

## Hard-rod fluid: Scaled particle theory revisited\*

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A scaled particle theory is developed for a fluid of hard spherocylindrical rods with fixed orientations. Unlike earlier scaled particle treatments of this system, it maintains thermodynamic consistency in that the Maxwell relation  $\partial\mu_i/\partial\rho_j = \partial\mu_j/\partial\rho_i$ , where  $\mu$  is the chemical potential and  $\rho$  is the number density, is satisfied for all orientations  $i$  and  $j$  without sacrificing the internal logic or consistency of the scaled particle approach. The resulting expression for the Helmholtz free energy is used to derive the equilibrium thermodynamics of hard spherocylinders that are free to rotate among an arbitrary set of allowed orientations. Numerical results are presented for two special cases: (i) rods with a continuous distribution of orientations and (ii) rods permitted to adopt only three mutually perpendicular orientations. In both instances, the properties of the nematiclike ordered phase and of the anisotropic  $\rightarrow$  isotropic phase transition are determined and compared with experimental data for nematic liquids, as well as with the predictions of other theories of the hard-rod fluid. This theory is shown to reduce to the Reiss, Frisch, and Lebowitz (or Percus-Yevick) theory of hard spheres when the length-to-breadth ratio of the spherocylinders decreases to unity.

### I. INTRODUCTION

Liquid-crystalline phases, or mesophases, exhibit properties intermediate between those of crystalline solids and isotropic liquids, that is, they are liquidlike in their flow behavior but resemble uniaxial crystals optically.<sup>1</sup> Of the three generally recognized types of liquid crystals—smectic, nematic, and cholesteric—the simplest are the nematic. Formed by elongated, rodlike molecules, nematic mesophases differ from isotropic liquids in only one respect: the average alignment of the molecular long axes along a preferred direction (i.e., nematic long-range orientational order).<sup>2</sup> Nematogenic substances undergo a first-order phase transition from the nematic phase, stable at lower temperatures and higher densities to the isotropic liquid phase, stable at higher temperatures and lower densities.

The hard-rod fluid, as its name implies, consists of rigid, rodlike particles which interact only through the infinite repulsion which prevents their overlapping. It is isotropic at low densities and then undergoes a first-order transition to an anisotropic higher-density phase with nematiclike order. Although not a realistic model for nematogenic systems, hard rods are quite useful in trying to understand the molecular “reasons” for the existence of nematic mesophases, particularly as regards the roles of molecular geometry and short-range repulsive interactions.

For the most part, the statistical-mechanical treatments of the hard-rod fluid have been of three types<sup>3</sup>: those utilizing (i) cluster expansions,<sup>4-7</sup> (ii) lattice models,<sup>8-11</sup> and (iii) scaled particle

theory.<sup>12-13</sup> The first of these is perhaps the most satisfying esthetically, since it utilizes an exact density expansion for the Helmholtz free energy. As the result of computational difficulties, however, no coefficients in the expansion beyond that of the linear term have been or are likely to be evaluated for the general case of rods with a continuous range of possible orientations. Truncating the series after the linear term (the so-called Onsager approximation<sup>4</sup>) yields an approximate theory which should be satisfactory for very long rods<sup>14</sup> but probably not for shorter rods. Of the remaining (and less rigorous) statistical approaches, the third seems preferable to the second since scaled particle theory does not restrict one to small sets of discrete orientations for the rods and is certainly less suspect for short rods than is the use of lattice models.<sup>15</sup>

Simple scaled particle theory provides a means of deriving approximate expressions for the chemical potential and pressure of a hard-particle fluid by considering the reversible work necessary to insert a scaled particle (i.e., a “solute” particle which is a scaled replica of the “solvent” particles) at some arbitrary point in the fluid. It was originally developed by Reiss, Frisch, and Lebowitz<sup>16</sup> to treat hard spheres and has since been applied to a number of other systems.<sup>17</sup> It is exact in one dimension and gives equations of state for two- and three-dimensional hard spheres that are in good agreement with “experiment,” i.e., with Monte Carlo and molecular-dynamics computations.<sup>18</sup>

The scaled particle approach has been applied to hard rods by Cotter and Martire<sup>12</sup> and by

Lasher.<sup>13</sup> Lasher, in his more general treatment, noted that the configurational partition function for a fluid in which each hard rod moves about with fixed orientation yields, after maximization with respect to the orientational distribution, the maximum term of the configurational partition function for the fluid of hard rods that are free to rotate (the system of most interest). He therefore applied the customary scaled particle procedure to a fluid of hard spherocylinders (i.e., cylinders capped on each end by a hemisphere) with fixed orientations, a system that must be regarded thermodynamically as a multicomponent mixture, each component consisting of all spherocylinders pointing in a particular direction. Unfortunately, the resulting expressions for the chemical potentials were not thermodynamically consistent in that the Maxwell relation

$$\left(\frac{\partial \mu_i}{\partial \rho_j}\right)_{T, \rho_{k \neq j}} = \left(\frac{\partial \mu_j}{\partial \rho_i}\right)_{T, \rho_{k \neq i}} \quad (1)$$

for a multicomponent system was not satisfied, where  $\mu_k$  is the chemical potential and  $\rho_k$  the number density of component  $k$ . The inconsistency was eliminated in a rather arbitrary manner by dropping from the expression for the chemical potential of each component the term responsible for Eq. (1) not being satisfied. This truncation is undesirable, however, in several respects. (i) The terms dropped, which are proportional to  $(1 - v_0 \rho)^{-2}$ , where  $v_0$  is the volume of a spherocylinder, are negligible numerically only at very low densities. (ii) The arbitrariness of the truncation is disturbing and its physical meaning is unclear. (iii) The resulting expressions for the thermodynamic variables do not reduce to the cor-

responding (impressively accurate) scaled particle expressions for hard spheres<sup>16</sup> when the length-to-breadth ratio of the spherocylinders is decreased to unity; as a consequence, the predictions of the truncated theory are somewhat suspect for short rods. It would certainly be desirable, therefore, to have a scaled particle theory of the hard-rod mixture in which thermodynamic consistency would be obtained without arbitrary truncation. Such a theory is presented in this paper. It is entirely within the spirit and logical framework of the original scaled particle theories and reduces, in the appropriate limits, to previously derived results for hard spheres<sup>16</sup> and perfectly ordered hard spherocylinders.<sup>12</sup> The hard-rod fluid is considered in greater detail in Sec. II, while the scaled particle theory is developed in Sec. III and used in Sec. IV to derive the equilibrium thermodynamics of hard spherocylinders that are free to rotate. Numerical results for two specific systems are presented in Sec. IV and their significance is discussed in Sec. V.

## II. HARD-ROD FLUID

Consider a fluid of  $N$  identical cylindrically symmetric hard rods contained in a volume  $V$ . The orientation of the  $\nu$ th rod can be specified by  $(\theta_\nu, \phi_\nu)$ , where  $\theta_\nu$  is the polar and  $\phi_\nu$  the azimuthal angle of the long axis of  $\nu$  with respect to a space-fixed coordinate system. (In other words,  $\theta$  and  $\phi$  are the Euler angles  $\beta$  and  $\alpha$ , respectively.) If there are no *a priori* restrictions on the possible orientations of a rod, the canonical ensemble partition function for the system is

$$Q(N, V, T) = \frac{Z(N, V, T)}{N! \Lambda^N} \quad (2)$$

$$= [N! \Lambda^N (4\pi)^N]^{-1} \int \cdots \int \int_V \cdots \int_V \exp[-\beta U_N(\bar{\mathbf{r}}_1, \Omega_1, \dots, \bar{\mathbf{r}}_N, \Omega_N)] \prod_{\nu=1}^N d\bar{\mathbf{r}}_\nu d\Omega_\nu, \quad (3)$$

where  $Z$  is the configurational partition function,  $\Lambda^{-1}$  is the kinetic energy (translational plus rotational) contribution to the single-particle partition function,  $U_N$  is the  $N$ -particle potential energy of interaction,  $\bar{\mathbf{r}}_\nu$  and  $\Omega_\nu$  are the position and orientation of rod  $\nu$ ,  $\beta = (kT)^{-1}$ , and  $d\Omega_\nu$

$= \sin \theta_\nu d\theta_\nu d\phi_\nu$ . (For hard rods, of course,  $U$  can have only two values, 0 and  $\infty$ .) If, on the other hand, each rod is allowed to point in only  $n$  discrete directions,  $1, 2, \dots, n$ , the partition function is given by

$$Q(N, V, T) = (N! \Lambda^N n^N)^{-1} \sum_{j_1=1}^n \cdots \sum_{j_N=1}^n \int_V \cdots \int_V \exp[-\beta U_N(\bar{\mathbf{r}}_1, j_1, \dots, \bar{\mathbf{r}}_N, j_N)] \prod_{\nu=1}^N d\bar{\mathbf{r}}_\nu, \quad (4)$$

where  $j_\nu$  denotes the orientation of the  $\nu$ th hard rod. Following Zwanzig,<sup>6</sup> let us introduce the quantity  $\Phi_N$ , defined by

$$V^N e^{-\beta \Phi_N} \equiv \int_V \cdots \int_V e^{-\beta U_N} d\bar{\mathbf{r}}_1 \cdots d\bar{\mathbf{r}}_N. \quad (5)$$

As has been noted,<sup>6,12</sup>  $\Phi_N(j_1, \dots, j_N)$  is just the

excess (Helmholtz) free energy of a hard-rod fluid with fixed orientations  $j_1, \dots, j_n$ , relative to an ideal, multicomponent hard-rod mixture. Actually,  $\beta\Phi_N$  depends only on the orientational distribution  $N_1, N_2, N_3, \dots$ , where  $N_i$  is the number of rods with orientation  $i$ , and the sum over configurations  $(j_1, \dots, j_n)$  in (4) can be converted to a sum over the set  $(N_1, \dots, N_n)$ . Replacing the resulting multiple sum by its maximum term, taking natural logarithms, and rearranging then gives

$$\begin{aligned} N^{-1} \ln Q &= 1 - \ln(n\Lambda\rho) - \sum_{i=1}^n \bar{s}_i \ln \bar{s}_i \\ &\quad - N^{-1} \beta\Phi_N(\rho, \bar{s}_1, \dots, \bar{s}_n) \\ &\equiv t(\bar{s}_1, \dots, \bar{s}_n), \end{aligned} \quad (6)$$

where

$$s_i = N_i/N, \quad (7)$$

$$\sum_i s_i = 1, \quad (8)$$

and the bars indicate that distribution  $\{s_1, s_2, \dots, s_n\}$  which maximizes  $\ln Q$  (and hence  $Q$ ). The corresponding expression for  $\ln Q$  when the range of possible orientations is continuous can be obtained from (6) by dividing the unit sphere into very small equal parts of solid angle  $\Delta\Omega$ . Then  $s_i = f(\Omega_i)\Delta\Omega$ ,  $n = 4\pi/\Delta\Omega$ , and in the limit  $\Delta\Omega \rightarrow 0$  (6) and (8) become

$$\begin{aligned} N^{-1} \ln Q &= 1 - \ln(\rho\Lambda) - \int \bar{f}(\Omega) \ln[4\pi\bar{f}(\Omega)] d\Omega \\ &\quad - N^{-1} \beta\Phi_N(\bar{f}(\Omega), \rho) \\ &\equiv t(\bar{f}(\Omega)), \end{aligned} \quad (9)$$

$$\int \bar{f}(\Omega) d\Omega = 1, \quad (10)$$

where  $f(\Omega)$  is the normalized orientational distribution function and the bar again indicates that distribution which maximizes  $\ln Q$ . Finally, it is clear that  $\ln Q$  can be obtained by first obtaining  $\Phi_N$  for an arbitrary distribution of orientations and then determining the most probable distribution by maximizing the quantity  $t$ . All the equilibrium thermodynamic properties of the hard-rod fluid can then be derived from  $\ln Q(N, V, T)$ .

### III. CONSISTENT SCALED PARTICLE THEORY

Before the scaled particle approach can be utilized to evaluate the excess free energy  $\Phi_N$ , the precise shape of the hard rods must be specified. Following Onsager,<sup>4</sup> Cotter and Martire,<sup>12,13</sup> and Lasher,<sup>14</sup> we shall consider spherocylindrical rods, where a spherocylinder is defined to be a

right circular cylinder capped at each end by a hemisphere.<sup>19</sup> More precisely, we shall determine  $\Phi_N$  for a fluid of  $N$  hard spherocylinders of radius  $a$  and cylindrical length  $l$  contained in a volume  $V$ , with each spherocylinder moving through the fluid so as to maintain a constant orientation with respect to some space-fixed coordinate system. Let us again denote by  $s_i$  the fraction of rods in the  $i$ th orientation, where  $i = 1, 2, \dots, n$  and the fluid must be regarded thermodynamically as an  $n$ -component system. (The limiting case of a continuous distribution of orientations will be considered later.) The chemical potential of a spherocylinder in orientation  $i$  is given by the exact relation<sup>13</sup>

$$\beta\mu_i = \beta\mu_0(\beta) + \ln(v_0\rho_i) + \beta[W_i(\alpha, \lambda, \rho)]_{\alpha=1, \lambda=1} \quad (11)$$

$$= \beta\mu_0(\beta) + \ln(v_0\rho_i)$$

$$- [\ln p_i^0(\alpha, \lambda, \rho)]_{\alpha=1, \lambda=1}, \quad (12)$$

where  $v_0$  is the volume of the spherocylinder,  $\beta\mu_0 + \ln(v_0\rho_i)$  is the chemical potential of component  $i$  in an ideal mixture,  $W_i(\alpha, \lambda)$  is the reversible work necessary to add a hard scaled spherocylinder of radius  $\alpha a$ , cylindrical length  $\lambda l$ , and orientation  $i$  at some arbitrary fixed point in the fluid, and  $p_i^0$  is the probability that such a scaled particle could be so added without overlapping any of the  $N$  "solvent" spherocylinders. Clearly,  $p_i^0$  and  $W_i$  are related by

$$p_i^0 = e^{-\beta W_i}. \quad (13)$$

Our principal task is to derive expressions for  $\ln p_i^0(\alpha, \lambda, \rho)$  ( $i = 1, 2, \dots, n$ ) which can be evaluated at  $\alpha = 1, \lambda = 1$  in order to obtain the chemical potentials  $\beta\mu_i$  from (12).

When  $\alpha$  and  $\lambda$  are sufficiently small so that three "solvent" spherocylinders cannot simultaneously be in contact with the scaled spherocylinder,  $p_i^0$  is given by<sup>20</sup>

$$\begin{aligned} p_i^0(\alpha, \lambda, \rho) &= 1 - \rho \sum_{k=1}^n s_k \mathbf{v}_{ik} \\ &\quad + \sum_{m_1} \sum_{m_2} \dots \sum_{m_n} \rho^2 \prod_{k=1}^n \frac{s_k^{m_k}}{m_k!} \\ &\quad \times \int_{\mathbf{v}_{ij_1}} \int_{\mathbf{v}_{ij_2}} g^{(2)}(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2, j_1, j_2) d\bar{\mathbf{r}}_1 d\bar{\mathbf{r}}_2 \end{aligned} \quad (14)$$

$$\equiv 1 - \rho \sum_{k=1}^n s_k \mathbf{v}_{ik} + F_2^{(i)}(\alpha, \lambda, \rho), \quad (15)$$

where the  $m_k$  are non-negative integers and  $\sum_{k=1}^n m_k = 2$  for each term in the sum over  $(m_1, \dots, m_n)$ .  $\mathbf{v}_{ik}$  is the volume excluded to a "solvent" spherocylinder with orientation  $k$  by the

presence of the scaled particle (with orientation  $i$ ) at some fixed point,  $g^{(2)}$  is the two-particle correlation function, and the integration with respect to  $\vec{r}_\nu$  ( $\nu=1$  or  $2$ ) is over all positions excluded to "solvent" spherocylinder  $\nu$  (with orientation  $j_\nu$ ) by the presence of the scaled particle. (The positions  $\vec{r}_1$  and  $\vec{r}_2$  are measured relative to the center of the scaled particle.) Onsager<sup>4</sup> has shown that

$$\mathbf{v}_{ik} = \pi a^2 l (1 + \alpha)^2 (1 + \lambda) + \frac{4}{3} \pi a^3 (1 + \alpha)^3 + 2a l^2 (1 + \alpha) \lambda |\sin \gamma_{ik}| \quad (16)$$

for spherocylinders, where  $\gamma_{ik}$  is the angle between directions  $i$  and  $k$ . For a point particle, moreover, it can be shown that<sup>22,23</sup>

$$F_2^{(i)} = \frac{\partial F_2^{(i)}}{\partial \alpha} = \frac{\partial F_2^{(i)}}{\partial \lambda} = \frac{\partial^2 F_2^{(i)}}{\partial \alpha \partial \lambda} = \frac{\partial^2 F_2^{(i)}}{\alpha^2} = \frac{\partial^3 F_2^{(i)}}{\alpha^2 \partial \lambda} = 0 \quad (\alpha=0, \lambda=0). \quad (17)$$

Therefore  $\ln p_i^0$ ,  $\partial \ln p_i^0 / \partial \alpha$ ,  $\partial \ln p_i^0 / \partial \lambda$ ,  $\partial^2 \ln p_i^0 / \partial \alpha \partial \lambda$ ,  $\partial^2 \ln p_i^0 / \alpha^2$ , and  $\partial^3 \ln p_i^0 / \alpha^2 \partial \lambda$  can be evaluated for all  $i$  at  $\alpha=0, \lambda=0$ . When  $\alpha$  and  $\lambda$  are both very large,  $W_i(\alpha, \lambda, \rho)$  must approach the reversible  $pV$  work necessary to produce a macroscopic spherocylindrical cavity of radius  $\alpha a$  and cylindrical length  $\lambda l$  in the fluid, from which all parts of all "solvent" spherocylinders are excluded. Hence,

$$\lim_{\alpha \rightarrow \infty, \lambda \rightarrow \infty} \ln p_i^0 = -\beta \lim_{\alpha \rightarrow \infty, \lambda \rightarrow \infty} W_i = -\beta p \left[ \pi (\alpha a)^2 \lambda l + \frac{4}{3} \pi (\alpha a)^3 \right], \quad (18)$$

where  $p$  is, of course, the pressure. These considerations suggest that

$$\ln p_i^0(\alpha, \lambda) = A_i + B_i \alpha + C_i \lambda + D_i \alpha \lambda + E_i \alpha^2 - (\pi a^2 l \beta p) \alpha^2 \lambda - \left( \frac{4}{3} \pi a^3 \beta p \right) \alpha^3 \quad (19)$$

might be a good approximation for all  $\alpha \geq 0, \lambda \geq 0$ .<sup>21</sup> This was the functional form used by Cotter and Martire in Ref. 12(c). Lasher, on the other hand, used only one scaling parameter and approximated  $\ln p_i^0$  by

$$\ln p_i^0 = A_i + B_i' s + C_i' s^2 - (\pi a^2 l + \frac{4}{3} \pi a^3) \beta p s^3 \quad (s \geq 0), \quad (20)$$

where the scaled spherocylinder was taken to have radius  $sa$  and cylindrical length  $sl$ .<sup>24</sup> When either (19) or (20) is used, the coefficients  $A_i, B_i, C_i, D_i, E_i$  or  $A_i, B_i', C_i'$ <sup>24</sup> determined from (15)–(17), and the pressure then obtained from (12) together with the Gibbs-Duhem equation in the form

$$\left( \frac{\partial(\beta p)}{\partial \rho} \right)_{s_1, \dots, s_n, \beta} = \sum_{k=1}^n \rho_k \left( \frac{\partial(\beta \mu_k)}{\partial \rho} \right)_{s_1, \dots, s_n, \beta} \quad (21)$$

or

$$\left( \frac{\partial(\beta p)}{\partial \rho_j} \right)_{\rho_i \neq j, \beta} = \sum_{k=1}^n \rho_k \left( \frac{\partial(\beta \mu_k)}{\partial \rho_j} \right)_{\rho_i \neq j, \beta}, \quad (22)$$

the resulting expressions for the chemical potentials are not thermodynamically consistent in that Eq. (1) is not satisfied. To eliminate this inconsistency in a nonarbitrary manner, a functional form somewhat more flexible than (19) or (20) must be adopted. Stillinger and Cotter<sup>25</sup> have demonstrated that an asymptotic expansion of  $\ln p^0$  for hard spheres in descending powers of the variable  $\xi = \frac{1}{2}(1 + \alpha)$  exists and has the form

$$\ln p^0(\xi) = \sum_{n=0}^{\infty} C_n \xi^{3-n}. \quad (23)$$

Their work suggests that if the right-hand side of (19) represents the leading terms of a similar (large scaled particle) asymptotic expansion, then the next term should be proportional to  $(1 + \alpha)^{-1}$ . Accordingly, let us assume that  $\ln p_i^0$  can be represented adequately by

$$\begin{aligned} \ln p_i^0(\alpha, \lambda, \rho) = & \frac{Q(\rho, \underline{s})}{1 + \alpha} + A_i(\rho, \underline{s}) + B_i(\rho, \underline{s}) \alpha \\ & + C_i(\rho, \underline{s}) \lambda + D_1(\rho, \underline{s}) \alpha \lambda + E_i(\rho, \underline{s}) \alpha^2 \\ & - (\pi a^2 l \beta p) \alpha^2 \lambda - \left( \frac{4}{3} \pi a^3 \beta p \right) \alpha^3 \quad (24) \end{aligned}$$

for all non-negative  $\alpha$  and  $\lambda$ .<sup>26</sup> ( $\underline{s}$  denotes the set  $\{s_1, \dots, s_n\}$ .) Equation (24) is the central assumption of our theory.

The coefficients  $A_i, B_i, C_i, D_i$ , and  $E_i$  are determined by equating each of  $\ln p_i^0(0, 0)$ ,  $(\partial \ln p_i^0 / \partial \alpha)_{\alpha=0, \lambda=0}$ ,  $(\partial \ln p_i^0 / \partial \lambda)_{\alpha=0, \lambda=0}$ ,  $(\partial^2 \ln p_i^0 / \partial \alpha \partial \lambda)_{\alpha=0, \lambda=0}$ , and  $(\partial^2 \ln p_i^0 / \alpha^2)_{\alpha=0, \lambda=0}$ , respectively, obtained from (24) with the same quantity obtained from (15)–(17). Equation (12) then becomes

$$\beta(\mu_i - \mu_0) = \ln \left( \frac{s_i v_0 \rho}{1 - v_0 \rho} \right) + \frac{6v_0 \rho (1 + \frac{2}{3} r \sum_{j \neq i} s_j |\sin \gamma_{ij}|)}{(1 - v_0 \rho)} + \frac{4v_0^2 \rho^2 (1 + \frac{1}{2} q) (1 - \frac{1}{4} q + r \sum_{j \neq i} s_j |\sin \gamma_{ij}|)}{(1 - v_0 \rho)^2} + \frac{1}{2} Q + \Pi, \quad (25)$$

where

$$\begin{aligned} v_0 &= \pi a^2 l + \frac{4}{3} \pi a^3, \\ x &= \frac{l}{2a} + 1, \\ q &= \frac{\frac{4}{3} \pi a^3}{v_0} = \frac{2}{(3x-1)}, \\ r &= \frac{al^2}{v_0} = \frac{6(x-1)^2}{\pi(3x-1)}, \\ \Pi &= v_0 \beta p, \end{aligned} \quad (26)$$

(i.e.,  $v_0$  is the volume of a spherocylinder,  $x$  is its length-to-breadth ratio, and  $\Pi$  is the dimensionless pressure-to-temperature ratio). We wish to evaluate  $Q$  and  $\Pi$  by demanding that the symmetry requirement (1) together with the Gibbs-Duhem equation (22) be satisfied simultaneously for all  $i$  and  $j$ . It is more convenient, however, to choose  $\rho, s_2, s_3, \dots, s_n$  (with  $s_1 = 1 - \sum_{i=2}^n s_i$ ) rather than  $\rho_1, \rho_2, \dots, \rho_n$  as independent variables. In terms

of the former set of variables, thermodynamic consistency requires that

$$\frac{1}{v_0} \left( \frac{\partial \Pi}{\partial \rho} \right)_{\underline{s}} = \rho \sum_{k=1}^n s_k \left( \frac{\partial (\beta \mu_k)}{\partial \rho} \right)_{\underline{s}}, \quad (27)$$

$$\left( \frac{\partial \Pi}{\partial s_i} \right)_{\rho, s_j \neq i} = v_0 \rho \sum_{k=1}^n s_k \left( \frac{\partial (\beta \mu_k)}{\partial s_i} \right)_{\rho, s_j \neq i}, \quad (28)$$

and

$$\begin{aligned} 0 &= \left( \frac{\partial \mu_i}{\partial \rho_1} \right)_{\rho_j \neq 1} - \left( \frac{\partial \mu_1}{\partial \rho_i} \right)_{\rho_j \neq i} \\ &= \left( \frac{\partial (\mu_i - \mu_1)}{\partial \rho} \right)_{\underline{s}} - \frac{1}{\rho} \left( \frac{\partial \mu_1}{\partial s_i} \right)_{\rho, s_j \neq i} \\ &\quad - \frac{1}{\rho} \sum_{k=2}^n s_k \left( \frac{\partial (\mu_i - \mu_1)}{\partial s_k} \right)_{\rho, s_j \neq k}, \end{aligned} \quad (29)$$

for all  $i=2, 3, \dots, n$ . [Given (25), it can readily be confirmed that condition (1) will be satisfied for all  $i$  and  $j$  if (29) is satisfied for all  $i$ .] Substituting (25) into (27)–(29) and simplifying yields

$$\begin{aligned} v_0^{-1} (1 - v_0 \rho) \left( \frac{\partial \Pi}{\partial \rho} \right)_{\underline{s}} &= 1 + \frac{v_0 \rho}{1 - v_0 \rho} + \frac{6v_0 \rho (1 + \frac{2}{3} r \sum_i \sum_k s_j s_k |\sin \gamma_{jk}|)}{(1 - v_0 \rho)^2} \\ &\quad + \frac{8v_0^2 \rho^2 (1 + \frac{1}{2} q) (1 - \frac{1}{4} q + r \sum_j \sum_k s_j s_k |\sin \gamma_{jk}|)}{(1 - v_0 \rho)^3} + \frac{\rho}{2} \left( \frac{\partial Q}{\partial \rho} \right)_{\underline{s}}, \end{aligned} \quad (30)$$

$$(1 - v_0 \rho) \left( \frac{\partial \Pi}{\partial s_i} \right)_{\rho, s_j \neq i} = \frac{4r v_0^2 \rho^2 (1 + \frac{1}{2} q v_0 \rho) \sum_{k=1}^n s_k (|\sin \gamma_{ik}| - |\sin \gamma_{1k}|)}{(1 - v_0 \rho)^2} + \frac{v_0 \rho}{2} \left( \frac{\partial Q}{\partial s_i} \right)_{\rho, s_j \neq i}, \quad (31)$$

and

$$\left( \frac{\partial \Pi}{\partial s_i} \right)_{\rho, s_j \neq i} = \frac{8r v_0^2 \rho^2 [1 + (1 + v_0 \rho) \frac{1}{4} q] \sum_{k=1}^n s_k (|\sin \gamma_{ik}| - |\sin \gamma_{1k}|)}{(1 - v_0 \rho)^3} - \frac{1}{2} \left( \frac{\partial Q}{\partial s_i} \right)_{\rho, s_j \neq i} \quad (32)$$

( $i=2, \dots, n$ ). These three partial differential equations are sufficient to determine  $\Pi(\rho, \underline{s})$  and  $Q(\rho, \underline{s})$ .  $\partial Q / \partial s_i$  can be eliminated from (31) and (32) with the result

$$\left( \frac{\partial \Pi}{\partial s_i} \right)_{\rho, s_j \neq i} = \frac{4r v_0^2 \rho^2 [1 + (1 + q) v_0 \rho] \sum_{k=1}^n s_k (|\sin \gamma_{ik}| - |\sin \gamma_{1k}|)}{(1 - v_0 \rho)^3}. \quad (33)$$

From (33), together with the boundary condition

$$\Pi(s_2 = s_3 = \dots = s_n = 0) = \frac{v_0 \rho [1 + v_0 \rho + \frac{2}{3} (1 + q - \frac{1}{2} q^2) v_0^2 \rho^2]}{(1 - v_0 \rho)^3}, \quad (34)$$

it can then be determined that

$$\Pi(\rho, \underline{s}) = \frac{v_0 \rho \{1 + [1 + 2r\Gamma(\underline{s})] v_0 \rho + \frac{2}{3} [1 + q - \frac{1}{2} q^2 + 3r(1 + q)\Gamma(\underline{s})] v_0^2 \rho^2\}}{(1 - v_0 \rho)^3}, \quad (35)$$

where

$$\Gamma(\underline{s}) = \sum_j \sum_k s_j s_k |\sin \gamma_{jk}|. \quad (36)$$

[(34) is just the scaled particle equation of state for a perfectly ordered fluid of hard spherocylinders.<sup>12(b)</sup>] Finally, differentiating (35) with re-

spect to  $\rho$  at constant  $\underline{s}$  and “plugging” the result into (30) gives

$$\frac{\rho}{2} \left( \frac{\partial Q}{\partial \rho} \right)_{\underline{s}} = \frac{4r v_0^2 \rho^2 (1 + \frac{1}{2} q) \Gamma(\underline{s})}{(1 - v_0 \rho)^2}, \quad (37)$$

whence

$$Q(\rho, \underline{s}) = \frac{4r(1 + \frac{1}{2}q)v_0^2 \rho^2 \Gamma(\underline{s})}{(1 - v_0 \rho)^2} \quad (38)$$

$[Q(\rho=0)=0]$ . It is easily ascertained that (38) yields the same expression for  $\partial Q/\partial s_i$ , as do (32) and (33). As an additional check, it can be verified that (25) together with (35) and (38) satisfy (1) and (22). We thus have a thermodynamically

consistent scaled particle theory of the hard-rod fluid with fixed orientations. Furthermore, (25) and (35) reduce to the corresponding scaled particle expressions of Reiss, Frisch, and Lebowitz (RFL)<sup>16</sup> for hard spheres when  $x=1$  and, therefore,  $q=1, r=0$ .

The excess free energy  $\Phi_N$  can now be determined as follows:

$$N^{-1} \beta \Phi_N = \sum_{i=1}^n s_i \beta (\mu_i - \mu_i^{\text{ideal}}) - \beta (p - p^{\text{ideal}})/\rho, \quad (39)$$

$$= 1 - \sum_{i=1}^n s_i \beta (\mu_i - \mu_i^{\text{ideal}}) - \Pi/(v_0 \rho), \quad (40)$$

$$= 1 - \ln(1 - v_0 \rho) - \frac{1 - [5 + 2r\Gamma(\underline{s})]v_0 \rho + [8 - q + \frac{1}{2}q^2 - 3rq\Gamma(\underline{s})]v_0^2 \rho^2/3}{(1 - v_0 \rho)^2} \quad (41)$$

#### IV. RESULTS

##### A. Discrete orientations

Substituting  $\Phi_N$  from (41) into (6), one obtains

$$-N^{-1} \ln Q = \ln \left( \frac{n\rho\Lambda \prod_{i=1}^n \bar{s}_i \bar{s}_i}{1 - v_0 \rho} \right) - \frac{\{1 - [5 + 2r\Gamma(\underline{s})]v_0 \rho + [8 - q + \frac{1}{2}q^2 - 3rq\Gamma(\underline{s})]v_0^2 \rho^2/3\}}{(1 - v_0 \rho)^2} = -t(\underline{s}) \quad (42)$$

for the partition function of a fluid of  $N$  hard spherocylinders, each of which is free to assume any of  $n$  discrete orientations. The Helmholtz free energy  $A$ , configurational entropy  $S_c$ , and Gibbs free energy  $G$  are, therefore,

$$N^{-1} \beta A = -N^{-1} \ln Q, \quad (43)$$

$$\frac{S_c}{Nk} = N^{-1} \ln Q + \ln \Lambda, \quad (44)$$

$$N^{-1} \beta G = \beta \mu = \ln \left( \frac{n\rho\Lambda \prod_{i=1}^n \bar{s}_i \bar{s}_i}{1 - v_0 \rho} \right) + \frac{6v_0 \rho [1 + \frac{2}{3}r\Gamma(\underline{s})]}{(1 - v_0 \rho)} + \frac{4v_0^2 \rho^2 (1 + \frac{1}{2}q) [1 - \frac{1}{4}q + \frac{3}{2}r\Gamma(\underline{s})]}{(1 - v_0 \rho)^2} + \Pi, \quad (45)$$

where  $\Pi$ , the dimensionless pressure-to-temperature ratio, is given by (35) with  $\underline{s} = \bar{\underline{s}}$ . An expression for any other equilibrium thermodynamic quantity can be derived from (42)–(45). To determine the most probable distribution  $\bar{\underline{s}}$ ,  $t(\underline{s})$  must be maximized with respect to  $s_1, \dots, s_n$  under the constraint  $\sum_{i=1}^n s_i = 1$ .

##### B. Continuous orientational distribution

When the range of possible orientations for the long axis of a spherocylinder is continuous, (35) and (42)–(45) become<sup>27</sup>

$$\Pi = \frac{v_0 \rho \{1 + v_0 \rho + \frac{2}{3}(1 + q - \frac{1}{2}q^2)v_0^2 \rho^2 + 2rv_0 \rho [1 + (1 + q)v_0 \rho] \langle \langle \sin \gamma(\Omega, \Omega') \rangle \rangle\}}{(1 - v_0 \rho)^3}, \quad (46)$$

$$N^{-1} \beta A = -\frac{S_c}{Nk} + \ln \Lambda = -N^{-1} \ln Q = \ln \left( \frac{\rho \Lambda}{1 - v_0 \rho} \right) + \langle \ln [4\pi \bar{f}(\Omega)] \rangle - \frac{[1 - 5v_0 \rho + (8 - q + \frac{1}{2}q^2)\frac{1}{2}v_0^2 \rho^2 - 2rv_0 \rho (1 + \frac{1}{2}qv_0 \rho) \langle \langle \sin \gamma(\Omega, \Omega') \rangle \rangle]}{(1 - v_0 \rho)^2}, \quad (47)$$

and

$$N^{-1} \beta G = \beta \mu = \ln \left( \frac{\rho \Lambda}{1 - v_0 \rho} \right) + \langle \ln [4\pi \bar{f}(\Omega)] \rangle + \frac{6v_0 \rho}{1 - v_0 \rho} + \frac{(4 + q - \frac{1}{2}q^2)v_0^2 \rho^2 + 4rv_0 \rho [1 + (1 + \frac{3}{2}q)\frac{1}{2}v_0 \rho] \langle \langle \sin \gamma(\Omega, \Omega') \rangle \rangle}{(1 - v_0 \rho)^2} + \Pi \quad (48)$$

where

$$\begin{aligned} \langle \ln[4\pi \bar{f}(\Omega)] \rangle &= \int \bar{f}(\Omega) \ln[4\pi \bar{f}(\Omega)] d\Omega, \\ \langle \langle \sin\gamma(\Omega, \Omega') \rangle \rangle &= \int \int \sin\gamma(\Omega, \Omega') \\ &\quad \times \bar{f}(\Omega) \bar{f}(\Omega') d\Omega d\Omega'. \end{aligned} \quad (49)$$

To determine the most probable distribution  $\bar{f}(\Omega)$ , we must maximize the functional  $t[f(\Omega)]$  with respect to  $f(\Omega)$  under the constraint (10) or, in other words, we must solve the variational equation

$$\delta \left[ t - \alpha^* \int f(\Omega) d\Omega \right] = 0, \quad (50)$$

where  $\alpha^*$  is a Lagrange multiplier. After the standard manipulations, (50) yields the nonlinear integral equation

$$\begin{aligned} \alpha^* - 1 &= \ln[4\pi \bar{f}(\Omega)] + \frac{4rv_0\rho(1 + \frac{1}{2}qv_0\rho)}{(1 - v_0\rho)^2} \\ &\quad \times \int \sin\gamma(\Omega, \Omega') \bar{f}(\Omega') d\Omega' \end{aligned} \quad (51)$$

for  $f(\bar{\Omega})$ . (51) is of the same form as the corresponding integral equations of Onsager<sup>4</sup> [his Eq. (69)] and of Lasher<sup>13</sup> [his Eq. (6)], namely,

$$\ln[4\pi \bar{f}(\Omega)] + \lambda^*(\rho, x) \int \sin\gamma(\Omega, \Omega') \bar{f}(\Omega') d\Omega' = C, \quad (52)$$

where  $C$  does not depend on  $\Omega$ . (The function  $\lambda^*(\rho, x)$  is, of course, not the same in the three cases.) Lasher has solved this equation (numerically) for a number of values of  $\lambda^*$ . He found that for small  $\lambda^*$  (low densities), the only solution to (52) is the isotropic distribution

$$\bar{f}(\Omega) = 1/4\pi, \quad (53)$$

but for  $\lambda^* > 8.88$ , there are two anisotropic solu-

$$\begin{aligned} r' &= \left[ \beta\mu^{\text{iso}}(v_0\rho^{\text{iso}}, r) - \ln\left(\frac{\rho^{\text{aniso}}\Lambda}{1 - v_0\rho^{\text{aniso}}}\right) - \frac{6v_0\rho^{\text{aniso}}}{1 - v_0\rho^{\text{aniso}}} - \langle \ln(4\pi \bar{f}^{\text{aniso}}) \rangle - \Pi \right. \\ &\quad \left. - \frac{(4 + q - \frac{1}{2}q^2)v_0^2\rho^{\text{aniso}}}{(1 - v_0\rho^{\text{aniso}})^2} \right] \frac{(1 - v_0\rho^{\text{aniso}})^2}{4v_0\rho^{\text{aniso}} [1 + (1 + \frac{3}{2}q)v_0\rho^{\text{aniso}}/2] \langle \langle \sin\gamma \rangle \rangle}. \end{aligned} \quad (57)$$

This procedure could simply have been continued until  $|r' - r|$  became negligibly small. Instead, however, the Wegstein iteration scheme<sup>30</sup> was used to hasten convergence to the final value of  $r$ . The results of these computations are displayed in Table I and Fig. 1.

In Fig. 1, the coexisting densities  $v_0\rho^{\text{aniso}}$  and  $v_0\rho^{\text{iso}}$  are plotted versus  $x$ , the length-to-breadth

tions as well. The isotropic state is thermodynamically stable (i.e., renders  $N^{-1}\ln Q$  a maximum or  $N^{-1}\beta A$  a minimum) when  $\lambda^* < 8.88$ , while the more ordered of the anisotropic states is stable for  $\lambda^* > 8.88$ . For a more detailed discussion of the properties of the function  $f(\Omega)$  at several values of  $\lambda^*$ , see Lasher, particularly his Figs. 1 and 2.

In order to "locate" the first-order phase transition between the isotropic (iso) and anisotropic (aniso) states for rods of length-to-breadth ratio  $x$ , it is necessary to solve the simultaneous equations

$$\Pi^{\text{aniso}}(v_0\rho^{\text{aniso}}, x) = \Pi^{\text{iso}}(v_0\rho^{\text{iso}}, x) \quad (54)$$

and

$$\beta\mu^{\text{aniso}}(v_0\rho^{\text{aniso}}, x) = \beta\mu^{\text{iso}}(v_0\rho^{\text{iso}}, x), \quad (55)$$

where  $\rho^{\text{iso}}$  and  $\rho^{\text{aniso}}$  are the densities of the coexisting phases at the transition and the pressures and chemical potentials are given by (46) and (48), respectively. Instead of fixing  $x$  and solving (51), (54), and (55) for  $v_0\rho^{\text{aniso}}$ ,  $v_0\rho^{\text{iso}}$ , and  $\bar{f}^{\text{aniso}}(\Omega)$ , it is much easier to fix  $\lambda^*$  [and therefore  $\bar{f}^{\text{aniso}}(\Omega)$ ] and to solve (54) and (55), together with

$$\lambda^* = \frac{4rv_0\rho^{\text{aniso}}(1 + \frac{1}{2}qv_0\rho^{\text{aniso}})}{(1 - v_0\rho^{\text{aniso}})^2}, \quad (56)$$

for  $x$ ,  $v_0\rho^{\text{aniso}}$ , and  $v_0\rho^{\text{iso}}$ . In his Tables I and II, Lasher has given  $\langle \ln 4\pi \bar{f} \rangle$  and  $\langle \langle \sin\gamma \rangle \rangle$  calculated with the stable anisotropic distribution function for twelve different values of  $\lambda^*$ , enabling us to determine the transition parameters at twelve different length-to-breadth ratios.<sup>28</sup> The following iterative procedure was employed: Given  $\lambda^*$ ,  $\langle \ln 4\pi \bar{f} \rangle$ , and  $\langle \langle \sin\gamma \rangle \rangle$ , we choose a trial value of  $r$  and calculate  $v_0\rho^{\text{aniso}}$  from (56) and then  $\Pi^{\text{aniso}}(v_0\rho^{\text{aniso}})$  from (46). Equation (54) then becomes a cubic equation which can be solved for  $v_0\rho^{\text{iso}}$ . Finally, we compute  $\beta\mu^{\text{iso}}(v_0\rho^{\text{iso}})$ <sup>29</sup> from (48) with  $\bar{f} = 1/4\pi$  and obtain a new value of  $r$ ,  $r'$ , from (55) rearranged to give

ratio of the spherocylinders. The behavior shown is typical of that found previously for hard-rod models<sup>8-13</sup>; that is, as  $x$  increases, there is a rather sharp decrease in the mean density at the transition, accompanied by an increase in the relative-density discontinuity  $\Delta\rho/\rho^{\text{aniso}}$ . Only for very short rods ( $x < 2$ ) is  $\Delta\rho/\rho^{\text{aniso}}$  of the same order of magnitude as available experimental values

TABLE I. Transition densities, density discontinuity, and degree of order at six values of the parameter  $\lambda^*$ . Comparison of consistent scaled particle theory (CSPT) with Lasher's truncated scaled particle theory (TSPT).

$\lambda^*$	S	CSPT				TSPT			
		$x$	$v_0\rho^{\text{aniso}}$	$v_0\rho^{\text{iso}}$	$\Delta\rho/\rho^{\text{aniso}}$	$x$	$v_0\rho^{\text{aniso}}$	$v_0\rho^{\text{iso}}$	$\Delta\rho/\rho^{\text{aniso}}$
9.1	0.572	1.43	0.784	0.783	0.002	1.93	0.869	0.867	0.002
9.3	0.627	2.15	0.627	0.620	0.012	3.56	0.643	0.631	0.019
9.5	0.666	2.98	0.527	0.514	0.026	5.46	0.490	0.469	0.043
9.7	0.697	4.21	0.437	0.418	0.044	8.18	0.367	0.341	0.071
9.9	0.722	6.08	0.354	0.330	0.067	12.14	0.270	0.243	0.10
10.2	0.753	12.96	0.216	0.192	0.11	25.12	0.146	0.126	0.14

for nematic substances, namely, several tenths of one per cent.<sup>31-34</sup> At length-to-breadth ratios typical of the more common nematogenic molecules ( $x=4-10$ , perhaps), the hard-rod relative-density discontinuities are roughly an order of magnitude too large.

The  $x$  dependence of the degree of order  $S$  in the anisotropic phase at the transition is also displayed in Fig. 1.  $S$  is defined by

$$S = \langle P_2(\cos\theta) \rangle = \frac{1}{2} \langle 3 \cos^2\theta - 1 \rangle, \quad (58)$$

where  $\theta$  is the angle between the long axis of a particle (molecule, rod, etc.) and the preferred direction, and the angular brackets denotes averaging over all particles and over time. It is an experimentally measurable order parameter<sup>35</sup> which vanishes in isotropic phases, is positive in nematic mesophases, and would be unity in a perfectly ordered system. At temperatures just below the nematic  $\rightarrow$  isotropic phase transition, typical values of  $S$  lie in the range 0.3-0.5.<sup>35</sup> It is clear, therefore, that our hard spherocylinder "mesophases" are considerably more ordered near the transition than are real nematic meso-

phases. When  $x=1$ , the only solution to (51) is  $\bar{f}=1/4\pi$ . In this limit, therefore,  $S=0$  at all densities and the transition to an ordered phase disappears. From the figure, however, it is clear that the degree of order in the anisotropic phase at the transition approaches a finite limiting value as  $x \rightarrow 1$ .

Table I compares the transition parameters  $x$ ,  $v_0\rho^{\text{aniso}}$ , and  $v_0\rho^{\text{iso}}$  obtained from our consistent scaled particle theory (CSPT) for six values of  $\lambda^*$  with the corresponding quantities obtained from Lasher's truncated scaled particle theory (TSPT).<sup>36</sup> The two approaches are in agreement for very long rods (both reduce to Onsager's theory in the limit  $l \rightarrow \infty$ ,  $a \rightarrow 0$ ,  $al^2$  finite) and their qualitative predictions are very similar for shorter rods. Clearly, however, there are appreciable quantitative differences at typical nematic length-to-breadth ratios. CSPT is probably more trustworthy for short rods since it reduces to the RFL theory of hard spheres when  $x=1$ .

Finally, the behavior of the isothermal compressibility  $\kappa$  near the transition was also determined, where

$$\frac{kT_\kappa}{v_0} = -\frac{1}{V} \left( \frac{\partial V}{\partial \rho} \right)_T = \left( \rho \frac{\partial \Pi}{\partial \rho} \right)^{-1} = \frac{(1 - v_0\rho)^4}{v_0\rho \{ 1 + 4v_0\rho + (3 + 2q - q^2)v_0^2\rho^2 + 4rv_0\rho [ 1 + 2(1 + \frac{3}{4}q)v_0\rho ] \langle \langle \sin\gamma(\Omega, \Omega') \rangle \rangle \}}, \quad (59)$$

and the compressibility was chosen as a typical representative of the "thermodynamic susceptibilities," i.e., the second derivatives of the free energy. As is well known, these quantities exhibit striking pretransition effects, similar to those occurring near so-called second-order phase transitions, on both sides of the nematic  $\rightarrow$  isotropic transition.<sup>37</sup> No such pretransition phenomena occur in our hard spherocylinder fluid, however, as can be seen from Fig. 2. This is in agreement with Alben<sup>11</sup> (see Ref. 3), who found no precursor effects in the anisotropic phase of the hard-rod fluid, but did observe such phenomena when a van der Waal's attractive term was added to the hard-rod potential energy.

### C. XYZ model

As a special case of the discrete orientations problem, let us consider a fluid of hard spherocylinders permitted to point in only three mutually perpendicular directions. In the limit  $l \rightarrow \infty$ ,  $a \rightarrow 0$ ,  $al^2$  finite, this system is rather well understood as a result of extensive cluster-expansion calculations.<sup>6,7</sup> It is also of interest because it is similar to a system of hard rods on a simple cubic lattice and can be used to probe differences between lattice and continuum models. For the sake of simplicity, let the three allowed directions 1, 2, and 3 correspond to the  $x$ -,  $y$ -, and  $z$ -axis directions, respectively, of a Cartesian coordinate



system and let us, therefore, "christen" this the XYZ model.

If we single out the  $z$  direction by some device such as the application of an infinitesimal field

$$\Pi(\rho, \bar{s}) = \frac{v_0 \rho \{1 + [1 + 8r\bar{s}(1 - \frac{3}{2}\bar{s})]v_0 \rho + \frac{2}{3}[1 + q - \frac{1}{2}q^2 + 12r(1+q)\bar{s}(1 - \frac{3}{2}\bar{s})]v_0^2 \rho^2\}}{(1 - v_0 \rho)^3}, \quad (60)$$

$$N^{-1}\beta A = -\frac{S_c}{Nk} + \ln \Lambda = -N^{-1} \ln Q = \ln \left( \frac{3\rho \Lambda \bar{s}^{2\bar{s}} (1 - 2\bar{s})^{(1-2\bar{s})}}{1 - v_0 \rho} \right) - \frac{\{1 - [5 + 8r\bar{s}(1 - \frac{3}{2}\bar{s})]v_0 \rho + [8 - q + \frac{1}{2}q^2 - 12rq\bar{s}(1 - \frac{3}{2}\bar{s})]\frac{1}{3}v_0^2 \rho^2\}}{(1 - v_0 \rho)^2} = -t(\bar{s}), \quad (61)$$

and

$$N^{-1}\beta G = \beta \mu = \ln \left( \frac{3\rho \Lambda \bar{s}^{2\bar{s}} (1 - 2\bar{s})^{(1-2\bar{s})}}{(1 - v_0 \rho)} \right) + \frac{6v_0 \rho [1 + \frac{2}{3}r\bar{s}(1 - \frac{3}{2}\bar{s})]}{(1 - v_0 \rho)} + \frac{4v_0^2 \rho^2 (1 + \frac{1}{2}q) [1 - \frac{1}{4}q + 6r\bar{s}(1 - \frac{3}{2}\bar{s})]}{(1 - v_0 \rho)^2} + \Pi(\rho, \bar{s}), \quad (62)$$

where

$$\bar{s}_1 = \bar{s}_2 = \bar{s}, \quad \bar{s}_3 = 1 - 2\bar{s}. \quad (63)$$

Maximizing  $t$  with respect to  $s$  yields

$$\ln \left( \frac{\bar{s}}{1 - 2\bar{s}} \right) + \frac{4rv_0 \rho (1 + \frac{1}{2}qv_0 \rho)(1 - 3\bar{s})}{(1 - v_0 \rho)^2} = 0. \quad (64)$$

At low densities, the only solution to (64) is  $\bar{s} = \frac{1}{3}$  (the isotropic solution for this model), but for

and assume that the most probable distribution  $(\bar{s}_1, \bar{s}_2, \bar{s}_3)$  is axially symmetric, (35) and (42)–(45) become

densities greater than a "critical" value  $v_0 \rho_0(x)$ , there are two anisotropic solutions as well, as is illustrated in Fig. 3. When  $v_0 \rho < v_0 \rho_0^* \approx v_0 \rho_c$ ,<sup>38</sup> the isotropic solution is thermodynamically stable, while when  $v_0 \rho > v_0 \rho^*$ , the more-ordered anisotropic solution (i.e., the lower anisotropic branch in Fig. 3) minimizes the free energy. (The less-ordered anisotropic solution can be disregarded since it always represents a local maximum in the free energy.) The "critical" disorder parameter

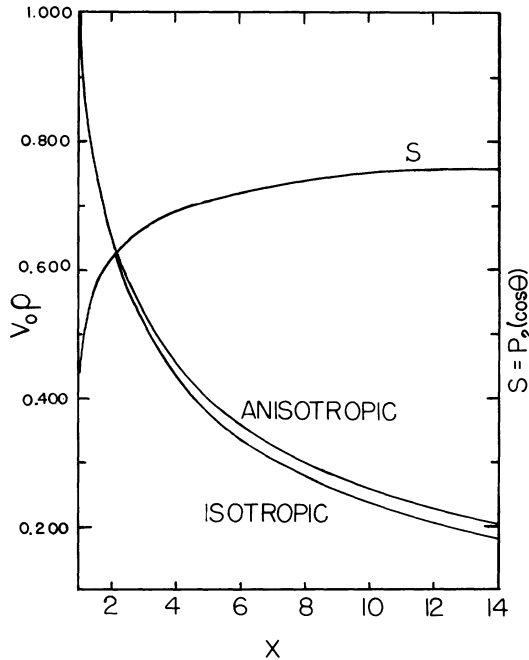


FIG. 1. Densities and degree of order at the anisotropic-isotropic phase transition as a function of the length-to-breadth ratio  $x$  of spherocylindrical rods with a continuous range of allowed orientations.

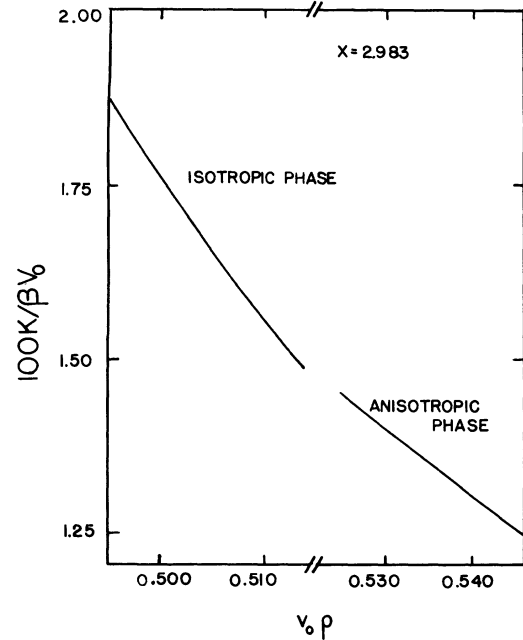


FIG. 2. Dimensionless isothermal compressibility  $\kappa/\beta v_0$  at densities near the anisotropic-isotropic phase transition for  $x = 2.983$ . The coexisting densities at the transition are  $v_0 \rho^{\text{aniso}} = 0.5271$  and  $v_0 \rho^{\text{iso}} = 0.5136$ .

$s_c$  is a constant approximately equal to 0.2076 and the "critical" density can be obtained for any  $x$  by substituting  $s_c$  and  $x$  into (64) and solving the resulting quadratic equation for  $v_0 \rho_c(x)$ .

The anisotropic-isotropic phase transition is located by simultaneously solving (64) (for the anisotropic phase), (54), and (55), with the pressures and chemical potentials obtained from (60) and (62). The solutions were determined numerically and the results are displayed in Fig. 4 and Table II. The behavior of the transition parameters is qualitatively similar to that shown in Fig. 1 for spherocylinders allowed to adopt all possible orientations, but quite different from the behavior of hard rods on a simple cubic lattice in that the lattice system undergoes no transition to an anisotropic state when  $x$  is less than approximately 3.65.<sup>11</sup> For the XYZ model,

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

$$= \frac{1}{2} \{ (1 - 2\bar{s})(2) + 2\bar{s}(-1) \} = 1 - 3\bar{s}, \quad (65)$$

and the system is considerably more ordered near the transition than is the hard spherocylinder fluid with a continuous range of allowed orientations. This is not surprising since most of the orientational disorder in the latter fluid is due to small angle deviations from the preferred direction and such deviations are not permitted in the XYZ model.

Table II compares consistent scaled particle theory (CSPT) with the simpler scaled particle theory (SPT) of Cotter and Martire<sup>12(c)</sup> (SPT). The latter is thermodynamically consistent for spherocylinders free to adopt any of the three allowed orientations, but inconsistent for the mixture of

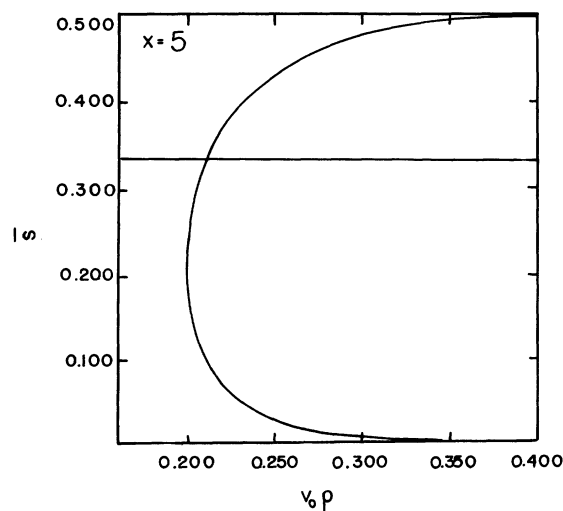


FIG. 3. Solutions  $\bar{s}$  to Eq. (64) as a function of density for  $x=5$ .

spherocylinders with fixed orientations in that

$$\left( \frac{\partial \mu_{\perp}}{\partial \rho_{\perp}} \right)_{\rho_{\parallel}} \neq \left( \frac{\partial \mu_{\parallel}}{\partial \rho_{\parallel}} \right)_{\rho_{\perp}}, \quad (66)$$

where  $\parallel$  denotes the preferred direction,  $\perp$  denotes the two equivalent perpendicular directions, and

$$\rho_{\parallel} = \rho_3 = (1 - 2s)\rho, \quad (67)$$

$$\rho_{\perp} = \rho_1 + \rho_2 = 2s\rho.$$

As can be seen from Table II, this underlying inconsistency, although very disturbing esthetically, is of rather little consequence numerically. The transition densities computed from CSPT are roughly (2-7)% larger than those computed from SPT, but the qualitative predictions of the two theories are the same.

## V. DISCUSSION AND CONCLUSIONS

The principle aim of this work was to vindicate the scaled particle theory of anisotropic fluids, i.e., to show that a straightforward application of the scaled particle approach need not lead to an inconsistent thermodynamics for the mixture of hard rods with fixed orientations. This goal has been attained: thermodynamic consistency has been achieved wholly within the procedures, framework, and spirit of simple scaled particle theory.

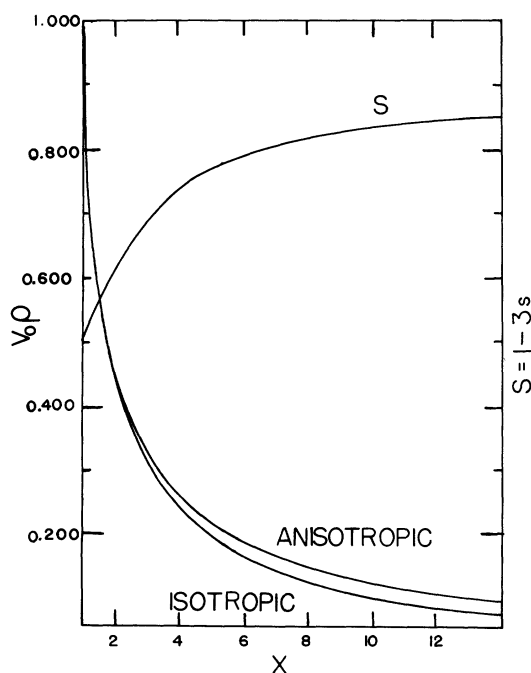


FIG. 4. Densities and degree of order at the anisotropic-isotropic phase transition as a function of the length-to-breadth ratio  $x$  of the spherocylindrical rods for the XYZ model.

TABLE II. Transition densities and degree of order for the XYZ model. Comparison of consistent scaled-particle theory (CSPT) with the scaled particle theory of Cotter and Martire (SPT).

$x$	$S$	CSPT		$S$	SPT	
		$v_0\rho^{\text{aniso}}$	$v_0\rho^{\text{iso}}$		$v_0\rho^{\text{aniso}}$	$v_0\rho^{\text{iso}}$
2	0.589	0.473	0.465	0.589	0.505	0.499
3	0.682	0.332	0.316	0.658	0.351	0.338
4	0.745	0.260	0.240	0.706	0.273	0.255
5	0.769	0.216	0.193	0.739	0.224	0.204
6	0.790	0.185	0.162	0.763	0.191	0.170
7	0.804	0.163	0.140	0.781	0.167	0.146
8	0.817	0.145	0.122	0.796	0.149	0.127
9	0.827	0.132	0.109	0.808	0.135	0.113
10	0.834	0.120	0.098	0.814	0.123	0.102

Hopefully, the scaled particle approach, which has proven quite useful for considering simple isotropic fluids,<sup>17</sup> may be of some help in investigating anisotropic fluids as well.

The numerical predictions of consistent scaled particle theory (CSPT) are qualitatively similar to those of several other approximate theories of the hard-rod fluid.<sup>11-13</sup> This is not too surprising since these approaches are all of the molecular-field variety in that short-range order in molecular positions and orientations is not considered. As was pointed out by Alben,<sup>11</sup> this neglect of short-range order may lead to serious underestimates of the configurational entropy, particularly when the rods are long and the system orientationally disordered, and this could mean that the theoretical predictions are at least partially artifacts of the mean-field approximation. To determine whether this is the case, computer-generated "experimental results" for the hard-rod fluid are needed but, unfortunately, are not available. Despite this difficulty, mean-field treatments seem at present to be the only mathematically tractable statistical-mechanical approaches to continuum (as opposed to lattice) models of rodlike molecules. Whatever the distortions produced by the neglect of fluctuations, such computations should still be useful for comparing systems with various sorts of intermolecular potentials. Among the various molecular-field approaches suggested to date, CSPT seems particularly promising because (i) when  $x$  is very large, it reduces (like its competitors) to the Onsager theory,<sup>4</sup> which should be satisfactory for very long rods<sup>14</sup>; (ii) at the opposite extreme of length-to-breadth ratios ( $x \rightarrow 1$ ), it reduces to the

rather successful RFL scaled particle theory of hard spheres.<sup>16</sup> In a subsequent publication, CSPT will be used to study rodlike molecules with hard cores and superimposed attractive interactions, in an effort to understand the roles of intermolecular attractions and repulsions in determining nematic stabilities.

Finally, the derivation of Sec. III makes the meaning of Lasher's truncation somewhat clearer. His truncated expression for the quantity  $\ln p_i^0$  is, in our notation,

$$\ln p_i^0 = \ln(1 - v_0\rho) - \frac{3v_0\rho\Gamma'(\underline{s})}{(1 - v_0\rho)} \zeta(1 + \zeta) - v_0\beta p \zeta^3, \quad (68)$$

where  $\zeta$  is Lasher's scaling parameter (previously called  $s$ ) and

$$\Gamma'(\underline{s}) = 1 + \frac{2}{3}r \sum_j s_j |\sin\gamma_{ij}|. \quad (69)$$

This means that the coefficient  $C'_i$  in Eq. (20) has been taken to be equal to  $-3v_0\rho\Gamma'(\underline{s})/(1 - v_0\rho)$ , which implies that the quantity  $(\partial^2 F^{2(i)}/\partial\zeta^2)_{\zeta=0}$  [see (14) and (15) for the definition of  $F_2^{(i)}$ ] is given by

$$\left(\frac{\partial^2 F^{2(i)}}{\partial\zeta^2}\right)_{\zeta=0} = \frac{9v_0^2\rho^2[\Gamma'(\underline{s})]^2}{(1 - v_0\rho)}, \quad (70)$$

and the discontinuity in  $\partial^2 \ln p_i^0/\partial\zeta^2$  by

$$\left(\frac{\partial^2 \ln p_i^0}{\partial\zeta^2}\right)_{\zeta \rightarrow 0^+} - \left(\frac{\partial^2 \ln p_i^0}{\partial\zeta^2}\right)_{\zeta \rightarrow 0^-} = \frac{9v_0^2\rho^2[\Gamma'(\underline{s})]^2}{(1 - v_0\rho)^2}. \quad (71)$$

Although it is known that  $\partial^2 F^{2(i)}/\partial\zeta^2$  does not vanish at  $\zeta=0$ , there is no particular reason to believe it is of the form (70). From the standpoint of the internal consistency of scaled particle theory, it might perhaps have been better to set  $C'_i$  equal to zero, thus eliminating any term proportional to  $\zeta^2$  from the expansion of  $\ln p_i^0$ , and yielding a truncated theory both thermodynamically and internally consistent, although having less exact information "built in" than does CSPT.

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<sup>1</sup>A good introduction to the subject of liquid crystals can be had from G. W. Gray, *Molecular Structure and the*

*Properties of Liquid Crystals* (Academic, London, England 1972) and A. Saupe, *Angew. Chem. (Int. Ed. Engl.)* **7**, 97 (1968).

- <sup>2</sup>The preferred direction is generally not uniform over an entire bulk nematic sample, but can be made so by applying a modest aligning field, either magnetic or electric. In the absence of such a field, the sample could be termed "poly-liquid-crystalline".
- <sup>3</sup>One treatment of the hard-rod fluid that fits into none of the three given categories is the free-volume theory of Alben (Sec. 4 of Ref. 11), in which the configurational entropy is calculated by means of an ingenious extension of the Flory-DiMarzio counting scheme for lattice configurations.
- <sup>4</sup>L. Onsager, *Ann. N. Y. Acad. Sci.* **51**, 627 (1949).
- <sup>5</sup>A. Isihara, *J. Chem. Phys.* **19**, 1142 (1951).
- <sup>6</sup>R. Zwanzig, *J. Chem. Phys.* **39**, 1714 (1963).
- <sup>7</sup>L. Runnels and C. Colvin, *J. Chem. Phys.* **53**, 4219 (1970).
- <sup>8</sup>P. J. Flory, *Proc. R. Soc. Lond.* **A234**, 73 (1956).
- <sup>9</sup>E. A. DiMarzio, *J. Chem. Phys.* **35**, 658 (1961).
- <sup>10</sup>M. A. Cotter and D. E. Martire, *Mol. Cryst. Liq. Cryst.* **7**, 295 (1969).
- <sup>11</sup>R. Alben, *Mol. Cryst. Liq. Cryst.* **13**, 193 (1971).
- <sup>12</sup>M. A. Cotter and D. E. Martire, *J. Chem. Phys.* (a) **52**, 1902; (b) **52**, 1909; (c) **53**, 4500 (1970).
- <sup>13</sup>G. Lasher, *J. Chem. Phys.* **53**, 4141 (1970).
- <sup>14</sup>J. P. Straley, *Proceedings of the Fourth International Liquid Crystal Conference* (to be published).
- <sup>15</sup>M. A. Cotter (to be published).
- <sup>16</sup>H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).
- <sup>17</sup>For a list of references to the various applications of scaled particle theory see D. M. Tully-Smith and H. Reiss, *J. Chem. Phys.* **53**, 4015 (1970).
- <sup>18</sup>Both Monte Carlo and molecular-dynamics computations for hard spheres are summarized in W. W. Wood, *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. L. Rowlinson, and G. S. Rushbrooke (Interscience, New York, 1968), Chap. 5.
- <sup>19</sup>The spherocylindrical shape is so popular because the mutual exclusion volume of two hard spherocylinders has a particularly simple functional dependence on their relative orientations. [See Eq. (16) of the text.]
- <sup>20</sup>Equation (14) is derived in Ref. 13 for the special case  $n = 3$ . The generalization of that derivation is trivial.
- <sup>21</sup>Equation (19), or its successor, Eq. (24), cannot be exact since  $\ln p_i^0$  is not an analytic function of  $\alpha$  and  $\lambda$  for all  $\alpha \geq 0$ ,  $\lambda \geq 0$ . Neither  $(\partial^2 F_2^{(i)} / \partial \lambda^2)_{\alpha=0, \lambda=0}$  nor  $(\partial^2 F_2^{(i)} / \partial \alpha^3)_{\alpha=0, \lambda=0}$  vanishes and, therefore  $(\partial^2 \ln p_i^0 / \partial \lambda^2)$  and  $(\partial^3 \ln p_i^0 / \partial \alpha^3)$  are discontinuous at  $\alpha = 0$ ,  $\lambda = 0$ . Moreover, progressively weaker nonanalyticities should occur at those points ( $\alpha > 0, \lambda > 0$ ) at which successive terms (involving  $g^{(3)}$ ,  $g^{(4)}$ , etc.) must first be added to the Mayer-Montroll expansion (14).
- <sup>22</sup>M. A. Cotter, Doctoral dissertation (Georgetown University, 1969) (Appendix III).
- <sup>23</sup>M. A. Cotter (unpublished results).
- <sup>24</sup>To obtain the coefficient  $C_i^j$  in (20),  $(\partial^2 \ln p_i^0 / \partial s^2)_{s=0}$  is needed. Unfortunately,  $\partial^2 \ln p_i^0 / \partial s^2$  is discontinuous at  $s = 0$ , but the magnitude of the discontinuity cannot be determined, that is,  $F_2^{(i)}(s, \rho)$  cannot be evaluated since no expression for  $g^{(2)}(\vec{r}_1, \vec{r}_2, j_1, j_2)$  is available, but it can be shown (Refs. 22, 23) that  $\partial^2 F_2^{(i)} / \partial s^2$  does not vanish at  $s = 0$ . In order to use (20) (with or without additional terms), one has to ignore the discontinuity. No such problem occurs with Eq. (19) [or (24)] because all the required partial derivatives of  $F_2^{(i)}$  vanish at  $\alpha = 0$ ,  $\lambda = 0$ . We have, therefore, used the two scaling parameters  $\alpha$  and  $\lambda$  to avoid making the additional approximation required by the use of only one such parameter.
- <sup>25</sup>F. H. Stillinger and M. A. Cotter, *J. Chem. Phys.* **55**, 3449 (1971).
- <sup>26</sup>One can, of course, write down more complicated functional forms than (24). More terms could be added and/or  $Q(\rho, s)$  could be replaced by  $Q_i(\rho, s)$ . However, the consistency requirements (1) and (22)—the only available exact relations—are not sufficient to determine the additional coefficients.
- <sup>27</sup>Equations (46)–(48) were obtained from (35); (42)–(45) in the same manner as (9) was obtained from (6), namely, by dividing the unit sphere into  $n = 4\pi/\Delta\Omega$  equal parts and letting  $\Delta\Omega \rightarrow 0$ .
- <sup>28</sup>Actually, Ref. 14 gives  $\langle\langle \sin \gamma \rangle\rangle$  and  $\langle\ln(4\pi\bar{r})\rangle$  only to three decimal places and this is not sufficient to determine the coexisting densities to three significant figures. However, Lasher (private communication) has very kindly supplied more precise values of both  $\langle\langle \sin \gamma \rangle\rangle$  and  $\langle\ln(4\pi\bar{r})\rangle$  for the twelve values of  $\lambda^*$  in his Tables I and II, and for a number of other values as well.
- <sup>29</sup>What we actually compute is not  $\beta\mu$  but  $\beta\mu + \ln(v_0/\Lambda)$ , the quantity Lasher calls  $\beta(\mu - \mu_0)$ .
- <sup>30</sup>G. N. Lance, *Numerical Methods for High Speed Computers* (Hiffe, London, England, 1960), pp. 134–138.
- <sup>31</sup>W. Maier and A. Saupe, *Z. Naturforsch. A* **15**, 287 (1960).
- <sup>32</sup>W. A. Hoyer and A. W. Nolle, *J. Chem. Phys.* **24**, 803 (1956).
- <sup>33</sup>A. Torgalkar, R. S. Porter, E. M. Barrall, and J. F. Johnson, *J. Chem. Phys.* **48**, 3897 (1968).
- <sup>34</sup>R. S. Porter and J. F. Johnson, *J. Appl. Phys.* **34**, 51 (1963).
- <sup>35</sup>The degree of order is most commonly measured by means of proton magnetic resonance, since uniformly oriented magnetic samples can be produced by modest magnetic fields and the direct proton-proton couplings therein are proportional to  $S$ . Saupe (Ref. 1) has summarized and discussed experimentally determined order parameters for common nematic liquids.
- <sup>36</sup>Use of the abbreviations CSPT and TSPT might be somewhat misleading. Let us again emphasize, therefore, that both theories are thermodynamically consistent. The difference between them lies in the way consistency is achieved.
- <sup>37</sup>For a list of the numerous references to experimental observations of such pretransition phenomena, see Ref. 11.
- <sup>38</sup>The behavior of the Helmholtz free energy in the vicinity of  $\rho_c$  is rather complicated and we must distinguish among three densities  $\rho_c$ ,  $\rho^*$ , and  $\rho^+$ , where  $\rho_c < \rho^* < \rho^+$ . When  $\rho$  is less than  $\rho_c$  only an isotropic distribution is possible. For  $\rho < \rho^+$ , the isotropic distribution represents a local minimum in the free energy; for  $\rho > \rho^+$  it represents a local maximum, while the more ordered anisotropic distribution gives a local minimum for all  $\rho > \rho_c$ . The absolute minimum in the free energy is obtained with the isotropic distribution when  $\rho < \rho^*$ , but with the anisotropic distribution when  $\rho > \rho^*$ .