

On the Statistics of a Three-Dimensional Gas of Long Thin Rods

Katja Lakatos¹

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A gas of long thin rods undergoes an order-disorder phase transition as a function of rod concentration. We have evaluated the critical concentration at which this first-order transition occurs using Onsager's hard-core interaction model. We obtain the nematic angular distribution function of rods in the ordered phase expanded in a series of Legendre polynomials.

KEY WORDS: long thin rods; order-disorder phase transition; critical concentration; angular distribution function.

1. INTRODUCTION

A gas of long thin rods undergoes an order-disorder phase transition as a function of rod concentration. Such a phase transition has been observed experimentally^(1,2,3) in systems of rodlike molecules in solution (e.g., tobacco mosaic virus), and theoretical results have been obtained using hard-core interaction models.⁽⁴⁻⁸⁾ At low rod concentrations, such a gas is isotropic; the long axes of the rods point in random directions. As the concentration is increased, the rods get in each other's way with a high cost in energy. Finally, at a critical concentration, the rods tend to line up to avoid each other, the decrease in entropy being more than counteracted by the gain in energy.

Two theoretical approaches have been applied to the problem. Flory's theory⁽⁶⁾ and its extension by DiMarzio⁽⁷⁾ to molecules of various shapes is based on the lattice model. The other approach, formulated by Onsager⁽⁴⁾ and also used by Isihara⁽⁵⁾ and Zwanzig,⁽⁸⁾ uses Mayer cluster expansion theory with successive

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¹Department of Chemistry, University of California, San Diego, La Jolla, California.

cluster contributions proportional to powers of parameters involving the concentration of rods and their geometry.

In this paper we will follow Isihara's extension of Onsager's formulation to calculate the critical concentration and degree of anisotropy near the phase transition.⁽⁵⁾ Our results, however, differ from those of Isihara, as discussed in Sections 3 and 4.

2. EQUATION DETERMINING MOLECULAR ORIENTATION

We briefly outline Onsager's⁽⁴⁾ formulation and its extension by Isihara.⁽⁵⁾ The colloidal particles are assumed to be in solution, in dialytic equilibrium with a solvent of constant composition across an osmometer membrane. The rods in solution are in the configuration which minimizes the quantity

$$\begin{aligned} F &= F_{\text{solution}} - F_{\text{solvent}} \\ &= N_p \mu_p^0(T, \text{solvent}) - kT \log B_p(N_p, V, T) \end{aligned} \quad (1)$$

Here F is the free energy, N_p is the number of rods and B_p is the configuration integral

$$B_p(N_p, V, T) = \int \exp(-W/kT) \frac{d\tau}{N_p!} \quad (2)$$

$$W = W_{N_p}[(q_1), (q_2), \dots, (q_{N_p})] \quad (3)$$

W is the potential of the average forces which act between the particles in a configuration described by the sets of coordinates $(q_1), (q_2), \dots, (q_{N_p})$ of particles 1, 2, ..., N_p . It is necessary to specify the orientation of the rods, as well as the positions of their centers, and the work against the corresponding torques must be included in W .

The configuration integral in (2) is treated by the usual Mayer cluster expansion theory. Assuming additive forces

$$W = \sum_{i < j} W_{ij}[(q_i), (q_j)] \equiv \sum_{i < j} W_{ij} \quad (4)$$

and defining

$$\phi_{ij} \equiv \exp(-W_{ij}/kT) - 1 \quad (5)$$

gives

$$\log B_p = N_p [1 + \log(V/N_p) + \frac{1}{2}(N_p/V) \beta_1 + \frac{1}{8}(N_p/V)^2 \beta_2 + \dots] \quad (6)$$

with

$$\beta_1 = \frac{1}{V} \int \phi_{12} d\tau_1 d\tau_2; \quad (7)$$

$$\beta_2 = \frac{1}{V} \int \phi_{12} \phi_{23} \phi_{31} d\tau_1 d\tau_2 d\tau_3; \text{ etc.} \quad (8)$$

Instead of including an integral over all particle orientations in $\int d\tau$, Onsager introduces the artifice of treating particles of different orientations as particles of

different kinds. The number of particles in a solid angle $\Delta\Omega_\nu$ surrounding direction $\vec{\alpha}_\nu$, measured from an arbitrarily chosen fixed axis is

$$\Delta N_\nu \equiv N_p f(\vec{\alpha}_\nu) \Delta\Omega_\nu \quad \nu = 1, 2, \dots, s \quad (9)$$

where

$$\sum_{\nu=1}^s \Delta N_\nu = N_p \quad (10)$$

and $f(\vec{\alpha}_\nu)$ is an as yet undetermined function which depends on the rod configuration. The free energy of this assembly of particles of different kinds is additive if due allowance is made for the entropy of mixing:

$$\begin{aligned} \log B_p = & \sum_{\nu} \Delta N_\nu [1 + \log(V\Delta\Omega_\nu/4\pi N_\nu)] + \frac{1}{2V} \sum_{\nu, \nu'} \beta_1(\vec{\alpha}_\nu, \vec{\alpha}_{\nu'}) \Delta N_\nu \Delta N_{\nu'} \\ & + \frac{1}{3V^2} \sum_{\nu, \nu', \nu''} \beta_2(\vec{\alpha}_\nu, \vec{\alpha}_{\nu'}, \vec{\alpha}_{\nu''}) \Delta N_\nu \Delta N_{\nu'} \Delta N_{\nu''} + \dots \end{aligned} \quad (11)$$

The cluster integrals in (7), (8), etc., are now evaluated for fixed orientations $\vec{\alpha}_\nu$ of the particles involved.

Finally, the sums over angular orientations are replaced by integrals involving the normalized angular distribution function $f(\vec{\alpha})$:

$$\int f(\vec{\alpha}) d\Omega(\vec{\alpha}) = 1 \quad (12)$$

and (11) becomes

$$\begin{aligned} \log B_p = & N_p \left\{ 1 + \log\left(\frac{V}{N_p}\right) - \int f(\vec{\alpha}) \log[4\pi f(\vec{\alpha})] d\Omega(\vec{\alpha}) \right. \\ & + \frac{N_p}{2V} \iint \beta_1(\vec{\alpha}, \vec{\alpha}') f(\vec{\alpha}) f(\vec{\alpha}') d\Omega d\Omega' \\ & \left. + \frac{N_p^2}{3V^2} \iiint \beta_2(\vec{\alpha}, \vec{\alpha}', \vec{\alpha}'') f(\vec{\alpha}) f(\vec{\alpha}') f(\vec{\alpha}'') d\Omega d\Omega' d\Omega'' + \dots \right\} \end{aligned} \quad (13)$$

The unknown angular distribution function $f(\vec{\alpha})$ is now determined by requiring that the free energy of (1) be a minimum, or that $\log B_p$ be a maximum, subject to condition (12). Performing a functional differentiation of (13) with respect to f , including condition (12) by the usual method of Lagrange multipliers, and setting the result equal to zero, gives a nonlinear integral equation for f :

$$f(\vec{\alpha}) = \frac{\exp[\rho \int \beta_1(\vec{\alpha}, \vec{\alpha}') f(\vec{\alpha}') d\Omega' + \rho^2 \iint \beta_2(\vec{\alpha}, \vec{\alpha}', \vec{\alpha}'') f(\vec{\alpha}') f(\vec{\alpha}'') d\Omega' d\Omega'' + \dots]}{\int \exp[\rho \int \beta_1(\vec{\alpha}, \vec{\alpha}') f(\vec{\alpha}') d\Omega' + \rho^2 \iint \beta_2(\vec{\alpha}, \vec{\alpha}', \vec{\alpha}'') f(\vec{\alpha}') f(\vec{\alpha}'') d\Omega' d\Omega'' + \dots] d\Omega} \quad (14)$$

where $\rho = N_p/V$ is the number concentration of rods. Among the solutions to this equation is the one that minimizes the free energy. The orientational degeneracy

of the solutions is eliminated by looking only for solutions which have cylindrical symmetry about the axis from which direction $\vec{\alpha}$ is measured [see comments preceding (9)]. This is then the axis about which we will look for a preferential alignment of the rods.

Onsager has shown on general grounds that for a three-dimensional gas of rods it is sufficient to retain only the first cluster integral in (14) to obtain an order-disorder phase transition.

$$f(\vec{\alpha}) = \frac{\exp[\rho \int \beta_1(\vec{\alpha}, \vec{\alpha}') f(\vec{\alpha}') d\Omega']}{\int \exp[\rho \int \beta_1(\vec{\alpha}, \vec{\alpha}') f(\vec{\alpha}') d\Omega'] d\Omega} \quad (15)$$

The cluster integral $\beta_1(\vec{\alpha}, \vec{\alpha}')$ for cylindrical rods interacting *via* a hard-core potential has been evaluated in detail by Onsager. For rods of length L and diameter d , the result is

$$\beta_1(\gamma) = -[2L^2d + (\pi/2)d^3] \sin \gamma + [(\pi/2)(1 + |\cos \gamma|) + 2E(\sin \gamma)] Ld^2 \quad (16)$$

where $0 \leq \gamma \leq \pi/2$ and $E(\sin \gamma)$ is the complete elliptic integral of the second kind:

$$E(\sin \gamma) = \int_0^{\pi/2} (1 - \sin^2 \gamma \sin^2 \phi)^{1/2} d\phi \quad (17)$$

For $L \gg d$

$$\beta_1(\gamma) \approx -2L^2d \sin \gamma \quad (18)$$

To estimate the critical concentration, Onsager chooses a trial function $f(\theta)$ which is peaked about $\theta = 0$ and contains an arbitrary parameter α :

$$f(\theta) = \frac{\alpha}{4\pi \sinh \alpha} \cosh(\alpha \cos \theta) \quad (19)$$

The free energy is then minimized with respect to α and the resulting free energy is compared to that of an isotropic gas of rods [$f(\theta) = \frac{1}{4}\pi$]. The critical concentration is then the one at which the anisotropic $f(\theta)$ begins to give a lower free energy than the isotropic one as ρ is increased. Using (18), his result is

$$L^2 d\rho_c = 5.1085 \quad (20)$$

Independently of his choice of $f(\theta)$, Onsager shows on general grounds that the phase transition is of first order. The function $f(\theta)$ is discontinuous with respect to rod concentration at the phase transition. The usual van der Waals loop can be constructed by equating the pressures and chemical potentials of the isotropic and anisotropic phases at the critical point.

Isihara⁽⁵⁾ goes about solving the integral equation (15) in a more systematic manner, by expanding both the cluster integral and the angular distribution function

in Legendre polynomials. By the symmetry of the system, only even Legendre polynomials are necessary.

$$\beta_1(\gamma) = \sum_{l=0}^{\infty} B_l P_{2l}(\cos \gamma) \tag{21}$$

$$f(\theta) = \sum_{l=0}^{\infty} C_l P_{2l}(\cos \theta) \tag{22}$$

Substituting (21) and (22) into (15) and using the addition theorem of spherical harmonics immediately gives

$$f(\theta) = \frac{\exp \left[\rho \sum_{l=1}^{\infty} \frac{4\pi}{4l+1} B_l C_l P_{2l}(\cos \theta) \right]}{2\pi \int_0^{\pi} \exp \left[\rho \sum_{l=1}^{\infty} \frac{4\pi}{4l+1} B_l C_l P_{2l}(\cos \theta) \right] \sin \theta d\theta} \tag{23}$$

and

$$C_l = \frac{4l+1}{4\pi} \frac{\int_0^{\pi/2} f(\theta) P_{2l}(\cos \theta) \sin \theta d\theta}{\int_0^{\pi/2} f(\theta) \sin \theta d\theta} \tag{24}$$

where the orthogonality properties of Legendre polynomials have been used. These are the transcendental equations to determine the expansion coefficients C_l .

3. EVALUATION OF CRITICAL CONCENTRATION AND ANGULAR DISTRIBUTION FUNCTION

To find an approximate solution for (23) and (24) we first leave out the terms corresponding to $l \geq 2$. This is *not* meant to imply that the higher-order coefficients $C_{l \geq 2}$ are much smaller than C_1 (in fact we show later that they are not). However, in this manner an equation is obtained which is at least numerically tractable and whose solution can be used as a first step in an iteration procedure. The resulting equation involves only C_1 ; we denote its solution by C_1^0 :

$$C_1^0 = \frac{5}{4\pi} \frac{\int_0^1 \exp \left[-\frac{4\pi}{5} \rho B_1 C_1^0 P_2(x) \right] P_2(x) dx}{\int_0^1 \exp \left[-\frac{4\pi}{5} \rho B_1 C_1^0 P_2(x) \right] dx} \tag{25}$$

Equation (25) can be solved numerically for C_1^0 as a function of ρ . For small ρ it has only one solution, namely, $C_1^0 = 0$ (isotropic rod distribution). When ρ increases beyond the critical value given by

$$\rho_c B_1 = 4.4876 \tag{26}$$

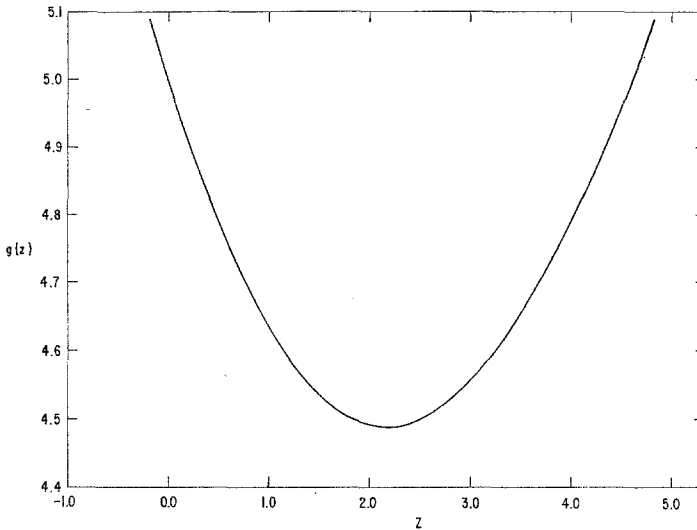


Fig. 1. Plot of Eq. (27).

two additional solutions emerge. This is best shown graphically by rewriting (25). Simple manipulation leads to

$$\rho B_1 = \frac{8z^2}{\frac{9e^z}{\int_0^1 e^{zx^2} dx} - 6z - 9} \equiv g(z) \quad (27)$$

where $z = 6\pi\rho B_1 C_1^0/5$. Figure 1 is a plot of $g(z)$, with a minimum at $z = 2.1609$. Since the left side of (27) is proportional to $z(\rho B_1 = 5z/6\pi C_1^0)$, the two values of C_1^0 for each ρ are found from the intersections of Fig. 1 with the line $g(z) = \text{const} \cdot z$ of appropriate slope. The resulting values of C_1^0 are shown in Fig. 2. The broken line corresponds to the values of C_1^0 obtained from Fig. 1 for $z < 2.1609$. We disregard this solution for the reasons given in Section 4. (Isihara⁽⁵⁾ chooses this solution, with $\rho_e B_1 = 5$). The solution we choose is given by the solid line. There C_1^0 increases continuously with increasing ρB_1 starting from the value $C_1^0 = 0.1277$ at $\rho = \rho_e$. This branch corresponds to a first order phase transition: C_1^0 jumps discontinuously from its isotropic value ($C_1 = 0$) to its value at ρ_e , giving a finite degree of anisotropy.

Using the approximate cluster integral of (12) whose expansion in terms of Legendre polynomials is given by

$$\beta_1(\gamma) \approx \pi L^2 d \left\{ -\frac{1}{2} + \sum_{l=1}^{\infty} \frac{(4l+1)(2l-3)!!(2l-1)!!}{2^{2l+1}l!(l+1)!} \right\} P_{2l}(\cos \gamma) \quad (28)$$

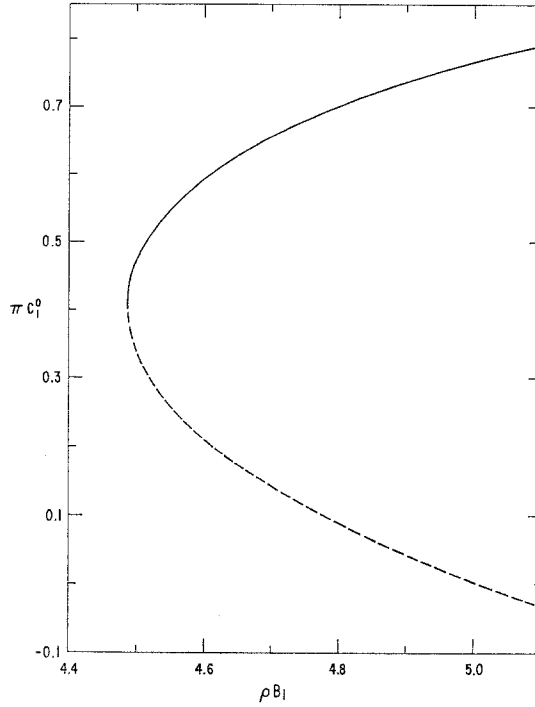


Fig. 2. C_1^0 as a function of rod concentration.

we obtain

$$B_1 = \frac{5}{16} \pi L^2 d \tag{29}$$

and

$$L^2 d \rho_c = 4.5710 \tag{30}$$

This value is 10% lower than Onsager's result.

To approximate some of the higher-order expansion coefficients C_n of $f(\theta)$ at various concentrations we iterate truncated forms of (23) and (24). Using the relation

$$\rho B_l = \frac{(4l + 1)(2l - 3)!! (2l - 1)!!}{(5)(2^{2l-3}l! (l + 1)!)} \rho B_1 \tag{31}$$

obtained from (28), we use as initial values for the iteration

$$C_n^0 = \frac{\int_0^1 \exp \left[\frac{4\pi}{5} \rho B_1 \sum_{i=1}^{n-1} \frac{(2l - 3)!! (2l - 1)!!}{2^{2l-3}l! (l + 1)!} C_i^0 P_{2l}(x) \right] P_{2n}(x) dx}{\int_0^1 \exp \left[\frac{4\pi}{5} \rho B_1 \sum_{i=1}^{n-1} \frac{(2l - 3)!! (2l - 1)!!}{2^{2l-3}l! (l + 1)!} C_i^0 P_{2l}(x) \right] dx} \tag{32}$$

$n = 2, 3, \dots, s$

Table I. Initial Values of C_1^0 —Solution of Eq. (25)

ρB_1	C_1^0
4.4876	0.12773
4.4891	0.13652
4.5020	0.15085
4.5685	0.17984
4.6594	0.20120
4.9270	0.23743
5.0950	0.25197

where C_s is the highest coefficient included. With these initial values we then iterate the equations

$$C_n^i = \frac{\int_0^1 \exp \left[\frac{4\pi}{5} \rho B_1 \sum_{l=1}^s \frac{(2l-3)!! (2l-1)!! C_l^{i-1}}{2^{2l-3} l! (l+1)!} P_{2l}(x) \right] P_{2n}(x) dx}{\int_0^1 \exp \left[\frac{4\pi}{5} \rho B_1 \sum_{l=1}^s \frac{(2l-3)!! (2l-1)!! C_l^{i-1}}{2^{2l-3} l! (l+1)!} P_{2l}(x) \right] dx} \quad (33)$$

Using the initial values C_1^0 of Table I, the iterations were performed using Gauss' numerical integration method with 16 points, until the results changed by less than 1%. The results for various rod concentrations are shown in Table II. The resulting angular-distribution function $f(\theta)$ is shown in Figs. 3 and 4 for various rod concentrations.

The free energy in terms of the expansion coefficients C_n is found from Eqs. (1), (13), (21), (22), and (23) to be:

$$\begin{aligned} \frac{F - N_p \mu_p^0}{N_p k T} = & -1 + \log \rho + \frac{\rho}{2} \sum_{l=0}^{\infty} B_l C_l^2 \left(\frac{4\pi}{4l+1} \right)^2 \\ & - \log \int_0^{\pi/2} \exp \left[\rho \sum_{l=0}^{\infty} B_l C_l \left(\frac{4\pi}{4l+1} \right) P_{2l}(\cos \theta) \right] \sin \theta d\theta \quad (34) \end{aligned}$$

Table II. Expansion Coefficients C_n

C_n	ρB_1						
	4.4876	4.4891	4.5020	4.5685	4.6594	4.9270	5.0950
C_1	0.23629	0.23665	0.23965	0.25289	0.26703	0.29524	0.30743
C_2	0.19157	0.19219	0.19738	0.22141	0.24926	0.31279	0.34420
C_3	0.10480	0.10532	0.10977	0.13135	0.15835	0.22814	0.26705
C_4	0.046423	0.046740	0.049454	0.063221	0.081763	0.13590	0.16967
C_5	0.018023	0.018179	0.019529	0.026684	0.037042	0.071079	0.094659
C_6	0.0063680	0.0064348	0.0070162	0.010232	0.015214	0.033493	0.047392
C_7	0.0019582	0.0019819	0.0021890	0.0033756	0.0053170	0.013084	0.019413
C_8	0.0000047	0.0000047	0.0000048	0.0000053	0.0000060	0.0000076	0.0000086
C_9	0	0	0	0	0	0	0

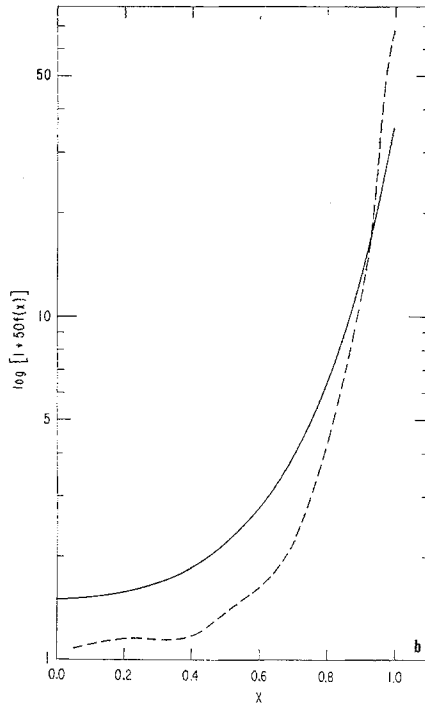
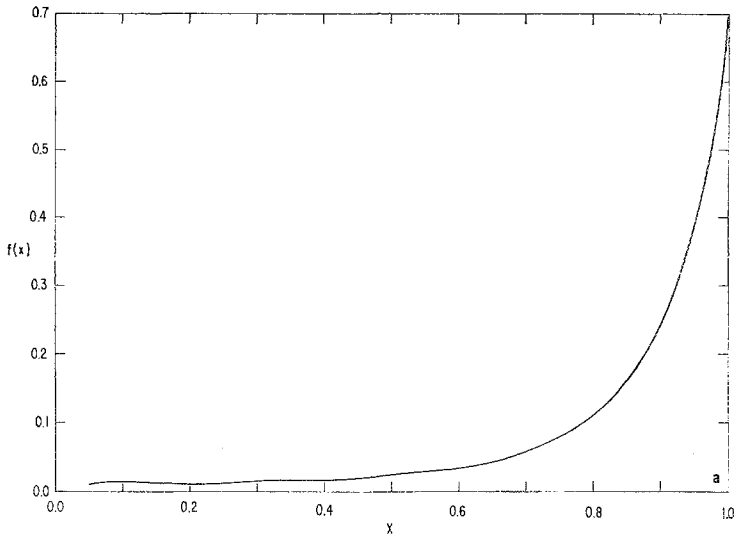


Fig. 3. (a) Angular distribution function at the critical rod concentration $\rho_c B_1 = 4.4876$. (b) Logarithmic plot of the angular distribution function for $\rho_c B_1 = 4.4876$ (solid line) and $\rho B_1 = 5.0950$ (broken line).

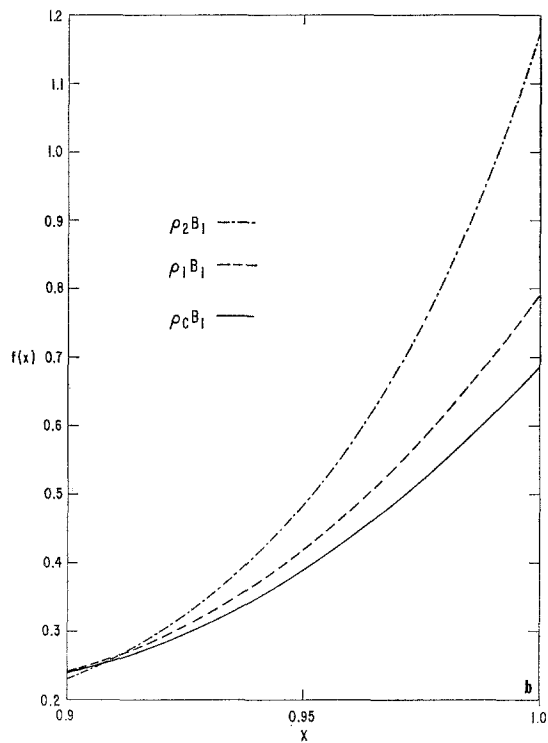
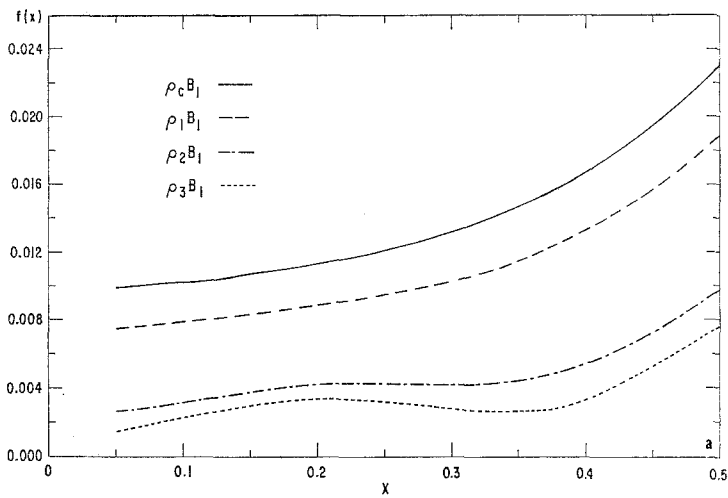


Fig. 4. (a) Large-angle plot of the angular-distribution function for several concentrations: $\rho_0 B_1 = 4.4876$; $\rho_1 B_1 = 4.5685$; $\rho_2 B_1 = 4.9270$; $\rho_3 B_1 = 5.0950$. (b) Small-angle plot of the angular distribution function for several concentrations.

or equivalently

$$\begin{aligned} \frac{F - N_p \mu_p^0}{N_p k T} = & -1 + \log \rho + \log 4\pi - \frac{\rho}{2} \sum_{l=0}^{\infty} B_l C_l^2 \left(\frac{4\pi}{4l+1} \right)^2 \\ & - 4\pi \int_0^{\pi/2} \sum_{l=0}^{\infty} C_l P_{2l}(\cos \theta) \log \left[\sum_{l=0}^{\infty} C_l P_{2l}(\cos \theta) \right] \sin \theta d\theta \quad (35) \end{aligned}$$

The free-energy differences between the isotropic and anisotropic solutions are given in Table III, where we have evaluated the quantity

$$\Delta \equiv \left[\frac{F - N_p \mu_p^0}{N_p k T} \right]_{\text{isotropic}} - \left[\frac{F - N_p \mu_p^0}{N_p k T} \right]_{\text{anisotropic}} \quad (36)$$

using Eqs. (34) and (35). The similarity of the two results is an additional check on our solution. The free-energy difference Δ vs. ρB_1 curve is practically a straight line for small Δ . If one extrapolates this line to $\Delta = 0$, one obtains

$$\rho B_1 |_{\Delta=0} = 4.435 \quad (37)$$

Since Δ is discontinuous at a first-order phase transition, this gives a lower bound on the critical concentration which is only 1.2% away from our value for $\rho_c B_1$

$$\rho_c B_1 > 4.435 \quad (38)$$

Finally, we also solved for $\rho_c B_1$ by truncating Eqs. (23) and (24) at $l = 2$ instead of $l = 1$, as in (25). We obtain

$$\rho_c B_1 = 4.482 \quad (39)$$

only an 0.1% change from (26). We have therefore found a very accurate value of the critical concentration in this model. The angular-distribution function is of course much more sensitive to approximations than the critical concentration.

Table III. Isotropic-Anisotropic Free-Energy Difference of Eq. (36) Using Eqs. (34) and (35)

ρB_1	Δ [Eq. (34)]	Δ [Eq. (35)]
4.4876	0.01078	0.01078
4.4891	0.01106	0.01107
4.5020	0.01346	0.01343
4.5685	0.02679	0.02681
4.6594	0.04729	0.04731
4.9270	0.11952	0.11953
5.0950	0.17203	0.17204

4. DISCUSSION

We have found an accurate value of the critical concentration at which a hard-core gas of long thin rods undergoes a first-order phase transition. We have also found the angular distribution function of the rods as a function of rod concentration by doing a systematic expansion in terms of Legendre polynomials. The low-concentration phase is isotropic; in the high-concentration phase, the rods tend to align with their long axes parallel to each other. The ordered-phase configuration is that of a nematic liquid crystal.

We have disregarded one of the two anisotropic solutions appearing for $\rho > \rho_c$. For $\rho B_1 > 5$, as chosen by Isihara, this solution would correspond to a second-order phase transition in which the rods would go from the isotropic phase to a phase in which the long axes of the rods tend to be perpendicular to a preferred axis, reminiscent of a cholesteric liquid crystal. It could also correspond to a first-order phase transition between ordered phases. We have analyzed this solution in detail in Zwanzig's model, where the rods are rectangular and can lie in only three mutually perpendicular directions. This solution gives a saddle point rather than a minimum in the free energy. A small external field or a small anisotropic interaction in addition to the hard-core interaction between rods would probably be sufficient to turn the saddle point in the free energy into at least a relative minimum in the free energy, making the "cholesteric" configuration metastable.

APPENDIX A—QUADRATIC EQUATIONS FOR EXPANSION COEFFICIENTS

The system of coupled exponential equations (23) and (24) can be transformed to a system of coupled quadratic equations for the C_n . In principle, the latter set of equations should be easier to handle mathematically than the former. In the present problem, however, Eqs. (23) and (24) have been used because when they are truncated they yield an anisotropic minimum free energy result. This is not the case with the quadratic equations given below: the anisotropic solutions that emerge upon decoupling do not correspond to a minimum in the free energy of the system. To find the anisotropic angular-distribution function, the entire system of coupled equations must be solved exactly.

Let

$$S_l = \frac{4\pi}{4l+1} \rho B_l \quad (\text{A1})$$

Equations (22) and (23) then are

$$f(x) = \sum_{l=0}^{\infty} C_l P_{2l}(x) = K \exp \left[\sum_{l=1}^{\infty} S_l C_l P_{2l}(x) \right] \quad (\text{A2})$$

where $x = \cos \theta$ and

$$K = \left[4\pi \int_0^1 \exp \left[\sum_{l=1}^{\infty} S_l C_l P_{2l}(x) \right] dx \right]^{-1} \quad (\text{A3})$$

Assuming that at any fixed concentration f is a continuous function of angle we can differentiate (A2) with respect to x :

$$\frac{df}{dx} = \sum_{l=1}^{\infty} C_l \frac{dP_{2l}(x)}{dx} = f(x) \sum_{l=1}^{\infty} S_l C_l \frac{dP_{2l}(x)}{dx} \quad (\text{A4})$$

which gives

$$\sum_{l=1}^{\infty} C_l \frac{dP_{2l}(x)}{dx} = \left[\sum_{l=0}^{\infty} C_l P_{2l}(x) \right] \left[\sum_{l=1}^{\infty} S_l C_l \frac{dP_{2l}(x)}{dx} \right] \quad (\text{A5})$$

Multiplying both sides of this equation by $(x^2 - 1)$ and using the recursion relation

$$(x^2 - 1) \frac{dP_{2l}(x)}{dx} = \frac{2l(2l + 1)}{4l + 1} [P_{2l+1}(x) - P_{2l-1}(x)] \quad (\text{A6})$$

gives

$$\begin{aligned} & \sum_{n=1}^{\infty} \left[\frac{(2n)(2n + 1)}{4n + 1} C_n - \frac{(2n - 2)(2n - 1)}{4n - 3} C_{n-1} \right] P_{2n-1}(x) \\ &= \left\{ \sum_{l=0}^{\infty} C_l P_{2l}(x) \right\} \left\{ \sum_{n=1}^{\infty} \left[\frac{(2n)(2n + 1)}{4n + 1} S_n C_n - \frac{(2n - 2)(2n - 1)}{4n - 3} S_{n-1} C_{n-1} \right] P_{2n-1}(x) \right\} \end{aligned} \quad (\text{A7})$$

Finally, using the orthogonality properties of Legendre polynomials and the expansion

$$\begin{aligned} P_n(x) P_m(x) &= \sum_{k=0}^{\infty} \frac{a_{m-k} a_k a_{n-k}}{a_{n+m-k}} \frac{(2n + 2m - 4k + 1)}{(2n + 2m - 2k + 1)} P_{n+m-2k}(x) \quad (\text{A8}) \\ a_k &= \frac{(2k - 1)!!}{k!}; \quad m \leq n \end{aligned}$$

yields

$$\begin{aligned} & \frac{(2m)(2m + 1)}{(4m - 1)(4m + 1)} C_m (1 - S_m C_0) - \frac{(2m - 2)(2m - 1)}{(4m - 3)(4m - 1)} C_{m-1} (1 - S_{m-1} C_0) \\ &= \sum_{l=1}^{\infty} \sum_{n=\text{Max}(m-l, l-m+1)}^{m+l} \left\{ \left[\frac{a_{l-m+n} a_{l+m-n} a_{m-l+n-1}}{(l + m + n) a_{l+m+n}} \right] \right. \\ & \quad \cdot \left. \left[\frac{2n(2n + 1)}{4n + 1} S_n C_n - \frac{(2n - 2)(2n - 1)}{4n - 3} S_{n-1} C_{n-1} \right] C_l \right\} \end{aligned} \quad (\text{A9})$$

The normalization of f gives

$$C_0 = \frac{1}{4\pi} \quad (\text{A10})$$

If, for example, we consider the equation for $m = 1$ and leave out all $C_{l \geq 2}$ [see Eq. (25)] we have

$$\frac{6}{5} C_1 = \frac{6}{5} S_1 C_1 C_0 + \frac{6}{35} S_1 C_1^2 \quad (\text{A11})$$

with solutions

$$C_1 = 0 \quad (\text{isotropic distribution}) \quad (\text{A12})$$

and

$$C_1 = \frac{7}{4\pi\rho B_1} (5 - \rho B_1) \quad (\text{A13})$$

Letting $\rho B_1 = 5 + \Delta\rho B_1$, for small $\Delta\rho B_1$ Eq. (A13) becomes

$$C_1 \approx -\frac{7}{20\pi} \Delta\rho B_1 \quad (\text{A14})$$

APPENDIX B—EXPANSION OF ANGULAR-DISTRIBUTION FUNCTION IN POWERS OF CONCENTRATION

Once the angular-distribution function $f(\theta)$ has been determined at some concentration $\rho_0 > \rho_c$, it can be determined for other concentrations $\rho_c < \rho < 2\rho_0 - \rho_c$ by a set of *linear* integral equations instead of the nonlinear equation (15). Let the solution of (15) at $\rho = \rho_0$ be denoted by $f(\rho_0, x)$, where $x = \cos \theta$. Then for $\rho_c < \rho < 2\rho_0 - \rho_c$,

$$f(\rho, x) = \sum_{n=0}^{\infty} \frac{(\rho - \rho_0)^n}{\rho_0^n} f_n(\rho_0, x) \quad (\text{B1})$$

It is now easy to derive the equations satisfied by the successive f_n . Let

$$\alpha \equiv \frac{\rho - \rho_0}{\rho_0}; \quad \rho = \alpha\rho_0 + \rho_0 \quad (\text{B2})$$

Then from (B1) and (15)

$$\begin{aligned} \frac{\partial f(\rho, x)}{\partial x} &= \sum_{n=0}^{\infty} \alpha^n \frac{\partial f_n(\rho_0, x)}{\partial x} \\ &= (\alpha\rho_0 + \rho_0) \left[\sum_{n=0}^{\infty} \alpha^n f_n(\rho_0, x) \right] \left[\sum_{n=0}^{\infty} \alpha^n \frac{\partial}{\partial x} \int \beta_1(\Omega, \Omega') f_n(\rho_0, x') d\Omega' \right] \end{aligned} \quad (\text{B3})$$

Equating coefficients of each power of α gives an equation for each f_n . For f_0 we have:

$$\frac{\partial f_0(\rho_0, x)}{\partial x} = \rho_0 f_0(\rho_0, x) \frac{\partial}{\partial x} \int \beta_1(\Omega, \Omega') f_0(\rho_0, x') d\Omega' \quad (\text{B4})$$

and integration gives

$$f_0(\rho_0, x) = K_0(\rho_0) \exp \left[\rho_0 \int \beta_1(\Omega, \Omega') f_0(\rho_0, x') d\Omega' \right] \quad (\text{B5})$$

where $K_0(\rho_0)$ is a constant of integration. Since $f(\rho_0, x) = f_0(\rho_0, x)$, Eq. (B5) is the same as Eq. (15) at $\rho = \rho_0$. This fixes the constant of integration and we have

$$f_0(\rho_0, x) = \frac{\exp[\rho_0 \int \beta(\Omega, \Omega') f_0(\rho_0, x') d\Omega']}{\int \exp[\rho_0 \int \beta(\Omega, \Omega') f_0(\rho_0, x') d\Omega'] d\Omega} \quad (\text{B6})$$

f_1 satisfies the equation

$$\begin{aligned} \frac{\partial f_1(\rho_0, x)}{\partial x} &= \rho_0 f_0(\rho_0, x) \frac{\partial}{\partial x} \int \beta(\Omega, \Omega') f_0(\rho_0, x') d\Omega' \\ &+ \rho_0 f_0(\rho_0, x) \frac{\partial}{\partial x} \int \beta(\Omega, \Omega') f_1(\rho_0, x') d\Omega' \\ &+ \rho_0 f_1(\rho_0, x) \frac{\partial}{\partial x} \int \beta(\Omega, \Omega') f_0(\rho_0, x') d\Omega' \end{aligned} \quad (\text{B7})$$

Using (B4) and rearranging terms gives

$$\frac{\partial}{\partial x} \frac{f_1(\rho_0, x)}{f_0(\rho_0, x)} = \frac{1}{f_0(\rho_0, x)} \frac{\partial}{\partial x} f_0(\rho_0, x) + \rho_0 \frac{\partial}{\partial x} \int \beta(\Omega, \Omega') f_1(\rho_0, x') d\Omega' \quad (\text{B8})$$

which can be integrated directly to yield

$$\frac{f_1(\rho_0, x)}{f_0(\rho_0, x)} = \ln f_0(\rho_0, x) + \rho_0 \int \beta(\Omega, \Omega') f_1(\rho_0, x') d\Omega' + K_1(\rho_0) \quad (\text{B9})$$

The constant of integration $K_1(\rho_0)$ can be determined from the normalization condition on f . We have

$$\int f(\rho, x) d\Omega = 1 \quad (\text{B10})$$

and also [see Eq. (B6)]

$$\int f_0(\rho_0, x) d\Omega = 1 \quad (\text{B11})$$

Hence

$$\int f_n(\rho_0, x) d\Omega = 0 \quad \text{for all } n \geq 1 \quad (\text{B12})$$

For $n = 1$, Eqs. (B9) and (B6) give

$$K_1(\rho_0) = - \int \ln f_0(\rho_0, x) [f_0(\rho_0, x) + f_1(\rho_0, x)] d\Omega \quad (\text{B13})$$

and finally

$$\begin{aligned} \frac{f_1(\rho_0, x)}{f_0(\rho_0, x)} &= \ln f_0(\rho_0, x) + \rho_0 \int \beta(\Omega, \Omega') f_1(\rho_0, x') d\Omega' \\ &- \int \ln f_0(\rho_0, x) [f_0(\rho_0, x) + f_1(\rho_0, x)] d\Omega \end{aligned} \quad (\text{B14})$$

This is a linear integral equation for $f_1(\rho_0, x)$ in terms of the known function $f_0(\rho_0, x)$.

Similar derivations give the equations for higher order f_n . Thus, for example,

$$\begin{aligned} \frac{f_2(\rho_0, x)}{f_0(\rho_0, x)} &= \frac{1}{2} \left[\frac{f_1(\rho_0, x)}{f_0(\rho_0, x)} \right]^2 - \frac{1}{2} \int \frac{f_1^2(\rho_0, x)}{f_0(\rho_0, x)} d\Omega \\ &+ \rho_0 \int \beta(\Omega, \Omega') [f_1(\rho_0, x') + f_2(\rho_0, x')] d\Omega' \\ &- \int \ln f_0(\rho_0, x) [f_1(\rho_0, x) + f_2(\rho_0, x)] d\Omega \end{aligned} \quad (\text{B15})$$

and

$$\begin{aligned} \frac{f_3(\rho_0, x)}{f_0(\rho_0, x)} &= -\frac{1}{3} \left[\frac{f_1^3(\rho_0, x) - 3f_0(\rho_0, x)f_1(\rho_0, x)f_2(\rho_0, x)}{f_0^3(\rho_0, x)} \right] \\ &+ \frac{1}{3} \int \frac{f_1^3(\rho_0, x) - 3f_0(\rho_0, x)f_1(\rho_0, x)f_2(\rho_0, x)}{f_0^3(\rho_0, x)} d\Omega \\ &+ \rho_0 \int \beta(\Omega, \Omega') [f_2(\rho_0, x') + f_3(\rho_0, x')] d\Omega' \\ &- \int \ln f_0(\rho_0, x) [f_2(\rho_0, x) + f_3(\rho_0, x)] d\Omega \end{aligned} \quad (\text{B16})$$

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