

Research Article

A Simple Free Energy for the Isotropic-Nematic Phase Transition of Rods

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A free energy expression is proposed that describes the isotropic-nematic binodal concentrations of hard rods. A simple analytical form for this free energy was yet only available using a Gaussian trial function for the orientation distribution function (ODF), leading, however, to a significant deviation of the predicted binodals. The new free energy proposed here is based upon a rationalized correction to the orientational and packing entropies when using the Gaussian ODF. In combination with Parsons-Lee theory or scaled particle theory, it enables describing the isotropic-nematic phase coexistence concentrations of rods accurately using the simple Gaussian ODF for a wide range of aspect ratios.

1. Introduction

Liquid crystal phases are found in a wide variety of soft matter systems including solutions of amphiphilic molecules, polymer solutions, and colloidal dispersions (viruses, DNA, cellulose, boehmite, and vanadia) [1]. These materials are composed of particles that can assume a preferred orientation making them suitable for applications due to special rheological and optical properties. Liquid crystal displays have been used since the 1980s and were later used in mobile phones, laptops, and flat screen televisions (see, e.g., [2] and references therein).

The basic understanding of the origin of liquid crystalline phases commenced thanks to theoretical work on the ability of hard rods to form a nematic, the simplest liquid crystal phase. In the 1940s, Onsager showed that an isotropic fluid of very thin, hard rods undergoes a transition to a nematic phase upon concentrating the rods [3, 4]. In the isotropic phase, the rods are oriented randomly whereas in the nematic phase they have a preferred, more parallel orientation. Onsager argued that the randomly oriented rods in the isotropic phase

reserve less free volume per particle than the aligned rods in the nematic phase. Hence the entropy loss associated with the orientational ordering in the nematic phase is more than compensated by the reduction of excluded volume between pairs of rods [5].

For very thin, rigid, hard rods, the phase transition occurs at a very low volume fraction and the virial expansion may therefore be truncated at the level of the second (osmotic) virial coefficient, leading to an exact theory for infinitely thin particles [4–6]. This rigorous demonstration of an entropy-driven phase transition in hard particle dispersions received significant impetus [7]. It stimulated computer simulation work that revealed highly ordered smectic phases in concentrated suspensions of hard rods [8].

In the following, a brief exposition of Onsager's theory for long rods is given in Section 2. Then the Gaussian approximation to the orientational distribution function is introduced in Section 3 that gives analytical results for the binodal concentrations. Subsequently, the new equation of state is proposed in Section 4 after which it is extended towards a description for arbitrary aspect ratio L/D using both Parsons theory

and scaled particle theory (Section 5). The new results are compared to computer simulations, followed by conclusions in Section 6.

2. Onsager Theory

The Helmholtz free energy A for a dispersion of N hard rods, modeled as spherocylinders with length L and diameter D in a volume V , can be written in the second virial approximation (valid for $L \gg D$) [5] as

$$\frac{A}{NkT} = \text{const} + \ln c + \sigma + c\rho, \quad (1)$$

with Boltzmann constant k and temperature T . The quantity c is the dimensionless concentration $c = bn$, where $n = N/V$ is the number density of the rods and $b = (\pi/4)L^2D$ is the second virial coefficient of a suspension of rods in the isotropic state. Note that (1) holds up to the binary collision limit [5, 6] and is thus valid for long, thin hard rods only. The quantity σ is related to the orientational entropy loss per particle $s_{\text{or}} = -k\sigma$ and ρ to the packing entropy loss per particle $s_{\text{pack}} = -k\rho$.

The quantity $\sigma[f]$ can be computed from [5]

$$\sigma[f] = \int d\Omega f(\Omega) \ln [4\pi f(\Omega)], \quad (2)$$

with $d\Omega$ being an infinitesimal surface element on the unit sphere. The orientational distribution function (ODF) f is normalized according to

$$\int d\Omega f(\Omega) = 1. \quad (3)$$

The quantity ρ can be computed from integration over the orientations between two rods:

$$\rho[f] = \frac{4}{\pi} \int \int |\sin \Theta| f(\Omega) f(\Omega') d\Omega d\Omega', \quad (4)$$

where Θ is the angle between the rods which depends on their orientations Ω and Ω' .

It is noted here that f does not depend on the azimuthal angle φ but only on the polar angle θ (differing from Θ). Furthermore, the distribution function $f(\theta)$ must satisfy inversion symmetry, implying that the angles θ and $\pi - \theta$ are equivalent.

For the isotropic phase, σ and ρ attain the values

$$\begin{aligned} \sigma_I &= 0, \\ \rho_I &= 1. \end{aligned} \quad (5)$$

And hence the free energy in the isotropic phase follows as

$$\frac{A_I}{NkT} = \text{const} + \ln c + c. \quad (6)$$

From (6) and (for the nematic phase) (1), standard thermodynamics provide the chemical potentials and pressures in each

phase. Numerically solving the ODF $f(\theta)$ and simultaneously the coexistence equations

$$\begin{aligned} P_I &= P_N, \\ \mu_I &= \mu_N \end{aligned} \quad (7)$$

yields the coexistence concentrations [5]:

$$\begin{aligned} c_I &= 3.29, \\ c_N &= 4.19. \end{aligned} \quad (8)$$

Note that the computation is involved since solving the coexistence concentrations includes numerical minimization of the ODF at each concentration of rods in the nematic phase; see [9] for an explanation of an efficient numerical approach.

3. Gaussian Orientational Distribution Function

It is quite useful for experimentalists and engineers to have analytical approximations at hand to estimate the concentrations at the isotropic-nematic (I - N) phase transition for practical purposes. Several trial functions (e.g., [4, 6, 10, 11]) for the ODF have been proposed in order to avoid numerical minimization [9] and retain insight into the expressions. Onsager [4] proposed a trial function that describes exact results quite reasonably but is numerically still quite demanding [11].

Odijk [6] realized that for rather aligned rods f can be approximated as a Gaussian distribution function:

$$\begin{aligned} f_G &= \tilde{N}(\alpha) \exp\left(-\frac{1}{2}\alpha\theta^2\right) \quad 0 \leq \theta \leq \frac{\pi}{2} \\ &= \tilde{N}(\alpha) \exp\left(-\frac{1}{2}\alpha(\pi - \theta)^2\right) \quad \frac{\pi}{2} \leq \theta \leq \pi, \end{aligned} \quad (9)$$

where the normalization factor $\tilde{N}(\alpha) \sim \alpha/4\pi$ for large α . When using the Gaussian ODF, the only parameter that needs to be determined from minimization of A is α . The advantage of this Gaussian distribution function is that the quantities σ and ρ can be calculated analytically for large values of α [5]:

$$\begin{aligned} \sigma_G &= \ln \alpha - 1, \\ \rho_G &= \frac{4}{\sqrt{\pi\alpha}}. \end{aligned} \quad (10)$$

This leads to the following expression for the free energy in the nematic phase:

$$\frac{A_N}{NkT} = \text{const} + \ln c + \ln \alpha - 1 + \frac{4c}{\sqrt{\pi\alpha}}. \quad (11)$$

Minimizing this expression with respect to α leads to

$$\alpha = \frac{4c^2}{\pi}. \quad (12)$$

Hence

$$\frac{A_N}{NkT} = \text{const} + \ln \frac{4}{\pi} + 3 \ln c. \quad (13)$$

The coexistence equations now take the simple forms

$$\begin{aligned} c_I + c_I^2 &= 3c_N \\ \ln c_I + 2c_I &= 3 \ln c_N + \ln \left(\frac{4}{\pi} \right) + 3, \end{aligned} \quad (14)$$

resulting in the following coexisting concentrations:

$$\begin{aligned} c_I &= 3.45, \\ c_N &= 5.12. \end{aligned} \quad (15)$$

The deviations from the numerical results $c_I = 3.29$ and $c_N = 4.19$ are considerable, being 5% for the isotropic and even 22% for the nematic phase coexistence concentrations.

4. Correction to the Free Energy

It should be realized that the Gaussian approximation to the ODF is an extremely rough approximation that only holds asymptotically for highly aligned rods. Within the Gaussian approach, the deviation between the results for the isotropic-nematic coexistence concentrations ((15) versus (8)) mainly arises from an ODF that is too sharply peaked. One can try to restore this by realizing that the orientational entropy loss s_{or} per rod is overestimated due to a description of the rods that is too aligned. Further, the packing entropy gain is also not adequately described by the Gaussian ODF. Hence one might attempt to correct the orientational and packing entropy contributions with an unknown amount Δs :

$$\frac{A_N}{NkT} = \text{const} + \ln \frac{4}{\pi} + 3 \ln c - \frac{\Delta s}{k}. \quad (16)$$

The value of Δs can be computed from the difference between exact and (Gaussian) approximated packing and orientational entropy:

$$\frac{\Delta s}{k} = \sigma_G - \sigma_{\text{num}} + c_N (\rho_G - \rho_{\text{num}}). \quad (17)$$

This is done at the numerically exact concentration $c_N = 4.19$. From (12), it follows that $\alpha = 22.36$ at c_N . From expressions (10), this gives $\sigma = 2.107$ and $\rho = 0.477$.

The exact numerical results are $\sigma = 1.601$ and $\rho = 0.565$ [12]. This means the entropy correction should be $\Delta s/k = 2.107 - 1.601 + 4.191(0.477 - 0.565) = 0.139$.

For $\Delta s = 0.139k$ the coexistence concentrations from (1) and (16) become

$$\begin{aligned} c_I &= 3.26, \\ c_N &= 4.62. \end{aligned} \quad (18)$$

The deviations from the exact Onsager results (see (8)) are now 1% for the isotropic phase and 10% for the nematic phase. This is a severe reduction of the deviation (a factor of 5 for the isotropic phase and a factor of 2 for the nematic phase) with respect to the uncorrected Gaussian approximation.

5. Aspect Ratio Dependence

The correction to the free energy upon using the Gaussian approximation for the ODF is now extended towards hard spherocylinders for arbitrary aspect ratio L/D . This means that interactions between the rods should be accounted for beyond the level of the second virial coefficient. Theoretically, at significant rod volume fractions, this is not possible without approximate descriptions. Here we use two approaches, scaled particle theory (SPT) and Parsons-Lee theory, the latter being used frequently by engineers.

5.1. Parsons-Lee Theory. Parsons [13] derived an expression for the excess free energy of hard spherocylinders that can be considered as an extension of the Carnahan-Starling equation of state for hard spheres [14]. The excess part of the Carnahan-Starling equation is multiplied by the ensemble-averaged excluded volume of a spherocylinder, normalized with its volume. This free energy expression was extended by Lee [15, 16] to describe the isotropic-nematic phase transition of hard spherocylinders. The phase transition concentrations and osmotic pressure at coexistence, obtained after numerical minimization, have been shown to correspond quite reasonably with computer simulations [5].

For the isotropic phase, the Parsons result is

$$\frac{A_I}{NkT} = \text{const} + \ln \frac{L}{D} + \ln \phi + \frac{L}{D} \phi g(\phi), \quad (19)$$

where $g(\phi)$ is defined by

$$g = \frac{4 - 3\phi}{4(1 - \phi)^2}, \quad (20)$$

and derives from the Carnahan-Starling equation of state, which in itself accurately describes the (osmotic) pressure of a collection of hard spheres in the fluid state up to a packing fraction of ≈ 50 vol%. Here, ϕ , the volume fraction of rods, which equals nv_R , where $v_R = \pi D^3/6 + \pi D^2 L/4$, is the volume of a rod. Hence, using $c = bn$, c and ϕ are related via

$$\phi = c \left[\frac{D}{L} + \frac{2}{3} \left(\frac{D}{L} \right)^2 \right]. \quad (21)$$

For the nematic phase, the Parsons result reads

$$\begin{aligned} \frac{A_N}{NkT} &= \text{const} + \ln \frac{L}{D} + \ln \phi + \sigma + \frac{L}{D} \rho \frac{4\phi - 3\phi^2}{4(1 - \phi)^2} \\ &\quad - 0.139, \end{aligned} \quad (22)$$

including the proposed correction $\Delta = 0.139k$. For ρ and σ , (10) from the Gaussian approximation are used and inserted into the free energy in (22). Minimization of this free energy with respect to α then leads to the following closed expression for the variational parameter:

$$\alpha = \frac{L}{D} \frac{(4\phi - 3\phi^2)^2}{4\pi(1 - \phi)^4}. \quad (23)$$

Now the isotropic-nematic coexistence concentrations can be obtained straightforwardly; the minimization of the ODF is incorporated into (23).

For the sake of completeness, we write down the analytical expressions for the osmotic pressure and chemical potential. The chemical potential $\mu = (\partial A / \partial N)_{V,T}$ follows from the Helmholtz energy A as $\mu = (\partial [A\phi/N] / \partial \phi)_{V,T}$, and the osmotic pressure $P = -(\partial A / \partial V)_{N,T}$ can be found from $Pv_R = \phi^2 (\partial [\phi A/N] / \partial \phi)_{N,T}$. The free energy of (19) yields the following results for the chemical potential of a spherocylinder in the isotropic phase:

$$\frac{\mu_I}{kT} = \text{const} + \ln \frac{L}{D} + \ln \phi + \frac{L}{D} \frac{8 - 9\phi + 5\phi^2}{4(1 - \phi)^3}. \quad (24)$$

For the chemical potential of the rods in the nematic phase, (22) yields

$$\frac{\mu_N}{kT} = \text{const} + \ln \frac{L}{D} + \ln \phi + \sigma + \frac{L}{D} \rho \frac{8 - 9\phi + 5\phi^2}{4(1 - \phi)^3} - 0.139. \quad (25)$$

The result for the osmotic pressure is

$$\frac{Pv_R}{kT} = \phi + \frac{L}{D} \rho \frac{2\phi^2 - \phi^3}{2(1 - \phi)^3}. \quad (26)$$

The results for the *I-N* binodals using Parsons-Lee theory for spherocylinders with a correction for the entropy are plotted in Figure 1. The new results are confronted with computer simulations on dispersions of rods to determine the rod concentrations at isotropic-nematic coexistence. These have been performed on relatively short rods first [18] but were performed for L/D up to 50 by Bolhuis and Frenkel [17] soon after. Their results are represented as the open symbols in Figure 1. The results are plotted in terms of the dimensionless (Onsager) concentration $c = bn$. It is clear that the simulation data are quite well described using the proposed new free energy expressions as a function of L/D , except for a slight overestimation of the concentration of rods in the coexisting nematic phase for long rods.

5.2. Scaled Particle Theory. Scaled particle theory has the advantage that it also allows incorporating attractions in a direct manner [19] and also via, for instance, the contribution of nonadsorbing polymer chains [20]. The SPT approach of Cotter [21] is used, deriving a SPT expression for the Helmholtz energy F of a dispersion of rods. For the isotropic phase, the result is

$$\frac{A_I}{NkT} = \text{const} + \ln \frac{L}{D} + \ln y + ay + \frac{1}{2}by^2, \quad (27)$$

where a and b are

$$a = 3 + \rho \frac{3(\gamma - 1)^2}{3\gamma - 1}, \quad (28)$$

$$b = \frac{12\gamma(2\gamma - 1)}{(3\gamma - 1)^2} + \rho \frac{12\gamma(\gamma - 1)^2}{(3\gamma - 1)^2},$$

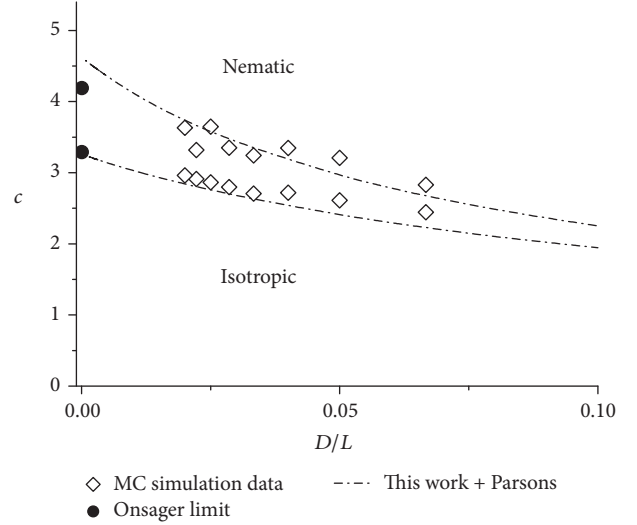


FIGURE 1: Aspect ratio dependence of the isotropic-nematic phase coexistence for hard spherocylinders. Dashed dotted curves are predictions using the proposed free energy correction inserted into Parsons-Lee theory. Monte Carlo (MC) computer simulation data were taken from Bolhuis and Frenkel [17].

involving the ODF via ρ . Here γ is the overall length-to-diameter ratio $L/D + 1$. The quantity y is defined as $y = \phi/(1 - \phi)$.

For the nematic phase, the SPT result reads

$$\frac{A_N}{NkT} = \text{const} + \ln \frac{L}{D} + \ln y + \sigma + Py + \frac{1}{2}Qy^2 - 0.139, \quad (29)$$

including the added proposed correction. Minimization of A with respect to α yields

$$\alpha = \frac{36}{\pi} \frac{(\gamma - 1)^4}{(3\gamma - 1)^2} \left(y + \frac{2\gamma}{3\gamma - 1} y^2 \right)^2. \quad (30)$$

The binodal isotropic-nematic concentrations can now be computed from (27)–(30).

The scaled particle free energy of (27) yields the following results for the chemical potential of a spherocylinder in the isotropic phase:

$$\frac{\mu_I}{kT} = \text{const} + \ln \frac{L}{D} + \ln y + [1 + 2a] y + \left(a + \frac{3}{2}b \right) y^2 + by^3. \quad (31)$$

For the chemical potential in the nematic phase, (29) yields

$$\frac{\mu_N}{kT} = \text{const} + \ln \frac{L}{D} + \sigma + \ln y + [1 + 2a] y + \left(a + \frac{3}{2}b \right) y^2 + by^3 - 0.139. \quad (32)$$

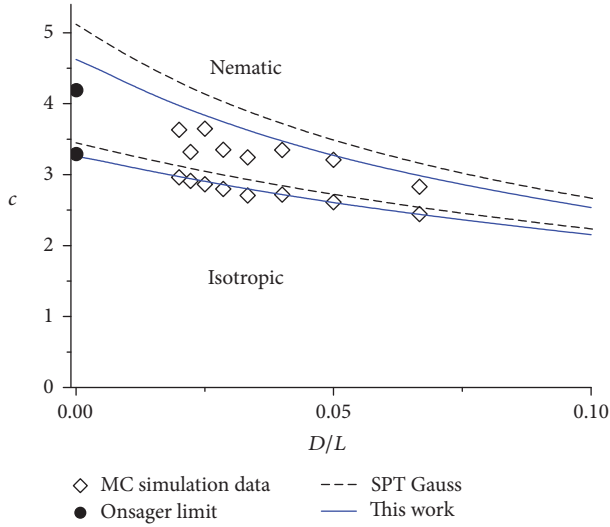


FIGURE 2: Isotropic-nematic phase coexistence for hard spherocylinders as a function of the inverse of the aspect ratio L/D . Scaled particle theory results without (dashed curves) and with (solid curves) correction to the free energy are compared with Monte Carlo (MC) computer simulation data [17] and the Onsager limit.

The result for the osmotic pressure is

$$\frac{Pv_R}{kT} = y + ay^2 + by^3, \quad (33)$$

where a and b in the above equations differ in the isotropic and nematic phase because of ρ . It is noted that the above Parsons-Lee and SPT expressions for the free energy are semiempirical; third- and higher-order virial terms are included approximately [5]. Implicitly, it is assumed that the correction needed to account for the Gauss ODF that is too sharply peaked in the Onsager limit remains similar when the aspect ratio L/D gets smaller.

The results using scaled particle theory with a correction for the entropy for the I - N coexistence concentrations of spherocylinders are plotted in Figure 2. They are compared to SPT results using the Gaussian ODF without correction (dashed curves). Again we compare the results with computer simulations of [17], represented as the open symbols in Figure 2. Also when using SPT the simulation data are quite well described using the proposed corrected free energy expressions. Obviously, the free energy correction via the rationalized Δs correction now enables describing the I - N transitions quite well and is certainly a severe improvement to the (uncorrected) Gaussian approximation.

6. Concluding Remarks

A simple free energy correction was presented for the isotropic-nematic phase transition of hard spherocylinders. Basically, Onsager's free energy with a simple Gaussian orientational distribution function (ODF) was modified by realizing that this ODF is too sharply peaked. The proposed corrected free energy provides quite accurate predictions for the isotropic-nematic phase coexistence concentrations.

It can also be extended to include interactions beyond the pair level using Parsons-Lee or scaled particle theory. It is shown that inclusion of the proposed corrections into these simple approximate theories gives a fair description of the isotropic-nematic phase behavior for arbitrary rod length over diameter ratios. For more complicated applications of dispersions of rods beyond hard interactions, numerical approaches rapidly become more involved. Then this (still) simple, yet (more) accurate description of isotropic-nematic equilibria may become quite useful.

Competing Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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