

# Isotropic–nematic transition in micellized solutions<sup>a)</sup>

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We treat the isotropic-to-nematic transition in polydisperse suspensions of micellar rods. By generalizing an early theory of Onsager, we obtain a first-order transition in which the ordered rods are significantly longer than those in the (coexisting) isotropic phase. We show that this “growth” is driven by the free energy term arising from loss of orientational entropy upon alignment. For large aggregates the product  $\bar{\rho}\bar{L}^2D$  (where  $\bar{L}$  is a number-averaged length,  $D$  the diameter of the rods, and  $\bar{\rho}$  the number density of aggregates) is roughly constant for each phase at coexistence. The transition value of the (nematic) order parameter ( $\simeq\langle P_2(\cos\theta)\rangle$ ) first increases linearly with aggregation number  $s$  (for small rods) and approaches unity asymptotically (for large  $s$ ). We compare our results to those of an earlier, monodisperse treatment of this system and interpret the nematic-induced growth in terms of coupling between rod size and alignment in micellar solutions.

## I. INTRODUCTION

Suspensions of rigid anisotropic particles have long been known to exhibit an order–disorder phase transition at high enough density.<sup>1</sup> This isotropic-to-nematic transition results from a lowering of the thermodynamic free energy upon orientationally ordering the particles. Mixtures of hard rods of various sizes,<sup>2–4</sup> or of rods and disks<sup>5–7</sup> undergo the same phase change, though the extra components complicate their phase diagrams somewhat. Similar nematic behavior must be expected as well in concentrated-enough micellar solutions consisting of anisotropic aggregates. Experiments performed on several aqueous amphiphilic systems verify this idea<sup>8,9</sup>: at volume fractions of order 10%–40%, solutions of rodlike micelles show a birefringent fluid phase. At slightly higher densities, the nematic state becomes unstable with respect to a perfectly ordered, hexagonally packed phase of infinite cylinders.

What distinguishes the micellar colloids described in this work from the usual polydisperse mixture of rodlike particles is the former’s ability to change its size distribution via exchange of molecules. An ordinary colloidal solution (e.g., a polydisperse suspension of rigid macromolecules) consists of interacting particles *each of which must maintain its physical integrity*. In the *exchange* (micellar) colloids, on the other hand, species of a given size are *not* conserved upon changing the thermodynamic state of the system. Only the *total* amount of “monomer” (surfactant) must remain constant. In particular, either concentrating (or warming/cooling) the system, or going

to a nematic state, may alter the “particle” (aggregate) size distribution.

Although theories<sup>10,11</sup> of micellar self-assembly superficially treat each different size (and shape) aggregate as a separate species, the species are linked by equations of chemical equilibrium between monomer and aggregated particles. With  $s$  subscript denoting a micelle of size (aggregation number)  $s$ , and  $A$  labeling the monomer, we have

$$s\mu_A = \mu_s.$$

There is one such equation for the chemical potential  $\mu_s$  of each aggregate, and hence only a single independent species (e.g., the monomer). The exchange colloid is a single-component system, the ordinary (polydisperse) one a multicomponent mixture.

With few exceptions<sup>12,13</sup> theorists working on models for self-aggregation have ignored the interactions that may exist between micelles. They have concentrated generally on approximate, often phenomenological, theories of aggregation at the single micelle level. Still less effort has been devoted toward treating the effects of anisotropic interactions between micelles on fluid phase stability. An earlier study<sup>14</sup> of the  $I \rightarrow N$  transition had suppressed polydispersity contributions, focusing on the most-probable-sized micelle. Because the interactions between aggregates depend upon their size distribution, and their size distribution upon the interactions between them, a more complete treatment of the problem appears unreasonably complicated at first. Indeed, the usual approach to multicomponent systems of constant composition is to write a separate orientational distribution function for each component of given concentration. In the present situation, however, we are not free to arbitrarily

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fix the size distribution since it is coupled to the state of alignment. This dilemma becomes especially significant in view of the large amount of experimental and practical interest in isotropic-to-nematic phase transitions in surfactant solutions.<sup>8,9</sup>

In this paper we treat the isotropic-to-nematic phase transition in a polydisperse system of long (spherocylindrical) hard rods built up from monomer. Our approach allows for full coupling between polydispersity and inter-aggregate interactions. We generalize the usual Onsager theory of monodisperse hard particles to our system and derive expressions for the size-and-orientational distribution function, osmotic pressure, and chemical potential. The results obtained are quite general and would apply to any exchange colloid in which second virial terms are dominant. We apply this formalism in particular to micellar aggregates, using current models for the standard chemical potentials. These results are discussed in connection with the monodisperse case and used to arrive at a qualitative characterization of the coupling between micellar size and alignment in the isotropic/nematic transition in simple soap solutions.

During the refereeing of this paper, the authors learned about a series of articles by R. W. Briehl and J. Herzfeld [Macromol. **14**, 397, 1209 (1981); Ferroelectrics **30**, 125 (1980); Proc. Natl. Acad. Sci. U.S.A. **76**, 2740 (1979)] which treat the coupling of growth and alignment in systems of reversibly polymerizing macromolecules. Despite the differences in physical contexts, and in statistical mechanical approximations, their discussion of the joint equilibration of rod lengths and orientations is phenomenologically similar to ours. In both cases the length distributions are determined by thermodynamics, rather than by the choice of system.

## II. THEORY

### A. Statistical thermodynamics

Consider a suspension of rodlike "particles" (e.g., micelles) of different sizes, in chemical equilibrium with each other. We regard the solution as dilute in each species, *but not as ideal*. Let  $N_A$  be the total number of monomers (incorporated into micelles) and  $N_A f(\Omega, s)$  be the number of rods per unit solid angle having size  $s$  and orientation  $\Omega$ . Regarding rods with different  $\Omega$  as distinct species, expanding the excess (over that of pure solvent) Helmholtz free energy  $\Delta A$  in a virial series, and neglecting three-body and higher-order terms, we write ( $\rho_A = N_A/V$  and  $\beta = 1/kT$  as usual)

$$\frac{\beta \Delta A}{N_A} = \int \left\{ \beta \mu_s^* + \ln 4\pi f(\Omega, s) - \ln 4\pi + \ln \rho_A - 1 - \frac{\rho_A}{2} \int \beta_1(s, s', \Omega, \Omega') f(\Omega', s') d\Omega' ds' \right\} \times f(\Omega, s) d\Omega ds. \quad (1)$$

Here  $\mu_s^*$  is the standard chemical potential of an  $s$  rod [defined so that  $\beta \mu_s \rightarrow \beta \mu_s^* + \ln \rho_s$ ,  $\rho_s \equiv \rho_A \int d\Omega f(\Omega, s) \rightarrow 0$ ] and  $\beta_1(s, s'; \Omega, \Omega')$  is the cluster integral for two

rods with sizes  $s$  and  $s'$  and orientations  $\Omega$  and  $\Omega'$ . To the extent that the micelles behave like "hard" particles (i.e., for nonionic surfactants, or in the high salt—short Debye length—limit),  $-\beta_1$  becomes simply the volume excluded to the geometrical center of one rod by the other. Note that  $\mu_s^*$  contains contributions from the internal micellar degrees of freedom, as well as the usual integrations over translational and rotational momenta; it also includes the direct interactions of each aggregate with the solvent.<sup>15,16</sup>

Performing a functional minimization of Eq. (1) [ $\delta(\beta \Delta A/N_A) = 0$ ] with respect to  $f$ , subject to the constraint

$$\int s f(\Omega, s) ds d\Omega = 1, \quad (2)$$

we obtain

$$f(\Omega, s) = \frac{e^{-\beta \mu_s^*}}{\rho_A} e^{\lambda s} \exp \left[ \rho_A \int \beta_1(s, s'; \Omega, \Omega') \times f(\Omega', s') d\Omega' ds' \right]. \quad (3)$$

Here  $\lambda$  is the Lagrange multiplier conjugate to the normalization condition (2). (Soon we identify  $\lambda$  with the chemical potential of monomer in solution.) Equation (3) is a nonlinear integral equation for  $f(\Omega, s)$  which we will solve (approximately) numerically. Armed with  $f(\Omega, s)$  we can evaluate  $\Delta A$  and any other macroscopic property using Eq. (1) and appropriate thermodynamic identities.

To observe a coexistence between nematic and isotropic phases of rodlike aggregates, we need to consider the system under conditions of constant pressure and temperature. At some critical density, before  $(\Delta A)_{\text{nematic}} = (\Delta A)_{\text{isotropic}}$ , the chemical potential of the isotropic phase will become equal to that of a nematic phase of higher density. The solution will begin separating into these isotropic and nematic phases upon further increase in concentration. This will continue until the overall solution density equals that of the nematic phase. From that point on, the equilibrium state of the system will be nematic.

Along the line of coexistences, the conditions for chemical equilibrium are that the chemical potential  $\mu_A$  of monomer in both phases be equal (by the equilibrium condition between  $s$  monomers and an  $s$  aggregate,  $s\mu_A = \mu_s$ ; this implies that the chemical potentials per monomer in aggregates of all sizes are equal between both phases), and that each phase have the same osmotic pressure  $\Pi$ . From  $\Pi = -(\partial \Delta A / \partial V)_{T, N_A}$  and Eq. (1) we have

$$\beta \Pi = \rho_A \left[ \left\langle \frac{1}{s} \right\rangle - \frac{\rho_A}{2} \int \int \beta_1(\Omega, s; \Omega', s') f(\Omega, s) \times f(\Omega', s') d\Omega' ds' \right]. \quad (4)$$

Bracketed quantities denote averages over  $s$  and  $\Omega$  according to

$$\langle \Psi \rangle \equiv \int ds d\Omega \Psi(\Omega, s) s f(\Omega, s). \quad (5)$$

The chemical potential of the monomers is

$$\beta\mu_A = \frac{\beta\Delta G}{N_A} = \frac{\beta(\Delta A + \Pi V)}{N_A}. \quad (6)$$

Combining Eqs. (1), (3), and (4) gives the general result

$$\beta\mu_A = \lambda. \quad (6')$$

Hence to locate the coexistence point, we must find the densities at which, after solving for the distribution function, the Lagrange multipliers of both phases are equal and  $(\beta\Pi)_{\text{isotropic}} = (\beta\Pi)_{\text{nematic}}$ .

## B. Treatment of long rods

As suggested by Onsager and later shown by Straley,<sup>17</sup> truncation of the virial expansion at  $\beta_1$  for hard, mono-dispersed rods is valid only for sufficiently anisotropic rods. We expect the same considerations to apply to a polydisperse system of such particles, and thus confine the remainder of this development to rods with large aggregation numbers (and thus large length-to-diameter ratios)—see, however, discussion in Sec. IV.

For long spherocylinders,  $\beta_1$  has the simple form

$$\beta_1 = -LL'(D + D')\sin \gamma, \quad (7)$$

with  $L(L')$  and  $D(D')$  the cylinder length and diameter of an  $s(s')$  rod.  $\gamma$  is the angle between the two rods. If a rod contains  $m$  monomers in its spherical caps, has a fixed diameter (independent of  $s$ ) of  $2l$ , and each monomer has a volume  $v$ , then

$$L = (s - m)v/\pi l^2. \quad (8)$$

(A minimum aggregation number  $m$  corresponding to the two hemispherical caps, and a fixed diameter  $2l$  equal to twice the "length" of a monomer, is basic to earlier discussions of micellar colloids.<sup>12,13</sup>) From Eqs. (7) and (8),

$$\begin{aligned} \rho_A \int \beta_1(s, s'; \Omega, \Omega') f(\Omega', s') d\Omega' ds' \\ = -\frac{4v^2}{\pi^2 l^3} \rho_A (s - m) \int (s' - m) \sin \gamma(\Omega, \Omega') \\ \times f(\Omega', s') d\Omega' ds'. \end{aligned} \quad (9)$$

Next, using an expansion for  $\sin \gamma$  in terms of Legendre polynomials  $P_n$ ,<sup>18</sup> and the addition theorem for spherical harmonics,<sup>19</sup> Eq. (1) becomes

$$\frac{\beta\Delta A}{N_A} = \lambda - \frac{1}{m} + \frac{4\alpha_1}{\pi m} - 2\frac{B\alpha_1^2}{\pi} + \frac{16}{5}\frac{B\alpha_2^2}{\pi}, \quad (10)$$

with

$$B = \frac{4v^2 \rho_A}{\pi^2 l^3}, \quad (11)$$

$$\alpha_1 = \frac{\pi}{4} (1 - m\langle 1/s \rangle), \quad (12)$$

and

$$\alpha_2 = \frac{5\pi}{32} \left\langle \left( 1 - \frac{m}{s} \right) P_2(\cos \theta) \right\rangle. \quad (13)$$

From Eq. (3) we have similarly that

$$\begin{aligned} f(\Omega, s) = \frac{e^{-\beta\mu_s^*}}{\rho_A} e^{\lambda s} \exp\{-B(s - m) \\ \times [\alpha_1 - \alpha_2 P_2(\cos \theta)]\}, \end{aligned} \quad (14)$$

reducing to the proper form<sup>13</sup> for isotropic phases (with  $\lambda$  the chemical potential of monomer) when  $\alpha_2 = 0$ . At low densities (low  $B$ ), we should find only the isotropic ( $\alpha_2 = 0$ ) solution, while at higher densities we expect as well a nematic ( $\alpha_2 \neq 0$ ) solution. Finally, from Eq. (4) we have

$$\beta\pi = \rho_A \left\{ \frac{1}{m} - \frac{4\alpha_1}{\pi m} + \frac{B}{2} \left[ \frac{4}{\pi} \alpha_1^2 - \frac{32}{5\pi} \alpha_2^2 \right] \right\}. \quad (15)$$

In deriving Eqs. (10) through (15) we have truncated the Legendre polynomial expansions at the  $P_2$  level; as shown by others<sup>2,18</sup> in calculations on monodispersed systems, this approximation gives qualitatively correct results for all properties of interest. To obtain the distribution function  $f(\Omega, s)$  [see Eq. (14)], for example, we simply solve Eqs. (2), (12), and (13) for  $\lambda$ ,  $\alpha_1$ , and  $\alpha_2$ . The  $I/N$  coexistence point then follows from the values of  $\rho_A^I$  and  $\rho_A^N$  which equalize the chemical potentials ( $\beta\mu_A$ ) and osmotic pressures ( $\beta\Pi$ ) for the two phases.

## C. Application to micelles

The standard chemical potential,  $\mu_s^*$ , of an  $s$  rod can be written<sup>15</sup>

$$\beta\mu_s^* = \ln \left[ \frac{V\gamma_s^0}{q(s)} \right], \quad (16)$$

where  $q(s)$  is the "ideal-gas," single-particle partition function of an  $s$  rod excluding the integrations over its two orientational Euler angles, and  $\gamma_s^0$  ( $1/\gamma_s^0 = \langle\langle e^{-\beta\phi_s} \rangle\rangle$ ) where  $\langle\langle \rangle\rangle$  denotes an average over the configurational coordinates of solvent molecules and  $\phi_s = [(\text{the potential energy of an } s \text{ rod} + \text{solvent}) - (\text{the potential energy of the solvent only})]$ <sup>17</sup> is its direct interaction with pure solvent. In earlier work,<sup>15</sup> we showed for micellar aggregates that a consistent—from a statistical thermodynamical point of view—expression for the quantity  $q(s)/N_A\gamma_s^0 = e^{-\beta\mu_s^*}/\rho_A$  is

$$\frac{q(s)}{N_A\gamma_s^0} = [4\pi^{1/2}\Lambda^3, \Lambda_{\text{rot}}^3\rho_A]^{-1} s^{3/2} [R_A(s)R_B^2(s)]^{1/2} e^{-s\beta\mu_s^0}, \quad (17)$$

where

$$\Lambda_1 = (h^2/2\pi mkT)^{1/2},$$

$$\Lambda_{\text{rot}} = \Lambda_1/l,$$

and

$$\begin{aligned} \beta\tilde{\mu}_s^0 = \frac{2\gamma a_0}{kT} \left[ 1 + \frac{(1-y)^2}{4(1+y)} \right] \\ + \frac{m\gamma a_0}{6(1+y)kT} \frac{(5-2y-y^2)}{s}. \end{aligned}$$

Here  $h$  is Planck's constant,  $m_1$  the mass of monomer,  $l$  the length of a monomer (surfactant) tail, and  $\gamma$  the

interfacial energy per unit area at the surfactant-solvent (water) interface.  $a_0$  (units of area) and  $\gamma$  (dimensionless) are phenomenological parameters which characterize the optimum head group area and the packing and stretching of the hydrocarbon tails<sup>11</sup>:  $a_0 \equiv \nu/l(1 + \gamma)$ .  $R_A(s)$  and  $R_B(s)$  are dimensionless moments of inertia:

$$R_A(s) = \left(5s - \frac{m}{10}\right), \quad (18a)$$

$$R_B(s) = \frac{3m}{20} + \frac{s}{4} + \frac{4}{9m^2} \left[ \frac{(s-m)^3}{3} + (s-m)^2 \right] + \frac{(s-m)}{2m}. \quad (18b)$$

Equations (17), (18), and (14) define the full distribution of micelle sizes and orientations. For other types of aggregates we require an analogous, but algebraically different, set of equations [(17), (18)] for  $q(s)/N_A\gamma_s^0$ ; otherwise, the theory remains the same.

### III. RESULTS

Using the truncated versions of the distribution function [Eq. (14)], the Helmholtz free energy [Eq. (10)] and the osmotic pressure [Eq. (15)], we have solved numerically the consistency equations (12) and (13) and the chemical equilibrium conditions for micellar aggregates. Typical choices of input parameters, and the corresponding results, are shown in Table I.

In our computations we have chosen to vary  $\gamma$ , the interfacial free energy, but could have also varied the parameter (i.e.,  $\gamma$ ) which govern the relative stabilities of packing in different micellar curvatures. As has been shown elsewhere<sup>10,11,13</sup> the average micelle size at a fixed total amphiphile concentration in an isotropic phase increases with the interfacial free energy. These bigger micelles give rise to a nematic phase at a lower amphiphile molefraction. Table I lists the number-average size of micelles in the coexisting isotropic and nematic phases. This quantity is trivially related to  $\alpha_1$  by [see Eq. (12)],

$$S_N = m \left/ \left(1 - \frac{4\alpha_1}{\pi}\right)\right., \quad (19)$$

since  $S_N \equiv 1/\langle 1/s \rangle$ . Also included are the molefractions ( $X$ ) of amphiphile in the isotropic and nematic phases,  $\alpha_2$  in the nematic phase, and the common chemical potential and osmotic pressure.

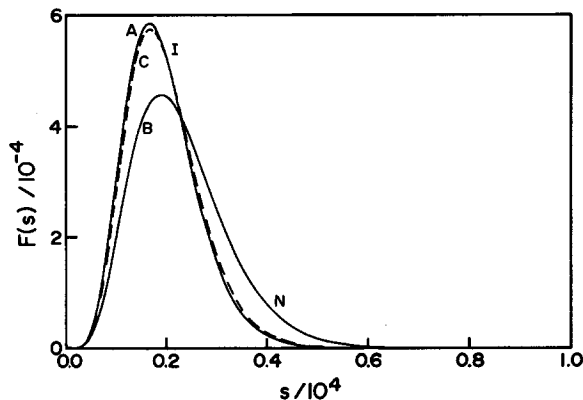


FIG. 1. Size distributions of rod-shaped micelles for the coexisting isotropic (I) and nematic (N) phases corresponding to the  $\gamma = 0.20kT/\text{\AA}^2$  case of Table I. [For a precise definition of  $F(s)$  see the text.] The dashed curve shows the size distribution of an isotropic phase with the same amphiphile concentration ( $X = 52.33 \times 10^{-4}$ ) as the nematic.

Figures 1(A) and 1(B) are size distributions of rod-shaped micelles at the phase transition for the  $\gamma = 0.20(kT/\text{\AA}^2)$  case of Table I. The dashed curve, Fig. 1(C), shows the size distribution of an isotropic phase with the same amphiphile concentration as in Fig. 1(B). The ordinate of these plots is the “reduced” distribution function, i.e., the fraction of monomers incorporated into rods of size  $s$ :

$$F(s) = \int sf(s, \Omega)d\Omega. \quad (20)$$

Upon passing from the isotropic to nematic phase, these distributions do not change their basic shape. The nematic distribution is simply broader and peaked about a higher aggregation number as compared with the virtually indistinguishable isotropic plots.

Figure 2 shows how the alignment of rods varies with their size. Here, we plot the orientational order parameter

$$\langle P_2 \rangle_s = \frac{\int P_2(\cos \theta)sf(s, \Omega)d\Omega}{\int sf(s, \Omega)d\Omega} \quad (21)$$

vs  $s$ . This quantity increases nearly linearly with  $s$  for small rods and then goes asymptotically to 1.0 for large ones.

TABLE I. Characteristics of the coexisting isotropic and nematic phases, for different values of the interfacial tension  $\gamma$  and the intramicelle chemical potential difference  $\delta$ . The amphiphile molefraction  $X$ , number-average size  $S_N$  and order parameters  $\alpha_1$  and  $\alpha_2$  are defined in the text.<sup>a</sup>

$\gamma(kT/\text{\AA}^2)$	$\delta^b$	Isotropic phase					Nematic phase					
		$X(\times 10^4)$	$S_N$	$\alpha_1$	$\bar{\rho}\bar{L}^2D$	$X(\times 10^4)$	$S_N$	$\alpha_1$	$\alpha_2$	$\bar{\rho}\bar{L}^2D$	$\beta\mu_A$	$\beta\pi$ (cm <sup>-3</sup> /10 <sup>16</sup> )
0.24	90	6.835	10 790	0.784	3.724	7.911	12 400	0.784	0.313	4.972	22.499 98	0.814
0.22	82.5	17.53	4 230	0.781	3.723	20.29	4 880	0.782	0.313	4.978	20.624 95	5.324
0.20	75	45.25	1 660	0.775	3.716	52.33	1 910	0.777	0.311	4.961	18.749 88	34.98
0.1812	67.95	112.1	692	0.762	3.708	129.4	797	0.765	0.306	4.968	16.987 26	207.6

<sup>a</sup> Molecular parameters:  $\nu = 360 \text{\AA}^3$ ,  $l = 12 \text{\AA}$ ,  $\gamma = 0.5$ ,  $m_1 = 4.4 \times 10^{-22} \text{ g}$ ,  $\rho = 0.033 \text{\AA}^{-3}$ .

<sup>b</sup>  $\delta = m\gamma a_0(5 - 2\gamma - \gamma^2)/6(1 + \gamma)kT$ , where  $m = 4\pi l^3/3\nu$  and  $a_0 = \nu/l(1 + \gamma)$ .

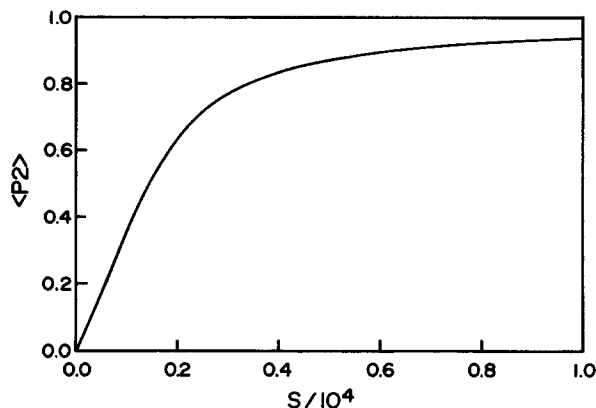


FIG. 2.  $P_2$ -order parameter vs size for micellar rods in the nematic phase shown in Fig. 1: see the text for details.

#### IV. DISCUSSION

In the usual discussion of the isotropic-to-nematic phase change in mixtures of anisotropic particles<sup>1,2</sup> the transition is explained in terms of a competition between orientational and packing entropy. In a *monodisperse* system, where the distribution function  $h(\Omega)$  gives the fraction of particles within  $d\Omega$  of orientation  $\Omega$ , the orientational entropy is

$$\sigma = - \int h(\Omega) \ln 4\pi h(\Omega) d\Omega \quad (22)$$

and the packing entropy

$$P = + f_2 \int \beta_1(\Omega, \Omega') h(\Omega) h(\Omega') d\Omega d\Omega'. \quad (23)$$

In a *polydisperse* system of anisotropic particles of *fixed* size and shape,  $\sigma$  and  $P$  become

$$\sigma = - \sum_i X_i \int h_i(\Omega) \ln 4\pi h_i(\Omega) d\Omega - \sum_i X_i \ln X_i \quad (22')$$

and

$$P = + f_2 \sum_{i,j} X_i X_j \int \beta_{1,ij}(\Omega, \Omega') h_i(\Omega) h_j(\Omega') d\Omega d\Omega'. \quad (23')$$

Here  $X_i$  is the mole fraction of species  $i$  and  $h_i(\Omega)$  its orientational distribution function. We see that the  $\sigma$  in [Eq. (22')] contains the entropy of mixing  $-\sum_i X_i \ln X_i$  as well as the "orientational entropy" for each component. The packing entropy is a weighted average of the pair-excluded volume, including packing contributions from all possible two-body interactions.

As we emphasized in Sec. I, an exchange colloid's ability to change its size distribution distinguishes it from a polydisperse system of rigid, nonassociating particles. In other words, particles of a given size are not conserved when the thermodynamic state of the exchange colloid changes. For example, either concentrating the solution or going to a nematic state enhances the average size of rods. For polydisperse mixtures of "fixed" rods, it has been shown that the longer rods partition preferentially into the nematic phase at the coexistence. In the case of micellar systems, there is *also* an *actual growth* of rods in the nematic phase, due to size-alignment coupling. A

comparison of Figs. 1(B) and 1(C) shows that this is not just a concentration effect.

Despite this difference, considerable insight can be gained by analyzing the exchange colloid's isotropic-to-nematic transition in the conventional language. Referring to Eq. (1), we note that the free energy  $(\beta\Delta A)/N_A$  contains terms corresponding to the orientational and packing entropies [Eqs. (22') and (23')]. More explicitly,

$$\sigma = - \int f(\Omega, s) \ln [4\pi f(\Omega, s)] d\Omega ds \quad (24)$$

and

$$P = + \frac{\rho_A}{2} \int \int \beta_1(s, s'; \Omega, \Omega') f(\Omega, s) \times f(\Omega', s') d\Omega ds d\Omega' ds'. \quad (25)$$

Equation (1) also contains two other contributions: (1) a number-weighted average of the standard chemical potential per aggregate; and (2) an average over the number of particles of each size. If we designate these quantities by  $\bar{\mu}^*$  and  $\bar{n}$ , respectively, we have

$$\bar{\mu}^* = \int f(\Omega, s) \beta \mu_s^* d\Omega ds \quad (26)$$

and

$$\bar{n} = - \int f(\Omega, s) \left( \ln \frac{4\pi}{\rho_A} + 1 \right) d\Omega ds. \quad (27)$$

Let us define an orientational distribution function,  $R(\Omega, s)$ , in terms of the earlier  $F(s)$ , so that  $sf(\Omega, s) \equiv F(s)R(\Omega, s)$ . Recall that  $F(s)$  is the fraction of surfactant contained in rods of size  $s$  regardless of their orientation:  $R(\Omega, s)$  is the fraction of  $s$  rods with orientation  $\Omega$ . From Eq. (14):

$$F(s) \equiv \int sf(\Omega, s) d\Omega = \frac{e^{-\beta\mu_s^*}}{\rho_A} s e^{\lambda s} e^{-B(s-m)\alpha_1} \int d\Omega e^{B(s-m)\alpha_2 P_2(\cos\theta)} \quad (28)$$

and

$$R(\Omega, s) = e^{B(s-m)\alpha_2 P_2(\cos\theta)} / \int d\Omega e^{B(s-m)\alpha_2 P_2(\cos\theta)}. \quad (29)$$

Using  $R(\Omega, s)$  and  $F(s)$  we can rewrite  $\sigma$  in Eq. (24) as the sum of a "mixing-like" entropy and a number-weighted orientational entropy:

$$-\sigma = \int \frac{F(s)}{s} \ln \frac{F(s)}{s} ds + \int \frac{F(s)}{s} \left[ \int R(\Omega, s) \ln 4\pi R(\Omega, s) d\Omega \right] ds \quad (30)$$

or

$$\sigma = \sigma_{\text{mix.}} + \sigma_{\text{orient.}} \quad (30')$$

in analogy with the two-term  $\sigma$  given in Eq. (22').  $P$  [Eq. (25)] similarly takes the form

$$-P = \int F(s) \left(1 - \frac{m}{s}\right) \times \left[ \alpha_1 - \alpha_2 \int R(\Omega, s) P_2(\cos \theta) d\Omega \right] ds \quad (31)$$

while for  $\bar{\mu}^0$  and  $\bar{n}$  [Eqs. (26) and (27)] we have

$$\bar{\mu}^0 = \int F(s) \frac{\beta\mu_s^*}{s} ds \quad (32)$$

and

$$\bar{n} = \int F(s) \frac{1}{s} \left( \ln \frac{4\pi}{\rho_A} + 1 \right) d\Omega ds. \quad (33)$$

The Helmholtz free energy,  $(\beta\Delta A)/N_A = \bar{\mu}^* + n - \sigma - P$ , can also be written as an integral of the form

$$\frac{\beta\Delta A}{N} = \int F(s) \hat{a}(s) ds, \quad (34)$$

where  $\hat{a}(s)$  can be thought of as a "free-energy density." Inspection of Eqs. (30)–(33) shows that  $\hat{a}(s)$  is given by

$$\begin{aligned} \hat{a}(s) = & \frac{1}{s} \ln \frac{F(s)}{s} + \frac{1}{s} \left[ \int R(\Omega, s) \ln 4\pi R(\Omega, s) d\Omega \right] \\ & + \frac{B}{2} \left(1 - \frac{m}{s}\right) \left[ \alpha_1 - \alpha_2 \int R(\Omega, s) P_2(\cos \theta) d\Omega \right] \\ & + \frac{1}{s} \beta\mu_s^* - \frac{1}{s} \left( \ln \frac{4\pi}{\rho_A} + 1 \right). \end{aligned} \quad (34a)$$

In an isotropic phase,  $R(\Omega, s) \equiv 1/4\pi$ ,  $\alpha_2 = 0$ , and  $\sigma_{\text{orient}} = 0$ . Increasing the total monomer concentration (recall  $B \sim \rho_A$ ) crowds the aggregates, making the third ("packing") term in Eq. (34a) large, positive, and hence unfavorable for all  $s$ . When the concentration gets high enough, the rods align to reduce this term although doing so makes  $-\sigma_{\text{orient}} > 0$ . To partially offset this loss in orientational entropy, the system reorganizes into larger rods since  $1/s \left[ \int R(\Omega, s) \ln 4\pi R(\Omega, s) d\Omega \right]$  decreases with  $s$ . Furthermore, the packing free energy is most effectively reduced by large values of  $s$  when  $\alpha_2 \neq 0$  (the integral increases with  $s$ ).

If the packing and orientational entropies were the only portions of the free energy affecting rod size, the micelles would "explode" into infinite aggregates upon alignment. What limits this growth is the cumulative effect of the other three terms in Eq. (34a)  $(1/s)\beta\mu_s^*$  favors growth up to—but not beyond—the size of minimum standard chemical potential per monomer; and  $-1/s \times \left[ \ln(4\pi/\rho_A) + 1 \right]$  is most negative, and thus most favorable, for small  $s$ . To minimize the free energy,  $F(s)$  must be large at those values of  $s$  where the sum of these four contributions is lowest, but not so large that the mixing-entropy portion,  $(1/s)\ln[F(s)/s]$ , increases unfavorably. The mixing entropy favors a large number of small rods rather than a few large ones and provides a "built-in feedback" against the explosion into infinite aggregates.

From the definition of  $R(\Omega, s)$  we notice [Eq. (29)] that each aggregate's strength of coupling to the aligning

field increases exponentially with its size. That is, large rods are more effectively oriented by the nematic than small ones. Figure 2 reflects this phenomenon. As  $s \rightarrow \infty$ , no matter how weakly ordered the nematic (i.e., no matter how small  $\alpha_2$ ),  $\langle P_2 \rangle_s = \int [P_2(\cos \theta) R(\Omega, s)] d\Omega \rightarrow 1$ . At very small values of  $s$  the order varies linearly with  $(s - m)$ . More explicitly—cf. Eq. (29), with  $P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$

$$\langle P_2 \rangle_s = \frac{\frac{3}{2} \int_0^1 dx x^2 e^{zx^2}}{\int_0^1 dx e^{zx^2}} - \frac{1}{2}, \quad (35)$$

where  $z = \frac{3}{2}B(s - m)\alpha_2$ . Expanding the exponentials and integrating yields (for small  $z$ )

$$\begin{aligned} \langle P_2 \rangle_s \approx & \frac{1}{3}B(s - m)\alpha_2 + \frac{1}{35}B^2(s - m)\alpha_2^2 \\ & - \frac{2}{525}B^3(s - m)^3\alpha_2^3. \end{aligned} \quad (36)$$

The initial slope of  $\langle P_2 \rangle_s$  vs  $(s - m)$  is  $\frac{1}{2}B\alpha_2$ , in agreement with Fig. 2. In the long rod limit, on the other hand, one can show that

$$\langle P_2 \rangle_s \approx 1 - \frac{1}{B(s - m)\alpha_2}. \quad (37)$$

This expression also agrees quite well with Fig. 2 for  $(s - m) \gtrsim 6000$  (with  $B\alpha_2 = 1.63 \times 10^{-3}$ ). In fact, comparing the results predicted by Eq. (37) with the actual numerical ones reveals  $[\langle P_2 \rangle_{s, \text{Eq. (42)}} - \langle P_2 \rangle_{s, \text{(numerical)}}] / [1 - \langle P_2 \rangle_{\text{numerical}}] \leq 4\%$  for  $s > 6000$ —a very sensitive test of the approximate form.

In the case of monodispersed hard rods, the transition occurs at a critical number density given by  $\rho L^2 D = \text{constant}$ , where  $L$  and  $D$  are the length and diameter of the rods. Such a relation exists for both the isotropic and nematic phases at the coexistence. In Table I, we have tabulated an analogous quantity

$$C_1 = \bar{\rho} \bar{L}^2 D \quad (38)$$

for our polydisperse rods. Here  $\bar{\rho} = \rho_A/S_N$  is the total number of aggregates per unit volume,  $\bar{L} = (S_N - m)v/\pi l^2$  is the average length of a rod and  $D = 2l$  is the diameter of a rod. As in the monodisperse case this quantity is indeed (nearly) a constant at the transition, different for each phase (and close to the monodisperse value).

Note that it is the number average,  $S_N \equiv 1/\langle 1/s \rangle$ , instead of the weight average  $S_w \equiv \langle s \rangle$  that enters into Eq. (38). A rigorous treatment of this fact would probably prove unilluminating because the algebra is not sufficiently simple. However, the number average—not a different moment—appears throughout the theory. We just replace the density  $\rho$  that arises in the monodisperse theory by the total number of aggregates per unit volume  $\bar{\rho}$ , and the length  $L$  by the average length (which must be calculated according to the number average). The polydisperse system presented here behaves like the monodisperse one in other ways as well. For example,  $\alpha_2$  saturates

to a constant value ( $\approx 0.313$ ; Table I) as the rods at the transition get larger, reminiscent of the transition order parameter,  $\langle P_2(\cos \theta) \rangle$  being constant in the  $L \rightarrow \infty$  monodispersed case. Simple relations of this kind do not hold for mixtures of particles of various anisometry.

In an earlier paper, we approximated the present polydisperse system by a monodispersed one of "most-probable" aggregates.<sup>14</sup> We used asymptotic forms (based on large rods) for the orientational and packing entropies. Though differing quantitatively, the results of the present work support the simplified model's qualitative conclusions. In both versions, nematic ordering increases the size (or average size) of the rods. The aggregates at the transition in the simpler case are slightly smaller, however, the quantity  $[(S_N)_{\text{nematic}} - (S_N)_{\text{isotropic}}]^{1/2} [(S_N)_{\text{nematic}} + (S_N)_{\text{isotropic}}]$  a little larger, and  $\bar{\rho} \bar{L}^2 D$  about 4.3 in the nematic and 3.1 in the isotropic phase. [More explicitly, compare the  $\gamma = 0.18$  results (Table I) with the calculations presented in our earlier account. The transition occurs at a volume fraction of about 15% in both cases, but the aggregation numbers 790 and 690 compare to 300 and 220.] The results reported here for  $(\bar{\rho} \bar{L}^2 D)$  nematic and  $(\bar{\rho} \bar{L}^2 D)$  isotropic most closely resemble those determined elsewhere for monodispersed systems of hard, nonreacting rods.<sup>1,2</sup>

We next discuss the approximation made in deriving the distribution function [Eq. (14)]. Our results should be correct if  $\bar{L}/D \gg 1$ . Consider the smallest aggregates reported in Table I ( $S_N = 692$ ). Using Eq. (8),  $D = 2l$ ,  $m = 20$ , and  $s = 692$ , we find  $\bar{L}/D = 22$ . Straley has shown that when  $4D \gtrsim 100$ , truncation of the virial expansion is appropriate for monodispersed hard rods. For rods with  $\bar{L}/D = \theta(10)$  however, we can still expect qualitatively reliable results; for the still larger aggregates (e.g.,  $\gamma = 0.24$  and  $\bar{L}/D > 300$ ) we need of course to be concerned about flexibility.

The precise numerical results depend critically on the parameters used (e.g.,  $\gamma$ ) and on the details of the standard chemical potential. On the other hand, in the orientational distribution function, we have a nearly exact result for large rods. For larger aggregates,  $\alpha_{2n} = d_{2n} \langle (1 - m/s) P_{2n}(\cos \theta) \rangle \approx d_{2n} \langle P_{2n}(\cos \theta) \rangle$  and the orientational moments do not vary much with the size distribution. Referring to Eq. (29) or the analogous part of Eq. (14) we find the interesting result that in a nematic phase, each rod behaves as though its coupling to the nematic field is proportional to its length—i.e., proportional to  $(s - m)$ . This final observation may prove valuable in approximate treatments of polydisperse, orientationally ordered systems.

Had we used smaller values for the interfacial free energy, we would have observed smaller rods at the transition. This would be more in agreement with experiment.<sup>8,9</sup> In this vein we can estimate, based on the constancy of the product  $\bar{\rho} \bar{L}^2 D$ , how small our rods would get in the concentration range normally associated with the isotropic-to-nematic transition in micellar systems. As explained in the Introduction, the transition normally occurs when the volume fraction is in the range 10%–30%. In Table I, we see that for  $X \approx 0.01$ , the transition

occurs at  $\bar{L}/D = 22 (S_N = 692)$ . This corresponds to a volume fraction of  $\approx 10\%$ . If  $\gamma$  were small enough to have the transition occur at a volume fraction of 30%, we would expect rods characterized by  $\bar{L}/D \approx 7 (\bar{L}/D \sim 1/v)$  on the average. This is of the right order of magnitude ( $\bar{L}/D \approx 2-3$ ) to compare with experiment,<sup>8</sup> but going to such small rods and high concentrations requires that we account for higher-order many-body terms in the virial expansion.

Finally, we comment on the approximation of using a hardcore potential to describe intermicellar interactions. As mentioned previously, only highly screened (via added electrolyte) ionic micelles would behave like hard objects. In real systems, the range of intermicelle forces could certainly exceed those of a hard-core potential. The longer-ranged potential might reduce the rods' anisotropy and bring about a "delayed" and "softer" (higher density, smaller micelles) transition, in agreement with experiment. But then we would once again require a higher-order, many-body theory that could deal with smaller aggregates interacting through a Coulombic or Yukawa potential.<sup>20</sup>

## SUMMARY

The coupling between polydispersity and orientational order affects the isotropic-to-nematic phase change. Compared to a simpler model which treats only the most probable size, the inclusion of polydispersity softens the transition ( $\Delta s/\bar{s}$  is smaller), and necessitates larger aggregation numbers or a higher density. In many respects however, the polydisperse system behaves like the monodispersed one. For example, rods in the nematic phase are larger than those in the isotropic one, the volume fraction varies as the reciprocal of the average length, and the nematic order parameter is nearly constant at the transition. Though large quantitative differences exist, the more systematic treatment presented here supports the earlier effort's qualitative conclusions.

The rods in a nematic are larger than those in a coexisting isotropic phase because less orientational entropy is lost when the aggregates rearrange into a few, large, aligned rods than by aligning more small ones. Large rods are also more efficient at reducing the packing free energy in the nematic. The mixing entropy, and averages over the standard chemical potential and numbers of aggregate all serve further to inhibit the micelles from becoming infinite upon alignment.

At low enough aggregation numbers, the order parameter  $\langle P_2(\cos \theta) \rangle$  in the nematic phase increases linearly with the rod length  $\sim (s - m)$ . For much larger aggregates,  $\langle P_2(\cos \theta) \rangle$  approaches 1 asymptotically according to  $\langle P_2(\cos \theta) \rangle \sim 1 - \text{constant}/(s - m)$ .

The formalism presented here is applicable to any type of exchange colloid or associating particles where two-body virial interactions dominate. One can, for example, envisage a treatment of polymer melts in which persistence lengths correspond to the (rod-shaped) aggregates we have treated. The only required input is a set of standard chemical potentials for each size (and shape) of "aggregate."

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