Isotropic-symmetry-breaking bifurcations in a class of liquid-crystal models

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The isotropic-symmetry-breaking bifurcations occurring in a class of liquid-crystal models describing particles with the symmetry of rectangular slabs are studied. The model free-energy functional employed is appropriate to both the mean-field treatment of anisotropic dispersion forces and the Onsager approximation for hard anisometric particles. The symmetry of the bifurcating solutions to the stationary-phase equations is classified in terms of the eigenvalues of the effective pair interaction. Explicit conditions are derived for systems exhibiting crossover behavior between rodlike and platelike ordering. The results are applied to the question of the existence of biaxial phases in systems of uniaxial particles, and to two models for nonaxially symmetric particles: the hard spheroplatelet fluid and the Straley model.

I. INTRODUCTION

The notions of bifurcation theory were introduced to the study of orientational order-disorder transitions in liquid crystals by Kayser and Raveché.[1] They showed how Onsager's model for a fluid of elongated hard rods[2] can be analyzed in terms of a nonlinear eigenvalue equation. This equation is then shown to possess an isotropic-symmetry-breaking bifurcation. The solution branching off from the isotropic phase at the bifurcation point, albeit metastable, eventually connects to the stable branch of ordered solutions describing the nematic phase of the model. The qualitative properties of the model, i.e., its first-order phase transition, can already be inferred from the behavior of the solution close to the bifurcation point, since the direction of branching indicates the existence of a van der Waals type of loop in the equation of state. In their introduction Kayser and Raveché mention that their analysis, although elaborated for the Onsager model, is applicable to all other models of liquid crystals having the same formal structure as the Onsager model, e.g., mean-field theories of anisotropic long-ranged interactions. Since, then, however, no new applications seem to have been considered. The aim of this interest in the method as applied to orientation-dependent interactions by using it to study the symmetry properties of the bifurcating solutions of a class of liquid crystal models. We thus consider questions regarding the relation between the symmetry of the particles involved (or the symmetry of the defining interparticle interaction) and the symmetry of phases that develop from the isotropic phase.

The class of models we choose to study is that of the effective orientation-dependent pair interaction models appropriate to rigid particles possessing three mutually orthogonal planes of mirror symmetry, e.g., rectangular slabs, ellipsoids with three different major axes. This class of models encompasses most of the models for nonchiral, inversion-symmetric particles considered so far.[3] Note that the uniaxially symmetric particles form a subclass of the one considered here, so that the classical Maier-Saupe[4] and Onsager models are included.

Our main result will be the classification of the symmetries of the bifurcating solutions to the equations describing the stationary phases of our model free-energy functional in terms of eigenvalues of the effective pair interaction. The majority of systems will form either a uniaxially symmetric rodlike nematic phase $N_{(+)}$ or a platelike nematic phase $N_{(-)}$. These two classes are divided by the systems in which the tendencies towards rodlike and platelike behavior balance, resulting in a continuous transition to a phase with lower than uniaxial symmetry: the biaxial nematic phase B.

The rest of the paper is organized as follows. In Sec. II we introduce the free-energy functional that defines our models (II A), describe the properties of the effective pair interaction for the class of particles considered (II B), and discuss the solution space to which we restrict ourselves, thereby defining the order parameters appearing in the description (II C). Section III deals with the bifurcation analysis of the stationary-phase equations of the free-energy functional, starting with a definition of the relevant equations (III A), followed by a discussion of their solutions (III B) and closing with an interpretative comparison with Landau theory (III C). Applications of our results are presented in Sec. IV, where the question of the existence of biaxial phases in systems with uniaxial particles is discussed (IV A) and two models for nonaxially symmetric particles are analyzed: the hard spheroplatelet fluid (IV B) and the Straley model (IV C). Some comments on the theory and suggests for further research are gathered together in the concluding section V. An appendix discusses the details of the computation of the interaction coefficients of the hard spheroplatelet fluid.

II. FORMULATION OF THE MODEL

A. Free-energy functional

The starting point of our study is the free-energy functional defining our class of models. For details of the derivation of the functional as an approximation arising

in either the mean-field treatment of anisotropic dispersion forces or the Onsager treatment of hard interactions we refer the reader to Ref. 3,

$$\beta f[\psi]=\int d\Omega\,\psi(\Omega)\ln\psi(\Omega) + \tfrac{1}{2}\lambda\int d\Omega\int d\bar{\Omega}\,\psi(\Omega)\psi(\bar{\Omega})\mathcal{K}(\Omega,\bar{\Omega})+\beta\tilde{f}(\lambda)\ . \tag{2.1}$$

Here f denotes the free energy per particle, considered as a functional of the one-particle orientational distribution function (ODF) ψ, which has unit norm with respect to the invariant measure $d\Omega$. The orientation of the particles, here denoted by Ω, will, when necessary, be parametrized by the standard Euler angles (α,β,γ) defining the active rotation carrying a fixed reference frame $\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\}$ into a particle-fixed frame $\{\hat{\mathbf{u}},\hat{\mathbf{v}},\hat{\mathbf{w}}\}$, in which case the invariant measure is given by $d\Omega=d\alpha\sin(\beta)d\beta d\gamma$. We further introduce the control parameter λ and the effective pair-interaction kernel $\mathcal{K}(\Omega,\bar{\Omega})$. In the mean-field case the control parameter will be $\beta=(k_BT)^{-1}$ and the interaction kernel equal to the effective pair potential obtained from an averaging over the spatial degrees of freedom. In the Onsager case the control parameter will be the number density ρ and the interaction kernel equal to the pair-excluded volume at fixed relative orientation of the two particles. In either case the control parameter functions as a coupling parameter with $\lambda=0$ defining the noninteracting, ideal-gas system and $\lambda\to\infty$ the strong-coupling limit. Likewise, the properties of the specific model are completely defined by the interaction kernel $\mathcal{K}$ regardless of its origin. Finally we have the contributions to the free energy that do not depend on the ODF, but possibly on the control parameter, e.g., kinetic energy; they are denoted by $\tilde{f}(\lambda)$, but do not figure in the further developments.

A necessary condition for an equilibrium ODF of a system described by a free-energy functional like (2.1) is that it satisfies the stationarity condition

$$\frac{\delta\omega[\psi]}{\delta\psi(\Omega)}\equiv\frac{\delta}{\delta\psi(\Omega)}\left[f[\psi]-\tilde{\mu}\int d\Omega\,\psi(\Omega)\right]=0\ , \tag{2.2}$$

the chemical-potential-like multiplier $\tilde{\mu}$ being adjusted to ensure the normalization of the ODF. For a solution of (2.2) to describe a thermodynamically stable phase an additional minimum criterion will have to be satisfied, the appropriate criterion depending on whether we are considering a mean-field model or an Onsager model. In the mean-field case the free energy itself is the relevant potential, hence the mean-field equilibrium ODF $\psi_{\rm eq}^{\rm MF}$ satisfies the following inequality for all normed ψ:

$$f[\psi_{\rm eq}^{\rm MF}]\le f[\psi]\ , \tag{2.3}$$

while in the Onsager case the chemical potential plays this role and the equilibrium ODF $\psi_{\rm eq}^{\rm ON}$ satisfies

$$\mu[\psi_{\rm eq}^{\rm ON}]\le\mu[\psi]\equiv f[\psi]+\rho\frac{\partial}{\partial\rho}f[\psi]\ . \tag{2.4}$$

B. Properties of the effective pair interaction

We now turn to the properties of the effective pair interactions, as specified by the kernel $\mathcal{K}$, that follow from our choice of particle symmetry. We first note some general properties that have to be satisfied by $\mathcal{K}$: (i) reality, (ii) global rotational invariance, i.e., for an arbitrary rotation R we have $\mathcal{K}(R\Omega,R\bar{\Omega})=\mathcal{K}(\Omega,\bar{\Omega})$, and (ii) symmetry under particle interchange, i.e., $\mathcal{K}(\Omega,\bar{\Omega})=\mathcal{K}(\bar{\Omega},\Omega)$. These three requirements constrain $\mathcal{K}$ to be fully determined by an inversion-symmetric, real function of the relative orientational $\tilde{\Omega}=\bar{\Omega}^{-1}\Omega$ alone, which we will denote by K:

$$\mathcal{K}(\Omega,\bar{\Omega})=K(\tilde{\Omega})=K(\tilde{\Omega}^{-1})\ . \tag{2.5}$$

The symmetry of the individual particles is implemented by requiring that

$$\mathcal{K}(\Omega,\sigma\bar{\Omega})=\mathcal{K}(\Omega,\bar{\Omega})\ , \tag{2.6}$$

where σ is any element of the symmetry group of the particles. In our case the symmetry group of the particles is generated by the reflections in the three mutually orthogonal mirror planes that characterize our class of particles. The particle-fixed frame is defined by the intersection of the mirror planes (see Fig. 1). Labeling the axes by $\{u,v,w\}$, the generators of the symmetry group are $\{\sigma_{\langle u,v\rangle},\sigma_{\langle u,w\rangle},\sigma_{\langle v,w\rangle}\}$, where $\sigma_{\langle u,v\rangle}$ is the reflection in the $\langle u,v\rangle$ plane, etc. The action of these operations on the standard[5] rotation matrix elements $\mathcal{D}^{(l)}_{m,n}$ is given by

$$\begin{aligned}\mathcal{D}^{(l)}_{m,n}(\sigma_{\langle u,v\rangle}\Omega)&=(-)^{l+n}\mathcal{D}^{(l)}_{m,n}(\Omega)\ ,\\ \mathcal{D}^{(l)}_{m,n}(\sigma_{\langle u,w\rangle}\Omega)&=(-)^{n}\mathcal{D}^{(l)}_{m,-n}(\Omega)\ ,\\ \mathcal{D}^{(l)}_{m,n}(\sigma_{\langle v,w\rangle}\Omega)&=\mathcal{D}^{(l)}_{m,-n}(\Omega)\ .\end{aligned} \tag{2.7}$$

Combining (2.7) with (2.5) shows that K can be expanded in the following set of symmetry-adapted functions:

$$\Delta^{(l)}_{m,n}(\tilde{\Omega})=(\tfrac{1}{2}\sqrt{2})^{2+\delta_{m,0}+\delta_{n,0}}\sum_{\sigma,\sigma'=\{-1,1\}}\mathcal{D}^{(l)}_{\sigma m,\sigma' n}(\tilde{\Omega})\ , \qquad l,\ \text{even};\ 0\le m,n\le l,\ \text{even}\ . \tag{2.8}$$

The prefactor in (2.8) is chosen such that the $\Delta^{(l)}_{m,n}$'s satisfy the following orthogonality relations:

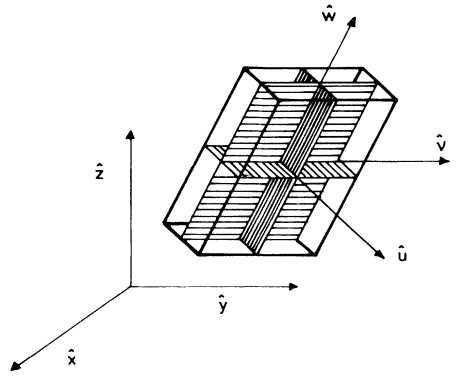

FIG. 1. Definition of the particle fixed frame $\{\hat{\mathbf{u}},\hat{\mathbf{v}},\hat{\mathbf{w}}\}$ using the intersections of the mirror-symmetry planes that define the particle symmetry.

fy the following orthogonality relations:

$$\int d\Omega\, \Delta^{(l)}_{m,n}(\Omega)\Delta^{(l')}_{m',n'}(\Omega)=\frac{8\pi^2}{(2l+1)}\delta_{l,l'}\delta_{m,m'}\delta_{n,n'} . \quad (2.9)$$

The expansion of K can then be given as

$$K(\tilde{\Omega})=\sum_{l,m,n}\frac{(2l+1)}{8\pi^2}K_{l,mn}\Delta^{(l)}_{m,n}(\tilde{\Omega}) , \quad (2.10)$$

where the sum is taken over all allowed values of l, m, and n. Due to the particle interchange symmetry the coefficients $K_{l,mn}$ are symmetric in the indices m and n.

At this point it will be convenient to introduce a more compact notation. Following Kayser and Raveché we therefore define an inner-product structure on the space of integrable, real functions of orientation $\mathcal{L}_\Omega$ through the definition

$$\langle f,g\rangle=\int d\Omega\, f(\Omega)g(\Omega), \quad f,g\in\mathcal{L}_\Omega \quad (2.11)$$

and henceforth drop the function arguments for elements of $\mathcal{L}_\Omega$ unless clarity demands otherwise. Furthermore each element of $\mathcal{L}_\Omega$ is also interpreted as a linear operator on $\mathcal{L}_\Omega$ by defining

$$f[g](\Omega)=\int d\bar{\Omega}\, f(\bar{\Omega}^{-1}\Omega)g(\bar{\Omega}) . \quad (2.12)$$

Note that with these definitions K becomes a Hermitian operator on $\mathcal{L}_\Omega$, i.e.,

$$\langle f,K[g]\rangle=\langle K[f],g\rangle . \quad (2.13)$$

The free energy (2.1) is now compactly rewritten as

$$\beta f[\psi]=\langle\psi,\ln\psi\rangle+\tfrac{1}{2}\lambda\langle\psi,K[\psi]\rangle+\beta\tilde{f}(\lambda) . \quad (2.14)$$

C. Solution space and order parameters

In principle the solution space appropriate to finding the stationary distributions of the free-energy functional (2.1) is the space of all real positive functions of orientation of unit norm. Intuition, however, suggests that it is sufficient to look at the subspace of distributions that possess the same symmetry as the particles in question. Most liquid-crystalline-state physicists would either take this point of view for granted or quote a statement like "you cannot get a homogeneous (i.e., nonspatially ordered) liquid crystalline phase that has a symmetry lower than that of the constituent particles" without supplying a reference. To our knowledge this question has not been studied in any generality. We nevertheless proceed on the assumption that the above-mentioned statement holds, and profit from the reduction of degrees of freedom that it entails. Later on, in Sec. IV A, we will bring some of the results of our work to bear on the question of the existence of biaxial phases in uniaxial-particle systems. Since in Sec. II B we have already derived a set of symmetry-adapted basis functions, our assumption translates into the statement that the ODF is completely specified by its expansion in this same set of functions

$$\psi=\sum_{l,m,n}\frac{(2l+1)}{8\pi^2}\psi_{l,mn}\Delta^{(l)}_{m,n} . \quad (2.15)$$

The normalization of ψ fixes the first coefficient

$$\psi_{0,00}=\langle\Delta^{(0)}_{0,0},\psi\rangle=\langle 1,\psi\rangle=1 . \quad (2.16)$$

As primary order parameters we will take the coefficients with angular momentum index $l=2$, corresponding to the most large-scale features of the distribution. They are the distribution averages of the following four functions:

$$\Delta^{(2)}_{0,0}(\Omega)=\tfrac{1}{2}(3\cos^2\beta-1) , \quad (2.17a)$$

$$\Delta^{(2)}_{0,2}(\Omega)=\tfrac{1}{2}\sqrt{3}\sin^2\beta\cos2\gamma , \quad (2.17b)$$

$$\Delta^{(2)}_{2,0}(\Omega)=\tfrac{1}{2}\sqrt{3}\sin^2\beta\cos2\alpha , \quad (2.17c)$$

$$\Delta^{(2)}_{2,2}(\Omega)=\tfrac{1}{2}(1+\cos^2\beta)\cos2\alpha\cos2\gamma - \cos\beta\sin2\alpha\sin2\gamma . \quad (2.17d)$$

Note that the functions with $m=0$ do not depend on the azimuthal angle α and are thus invariant under rotations around the reference z axis, in contrast to the set with $m=2$. The orderparameters $\psi_{2,00}$ and $\psi_{2,02}$ are thus associated with uniaxial order around the z axis, while nonzero values of $\psi_{2,20}$ and $\psi_{2,22}$ signal biaxiality of the distribution around this axis.

Having defined our solution space $\mathcal{S}_\Omega$, i.e., all positive functions satisfying an expansion of the type (2.15) with the constraint (2.16), we now inquire into the action of K onto the basis vectors of $\mathcal{S}_\Omega$. An explicit calculation shows that

$$\Delta^{(l)}_{m,n}[\Delta^{(l')}_{m',n'}]=\frac{8\pi^2}{(2l+1)}\delta_{l,l'}\delta_{m,n'}\Delta^{(l)}_{m',n} , \quad (2.18)$$

whence

$$K[\Delta^{(l)}_{m,n}]=\sum_p K_{l,np}\Delta^{(l)}_{m,p} . \quad (2.19)$$

Thus K induces a natural splitting of $\mathcal{S}_\Omega$ into invariant subspaces labeled by the angular momentum index l and the subindex m

$$\mathcal{S}_\Omega=\sum_{l,m}\oplus\mathcal{S}^{(l)}_m . \quad (2.20)$$

Moreover, for fixed l, K is represented by the same matrix in each m subspace $\mathcal{S}^{(l)}_m$.

III. BIFURCATION ANALYSIS

A. Bifurcation equations

In order to study the solutions of the equation (2.2) that describes the stationary distributions of the free energy (2.1) we explicitly perform the functional derivative yielding

$$\ln\psi+\lambda K[\psi]-\beta\tilde{\mu}=0 , \quad (3.1)$$

or upon eliminating $\tilde{\mu}$, using the condition $\langle 1,\psi\rangle=1$

$$\psi=\frac{\exp(-\lambda K[\psi])}{\langle 1,\exp(-\lambda K[\psi])\rangle} , \quad (3.2)$$

a form clearly displaying the role of $K[\psi]$ as a self-

consistent "mean field." A starting point for our analysis is the fact that the isotropic distribution $\psi_0=1/8\pi^2=\Delta^{(0)}_{0,0}/8\pi^2$ is a solution to (3.2) at all values of λ. This is a consequence of the global rotational invariance of K, whence $K[\psi_0]=\text{const}$. Bifurcation analysis now proceeds to look for solutions that branch off from the isotropic solution. To this end we construct a one-parameter family of solutions that connect to ψ_0 by inserting the following expansions in the arbitrary parameter ϵ into (3.2):

$$\begin{aligned}\psi&=\psi_0+\epsilon\psi_1+\epsilon^2\psi_2+\cdots\ ,\\ \lambda&=\lambda_0+\epsilon\lambda_1+\epsilon^2\lambda_2+\cdots\ ,\end{aligned}\tag{3.3}$$

where due to the normalization of ψ_0 we have $\langle 1,\psi_k\rangle=0$ for $k\geq 1$. Equating terms of equal order in ϵ left and right of (3.2) we find, to second order,

$$\psi_1=-\frac{\lambda_0}{8\pi^2}K[\psi_1]\tag{3.4}$$

and

$$\psi_2=-\frac{1}{8\pi^2}\left[\lambda_0K[\psi_2]+\lambda_1K[\psi_1]-\tfrac{1}{2}\lambda_0^2\left[K[\psi_1]^2-\frac{1}{8\pi^2}\langle 1,K[\psi_1]^2\rangle\right]\right]\ .\tag{3.5}$$

The first equation (3.4) is commonly referred to as the bifurcation equation. It is a linear eigenvalue equation that determines the bifurcation point(s), i.e., the value(s) of the control parameter λ where a nonisotropic solution with infinitesimal amplitude coexists with the isotropic one. Since the isotropic phase is stable in the absence of interaction ($\lambda=0$) we will be interested in the bifurcation point with the smallest value of λ, this being the point where the isotropic solution loses its property of being a local minimum of the free energy, the system thus becoming unstable with respect to nonisotropic perturbations.

B. Solutions and their symmetry

It is clear that an arbitrary eigenvector χ of K, with eigenvalue κ_χ solves the bifurcation equation (3.4) with the bifurcation point given by

$$\lambda_0^{(\chi)}=-\frac{8\pi^2}{\kappa_\chi}\ .\tag{3.6}$$

To obtain the "physical" bifurcation, as defined in Sec. III A, we have to determine the eigenvector with the absolutely largest, negative (N.B. $\lambda>0$) eigenvalue, which we assume to exist and denote by κ_*. Given the splitting induced by K on the solution space $\mathcal{S}_\Omega$ (2.20) the eigenvalues can be labeled by l, m, and q where $q=0,2,\ldots,l$, this last index chosen so that

$$\kappa_{l,m,0}\leq\kappa_{l,m,2}\leq\cdots\leq\kappa_{l,m,l}\ .\tag{3.7}$$

The label m is, in fact, redundant given the identical action of K in each subspace $\mathcal{S}^{(l)}_m$. In order to proceed we now make the following assumption:

$$\kappa_*=\kappa_{2,0,0}=\kappa_{2,2,0}\ .\tag{3.8}$$

The "physical" eigenvector is thus located in the $l=2$ subspace. This is, of course, an assumption on the form of the effective pair interaction. It is certainly satisfied by the reasonable class of effective interactions that have a single broad absolute minimum for total alignment of the two particles and no other local minima. Moreover, this choice is the only one consistent with our choice of the set (2.17) as our primary order parameters. We therefore incorporate it into the *definition* of the class of models considered.

Using (2.19), κ_* can be explicitly determined in terms of the expansion coefficients of K,

$$\kappa_*=\tfrac{1}{2}(K_{2,00}+K_{2,22})-\tfrac{1}{2}[(K_{2,00}-K_{2,22})^2+4K^2_{2,02}]^{1/2}\ ,\tag{3.9}$$

with the corresponding eigenvectors

$$\begin{aligned}\chi_0&=\Delta^{(2)}_{0,0}e_0+\Delta^{(2)}_{0,2}e_2\ ,\\ \chi_2&=\Delta^{(2)}_{2,0}e_0+\Delta^{(2)}_{2,2}e_2\ ,\end{aligned}\tag{3.10}$$

where the coefficients e_0 and e_2 are given by

$$\begin{aligned}e_0&=\frac{-K_{2,02}}{\{K^2_{2,02}+\tau^2\}^{1/2}},\quad e_2=\frac{\tau}{\{K^2_{2,02}+\tau^2\}^{1/2}}\ ,\\ \tau&=\tfrac{1}{2}(K_{2,00}-K_{2,22})+\tfrac{1}{2}[(K_{2,00}-K_{2,22})^2+4K^2_{2,02}]^{1/2}\geq 0\ .\end{aligned}\tag{3.11}$$

The general solution to the bifurcation equation is therefore

$$\psi_1=c_0\chi_0+c_2\chi_2,\quad \lambda_0=-\frac{8\pi^2}{\kappa_*}\ .\tag{3.12}$$

The as yet undetermined coefficients c_0 and c_2 can be obtained from the second-order bifurcation equation (3.5) using a consistency condition. We first note the identity

$$\langle\chi_0,\psi_2\rangle=\frac{-\lambda_0\kappa_*}{8\pi^2}\langle\chi_0,\psi_2\rangle=\frac{-\lambda_0}{8\pi^2}\langle K[\chi_0],\psi_2\rangle=\frac{-\lambda_0}{8\pi^2}\langle\chi_0,K[\psi_2]\rangle\ ,\tag{3.13}$$

and likewise

$$\langle\chi_2,\psi_2\rangle=\frac{-\lambda_0}{8\pi^2}\langle\chi_2,K[\psi_2]\rangle\ .\tag{3.14}$$

Taking the inner product of (3.5) with χ_0 and χ_2, respectively, and using (3.13) and (3.14) to eliminate the terms involving the unknown function ψ_2, we find

$$\begin{aligned}&\frac{8\pi^2}{5}\lambda_1\kappa_*c_0-\tfrac{1}{2}\lambda_0^2\kappa_*^2\{c_0^2\langle\chi_0,\chi_0^2\rangle+2c_0c_2\langle\chi_0^2,\chi_2\rangle+c_2^2\langle\chi_0,\chi_2^2\rangle\}=0\ ,\\ &\frac{8\pi^2}{5}\lambda_1\kappa_*c_2-\tfrac{1}{2}\lambda_0^2\kappa_*^2\{c_0^2\langle\chi_2,\chi_0^2\rangle+2c_0c_2\langle\chi_2^2,\chi_0\rangle+c_2^2\langle\chi_2,\chi_2^2\rangle\}=0\ .\end{aligned}\tag{3.15}$$

The inner products involving three χ's can be computed from (3.10) and the following triplet integrals of Δ's:

$$\langle \Delta^{(l)}_{m,n}, \Delta^{(l')}_{m',n'} \Delta^{(l'')}_{m'',n''} \rangle = 8\pi^2 \begin{pmatrix} l & l' & l'' \\ m & \sigma' m' & \sigma'' m'' \end{pmatrix} \begin{pmatrix} l & l' & l'' \\ n & \tau' n' & \tau'' n'' \end{pmatrix}, \tag{3.16}$$

where the round brackets denote 3-j symbols and $\sigma', \sigma'', \tau', \tau''$ are freely chosen from $\{-1,1\}$ to satisfy, if possible, the relations $m+\sigma' m'+\sigma'' m''=n+\tau' n''+\tau'' n''=0$. The relevant nonzero 3-j symbols are

$$\begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} = -\begin{pmatrix} 2 & 2 & 2 \\ 0 & 2 & -2 \end{pmatrix} = -\left\{\tfrac{2}{35}\right\}^{1/2} . \tag{3.17}$$

Using these facts and simplifying we arrive at

$$\begin{aligned} &\lambda_1 c_0 - \tfrac{1}{7}\lambda_0^2 \kappa_* \nu(K)\{c_0^2 - c_2^2\} = 0 , \\ &\lambda_1 c_2 + \tfrac{2}{7}\lambda_0^2 \kappa_* \nu(K)\{c_0 c_2\} = 0 , \end{aligned} \tag{3.18}$$

where

$$\nu(K) = e_0\{e_0^2 - 3e_2^2\} . \tag{3.19}$$

Here we have stressed the dependence of $\nu(K)$ on the interaction K through the formulas (3.11) for e_0 and e_2. There are now two separate cases to consider.

(i) $\nu(K)\neq 0$. In this case λ_1 can be consistently eliminated among the equations (3.18) yielding

$$c_2\{3c_0^2 - c_2^2\} = 0 . \tag{3.20}$$

Without loss of generality we can take $c_0^2 + c_2^2 = 1$ (this just defines the normalization of ψ_1) and therefore arrive at the following three solutions, up to sign

$$\begin{aligned} \psi_1^{(z)} &= \chi_0 , \\ \psi_1^{(y)} &= -\tfrac{1}{2}\chi_0 - \tfrac{1}{2}\sqrt{3}\chi_2 , \\ \psi_1^{(x)} &= -\tfrac{1}{2}\chi_0 + \tfrac{1}{2}\sqrt{3}\chi_2 . \end{aligned} \tag{3.21}$$

The solution $\psi_1^{(z)}$ is built up from the functions $\Delta^{(2)}_{0,0}$ and $\Delta^{(2)}_{0,2}$, which, as we remarked in Sec. II C, are functions invariant under rotations about the reference-frame z axis. It is now straightforward to check that the other two solutions $\psi_1^{(y)}$ and $\psi_1^{(x)}$ actually describe the same solution, but with the symmetry axis in the y and x directions, respectively. All solutions in this case thus have uniaxial symmetry, the only freedom left in our restricted solution space being the choice of the symmetry axis. (ii) $\nu(K)=0$. This case allows consistent solutions only if λ_1 is equal to zero. This leaves c_0 and c_2 to be determined by the next-order equation in the hierarchy of the bifurcation equations. The symmetry of the solution will however be lower than uniaxial, as we will show that this case marks the crossover between two different kinds of uniaxial order.

We therefore take a closer look at the quantity λ_1 that determines the direction of bifurcation. Solving (3.18) for λ_1 we find

$$\lambda_1 = \tfrac{1}{7}\lambda_0^2 \kappa_* \nu(K) c_0\{c_0^2 - 3c_2^2\} . \tag{3.22}$$

For the uniaxial solutions, in the case $\nu(K)\neq 0$, we expect the branch of stable nematic solutions to be connected to the bifurcating solutions with negative direction of bifurcation, as these give rise to the van der Waals looplike character of the equation of state, i.e., a range of λ for which there exist three (meta)stable phases. The overall sign of the bifurcating eigenvector ψ_1 now becomes important.

When $\nu(K)>0$ we have to choose the "positive" solutions as given in (3.21) in order to obtain $\lambda_1<0$ (remember that $\kappa_*<0$). These solutions describe the onset of ordering of the particle w axis *towards* the symmetry axis, associated with a positive value of the order parameter $S=\langle P_2(\hat{\mathbf{w}}\cdot\hat{\mathbf{s}})\rangle$, where $\hat{\mathbf{s}}$ is a unit vector along the symmetry axis. (In the case of solution $\psi_1^{(z)}$ we have $S=\psi_{2,00}$.) This type of order is commonly called rodlike nematic $N_{(+)}$. Indeed, for elongated uniaxial particles, with the w axis chosen along the particle symmetry axis, the only nonzero matrix element of K for $l=2$ will be $K_{2,00}$ leading to $e_0=1$ and $\nu(K)=1$.

When $\nu(K)<0$, the solutions for which $\lambda_1<0$ are the ones is (3.21) but with negative overall sign. These represent ordering of the particle w axis *away* from the symmetry axis ($S<0$). This is the type of order expected for platelike particles with the w axis in the plane of the plate, the so-called platelike nematic order $N_{(-)}$.

The case $\nu(K)=0$ clearly marks the separation between these two forms of uniaxial order. The vanishing of λ_1 in this case is also indicative for the occurrence of a phase transition of higher order towards the lower symmetry phase, which perforce is biaxial. Explicitly solving $\nu(K)=0$ yields the following expressions characterizing these systems of crossover type:

$$e_0 = 0 \Longrightarrow K_{2,02} = 0, \quad K_{2,00} - K_{2,22} > 0 \tag{3.23}$$

and

$$e_0^2 - 3e_2^2 = 0 \Longrightarrow K_{2,00} - K_{2,22} = \frac{-|K_{2,02}|}{\frac{1}{2}\sqrt{3}} . \tag{3.24}$$

The situation described above is illustrated in the schematic branching diagram (Fig. 2). A more physical

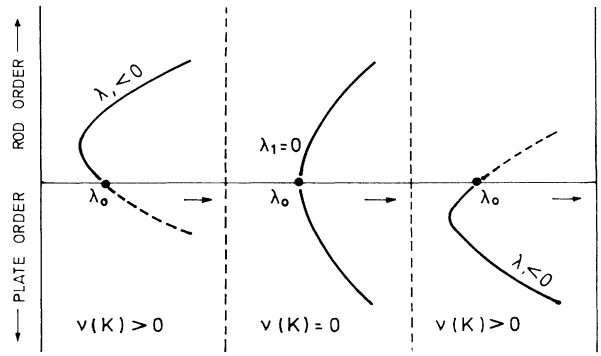

FIG. 2. Schematic branching diagram of the stationary-phase equation (3.2) showing the dependence on the sign of $\nu(K)$.

interpretation of the crossover phenomenon is deferred to the applications, where we will relate this behavior to actual particle parameters. In Sec. III C we look at this behavior from another point of view by studying the connection with Landau theory.

C. Connection with the Landau theory

A connection between the microscopic framework supplied by the density functional (2.1) and the more macroscopic, symmetry-oriented approach of the Landau theory of phase transitions,[6] can be made through our identification of the set (2.17) as primary order parameters. Inserting the expansion (2.15) for the ODF into the free-energy functional (2.1) and expanding in terms of the order parameters $\psi_{l,mn}$ we find the following structure:

$$\beta f[\{\psi_{l,mn}\}]=\Phi^{(0)}(\lambda)+\sum_{\substack{mm'\\nn'}}\Phi^{(2)}_{mn,m'n'}(\lambda,K)\psi_{2,mn}\psi_{2,m'n'}+\sum_{\substack{mm'm''\\nn'n''}}\Phi^{(3)}_{mn,m'n',m''n''}\times\psi_{2,mn}\psi_{2,m'n'}\psi_{2,m''n''}+\Phi^{(\text{rest})}(\lambda,K,\{\psi_{l,mn}\}) . \tag{3.25}$$

The summations all run over the appropriate ranges. Note that the interaction enters in the quadratic term but not in the cubic term which is due solely to the $\langle\psi,\ln\psi\rangle$ term in the free energy. The rest term $\Phi^{(\text{rest})}$ contains all higher-order invariant polynomials in the primary order parameters as well as the terms involving the secondary order parameters with $l\geq 4$. The relevant order parameters are those that develop a zero prefactor after diagonalization of the quadratic term in (3.25). These are exactly the amplitudes c_0 and c_2 of the eigenvectors of K with eigenvalue κ_*, which have been determined in Sec. III B, now interpreted as variational parameters. Performing the diagonalization and collectively denoting all nonrelevant order parameters by $\tilde{c}$ the free energy (3.25) is transformed into

$$\beta F[\{c_0,c_2,\tilde{c}\}]=\Phi^{(0)}(\lambda)+\frac{5}{2}\left[1+\frac{\lambda\kappa_*}{8\pi^2}\right](c_0^2+c_2^2)-\tfrac{25}{21}\nu(K)c_0(c_0^2-3c_2^2)+\tilde{\Phi}^{(\text{rest})}(\lambda,K,\{c_0,c_2,\tilde{c}\}) . \tag{3.26}$$

We recognize the bifurcation condition (3.12) in the prefactor of the quadratic term. The role of $\nu(K)$ in determining the presence of the cubic term in the Landau expansion is evident, supporting our interpretation of the crossover systems with $\nu(K)=0$ as the boundary between two classes exhibiting first-order transitions to nematic phases, they themselves exhibiting a second-order transition. In fact, we can directly compare our results with the Landau theory for the isotropic-nematic transition as developed by Gramsbergen, Longa, and de Jeu,[7] by noting that we can construct a second-rank tensor order parameter ($\mathbb{1}$ is the unit tensor)

$$\mathbb{Q}=c_0\{\tfrac{1}{2}(3\hat{\mathbf{z}}\otimes\hat{\mathbf{z}}-\mathbb{1})\}+c_2\{\tfrac{1}{2}\sqrt{3}(\hat{\mathbf{x}}\otimes\hat{\mathbf{x}}-\hat{\mathbf{y}}\otimes\hat{\mathbf{y}})\} \tag{3.27}$$

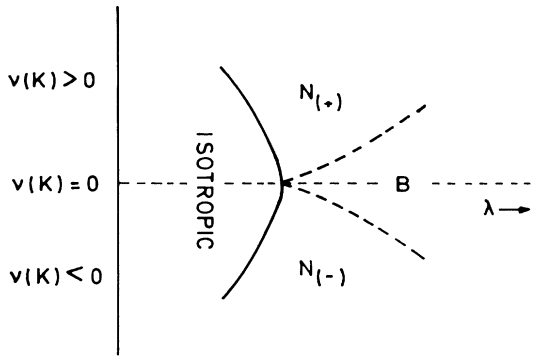

FIG. 3. Topology of the phase diagram in the neighborhood of the crossover points $\nu(K)=0$. Solid lines: first-order transitions. Dashed lines: second-order transitions.

that is equivalent to their macroscopic order parameter. The general expansion of the free energy in terms of this order parameter is given, up to sixth order, by

$$F[\mathbb{Q}]=F_0+a\,\mathrm{Tr}(\mathbb{Q}^2)+b\,\mathrm{Tr}(\mathbb{Q}^3)+c\,\mathrm{Tr}(\mathbb{Q}^2)^2+d\,\mathrm{Tr}(\mathbb{Q}^2)\mathrm{Tr}(\mathbb{Q}^3)+e\,\mathrm{Tr}(\mathbb{Q}^2)^3+e'\mathrm{Tr}(\mathbb{Q}^3)^2 , \tag{3.28}$$

where, by comparing with (3.26), we can identify $a\propto(\lambda_0-\lambda)$ and $b\propto\nu(K)$. Note that the presence and positivity of the even-order invariants is guaranteed in our case since they are generated by the noninteracting $\langle\psi,\ln\psi\rangle$ term in the free energy, for which the isotropic phase must be absolutely stable. We can therefore use their results and identify the cases $\nu(K)=0$ as Landau points in the phase diagram with $\nu(K)$ and λ as variables, i.e., the bicritical point in which the isotropic, rodlike nematic $N_{(+)}$, platelike nematic $N_{(-)}$ and biaxial B phases meet. The topology of this phase diagram in the neighborhood of the Landau point is sketched in Fig. 3. This feature of the phase diagram of nonuniaxially symmetry particles was first discussed by Alben.[8]

IV. APPLICATIONS

A. Uniaxially symmetric particles

As mentioned in the Introduction, the uniaxially symmetric particles from a subclass of the systems considered in this paper. The effective interaction between such particles depends only on the angle between their symmetry axes. Hence the only nonzero coefficients in the expansion of K (2.13) can be chosen to be the $K_{2,00}$'s. The minimal eigenvalue will be $\kappa_*=K_{2,00}$, with the two associated eigenvectors $\chi_0=\Delta^{(2)}_{0,0}$ and $\chi_2=\Delta^{(2)}_{2,0}$. The order parameter $\psi_{2,00}=S=\langle\psi,P_2(\cos\beta)\rangle$ is the well-known Maier-Saupe order parameter. The second relevant one—$\psi_{2,20}$—that signals biaxial order around the reference z axis, is commonly neglected on the grounds that "you cannot get biaxial phases from uniaxial particles" (see the discussion in Sec. II C). It does, however, appear naturally in the description of uniaxial particles. Consid-

er the second-rank tensor order parameter $\mathbb{S}$,

$$\mathbb{S}=\left\langle \sum_{i=1}^{N} \tfrac{1}{2}\{3\hat{\mathbf{w}}_i\otimes\hat{\mathbf{w}}_i-\mathbb{1}\}\right\rangle , \tag{4.1}$$

where the sum runs over the particles in the system and the angular brackets denote equilibrium averaging. Since $\mathbb{S}$ is a real, symmetric tensor there exists a reference frame in which it is diagonal. Using our definition of the ODF (2.15) we can explicitly express this reference $\mathbb{S}^\dagger$ in terms of our order parameters

$$\mathbb{S}^\dagger=\mathrm{diag}(-\tfrac{1}{2}\psi_{2,00}+\tfrac{1}{2}\sqrt{3}\psi_{2,20},\ -\tfrac{1}{2}\psi_{2,00}-\tfrac{1}{2}\sqrt{3}\psi_{2,20},\psi_{2,00}) . \tag{4.2}$$

The analysis of Sec. III B shows that for these systems the bifurcating solutions will be of uniaxial symmetry. Indeed one checks that the infinitesimal solutions (3.21) all yield the same $\mathbb{S}^\dagger$ up to interchange of the axis labels. Viewed from the Landau viewpoint, our analysis gives a microscopic justification of the argument given by Prokrovskii and Kats[9] for the absence of biaxial ordering in nematics when a nonzero third-order invariant is present in the free-energy expansion. The only invariant polynomials (with respect to the symmetry operations of our solution space $\mathcal{S}_\Omega$) that we can construct from the order parameters $\psi_{2,00}$ and $\psi_{2,20}$ are

$$\begin{aligned} I_2&=\psi_{2,00}^2+\psi_{2,20}^2\propto \mathrm{Tr}\{(\mathbb{S}^\dagger)^2\} ,\\ I_3&=\psi_{2,00}(\psi_{2,00}^2-3\psi_{2,20}^2)\propto \mathrm{Tr}\{(\mathbb{S}^\dagger)^3\} . \end{aligned} \tag{4.3}$$

The Landau free energy, neglecting secondary order parameters, will be a function of these two invariants: $\mathcal{F}(I_2,I_3)$. The stationary states are then selected by the criteria

$$\begin{aligned} \frac{\partial\mathcal{F}}{\partial\psi_{2,00}}&=2\frac{\partial\mathcal{F}}{\partial I_2}\psi_{2,00}+3\frac{\partial\mathcal{F}}{\partial I_3}(\psi_{2,00}^2-\psi_{2,20}^2)=0 ,\\ \frac{\partial\mathcal{F}}{\partial\psi_{2,00}}&=2\frac{\partial\mathcal{F}}{\partial I_2}\psi_{2,20}-6\frac{\partial\mathcal{F}}{\partial I_3}(\psi_{2,00}\psi_{2,20})=0 . \end{aligned} \tag{4.4}$$

The reader will recognize the analogs of the equations (3.18) leading the conclusions that the solutions will posses uniaxial symmetry in the case that $\partial\mathcal{F}/\partial I_3\neq 0$. Out theory predicts that close to bifurcation, where the order parameters are small, this is indeed the case given that $\nu(K)\neq 0$, the latter condition being automatically satisfied by the uniaxial systems. Let us stress again that this is a local argument. The question of the global stability of uniaxial solutions remains as yet unsettled.

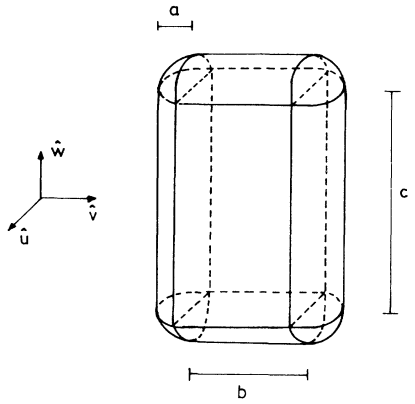

FIG. 4. Spheroplatelet.

B. Hard spheroplatelet fluid

The spheroplatelet as depicted in Fig. 4 is a natural generalization of the spherocylinder. It can be described as a rectangular block with dimensions $2a\times b\times c$, capped with quarter spheres of radius a and half-cylinders with radius a and lengths b and c such as to produce a piecewise smooth convex body. It is at present the only nonaxially symmetric convex body for which the pair-excluded volume at fixed relative orientation is known in closed form.[10] The explicit form of this excluded volume, which will play the role of effective interaction in our application, is given by

$$\begin{aligned} K(\Omega_1,\Omega_2)=&\frac{32\pi a^3}{3}+8\pi a^2 b+8\pi a^2 c+8abc+4abc\{\,|\hat{\mathbf{v}}_1\times\hat{\mathbf{w}}_2|+|\hat{\mathbf{w}}_1\times\hat{\mathbf{v}}_2|\,\}+4ab^2|\hat{\mathbf{v}}_1\times\hat{\mathbf{v}}_2|+4ac^2|\hat{\mathbf{w}}_1\times\hat{\mathbf{w}}_2|\\ &+b^2c\{\,|\hat{\mathbf{u}}_1\cdot\hat{\mathbf{v}}_2|+|\hat{\mathbf{v}}_1\cdot\hat{\mathbf{u}}_2|\,\}+bc^2\{\,|\hat{\mathbf{u}}_1\cdot\hat{\mathbf{w}}_2|+|\hat{\mathbf{w}}_1\cdot\hat{\mathbf{u}}_2|\,\} , \end{aligned} \tag{4.5}$$

where we refer to the figure for the assignment of the molecular frames $\{\hat{\mathbf{u}}_i,\hat{\mathbf{v}}_i,\hat{\mathbf{w}}_i\}$ and the cross $\times$ denotes the exterior product, and the bars $|\cdots|$ length or absolute value of the contained expression. This pair-excluded volume has a broad minimum for parallel orientation of the two particles and we will assume that criterion (3.8) holds and that the smallest eigenvalue of K is found in the $l=2$ subspace. In order to apply the theory developed in Sec. III, we need to determine the coefficients $K_{2,mn}$ as defined in (2.13). This can be accomplished by exploiting various symmetry relationships among the orientation-dependent terms in (4.5); the details of these calculations are given in the Appendix. The results are

$$\begin{aligned} K_{2,00}&=\tfrac{1}{2}\pi^2\{b^2c-2bc^2+2\pi abc-2\pi ac^2-\tfrac{1}{2}\pi ab^2\} ,\\ K_{2,02}&=K_{2,20}=\tfrac{1}{2}\sqrt{3}\pi^2\{bc^2+\pi abc-\tfrac{1}{2}\pi ab^2\} ,\\ K_{2,22}&=-\tfrac{3}{2}\pi^2\{b^2c+\tfrac{1}{2}\pi ab^2\} . \end{aligned} \tag{4.6}$$

For convenience we now choose a as our unit of length. The bifurcation density is found from (3.6) and (3.9)

$$\rho_0^{-1}=\tfrac{1}{16}[\{(b^2c+\pi bc-\tfrac{1}{2}\pi c^2)^2+(bc^2+\pi bc-\tfrac{1}{2}\pi b^2)^2$$
$$-(b^2c+\pi bc-\tfrac{1}{2}\pi c^2)(bc^2+\pi bc-\tfrac{1}{2}\pi b^2)\}^{1/2}$$
$$-(\pi bc-\pi b^2-\pi c^2-b^2c-bc^2)] \ . \qquad (4.7)$$

Solving the crossover conditions (3.23) and (3.24) we find the following relationships for the dimensions of the particles intermediate between rods and plates:

$$b^2+\pi b-\tfrac{1}{2}\pi c=0 \text{ or } c^2+\pi c-\tfrac{1}{2}\pi b=0 \ . \qquad (4.8)$$

The symmetry with respect to the interchange of b and c reflects the arbitrariness of the assignment of the $\hat{\mathbf{v}}$ and $\hat{\mathbf{w}}$ axes of the particles. The fact that there are two distinct branches of crossover systems is easily understood by considering a one-parameter family of related particles with b fixed and c variable. For $c \gg b > 1$ we have a rodlike particle, for $c=b$ the particle is platelike, and finally for $c=1$ the particle is rodlike again. Somewhere between these three regimes we must find the two crossover shapes. Figure 5 shows how the relations (4.8) divide the spheroplatelets in to subclasses with specific symmetry-breaking behavior.

These results permit us to build a tentative picture of the phase diagram of the hard spheroplatelet fluid in the Onsager approximation. In order to compare systems with different particle dimensions, we adopt the proper volume of the particles $v_0=\frac{4}{3}\pi+\pi b+\pi c+2bc$ as unit of volume and introduce the packing fraction $\eta=\rho v_0$. Figure 6 presents a plausible constant particle volume section of the phase diagram within our approximation. The first-order transition lines to the nematic phases and the, probably second-order, transition lines to the biaxial phase are of course "artist's impressions." The overall picture, however, agrees with the findings on other models. It is clear that the crossover (Landau) points play a striking role in determining the global features of the phase diagram. Whether the actual phase diagram of the hard spheroplatelet fluid retains any of the features present in this approximation is an open question. Certainly at higher packing fraction one will need to consider the formation of more ordered phases, i.e., smectic, crystalline, which are here neglected . Especially as regards the existence of the biaxial liquid-crystalline state in these systems, result from computer simulations seem to be indispensable. Our results, however, give an indication of which systems to consider, namely, those of crossover type, since it is for these shapes that the biaxial phase might be accessible from the low-density isotropic regime. Of course, if existent at all, the actual crossover dimensions will probably differ from the ones predicted here. Nevertheless, we believe that for c sufficiently larger than unity the order of the relation predicted between b and c, i.e., $b \approx c^{1/2}$ is correct.

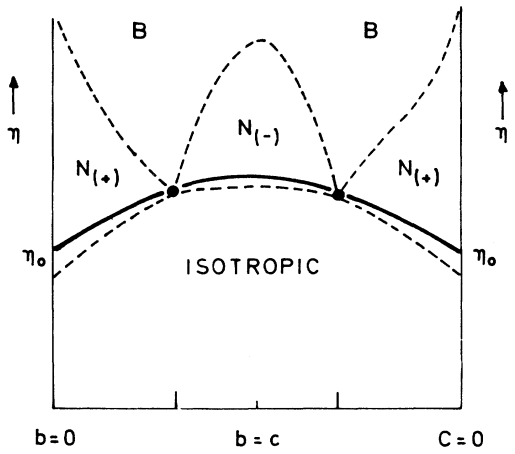

FIG. 6. Conjectured phase diagram of the hard spheroplatelet fluid in the Onsager approximations for a family of particles with constant volume v_0. Along the x axis we mark the progress from left to right along the dashed line defined in Fig. 5, along the y axis the packing fraction η. Solid line: calculated location of bifurcation. Closed circles: crossover points. Dashed lines: conjectured location of transitions between the phases.

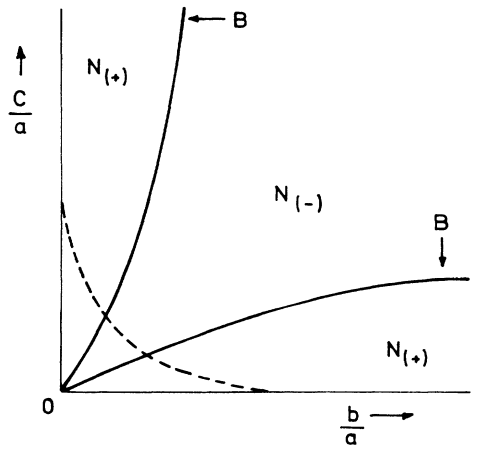

FIG. 5. Symmetry of bifurcating solutions as a function of the breadth b and length c at fixed width a of the spheroplatelets. Dashed line: family of particles with equal volume v_0.

C. Straley model

As a last application of our results, we turn to the first model to actually confront the full complexity of nonaxially symmetry orientational interactions.[11] Earlier work had either not incorporated a full set of order parameters[12] or had restricted itself to a lattice approximation with discrete orientations.[13] Straley was the first to introduce the order parameters (2.17). The model he proposed is of a hybrid type, being in the mean-field picture, but with the coefficients of the effective interaction fitted to the excluded volume of hard rectangular blocks with discrete orientations. The resulting parametrization of the effective interaction is complete in the sense that all values of the $K_{2,mn}$'s can be generated, albeit when we allow for negative particle dimensions. For positive values of his block parameters L (length), B (breadth), and W (width) his model trivially satisfies our requirement (3.8), since all higher-order eigenvalues are identically zero. Given our definitions for the $\Delta^{(2)}_{m,n}$'s and the expansion

(2.10) his coefficients are

$$K_{2,00}=\frac{8\pi^2}{5}[\tfrac{1}{3}\{-2B(W^2+L^2)-2W(B^2+L^2)+L(W^2+B^2)+6LBW\}], \quad (4.9a)$$

$$K_{2,02}=K_{2,20}=\frac{8\pi^2}{5}(\tfrac{1}{2}\sqrt{3})^{-1}[-\tfrac{1}{2}(L^2-BW)\times(B-W)], \quad (4.9b)$$

$$K_{2,22}=\frac{8\pi^2}{5}[-L(W-B)^2]. \quad (4.9c)$$

Two corrections have been made in Eqs. (4.9) with respect to the ones found in the printed version original paper. [In particular, the coefficients of the last term (LBW) in Eq. (4.9a) should read "6;" the prefactor $\frac{1}{2}$ of the quantity in square brackets in Eq. (4.9b) should carry a negative sign.] These errors where detected by applying our formulas for the crossover systems and finding disagreement with Straley's prediction that crossover occurs when $B=(LW)^{1/2}$. The discrepancy could be removed by making the indicated changes, which were, moreover, verified by recalculation of the original fitting procedure. The upshot of this is that, although its result is correct, as shown by his explicit numerical results, Straley's original argument for the location of crossover can*not* be correct. His argument is based on the observation that the transformation $(L,B,W)\rightarrow(L',B',W')=(W,LW/B,L)$, which maps a rodlike system with $L\gg B\approx W$ into a more platelike system with $B'\approx W'\gg L'$, induces the following transformation on the coefficient $K_{2,mn}$:

$$K'_{2,mn}=\frac{LW}{B^2}K_{2,mn}, \quad (4.10)$$

which therefore represents a system with identical interactions but at a different value of the control parameter $\lambda'=B^2/LW\lambda$. This immediately singles out the "self-dual" systems with dimensions $[L,(LW)^{1/2},W]$, which are fixed points of the transformation, leading Straley to the conclusion that the dividing line between rod and plate behavior is given by $B=(LW)^{1/2}$. Taking a closer look at the expressions (4.9) shows that they can all be written as linear combinations of the terms LBW, $L(B^2+W^2)$, $B(L^2+W^2)$, and $W(L^2+B^2)$ each of which independently satisfies the scaling (4.10). Thus all models whose interaction coefficients are given by arbitrary linear combinations of these terms would have their crossover predicted at $B=(LW)^{1/2}$, which, in view of our explicit expressions (3.23) and (3.24), cannot be the case. As remarked in Sec. IV B we expect this relation to be valid asymptotically, i.e., $L\gg B\approx W$ for all hard block-like particle models. The fact that in Straley's model this relation is exactly satisfied must be considered fortuitous. We conclude by giving the shape symmetry-breaking diagram for the model in Fig.7.

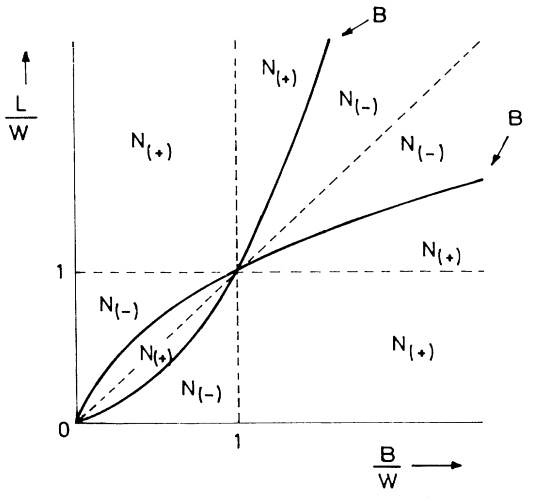

FIG. 7. Symmetry of bifurcation solutions as a function of block parameters of the Straley model. Dashed lines: uniaxially symmetry systems.

V. CONCLUDING REMARKS

The theory for the determination of the symmetries of the bifurcating solutions of the effective orientation-dependent pair interaction models presented here is clearly an elegant and useful tool for the questions considered. Care, however, has to be exercised in the interpretation of the results. Since the theory only deals with solutions (stable or metastable) that branch off from a known disordered solution, possibly stable solutions that do not connect to the reference solution are not taken into account. Especially cases where, due to the direction of bifurcation, the occurrence of a first-order transition is inferred merit caution. A pertinent example is the well-known observation by Alexander and McTague[14] that in the case of the liquid-solid transition symmetry considerations analogous to the ones employed here predict metastable crystalline solutions of bcc type, whereas the known stable crystalline phase often has a different symmetry. In these cases the bifurcating solution is thus pre-empted by a solution of different symmetry that does not bifurcate from the disordered phase. For the class of models considered here we were, of course, guided by more explicit numerical and analytic results on specific systems. We are thus confident of the interpretation given, but do not claim to have established generally that a phase diagram like the one presented in Fig. 6 exhausts the possibilities for the class of systems considered.

An obvious extension of the work done here would be to relax the symmetry imposed on the particles and consider, for instance, chiral particles. Of course, the relevant parameter space, i.e., the number of real numbers specifying the kernel K in the $l=2$ subspace, will grow in size, increasing the complexity of the problem. In the most general case of rigid particles with no assumed symmetry the parameter space will be effectively 14 dimensional. (There are 15 independent real components but an overall factor can always be absorbed into the definition of the coupling parameter λ.)

Another interesting development would be to go beyond the "mean-field" approximation for the free-energy functional and see which of the results derived

here remain valid. A possibility would be to study the contribution of a general diagram in the cluster expansion of the free energy to the symmetry properties at bifurcation.

Finally we remark that the theory developed here for orientation-dependent interactions is easily generalized to other types of interactions. Whenever the single-particle degrees of freedom are described by the elements of a (finite or compact) group G [in our case the rotation group SO(3)] the ODF's can be expanded in terms of the finite-dimensional irreducible representation matrices of this group and the effective interaction will be a Hermitian operator on the space spanned by the irreducible invariant vector spaces belonging to these representations. This reveals the essentially group-theoretical content of the approach, which, of course, closely parallels that of the Landau theory. The main difference is that it establishes an explicit link to interparticle interactions.

Note added in proof. Professor Straley has communicated to us that he has only recently become aware of the printing errors in his paper, as mentioned in Sec. IV C. In his calculations he has of course used the correct expressions for the expansion coefficients $K_{2,mn}$, as given by (4.9a)–(4.9c). Moreover, he points out that these expressions are the only ones consistent with the physically obvious requirements $K_{2,02}=K_{2,22}=0$ when $B=W$ (uniaxial particles), $K_{2,00}=0$ when $L=B=W$ (spherical particles), and one more requirement implementing the symmetry $L\leftrightarrow B$ at fixed W. This defuses the presented counterargument against the scaling rule for locating the crossover systems, since the proposed arbitrary linear combinations of basic scaling terms are not physically reasonable. What remains is complete agreement of the two methods for locating the crossover in the case of the model discussed. The power of the general method developed in this paper is that it does not rely on special properties of the interaction coefficients which are peculiar to a specific model. We are indebted to Professor Straley for his illuminating comments.

APPENDIX: DETERMINATION OF $K_{2,mn}$ FOR HARD SPHEROPLATELETS

In order to determine the coefficients $K_{2,mn}$ for the hard spheroplatelet fluid we have to consider the integrals

$$K_{2,mn}=\int d\Omega_{12}K(\Omega_{12})\Delta^{(2)}_{m,n}(\Omega_{12}) , \tag{A1}$$

where K is the pair-excluded volume explicitly given in (4.5). Consider two functions of relative orientation related through

$$f(\Omega_{12})=f(\Omega_1^{-1}\Omega_2)=g((\Omega_1 R_1)^{-1}\Omega_2 R_2) , \tag{A2}$$

where R_1 and R_2 are two given rotations. Integrals of the type (A1) over f can then be re-expressed into those over g through

$$\begin{aligned}\int d\Omega_{12}f(\Omega_{12})\Delta^{(2)}_{m,n}(\Omega_{12})&=\int d\Omega_{12}g(R_1^{-1}\Omega_{12}R_2)\Delta^{(2)}_{m,n}(\Omega_{12})\\&=\int d\Omega_{12}g(\Omega_{12})\Delta^{(2)}_{m,n}(R_1\Omega_{12}R_2^{-1}) .\end{aligned} \tag{A3}$$

TABLE I. Values of the integrals used in the calculation of the coefficients $K_{2,mn}$ for the hard spheroplatelet expressed in units of $8\pi^2$. The integrand is the product of the factors labeling the row and the column of the result.

	$\Delta^{(2)}_{0,0}$	$\Delta^{(2)}_{0,2}$	$\Delta^{(2)}_{2,0}$	$\Delta^{(2)}_{2,2}$
$\lvert\hat{\mathbf{w}}_1\times\hat{\mathbf{w}}_2\rvert$	$-\frac{\pi}{32}$	0	0	0
$\lvert\hat{\mathbf{v}}_1\times\hat{\mathbf{v}}_2\rvert$	$-\frac{\pi}{128}$	$-\frac{\pi}{128}\sqrt{3}$	$-\frac{\pi}{128}\sqrt{3}$	$-\frac{3\pi}{128}$
$\lvert\hat{\mathbf{v}}_1\times\hat{\mathbf{w}}_2\rvert$	$\frac{\pi}{64}$	0	$\frac{\pi}{64}\sqrt{3}$	0
$\lvert\hat{\mathbf{w}}_1\times\hat{\mathbf{v}}_2\rvert$	$\frac{\pi}{64}$	$\frac{\pi}{64}\sqrt{3}$	0	0
$\lvert\hat{\mathbf{w}}_1\cdot\hat{\mathbf{u}}_2\rvert$	$-\frac{1}{16}$	$\frac{1}{16}\sqrt{3}$	0	0
$\lvert\hat{\mathbf{u}}_1\cdot\hat{\mathbf{w}}_2\rvert$	$-\frac{1}{16}$	0	$\frac{1}{16}\sqrt{3}$	0
$\lvert\hat{\mathbf{v}}_1\cdot\hat{\mathbf{u}}_2\rvert$	$\frac{1}{32}$	$-\frac{1}{32}\sqrt{3}$	$\frac{1}{32}\sqrt{3}$	$-\frac{3}{32}$
$\lvert\hat{\mathbf{u}}_1\cdot\hat{\mathbf{v}}_2\rvert$	$\frac{1}{32}$	$\frac{1}{32}\sqrt{3}$	$-\frac{1}{32}\sqrt{3}$	$-\frac{3}{32}$

Choosing $R_1=Q_1=R(\pi/2,\hat{\mathbf{u}}_1)$ (a quarter turn around the $\hat{\mathbf{u}}_1$ axis) and likewise $R_2=Q_2=R(\pi/2,\hat{\mathbf{u}}_2)$, all orientation-dependent terms in the excluded volume can be related to the three expressions $\lvert\hat{\mathbf{w}}_1\cdot\hat{\mathbf{u}}_2\rvert$, $\lvert\hat{\mathbf{u}}_1\cdot\hat{\mathbf{w}}_2\rvert$, and $\lvert\hat{\mathbf{w}}_1\times\hat{\mathbf{w}}_2\rvert$, e.g., $\lvert\hat{\mathbf{v}}_1\times\hat{\mathbf{w}}_2\rvert=\lvert Q_1(\hat{\mathbf{w}}_1)\times\hat{\mathbf{w}}_2\rvert$, etc. These quarter turns respect the symmetry of our solution space $\mathcal{S}_\Omega$ and the basis functions $\Delta^{(l)}_{m,n}$ form an invariant set under their action

$$\begin{aligned}\Delta^{(2)}_{m,n}(Q_1\Omega_{12}Q_2^{-1})&=\Delta^{(2)}_{m,p}(Q_1)\Delta^{(2)}_{p,q}(\Omega_{12})\Delta^{(2)}_{q,n}(Q_2^{-1})\\&=\Delta^{(2)}_{m,p}(Q_1)\Delta^{(2)}_{n,q}(Q_2)\Delta^{(2)}_{p,q}(\Omega_{12}) ,\end{aligned} \tag{A4}$$

where summation over the appropriate ranges is implied. The Euler parameters for the quarter turns are given by $Q=(-\pi/2,\pi/2,\pi/2)$. As matrices realized on the basis $\{\Delta^{(2)}_{0,0},\Delta^{(2)}_{0,2},\Delta^{(2)}_{2,0},\Delta^{(2)}_{2,2}\}$ they are given by

$$\mathbb{Q}_1=\begin{bmatrix}-\frac{1}{2}&0&-\frac{1}{2}\sqrt{3}&0\\0&-\frac{1}{2}&0&-\frac{1}{2}\sqrt{3}\\-\frac{1}{2}\sqrt{3}&0&\frac{1}{2}&0\\0&-\frac{1}{2}\sqrt{3}&0&\frac{1}{2}\end{bmatrix} ,$$

$$\mathbb{Q}_2=\begin{bmatrix}-\frac{1}{2}&-\frac{1}{2}\sqrt{3}&0&0\\-\frac{1}{2}\sqrt{3}&\frac{1}{2}&0&0\\0&0&-\frac{1}{2}&-\frac{1}{2}\sqrt{3}\\0&0&-\frac{1}{2}\sqrt{3}&\frac{1}{2}\end{bmatrix} . \tag{A5}$$

The integrals left to be calculated are

$$\begin{aligned}&\int d\Omega_{12}\,\lvert\hat{\mathbf{w}}_1\times\hat{\mathbf{w}}_2\rvert\,\Delta^{(2)}_{m,n}(\Omega_{12}) ,\\&\int d\Omega_{12}\,\lvert\hat{\mathbf{w}}_1\cdot\hat{\mathbf{u}}_2\rvert\,\Delta^{(2)}_{m,n}(\Omega_{12})=\int d\Omega_{12}\,\lvert\hat{\mathbf{u}}_1\cdot\hat{\mathbf{w}}_2\rvert\,\Delta^{(2)}_{m,n}(\Omega_{12}) ,\end{aligned} \tag{A6}$$

where we have used $\Delta^{(2)}_{m,n}(\Omega_{12})=\Delta^{(2)}_{n,m}(\Omega_{21})$ to obtain the last identity. The only nonzero contributions come from the following integrals:

$$\int d\Omega_{12}|\hat{\mathbf{w}}_1\times\hat{\mathbf{w}}_2|\Delta^{(2)}_{0,0}(\Omega_{12})=(2\pi)^2\int_{-1}^{1}d\xi[1-\xi^2]^{1/2}P_2(\xi)=8\pi^2\{-\pi/32\}\ ,$$
$$\int d\Omega_{12}|\hat{\mathbf{w}}_1\cdot\hat{\mathbf{u}}_2|\Delta^{(2)}_{0,0}(\Omega_{12})=2\pi\int_0^{2\pi}d\gamma|\cos\gamma|\int_{-1}^{1}d\xi[1-\xi^2]^{1/2}P_2(\xi)$$
$$=8\pi^2\{-\tfrac{1}{16}\}\ , \tag{A7}$$
$$\int d\Omega_{12}|\hat{\mathbf{w}}_1\cdot\hat{\mathbf{u}}_2|\Delta^{(2)}_{0,2}(\Omega_{12})=\tfrac{1}{2}\sqrt{3}(2\pi)\int_0^{2\pi}d\gamma|\cos\gamma|\cos2\gamma\int_{-1}^{1}d\xi[1-\xi^2]^{3/2}P_2(\xi)$$
$$=8\pi^2\{\tfrac{1}{16}\sqrt{3}\}\ .$$

The relevant integrals can now all be calculated using the elements described above. We tabulate them in Table I.

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