Bifurcation in Onsager's model of the isotropic-nematic transition

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(Received 16 December 1977)

In this paper Onsager's theory of the orientational order in a three-dimensional system of hard rods is reanalyzed as a nonlinear eigenvalue problem. Bifurcation is found and the equation of state is calculated from the orientational distribution function for a nematic phase. We also investigate the corresponding two-dimensional system of hard lines. The existence and order of a phase transition are shown to depend on both the direction of bifurcation and on properties of the global solutions. The analysis can be adapted to other nonlinear equations obtained in theories of liquid crystals.

I. INTRODUCTION

At sufficiently low densities, systems of highly asymmetrical molecules behave ideally and the distribution of the molecular orientations is uniform or isotropic. At higher densities, on the other hand, the molecules begin to strongly interfere with one another and the system undergoes a phase transition to an ordered or anisotropic state.

There is a class of theories of the isotropic-nematic transition having a common aspect in terms of the orientational distribution function (ODF), $f(\vec{a})$, which gives the probability that a molecule is oriented about the direction $\vec{a}$. This is the fact that the ODF satisfies a nonlinear integral equation of the type

$$\ln[4\pi f(\vec{a})] = C + \lambda \int F(\vec{a},\vec{a}') f(\vec{a}')\, d\Omega' . \tag{1.1}$$

The unit vectors $\vec{a}$ and $\vec{a}'$ are taken to lie in small solid angles $d\Omega$ and $d\Omega'$ and C is a constant determined by the normalization,

$$\int f(\vec{a})\, d\Omega = 1 . \tag{1.2}$$

Different choices for the parameter λ and kernel $F(\vec{a},\vec{a}')$ lead to equations found in the hard-rod theories of Onsager[1] and others,[2] as well as in several recent treatments[3] which include orientation-dependent attractions via mean-field theory.

In the paper we view the equation for the ODF as a nonlinear eigenvalue problem and use bifurcation theory to investigate the existence of multiple solutions of (1.1). We concentrate on Onsager's model although the analysis applies directly to the above theories and, more generally, to any problem in which $F(\vec{a},\vec{a}')$ depends only on the angle between $\vec{a}$ and $\vec{a}'$. The purpose of this investigation is to give methods which show the connection between analytic features of (1.1), namely, the direction of bifurcation and properties of the global solutions, and the possible existence of a phase transition. Although neither the model nor the underlying equation are new, the methods and emphasis are new. Furthermore, the results obtained for the ODF are more accurate than those found previously by minimization of a free energy functional.[1,2]

The remainder of the article proceeds as follows. The analytical formulation and bifurcation analysis are given in Sec. II. In Sec. III, the global solutions are obtained. Thermodynamic properties and the location of a first-order phase transition are in Sec. IV. The summary is in Sec. V where we also present the corresponding results for a two-dimensional system of hard lines. It is shown that the direction of bifurcation is opposite to that found in three dimensions and this difference precludes the existence of a first-order transition.

II. ANALYTICAL FORMULATION

A. Preliminaries

We note that $f(\vec{a}) = 1/4\pi$, corresponding to a uniform distribution of orientations, satisfies (1.1) for all values of the parameter λ. For convenience the function $h(\vec{a})$ is introduced,

$$h(\vec{a}) = 4\pi f(\vec{a}) - 1 , \tag{2.1}$$

so that $h(\vec{a}) = 0$ corresponds to the isotropic distribution. Exponentiation of (1.1) and the use of (1.2) yields

$$h(\vec{a}) = -1 + \frac{\exp(\lambda \int F(\vec{a},\vec{a}')h(\vec{a}')\, d\Omega'/4\pi)}{(1/4\pi)\int \exp(\lambda \int F(\vec{a},\vec{a}')h(\vec{a}')\, d\Omega'/4\pi)\, d\Omega} \tag{2.2}$$

where the normalization

$$\frac{1}{4\pi}\int h(\vec{a})\, d\Omega = 0 \tag{2.3}$$

is incorporated into the equation.

We focus on the system considered by Onsager, that is, a fluid of long rigid cylinders of length l and diameter d at a density ρ and temperature T. For $l \gg d$, the parameter λ and kernel F are given by

$$\lambda = \rho B_2 = \tfrac{1}{4}\rho\pi l^2 d, \tag{2.4}$$

$$(1/4\pi)F(\vec{a},\vec{a}') = (-2/\pi^2)[1-(\vec{a}\cdot\vec{a}')^2]^{1/2}. \tag{2.5}$$

Owing to the rigid-body interactions, the ODF depends only on the density. The quantity B_2 is the second virial coefficient (averaged over the relative orientations of two cylinders) and throughout this paper we choose units such that $B_2 = 1$. Therefore, in all that follows, the symbol ρ denotes the dimensionless number density.[4] The kernel $F(\vec{a},\vec{a}')$ indicates how the volume excluded to two cylinders with fixed orientations, $\vec{a}$ and $\vec{a}'$, depends on the angle between them. Since the contribution of the third virial coefficient is negligible when $l \gg d$, (2.4) and (2.5) should represent a reasonable approximation.[1]

We seek nontrivial solutions $h(\vec{a})$ which correspond to cylinders preferentially oriented about a single special direction, $\vec{a}_0$. Such anisotropic distributions will necessarily have cylindrical and mirror symmetry about the direction $\vec{a}_0$; this requires

$$h(\vec{a}) = h(\vec{a}\cdot\vec{a}_0) = h(-\vec{a}\cdot\vec{a}_0) = h(-\vec{a}). \tag{2.6}$$

To express the integral on the right-hand side of (2.2) in terms of known angles, a rotation of the coordinate axes is performed so that $\vec{a}$ lies along the z axis and $\vec{a}_0$ lies in the xz plane in the new coordinate system. We change to the polar coordinates (θ',ϕ'), and denote the angle between $\vec{a}_0$ and $\vec{a}$ by θ. In order to write (2.2) in a compact form, we introduce some notation. With the inner product

$$\langle g_1, g_2\rangle = \frac{1}{4\pi}\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi\, g_1(\cos\theta) \times g_2(\cos\theta), \tag{2.7}$$

let H be the Hilbert space of functions g satisfying (2.3) and (2.6). In addition, an operator K is defined by

$$\frac{2}{\pi^2}\int_0^{\pi} d\theta' \sin^2\theta' \times \int_0^{2\pi} d\phi'\, h(\sin\theta\sin\theta'\cos\phi' + \cos\theta\cos\theta') = Kh(\cos\theta). \tag{2.8}$$

Equation (2.2) may now be written:

$$h(\cos\theta) = -1 + \frac{\exp[-\rho Kh(\cos\theta)]}{\langle 1, \exp[-\rho Kh]\rangle}. \tag{2.9}$$

This is the working form of the basic equation for the ODF. The analytical properties of (2.9) are similar to those for an equation derived for a theory of the fluid-solid transition in which bifurcation was found.[5] The analytical similarities are exploited in this paper to investigate the existence of anisotropic solutions of (2.9).

B. Bifurcation analysis

Since the operator K defined by (2.8) is invariant to all rotations of the frame of reference, Legendre polynomials must be its eigenfunctions. Symmetry further requires that they be of even order. To evaluate $KP_{2n}(\cos\theta)$ the addition formula for Legendre polynomials is used:

$$P_n(\sin\theta\sin\theta'\cos\phi' + \cos\theta\cos\theta') = P_n(\cos\theta)P_n(\cos\theta') + 2\sum_{m=1}^{n}\frac{(n-m)!}{(n+m)!}P_n^m(\cos\theta) \times P_n^m(\cos\theta')\cos m\phi'. \tag{2.10}$$

Upon substitution into (2.8), the complicated sum involving associated Legendre functions of the first kind vanishes in the integration over ϕ' yielding

$$KP_{2n}(\cos\theta) = \left(\frac{4}{\pi}\int_0^{\pi} d\theta' \sin^2\theta' P_{2n}(\cos\theta')\right) \times P_{2n}(\cos\theta) \equiv \lambda_{2n}P_{2n}(\cos\theta), \tag{2.11}$$

$$\lambda_{2n} = -4^{-2n+1}\frac{1}{n}\binom{2n-2}{n-1}\frac{1}{n+1}\binom{2n}{n} \quad (n \geq 1). \tag{2.12}$$

Each $P_{2n}(\cos\theta)$, $n \geq 1$, satisfies the conditions (2.3) and (2.6), so that the Legendre polynomials of even order constitute a complete set of orthogonal functions in the Hilbert space H.

The operator K is also compact, self-adjoint, and maps H into itself. Therefore, we can apply the same analytical techniques used in the theory of the fluid-solid transition[5] and we find that the existence of bifurcation in (2.9) depends on whether the associated linear equation,

$$w(\cos\theta) = -\rho K w(\cos\theta), \tag{2.13}$$

has eigenvalues. We seek solutions which satisfy the boundary conditions

$$w(1) = w(-1) = \text{maximum}, \quad w(\cos\theta) \text{ has no other maxima}. \tag{2.14}$$

The first part of (2.14) indicates that the ODF is largest in the special direction $\vec{a}_0$ and the second

part that there are no special directions other than $\vec{a}_0$. The bifurcation density is determined by

$$\rho^* = -w(\cos\theta)/Kw(\cos\theta). \tag{2.15}$$

Every eigenfunction of the K operator satisfies (2.13) but only $P_2(\cos\theta)$ has the behavior required by (2.14). From (2.12) with $n=1$,

$$KP_2(\cos\theta) = -\tfrac{1}{4}P_2(\cos\theta). \tag{2.16}$$

Since the eigenvalue $-\frac{1}{4}$ is simple we find bifurcation at the density determined by

$$\rho^* = 4. \tag{2.17}$$

Therefore anisotropic solutions to (2.9) possessing the required properties exist. This result and formulas from this section will be used next to construct global solutions.

III. CALCULATION OF THE ORIENTATIONAL DISTRIBUTION FUNCTION

A. Branching diagram

As a measure of the size of a solution to (2.9) at a given density, we calculate its norm,

$$\|h\| = \langle h, h\rangle^{1/2}, \tag{3.1}$$

and plot $\|h\|$ vs ρ. We obtain, by methods to be discussed in this section, the results shown in Fig. 1. The isotropic distribution is a solution for all values of ρ and is represented in Fig. 1 by the horizontal line $\|h\| = 0$. We observe that the branch of anisotropic solutions joins continuously to the isotropic solution at the bifurcation point. This curve is such that it branches to the left from ρ^*, bends back to the right at ρ_b and increases monotonically thereafter. As a consequence of the branching to the left, two anisotropic solutions exist between ρ_b and ρ^*. These aspects of the branching diagram will be reflected in the equation of state of the anisotropic phase and, in fact, make possible the existence of a first-order transition.

Two different techniques were used to calculate the ODF. In the region between ρ_b and ρ^* the solutions of smaller norm, indicated by closed circles in Fig. 1, were obtained by a parametrization expansion about the bifurcation point. The solutions on the upper portion of the branch were calculated by an iterative procedure and are denoted by open circles in Fig. 1. Our computations indicate that the methods do not overlap,[6] but that it is possible to find two solutions quite close to one another in the neighborhood of ρ_b.

B. Parametrization expansion

Equation (2.9) may be parametrized in terms of a quantity α, which is a measure of the distance from bifurcation, by writing

$$\ln[h(\cos\theta,\alpha)+1] - \langle 1, \ln[h(\alpha)+1]\rangle = -\rho(\alpha)Kh(\cos\theta,\alpha), \tag{3.2}$$

where the normalization factor has been written in a form more convenient for the present analysis. We expand h and ρ in Taylor series about $\alpha = 0$:

$$h(\cos\theta,\alpha) \equiv h(\alpha) = h'\alpha + h''\frac{\alpha^2}{2!} + \frac{h'''\alpha^3}{3!} + \cdots \tag{3.3}$$

and

$$\rho(\alpha) = \rho^* + \rho'\alpha + \rho''\alpha^2/2! + \rho'''\alpha^3/3! + \cdots, \tag{3.4}$$

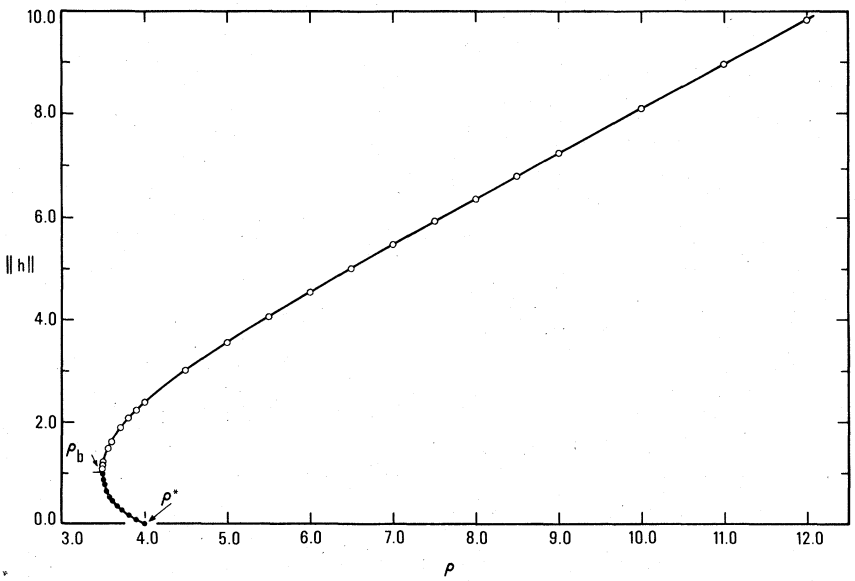

FIG. 1. Plot of $\|h\|$ vs ρ. The bifurcation point is indicated by ρ^* and the bending point by ρ_b. The closed circles are from solutions to (2.9) obtained by parametrization, the open circles from solutions obtained by the iterative procedure.

so that $\alpha = 0$ corresponds to $h = 0$ and $\rho = \rho^*$. The primes denote derivatives with respect to α evaluated at $\alpha = 0$. Successive differentiation of (3.2) with respect to α followed by setting $\alpha = 0$ leads to a set of coupled inhomogeneous integral equations for the quantities h', h'', h''', ..., ρ', ρ'', ρ''', ...:

$$h' - \langle 1, h' \rangle = -\rho^* K h' , \tag{3.5a}$$

$$h'' - (h')^2 - \langle 1, h'' - (h')^2 \rangle = -\rho^* K h'' - 2\rho' K h' , \tag{3.5b}$$

$$h''' - 3h''h' + 2(h')^3 - \langle 1, h''' - 3h''h' + 2(h')^3 \rangle = -\rho K h''' - 3\rho' K h'' - 3\rho'' K h' . \tag{3.5c}$$

In solving the system (3.5), we make use of the fact that $\langle 1, h' \rangle = \langle 1, h'' \rangle = \langle 1, h''' \rangle = \cdots = 0$, and note that h' is the eigenfunction at bifurcation, $h' = P_2(\cos\theta)$. The quantity ρ' may then be determined by taking the inner product of (3.5b) with h', using self-adjointness, and requiring that $\langle h', h'' \rangle = 0$. Once ρ' has been determined, h'' may be found from (3.5b). Similarly, ρ'' may be obtained by taking the inner product of (3.5c) with h' and requiring $\langle h', h''' \rangle = 0$, after which h''' may be found. By proceeding in this way it is possible to determine any number of terms in (3.3) and (3.4). The parametrization was carried to forty orders and the densities, norms, and equation of state obtained were correct to no fewer than six decimal places except near ρ_b. As is evident from the solid and open circles in Fig. 1, the technique is only capable of yielding the solutions on the lower portion of the branch in the region between ρ_b and ρ^*.[6]

Before describing the iterative solution of (2.9), we mention that the direction of branching is determined by the sign of the first nonvanishing quantity, $\rho', \rho'', \ldots$. Since α must be positive near the bifurcation point so that $h(\alpha)$ defined by (3.3) has its maximum value in the direction $\hat{\mathbf{a}}_0$, we will have branching to the left if the first nonvanishing derivative is negative and branching to the right if it is positive. Taking the inner product of (3.5b) with $h' = P_2(\cos\theta)$ yields

$$\rho' = -\tfrac{4}{7} < 0 , \tag{3.6}$$

so solutions of very small norm exist only at densities lower than the bifurcation density ρ^*.

C. Iterative solution

We start by rewriting (2.9) in iterative form,

$$h^{(i+1)}(\cos\theta) = -1 + \frac{\exp[-\rho K h^{(i)}(\cos\theta)]}{\langle 1, \exp(-\rho K h^{(i)}) \rangle} , \tag{3.7}$$

where the superscript (i) denotes the ith iteration. We assume that $h^{(i)}$ is known in the form

$$h^{(i)}(\cos\theta) = \sum_{j=1} a_j^{(i)} P_{2j}(\cos\theta) , \tag{3.8}$$

and determine the coefficients $a_j^{(i+1)}$ in a similar expansion of $h^{(i+1)}$. This is easily accomplished because the Legendre polynomials diagonalize K and are mutually orthogonal. The $a_j^{(i+1)}$ are then calculated by evaluation of the usual inner products.

The initial guess at a density near ρ^* can be taken to be the eigenfunction at bifurcation $P_2(\cos\theta)$. The converged solution is then used as the initial guess for the next value of the density. In the density region between ρ_b and ρ^*, where two distinct anisotropic solutions exist, the iterative procedure always converges to the one of higher norm.[6] At values of the density below ρ_b, the procedure converges to zero. Convergence was assumed when the norm of the difference between the results of two successive iterations became less than at least 10^{-10}.

IV. THERMODYNAMIC PROPERTIES

A. Equation of state

The formula for the pressure is

$$\beta P = \beta P|_{\text{iso}} + \tfrac{1}{2}\rho^2 \langle h, Kh \rangle , \tag{4.1}$$

where the pressure for a system of randomly oriented cylinders $\beta P|_{\text{iso}}$ is given by

$$\beta P|_{\text{iso}} = \rho(1 + \rho) . \tag{4.2}$$

When the ODF has a Legendre representation as in (3.8), the pressure takes the relatively simple form

$$\beta P = \beta P|_{\text{iso}} + \tfrac{1}{2}\rho^2 \sum_{j=1} \frac{a_j^2 \lambda_{2j}}{4j+1} . \tag{4.3}$$

Since the eigenvalues λ_{2j} are all negative, it is evident that the pressure of the anisotropic phase is always less than the pressure of the isotropic phase at the same density and temperature. When the second term of (4.3) is nonzero, $\beta P|_{\text{aniso}}$ will be written to indicate that the anisotropic phase is under consideration. The results for the equation of state calculated from formula (4.3) are shown in Fig. 2, where βP is plotted versus $1/\rho$. Because two anisotropic solutions exist between ρ^* and ρ_b, the pressure is double valued in this interval. It is important to discern that there must be, and is, a region of thermodynamic instability in this range, i.e., where $\partial(\beta P)/\partial(1/\rho) > 0$. The point at which this derivative is identically zero is the limit of stability of the ordered phase. Also shown in Fig. 2 is the quantity $\beta P|_{\text{OL}}$

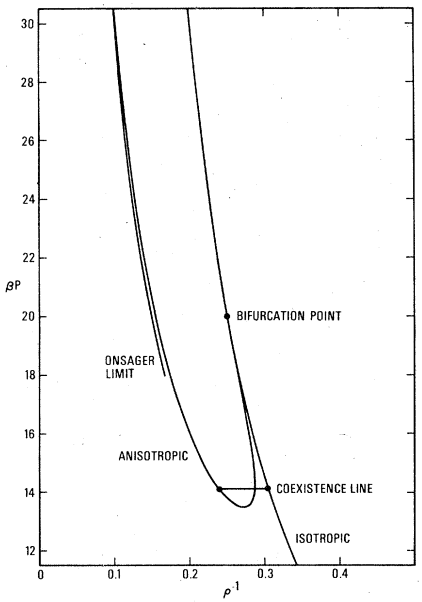

FIG. 2. The equations of state, βP vs $1/\rho$, for the isotropic phase, the anisotropic phase, and the limiting form predicted by Onsager; see Sec. IV C. The horizontal indicates the location of the isotropic-nematic phase transition.

$= 3\rho$, which is Onsager's high density limiting form of the anisotropic equation of state. Our results approach this limit quite accurately as $1/\rho$ becomes small, confirming Onsager's prediction.[1]

B. Free energy

Since $h(\cos\theta) \to 0$ continuously as $\rho \to \rho^*$, the existence of bifurcation leads to a natural choice of a standard state. That is, the free energies of the isotropic and anisotropic phases must become identical at the bifurcation point and we set this value equal to zero. Integration of the equation of state from $1/\rho^*$ to $1/\rho$ then yields the Helmholtz free energy of the system in excess of its value at $1/\rho^*$,

$$\beta A(1/\rho)/N = -\int_{1/\rho^*}^{1/\rho} \beta P \, d\left(\frac{1}{\rho}\right) . \tag{4.4}$$

The integration is carried out using a spline quadrature technique. The chemical potential μ is related to the free energy by

$$\beta\mu = \beta A/N + \beta P/\rho . \tag{4.5}$$

The conditions for the coexistence of the isotropic and anisotropic phases in stable equilibrium are that their pressures and chemical potentials be equal. In Fig. 3 is presented a plot of chemical potential versus pressure for the two phases in the neighborhood of the transition point. The point at which the curve corresponding to the isotropic

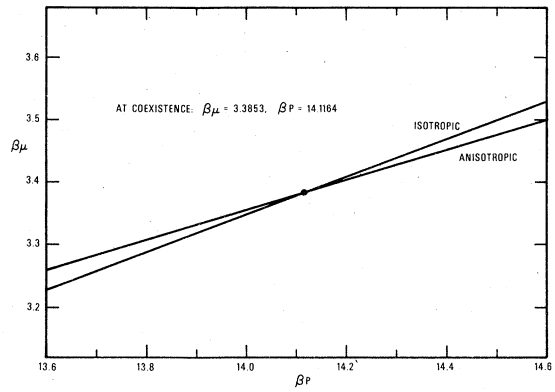

FIG. 3. Plot of the chemical potential μ vs βP for the isotropic and anisotropic phases. The intersection point gives the location of the tie-line in Fig. 2.

phase intersects that of the anisotropic phase determines the transition pressure and chemical potential:

$$\beta P|_{\text{trans}} = 14.1164 , \quad \beta\mu|_{\text{trans}} = 3.3853$$
$$1/\rho|_{\text{iso}} = 0.3039 , \quad 1/\rho|_{\text{aniso}} = 0.2368 . \tag{4.6}$$

The tie-line joining the two equations of state at the transition pressure is indicated in Fig. 2. We note that, since bifurcation implies continuity in the isotherm, the tie-line may also be located by the familiar Maxwell construction. The transition pressure given in (4.6) is lower than that of Onsager[1] by 2.7% (relative to our results) and that of Lasher[2] by only 0.5%. Their results, which are approximate, were calculated by minimization of a free-energy functional of the orientational distribution function and not by explicitly solving the nonlinear integral equation (2.9)

V. CONCLUDING REMARKS

The existence of bifurcation could have been inferred from Zwanzig's[7] "discretized" model of Onsager's original theory[1] and also from Lasher's[2] solution of the variational equation leading to (2.9). An equation similar to (2.9) can also be obtained from DiMarzio's lattice formulation of the hard-rod problem.[8]

In this paper, we have investigated the role of analytic features of the nonlinear equation for the ODF in determining the possibility of a phase transition. The existence of bifurcation leads naturally to a choice of a thermodynamic standard state for computing the free energy, and the direction of bifurcation affects the order of the transition. The double-valuedness shown in Fig. 1 is responsible for the isotherm shown in Fig. 2. We find it appropriate to note the suggestive similarity between the isotherm found in this paper and

that found from a theory of the fluid-solid transition in the hard-sphere system.[5]

The effect of the direction of bifurcation on the order of the phase transition can be illustrated further by considering the corresponding system of hard lines of length l in two dimensions. We point out, however, that Onsager's neglect of the third- and higher-order virial coefficients for the three-dimensional system is not justified in two dimensions. The following results must therefore be viewed as being merely suggestive rather than conclusive. The analog of the working equation (2.9) is given by

$$h(\theta)=-1+\frac{\exp\left[-\rho l^2\int_0^\pi \sin\theta' h(\theta-\theta')d\theta'/\pi\right]}{(1/\pi)\int_0^\pi \exp\left[-\rho l^2\int_0^\pi \sin\theta' h(\theta-\theta')d\theta'/\pi\right]d\theta} \tag{5.1}$$

and the linearization about the trivial solution $h=0$ is

$$w(\theta)=-\rho\frac{l^2}{\pi}\int_0^\pi \sin\theta' w(\theta-\theta')\,d\theta' . \tag{5.2}$$

Instead of the Legendre polynomials which were found to diagonalize the integral operator in three dimensions, the eigenfunctions of (5.2) are $\cos 2n\theta$, $n \geq 1$. Since we require the solutions of (5.1) to be such that $h(0)=h(\pi)$ is the only maximum of the ODF, we must choose the eigenfunction $\cos 2\theta$ as the solution to the linear equation. The associated eigenvalue is simple and leads to bifurcation at $\rho^* = 3\pi/2l^2$. By carrying out the same parametrization indicated in (3.3) and (3.4), we find that $\rho' = 0$ and $\rho'' = 9\pi/32l^2$. The direction of branching is therefore to the right, and the pressure of the anisotropic phase is found to lie below that of the isotropic phase and to increase with density near $1/\rho^*$. The free-energy curve of the anisotropic phase is also lower than that of the isotropic phase and is tangent to it at the bifurcation point. If, by extending the solutions of (5.1) globally, the pressure continued to increase with density (as we believe it does), the free energy of the anisotropic phase would be convex. The point $1/\rho^*$ would then be the only point of common tangency and the transition there would be of higher order than first. This is precisely the result found for the one-dimensional case of a theory of crystallization in the hard-sphere system,[5] and it is also consistent with the previous results of Zwanzig[7] and the earlier argument of Landau.[9] Similar connections between the order of a phase transition and the direction of branching apparently also occur in problems of large-scale instabilities.[10]

ACKNOWLEDGMENT

The authors wish to thank R. W. Zwanzig for his interest and trenchant comments.

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