Phase equilibria in solutions of platelike particles: Systems with steric and dispersive interactions between the platelets

Dagmara Sokolowska and Jozef K. Moscicki
Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland
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Our statistical thermodynamics model of solution of stiff, platelike, biaxial particles interacting solely via repulsion on contact (athermal limit) [Phys. Rev. E 62, 5011 (2000)] is extended to incorporate dispersion interactions between the particles. Dispersion forces between anisotropic particles are accounted for using the Imura-Okano approach. Numerical calculations specialized to solutions of either rods or disks show that besides the isotropic-nematic biphasic coexistence range, inclusion of attractive forces resulted in the appearance of nematic-nematic coexistence in both, disks and rods, solutions. The critical divergence of the difference between the order parameters and concentrations of the two nematics is observed while approaching the critical temperature. The minimum aspect ratio of rods or disks for the formation of the nematic phase is also discussed.

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I. INTRODUCTION

Nearly 80 years after the discovery of ordered phases in suspensions of highly anisotropic in shape colloidal particles [1–3], in recent years there is a substantial revival of interest in studying formation of mesophases by suspensions of naturally abundant and manmade rodlike and platelet nanoparticles [4–16], driven by potential applications of these systems. It is commonly accepted that both repulsive and attractive forces between particles are responsible for the formation of mesogenic phases [17]. Notwithstanding reservations towards applications of lattice models to small-molecule mesogenic systems, the lattice approach is quite convenient for the description of steric interactions between (macro)molecules with large axial ratios as in such cases molecular shapes can be simplified without substantial penalty, and spatial relations between them treated in a statistical manner [18–25]. However, when the reference lattice is in the laboratory frame, the allowed particle orientations are limited to a discrete set of directions only. Additionally, consideration of dispersive interactions in consistency with the statistical lattice model becomes awkward if particles are not rods in shape [26]. To overcome those problems an alternative concept of considering the reference lattice in the molecular frame was introduced by Warner [27] to model rodlike particles in a solution. As a result, the integrity of a rodlike molecule is preserved, i.e., discretization of rods is avoided and, consequently, also the molecular orientation distribution function is relieved from discretization characteristic of the Flory lattice approach [26,28].

In our previous paper (referred to as I) we extended Warner’s idea onto solutions of flat, rectangular parallelepipeds (platelets) exhibiting purely steric interactions [29]. The aim of this second in the series paper is to incorporate into the model dispersive interactions between the platelets.

Nonsteric interactions can be introduced into the model most conveniently as temperature dependent dispersion forces in the manner proposed by Imura and Okano [30,31]. For simplicity, we consider here dispersive forces only between anisotropic molecules, i.e., neglecting existence of such forces between solvent molecules and between solvent and solute molecules. Ultimately, the proposed model covers the systems of nonpolar, biaxial particles in a biaxial environment. Describing the average orientation of system particles through Euler’s angles, we show that the overall dispersive potential depends solely on four order parameters, on the absolute temperature, and on the anisotropic molecular polarizability. Detailed numerical calculations are limited to solutions of uniaxial particles, i.e., of either rods or square parallelepipeds with temperature-independent positive anisotropic polarizability (attractive dispersive interaction). The numerical algorithm proposed by Herzfeld et al. [32] is adopted to determine the phase diagrams of these systems.

II. THEORY

As in I, our discrete model system under consideration occupies $n_0$ cubic lattice cells, which are completely filled by $n_x$ solute monodisperse platelets $x_1 \times x_2 \times 1$ in size, and $n_s$ solvent $1 \times 1 \times 1$ cubes. All solute particles of the ensemble are incapable of interpenetrating each other—steric constraint. After placing the solute particles on the lattice, the remaining unoccupied cells are filled in by the solvent, i.e., solute-solvent and solvent-solvent steric interactions are disregarded. Thus there are no voids in the system, and $n_0 = n_x x_1 x_2 + n_s$; cf. I. Volume concentrations of solute and solvent molecules are then $n_x = x_1 x_2 n_x / n_0$ and $n_s = n_s / n_0$, respectively. Phase equilibrium analysis of such system requires evaluation of the thermodynamic Gibbs potential, $G = -kT \ln Z(n_x/n_s)$, and its subsequent minimization with respect to the orientation distribution function of the anisotropic species, $n_\parallel/n_\perp$, $n_\parallel$ being the number of platelets having orientation described by the solid angle $\Omega$. The partition function, $Z$ is factorable into configurational part $Z_{\text{comb}}$—comprising all steric interactions, the orientational part $Z_{\text{or}}$, and $Z_{\text{int}}$ accounting for other than steric interactions, such as, e.g., solute-solute (anisotropic dispersions), solvent-solute, solvent-solvent interactions or interactions with exter-
Particles in the system between two segments, say the inertia tensor axes coincide. The dispersion energy be-
anisotropic particles whose electric polarizability tensor and form of dispersion interaction between rodlike molecules molecules, and gives results consistent with Maier-Saupe defines expansion coefficients in terms of the polarizability Imura-Okano theory of dispersive forces two biaxial molecules in a biaxial environment following the equate for our model to evaluate interaction energy between experimentally observable physical quantities. We find it ad-
definition of expansion coefficients and their relation to ex-
tral atoms

dr_{ij}

test molecules

\[ C = \frac{1}{2} \left( \alpha_x + \alpha_y + \alpha_z \right), \] (3a)

\[ \alpha = \tilde{a}I + \Delta \alpha \text{diag} \left( \frac{1}{3}, -\frac{1}{3}, -\frac{1}{3} \right) + \Delta \alpha^t \text{diag} \left( -\frac{1}{3}, 0, 0 \right), \] (2)

\[ \Delta \alpha = \alpha_z - \frac{\alpha_x + \alpha_y}{2}, \] (3b)

\[ \Delta \alpha^t = \alpha_y - \alpha_z, \] (3c)

\[ \alpha_x, \alpha_y, \text{ and } \alpha_z \text{ being the principal components of the segment polarizability tensor } \alpha, \text{ and } I \text{ being the matrix identity.} \]

The original Imura-Okano model describes a system of anisotropic particles whose electric polarizability tensor and the inertia tensor axes coincide. The dispersion energy between two segments, say \( i \) and \( j \), belonging to two different particles in the system (cf. Fig. 1) can be approximated by

\[ \epsilon_{ij} = -\frac{C}{r_{ij}^6} \text{tr} (\alpha_i \alpha_j), \] (1)

where \( \alpha_i, \alpha_j \) are the polarizability tensors of the respective segments, \( r_{ij} \) is the distance between the centers of polarizability of those segments, and \( C \) is a constant. Each of the tensors can be represented in its principal frame as the sum of three parts of distinguished symmetries

\[ \tilde{a} = \frac{\alpha_x + \alpha_y + \alpha_z}{3}, \] (3a)

\[ \alpha = \tilde{a}I + \Delta \alpha \text{diag} \left( -\frac{1}{3}, -\frac{1}{3}, -\frac{1}{3} \right) + \Delta \alpha^t \text{diag} \left( -\frac{1}{3}, 0, 0 \right), \] (2)

\[ \Delta \alpha = \alpha_z - \frac{\alpha_x + \alpha_y}{2}, \] (3b)

\[ \Delta \alpha^t = \alpha_y - \alpha_z, \] (3c)

\( \alpha_x, \alpha_y, \text{ and } \alpha_z \text{ being the principal components of the segment polarizability tensor } \alpha, \text{ and } I \text{ being the matrix identity.} \]

The only limitation imposed by the lattice approach is that molecules are represented on the lattice by rectangular parallelepipeds. Let the \( Z \) axis of the laboratory frame \( \{XYZ\} \) coincides with the direction of the nematic director, \( n \). Let also molecular frames \( \{xyz\} \) and \( \{xyz^t\} \) of the test molecule and a randomly selected \( k \)th molecule of a system, respectively, be defined in such a way that the \( z \) axes are identified with the parallelepiped normals, and \( x \) and \( y \) axes coincide with the long edges of the same face of the parallelepipeds.

Mutual orientation of these reference frames is completely described by means of a set of Euler angles \( \Omega = (\alpha, \beta, \gamma) \) [29] (cf. Fig. 2):

\[ \{XYZ\} \longrightarrow \{xyz\}, \]

\[ \{XYZ\} \longrightarrow \{xyz^t\}, \]

In order to find the dispersion interactions of interest, we first express the polarizability tensor of a randomly selected \( k \)th molecule of a system, \( \alpha_k \), in the basis of the test molecule polarizability tensor, \( \alpha_{\text{test}} \). As a result, we get the interaction energy between the test molecule and a \( k \)th particle given in

\[ \{xyz\} \longrightarrow \{xyz^t\}. \]

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\[ \{xyz\} \longrightarrow \{xyz^t\}. \]
terms of the set of Euler angles, $\Omega_k$. This result has to be transformed to the laboratory frame, and we obtain the pairwise potential between two molecular segments (i.e., the $ith$ segment of a test molecule and the $jth$ segment of a $kth$ system particle) as a function of sets of Euler angles, $\Omega$ and $\Omega'$:

$$
\varepsilon_{ij}(\Omega, \Omega') = -\frac{C_{ij}}{r_{ij}^6} \left[ 3\bar{a}_i\bar{a}_j + \Delta \alpha_i \Delta \alpha_j \left( \frac{2}{3} s_1(\Omega)s_1(\Omega') + \frac{1}{2} s_2(\Omega)s_2(\Omega') \right) - \frac{\Delta \alpha_i \Delta \alpha_j}{2} \left( s_3(\Omega)s_1(\Omega') + s_1(\Omega)s_3(\Omega') \right) - \frac{\Delta \alpha_i \Delta \alpha_j}{2} \left( s_4(\Omega)s_4(\Omega') + \frac{3}{4} s_3(\Omega)s_3(\Omega') \right) \right] + \Phi(\Omega, \Omega'; \Delta \alpha_i, \Delta \alpha_j, \Delta \alpha^2_i, \Delta \alpha^2_j),
$$

(5)

where the functional $\Phi$ is a multicomponent sum of functions of $\sin \alpha$, $\sin \beta$, or $\sin \gamma$. Functions $s_1(\Omega)$, $s_2(\Omega)$, $s_3(\Omega)$, and $s_4(\Omega)$, when averaged over all possible orientations, yield a complete set of four biaxial order parameters [34,35,37]:

$$
S_1 = s_1(\Omega) = 1 - \frac{3}{2} \sin^2 \beta,
$$

(6a)

$$
S_2 = s_2(\Omega) = \sin^2 \beta \cos 2\alpha,
$$

(6b)

$$
S_3 = s_3(\Omega) = \sin^2 \beta \cos 2\gamma,
$$

(6c)

$$
S_4 = s_4(\Omega) = \frac{1}{2}(1 + \cos^2 \beta) \cos 2\alpha \cos 2\gamma - \cos \beta \sin 2\alpha \sin 2\gamma.
$$

(6d)

In case of apolar molecules ($\sin 2\alpha = \sin 2\beta = \sin 2\gamma = 0$), the order parameter $S_4$ simplifies to

$$
S_4 = s_4(\Omega) = \frac{1}{2}(1 + \cos^2 \beta) \cos 2\alpha \cos 2\gamma.
$$

(6d’)

Particular symmetries of the system or of the molecular shape are manifest in the zeroing of the relevant order parameters. For example, for particles with biaxial symmetry in the uniaxial system, $S_2 = S_3 = 0$. If, in addition, the molecules are uniaxial, $S_3 = 0$, the potential depends solely on the nematic order parameter, $S_1$. If we limit our interest to a system of apolar molecules, the average of $\Phi$ over the orientation distribution function is zero.

Assuming that molecules most efficiently interact with the nearest neighbors only, the mean field dispersion energy for $ith$ segment of a test molecule oriented at angle $\Omega$ with respect to the laboratory frame becomes

$$
e_{int} \equiv -\left( \frac{x_1 x_2 n_1}{2} \right) \bar{v}_i \left( \frac{k_B T^*}{\bar{v}} \right) \left( \frac{\overline{\Delta \alpha}}{\bar{\alpha}} \right)^2 \left( \frac{2}{3} S_1^2 + \frac{1}{2} S_3^2 + \frac{3}{8} S_4^2 \right),
$$

where $k_B T^* = \varepsilon_C/r^6$. In the process we assumed that since
the test molecule can be any molecule in the system, the test particle orientational distribution function is the same as of the system, \( \omega_{s1}^{x1} (\Omega) = \omega_{x1}^{s1} (\Omega') \). The supplementary factor of the platelet concentration, \( n_x \), reflects the assumption of the lack of interactions between solute and solvent particles. The \((x_1x_2n_x/2)\) factor slightly overestimates the number interacting pairs of segments, since it accounts also for pairs belonging to the same platelet, however, for very large \( n_x \), the error is negligible.

Dispersion attractions enter the Gibbs thermodynamic potential in two ways. There is a component, \( \Delta G_{\text{disp}}^1 \), coming out from \( Z_{\text{int}} \) factor of the partition function,

\[
\frac{\Delta G_{\text{disp}}^1}{k_B T} = -\ln Z_{\text{int}} = \frac{E_{\text{int}}}{k_B T} = -\left( \frac{x_1x_2n_x\Theta'}{2} \right) \left[ (\Delta \alpha)^2 - \frac{1}{3} S_1 (1 - S_1) + S_2 \right] = -\Delta \alpha \Delta \alpha' (S_1 S_3 + S_2 S_4) + (\Delta \alpha^2)^2 \left( \frac{1}{2} S_1^2 + \frac{3}{8} S_3^2 \right).
\]

The second component, \( \Delta G_{\text{disp}}^2 \), comes from the Boltzmann factor present in the molecular distribution function in equilibrium

\[
\frac{\Delta G_{\text{disp}}^2}{k_B T} = \frac{x_1x_2n_x\Theta'}{2} \left[ (\Delta \alpha)^2 - \frac{1}{3} S_1 (1 - S_1) + S_2 \right] \left[ (\Delta \alpha')^2 - \frac{1}{3} S_1 (1 - S_1) + S_2 \right] - \Delta \alpha \Delta \alpha' [2S_1 S_3 + 2S_2 S_4 - S_3 S_4] \left( \frac{1}{2} S_4^2 + \frac{3}{8} S_3^2 \right).
\]

The parameter \( \Theta' = T' / T \) is introduced as a measure of reduced inverse temperature. Thus we may write

\[
\frac{G}{k_B T} = \frac{G_{\text{ster}}}{k_B T} + \left( \frac{\Delta G_{\text{disp}}^1}{k_B T} + \frac{\Delta G_{\text{disp}}^2}{k_B T} \right),
\]

where \( G_{\text{ster}} \) denotes the Gibbs potential in the limit of steric repulsions only, and is derived in I. Note at this point that the molecular potential of the dispersive interaction experienced by the test molecule is

\[
\frac{U(\Omega)}{k_B T} = -\frac{x_1x_2\Theta'}{2} \left[ (\Delta \alpha)^2 (2 S_1 \sin^2 \beta + S_2 \sin^2 \beta \cos 2 \alpha) \right] + \frac{1}{2} \left[ (\Delta \alpha')^2 \left( \frac{1}{2} S_1^2 + \frac{3}{2} S_2^2 \right) \right]
\]

\[
+ \frac{1}{4} \left[ S_1 \sin^2 \beta \cos 2 \gamma + S_2 \sin^2 \beta \cos 2 \alpha \right] \left[ \frac{3}{4} S_1 \sin^2 \beta \cos 2 \gamma + \frac{1}{4} S_4 (1 + \cos^2 \beta) \right]
\]

\[
\times \cos 2 \alpha \cos 2 \gamma \right] - \Delta \alpha \Delta \alpha' \left[ \frac{3}{4} S_1 \sin^2 \beta \cos 2 \alpha \right]
\]

\[
+ \frac{1}{2} S_1 \sin^2 \beta \cos 2 \gamma + S_4 \sin^2 \beta \cos 2 \alpha
\]

\[
+ \frac{1}{2} S_2 (1 + \cos^2 \beta \cos 2 \alpha \cos 2 \gamma) \left( \frac{3}{8} S_3^2 + \frac{3}{8} S_4^2 \right) \right] \right).
\]

The phase coexistence condition requires the equality of the respective chemical potentials in two different phases, \( F_1 \) and \( F_2 \):

\[
(\mu_i^F - \mu_i^0) = (\mu_i^F - \mu_i^0)_{\text{ster}} + (\mu_i^F - \mu_i^0)_{\text{disp}}.
\]

Steric parts of chemical potentials are specified in I. The dispersion terms for the anisotropic phase (A) are

\[
\left( \frac{\mu_i^A}{k_B T} \right) = \frac{1}{2} \left[ (\Delta \alpha)^2 \left( \frac{1}{3} S_1^2 + \frac{1}{2} S_2^2 \right) - \Delta \alpha \Delta \alpha' (S_1 S_3 + 2S_2 S_4 - S_3 S_4) \right] \left( \frac{3}{8} S_4^2 + \frac{3}{8} S_3^2 \right) + C_x.
\]

for the solvent, and

\[
\left( \frac{\mu_i^A}{k_B T} \right) = \frac{x_1x_2\Theta'}{2} \left[ (\Delta \alpha)^2 \left( \frac{1}{2} S_1^2 + \frac{1}{2} S_2^2 \right) - \Delta \alpha \Delta \alpha' \left( S_1 S_3 + 2S_2 S_4 - S_3 S_4 \right) \right] \left( \Delta \alpha^2 \right)
\]

\[
+ \frac{1}{2} x_1x_2\Theta' \left( \frac{3}{8} S_4^2 + \frac{3}{8} S_3^2 \right) + C_x
\]

for the platelets. The terms \( C_x \) and \( C_s \) in Eq. (15) and Eq. (16) are chemical potentials of nonmixing mixtures, and are equal to the respective chemical potentials in the isotropic phase and, thus, cancel out when the two-phase coexistence condition is considered. In the isotropic phase the dispersive components of chemical potentials for both solute and solvent equal to zero.
III. CALCULATIONS AND DISCUSSION

The formalism presented here is sufficiently general to open the possibility for studying phase equilibrium in a vast range of molecular systems [33]. Here, for exemplary purpose we restrict our attention to two most common cases of the monodisperse uniaxial system, i.e., solutions of rods, and of square platelets (disks). In such cases, formalism simplifies substantially as outlined in Appendixes A and B. The dispersion interaction parameter, \( \Theta \), depends now solely on the inverse temperature (see Appendix A). As \( \Theta \) comprises the average polarizability factor, \( \Delta \alpha \), which in general can be either positive or negative [38], there are two possible ranges of interest for \( \Theta \), \( \Theta \geq 0 \) and \( \Theta \leq 0 \). In what follows we limit

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FIG. 4. Phase diagrams for solutions of (a)–(c) rods and (d)–(f) disks as a function of parallelepiped axial ratio \( x \): (a) 17.00, (b) 26.00, (c) 30.00, (d) 6.00, (e) 8.00, and (f) 11.00. Nematic (N), isotropic (I) and biphasic (I+N) regions are indicated. Note formation of \( (N_1+N_2) \) region for sufficiently asymmetric particles; \( \Theta_{III} \) and \( \Theta_{c} \) indicate a triple point, and a critical point for nematic-nematic \( (N_1+N_2) \) demixing, respectively.
considerations to attractive forces between the platelets (\(\Theta = 0\)) only, although it was argued that physically such a case is more likely for rods than for disks [38]. In addition, we assume that \(\Delta \alpha\) is independent of temperature. Numerical calculations used the method of Ref. [32], and details of the algorithm can be found in I. Results are summarized in Figs. 3–6.

First, we studied the interplay between steric and dispersive interactions in the formation of the nematic phase in the neat system (\(v_s = 1\)), as a function of the axial ratio. As anticipated, increasing strength of dispersive interactions, the higher dispersion parameter or lower the temperature, lowers the critical axial ratio for both the dislikle, and the rodlke systems; see Fig. 3. Extrapolation (exponential) of results gives the minimum critical molecular ratio, \(x_{\text{crit min}}\) for the formation of nematic phase in the uniaxial systems in the close-packing limit and in the inverse temperature limit, \(\Theta \rightarrow \infty\). We found that our model requires molecules to be aspherical for the nematic phase formation: \(x_{\text{crit min}} = 2.15 \pm 0.03\) for rods, and \(x_{\text{crit min}} = 1.66 \pm 0.01\) for disks. Our results do not depart significantly from those obtained by other authors. The values are similar to those obtained in the van der Waals approach [39] and scaled particle theory [40]. Numerical simulations based on the virial expansion give the limits ranging from \(x_{\text{min}} = 2.75\) for athermal lyotropic rods and disks in Monte Carlo simulations (in the ellipsoid of revolution approximation for the molecular shape) [41], to \(x_{\text{min}} = 1\) for spherocylinders [42].

Next, we generated phase diagrams for both systems of particles, for different axial ratios. In Fig. 4 are presented those results which are typical for particular ranges of the ratio values. \(\Theta = 0\) (the \(x\) axis) corresponds to the athermal limit studied in I, where isotropic-nematic demixing was entropically favored, according to the depletion mechanism, as argued in Ref. [43]. In all cases the biphasic range of coexistence is bottle-shaped: a narrow, bottleneck part for low values of \(\Theta\), and the broad one in the region where the attractive interactions become stronger. The transition between the narrow and the broad coexistence range is monotonous for small axial ratios. However, for systems with high enough axial ratio, a triple point, \(\Theta_{triple}\) appears on the biphasic-nematic border line, and separation of two nematic phases of the same spatial symmetry but with a different degree of orientational order, cf. Fig. 4(c) and Fig. 4(f).

Nematic-nematic demixing vanishes at the critical point, \(\Theta_{N-N}\), in the vicinity of which a critical behavior occurs. Such phase behavior has been observed experimentally in solutions of rodlike poly (\(\gamma\)-benzyl-L-glutamate) in benzyl alcohol [44]. Critical exponents for the divergence of \((S_{N-N}^1-S_{N-N}^2)\) were obtained by fitting the data within the range where critical divergence is clearly apparent. The best-fit lines to these fits are shown in Fig. 5 and the critical exponents are shown in Table I. NMR results show that the critical vicinity region of \(I-N\) transition for dislikle liquid crystals is up to two orders of magnitude smaller \((|T - T_{III}|/T_{III} \approx 10^{-5} - 10^{-4})\) than the corresponding range for rod-shaped thermotropic nematics \((|T - T_{III}|/T_{III} \approx 10^{-3} - 10^{-2})\) [8,45]. A similar tendency is visible in our results for \(N_1-N_2\) transition (cf. Fig. 5), although the difference is much less pronounced. To our knowledge, this is the first time when such critical behavior
of the nematic-nematic demixing in monodisperse system has been modeled quantitatively. The critical divergence shows up also in the volume concentration difference, \( \nu^N - \nu^S \); see Fig. 5. The best-fitted lines give critical exponents, \( \beta_2 \approx 0.50000 \pm 0.0004 \) and \( 0.495 \pm 0.001 \), for rods and disks, respectively, which are the mean-field values [46] within an experimental error. Additional numerical calculations verified that observed deviations of all our critical exponents from the mean field value of 0.5 are solely a consequence of numerical roundups and precision with which the order parameter is determined.

It is also interesting to follow the nematic ordering variation along the biphasic-nematic border of the isotropic-nematic coexistence region. The order parameter at the border, \( S_{1}^{**} \), is very sensitive to the strength of the dispersive interactions. In Fig. 6, the order parameter at the border as a function of \( \Theta \), and for several different axial ratios of rods and disks is presented. The universal character of \( S_{1}^{**} \) vs \( \Theta \) behavior is evident. Departing from the athermal limit (broken vertical line, \( \Theta = 0 \)), the order parameter decreases with increasing \( \Theta \), reaches a minimum, and starts to increase with increasing \( \Theta \). Clearly, the appearance of weak attractive forces stabilizes the nematic phase, as manifested in the shift of the biphasic-nematic border to lower concentrations; cf. Fig. 6, even at lower concentrations of solute, and in the lowering of the orientational order on the initial increase of \( \Theta \); cf. Fig. 6. This tendency, however, does not last too long on increasing the strength of attractive forces. Both the border concentration and the border order parameter begin, at some value of dispersion interactions, to increase monotonically with \( \Theta \). The nematic-nematic coexistence manifests itself in the \( S_{1}^{**} \) vs \( \Theta \) plot as the order parameter discontinuity at the triple point; cf. Fig. 6. At even stronger interactions, on increasing \( \Theta \) the order parameter saturates at the value close to unity for every axial ratio: the attractive dispersion forces overpower any steric constraints present in the system.

In the forthcoming papers we will address in turn the phase equilibrium calculations for solution of biaxial platelets, the platelet polydispersity—in particular rod-platelet binary mixtures, and the issues of solvent-solvent interactions [33].

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**APPENDIX A: UNIAXIAL DISKS**

The formalism simplifies if the plates are square, \( x_1 = x_2 = x \), i.e., for disks \( d \). The orientational distribution function reduces to the uniaxial one and depends solely on the Euler angle \( \Theta \):

\[
\omega_{x_{1}^{+2}}(\Omega) = \omega_{x_{1}}(\beta) = \omega_{d}(\beta)
\]

\[
\sin \beta \exp\left(- \sum_{i} b_{i} Q_{i} \exp\left(\frac{-U(\beta)}{k_{B}T}\right)\right) 
\int \sin \beta \exp\left(- \sum_{i} b_{i} Q_{i} \exp\left(\frac{-U(\beta)}{k_{B}T}\right)\right) d\beta
\]

\( i = X, Q \).  

(A1)

where the first exponent comes from steric repulsions [cf. Eqs. (B4)-(B7) in I], and the second exponent from attractive interactions with the potential

\[
\frac{U(\beta)}{k_{B}T} = \frac{3}{2} x^{2} \Theta v_{b} S_{1} \sin^{2} \beta,
\]

(A2)

and the dispersion interaction parameter \( \Theta \) is dependent on the inverse temperature...

---

**TABLE I. Comparison of critical exponents for divergence of the order parameter from the present study with those obtained by other workers (key to phase notation: \( I \), isotropic; \( N \), nematic; \( N_{BA} \), biaxial nematic, \( S_{A} \), smectic A)**

<table>
<thead>
<tr>
<th>Uniaxial system</th>
<th>Type of work</th>
<th>( I-N )</th>
<th>( N-N )</th>
<th>( N-S_{A} )</th>
<th>( N-N_{BA} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rodlike</td>
<td>Theory</td>
<td>0.5(^{a})</td>
<td>0.547(^{c})</td>
<td>0.94–1.00(^{d})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>0.2–0.3(^{e})</td>
<td></td>
<td></td>
<td>0.38–0.56(^{b})</td>
</tr>
<tr>
<td></td>
<td>Disklike</td>
<td>Theory</td>
<td>0.493(^{c})</td>
<td></td>
<td>0.3–0.36(^{f})</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td></td>
<td></td>
<td></td>
<td>0.34(^{g})</td>
</tr>
</tbody>
</table>

\(^{a}\)Mean field [46,47].
\(^{b}\)Tricritical pt. [48].
\(^{c}\)This work.
\(^{d}\)EPR [49].
\(^{e}\)Birefringence [50,51].
\(^{f}\)Static dielectric permittivity [52].
\(^{g}\)Renormalization [53].
\(^{h}\)Interferometry [54].
\(^{i}\)NMR [8].
\[ \Theta = \frac{2\pi C}{3\sqrt{\bar{T}}} (\Delta \bar{T})^2 \frac{1}{k_B T} \]  
(A3)

in analogy to Flory and Ronca’s $\bar{T}^{-1}$ [19].

The dispersive term of the Gibbs function in the nematic phase (N) is

\[ \left( \frac{G^N}{n_0 k_B T} \right)_{\text{disp}} \ = \ -(\nu_d^N)^2 S_1 \left( 1 - \frac{S_1}{2} \right) \Theta, \]  
(A4)

and the relevant parts of chemical potentials for solvent (s) and solute (d) are

\[ \left( \frac{\mu^N_s}{k_B T} \right)_{\text{disp}} \ = \ \frac{1}{2} \nu_d^N \Theta S_1^2, \]  
(A5)

\[ \left( \frac{\mu^N_d}{k_B T} \right)_{\text{disp}} \ = \ -\nu_d^N \Theta S_1 \left( 1 - \frac{1}{2} \nu_d^N S_1 \right), \]  
(A6)

respectively, and together with their counterparts from steric repulsions [cf. Eqs. (B9) and (B10) in I] they constitute the total chemical potentials of the components in the nematic phase.

Introduction of the dispersive attraction into the system does not alter Gibbs function or chemical potentials of the solute nor of the solvent in the isotropic phase; cf. Eqs. (33), (B11), and (B12) in I.

**APPENDIX B: LONG RODS**

Yet another limit of the general theory presented here is a solution of rods (r). In such case the substitution of either $x_1=1$ or $x_2=1$ simplifies the model formalism, and after inclusion of the attractive interactions between rods, the orientational distribution function becomes

\[ \omega_{x_1 x_2}(\Omega) = \omega_{x_1}(\beta) = \omega_{x_2}(\beta) \]

\[ \frac{\sin \beta \exp(b_x Q_{xy}) \exp \left( \frac{-U(\beta)}{k_B T} \right)}{\int \frac{\sin \beta \exp(-b_x Q_{xy}) \exp \left( \frac{-U(\beta)}{k_B T} \right) d\beta}, \]  
(B1)

where the first exponent in the numerator on RHS of Eq. (B1) comes from steric repulsions, see Eqs. (C17)-(C20) in I, and the potential of the pairwise dispersive interaction between rods is

\[ \frac{U(\beta)}{k_B T} = \frac{3}{2} x \Theta \nu_d^2 S_1 \sin^2 \beta, \]  
(B2)

where $\Theta$ is defined in Eq. (A3).

The nematic phase Gibbs function, and the chemical potential dispersive terms in the nematic phase are

\[ \left( \frac{G^N}{n_0 k_B T} \right)_{\text{disp}} = -(\nu_d^N)^2 S_1 \left( 1 - \frac{S_1}{2} \right) \Theta, \]  
(B3)

\[ \left( \frac{\mu^N_s}{k_B T} \right)_{\text{disp}} = \frac{1}{2} \nu_d^N \Theta S_1^2, \]  
(B4)

\[ \left( \frac{\mu^N_d}{k_B T} \right)_{\text{disp}} = -\nu_d^N \Theta S_1 \left( 1 - \frac{1}{2} \nu_d^N S_1 \right). \]  
(B5)

As for disks, the introduction of dispersive attraction into the system does not alter the Gibbs function or the chemical potentials of the solute nor of the solvent in the isotropic phase.