2\sigma^2}\right]. \quad (4.6)$$

The latter is the Lansing-Kraemer distribution with $\kappa_m=\exp(-\sigma^2/2)$ being the median of the distribution curve. Both distributions have the ratio

$$\bar{L}_W/\bar{L}=1+\sigma^2+\cdots. \quad (4.7)$$

The minimization condition in Eq. (3.7) is solved according to the iteration procedure described in Ref. [12], with the additional approximation of discretizing the function $x_N(\kappa)$. The transition densities ρ^I and ρ^N are then determined numerically by implementing the Newton algorithm for the chemical and pressure equilibrium conditions. These numerical results are compared with the perturbation results as shown in Figs. 2–5. In these figures, the solid lines are the physical quantities determined by the perturbation theory, the short-dashed curves are those from the Gauss model in (4.5), and the
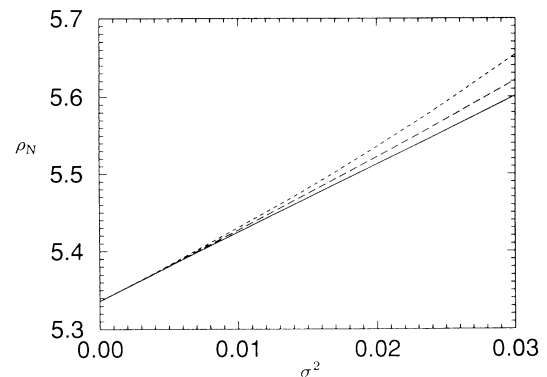

FIG. 4. Nematic density at the phase transition. The solid line is predicted by the perturbation theory (see Table II); the short-dashed and the long-dashed curves are the numerical results form solving the phase equilibrium condition for the two modeled nematic number fractions, in Eqs. (4.5) and (4.6).
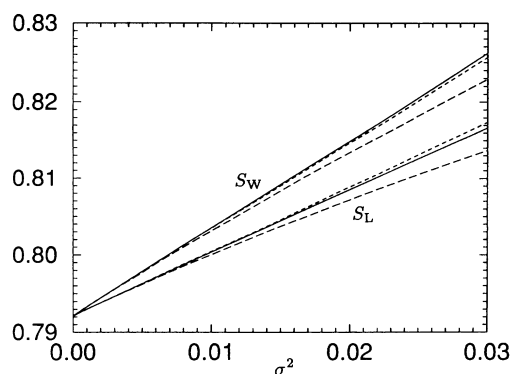
FIG. 5. Weight- and number-average orientational order parameter S_W and S_L defined in Eqs. (4.3) and (4.4). The solid line is predicted by the perturbation theory; the short-dashed and the long-dashed curves are the numerical results from solving the phase equilibrium condition for the two modeled nematic number fractions, in Eqs. (4.5) and (4.6).

long-dashed curves are those from the Lansing-Kraemer model. All curves fall into the same asymptotic behavior represented by the solid lines. As can be seen, our perturbation results describe accurately the asymptotic

behavior of these physical quantities near $\sigma = 0$. Even for $\sigma^2 = 0.03$, the perturbation results can still be used to give reasonable estimates for the numerical results. The error of the perturbation results are of order σ^3 at larger σ, which is consistent with our expectation.

Bidisperse rods are known to exhibit a possible reentrant phase transition [19]; two different nematic phases were also found by Birshtein, Kolegov, and Pryamitsyn for bidisperse rods [19]. These complications are outside the scope of the current paper.

In summary, the physical properties of the isotropic-nematic phase transition of polydisperse rigid rods can be studied through a second order perturbation theory. For systems that can be described by small σ^2, the leading correction terms to the isotropic and nematic densities, the orientational order parameter, and the ratio of the average lengths of rods in the isotropic and nematic phases calculated in this paper, should be adequate for describing the deviations from those of the monodisperse system.

ACKNOWLEDGMENT

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