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Solution of the excluded volume problem for biaxial particles

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We report the solution of the excluded volume problem for a pair of biaxial hard molecules; namely, sphero-platelets. As an application of this result we study the isotropic to nematic liquid crystal transition for a fluid composed of these particles in the Onsager limit (length $\gg$ breadth or width). We show that the range of stability of the isotropic phase decreases with increasing particle biaxiality.

1. Introduction

Hard particle fluids play a major role as models and reference systems for a wide variety of systems, varying from simple monatomic liquids to colloidal suspensions of molecular aggregates. At present, however, only the hard sphere fluid can be regarded as being adequately understood on a theoretical level [1]. Non-spherical hard particle systems studied so far were either formed by assemblies of fused hard spheres or convex shapes with one axis of rotational symmetry. The latter type of model has been extensively applied in the field of liquid crystal research [2]. This application was pioneered by Onsager [3], who was able to show how excluded volume effects can account for the transition to an orientationally ordered fluid phase in a system for very elongated hard rods. A crucial ingredient of this theory, as well as of most of its successors, is the determination of the pair excluded volume of the particles involved. Explicit analytical results for this quantity have been obtained so far for circular cylinders, sphero-cylinders [3] and ellipsoids of revolution [4]. As real molecules are in general not uniaxially symmetric, it is natural to inquire about the role of particle biaxiality in this type of model. This problem has already received some attention, but was studied either through effective potential approximations [5–8] or models with restricted particle orientations [9, 10]. It is our aim to carry the understanding of the role of particle biaxiality in hard particle fluids one step further, by giving, to our knowledge, the first explicit derivation of the excluded volume of two biaxial bodies with arbitrary fixed relative orientation. This paper is organized as follows. In §2 we introduce our biaxial particle, namely the sphero-platelet, and solve the excluded volume problem for sphero-platelets. Section 3 discusses order parameters and expansions of orientational distribution functions relevant to this system. As an application of our result the isotropic–nematic transition of the sphero-platelet fluid is studied in the Onsager limit in §4, resulting in a prediction for the upper-bound in the density of the transition as a function of particle biaxiality. Some conclusions and ideas for further research are presented in §5.

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2. Sphero-platelets and their excluded volume

The biaxial convex body we introduce is a direct generalization of the well-known sphero-cylinder, if we interpret this shape in a novel way. Instead of looking at it as a cylinder of length L and radius a capped with two hemispheres of the same radius, we can consider it to be the set bounded by those points, whose smallest distance to a straight line piece of length L is equal to a. More precisely (the concepts from the theory of convex bodies employed here can be found in [11]) the sphero-cylinder is a parallel body of a line piece. Using the definition of Minkowski addition we can denote it as

$$\mathrm{SC} = \mathscr{L} \oplus \mathscr{B}_a = \{\mathbf{x} \,|\, \mathbf{x} = \mathbf{l} + \mathbf{b}, \mathbf{l} \in \mathscr{L}, \mathbf{b} \in \mathscr{B}_a\}, \tag{2.1}$$

where $\mathscr{L}$ is a line piece of length L and $\mathscr{B}_a$ a sphere of radius a. The biaxial sphero-platelet immediately follows if we take a rectangular platelet as basis instead of a line piece, as illustrated in figure 1. Formally we have

$$\mathrm{SP} = \mathscr{R} \oplus \mathscr{B}_a, \tag{2.2}$$

where $\mathscr{R}$ is a rectangular platelet of length c and breadth b, where, as in the following we assume $c \geqslant b \geqslant a$. We recover the familiar cases of a sphero-cylinder and a sphere by setting b or b and c to zero respectively.

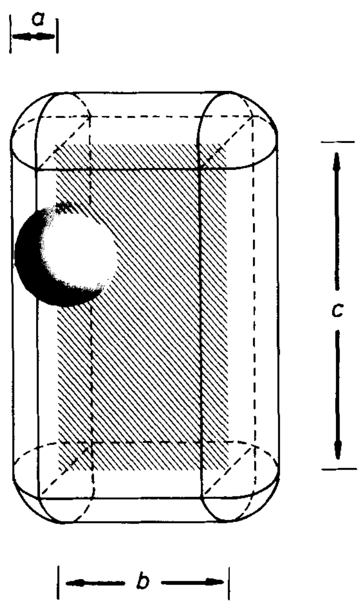

Figure 1. The sphero-platelet obtained by Minkowski adding a platelet and a sphere.

The quantity we are interested in is the excluded volume of two sphero-platelets with fixed orientations. The excluded volume $E(A, B)$ of two sphero-platelets, A and B, can be expressed as the volume of the Minkowsi sum of the two bodies

$$\begin{aligned} E(A, B) &= V[A \oplus B] = V[\mathscr{R}_A \oplus \mathscr{B}_a) \oplus (\mathscr{R}_B \oplus \mathscr{B}_a)], \\ &= V[(\mathscr{R}_A \oplus \mathscr{R}_B) \oplus \mathscr{B}_{2a}]. \end{aligned} \tag{2.3}$$

Here V is the volume-functional, and commutativity and associativity of Minkowski addition were applied. From equation (2.3) we see that we have to determine the volume of the parallel-body of radius $2a$ of the convex polyhedron $\mathscr{P}_{AB} = \mathscr{R}_A \oplus \mathscr{R}_B$. The volume of the parallel body of radius ϱ of a polyhedron $\mathscr{P}$ is given by the Steiner formula

$$V[\mathscr{P} \oplus \mathscr{B}_\varrho] = V[\mathscr{P}] + S[\mathscr{P}]\varrho + M[\mathscr{P}]\varrho^2 + \frac{4\pi}{3}\varrho^3, \tag{2.4}$$

where S is the surface-area functional and M the edge-curvature defined as

$$M[\mathscr{P}] = \frac{1}{2}\sum_{\text{edges}} s_j \Phi_j, \tag{2.5}$$

where s_j is the length of the edge j and Φ_j the angle between the normals of the faces meeting at edge j.

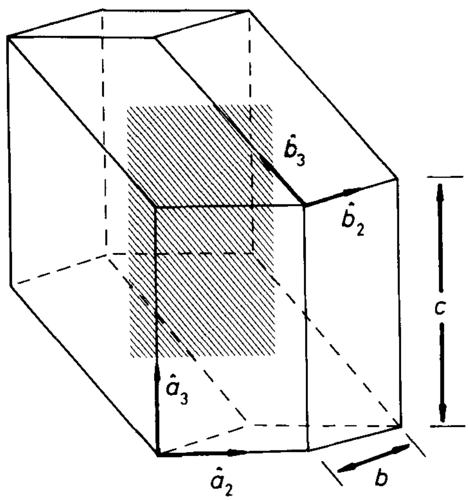

Figure 2. The polyhedron $\mathscr{P}_{AB}$; the excluded volume of two identical rectangular platelets.

We describe the sphero-platelets by orthonormal frames $\{\hat{a}_j\}_{j=1,2,3}$ and $\{\hat{b}_j\}_{j=1,2,3}$ with the 1 direction normal to the basis platelet. Figure 2 shows the polyhedron $\mathscr{P}_{AB}$ for a typical pair of orientations. Note that $\mathscr{P}_{AB}$ is generated by sweeping out space as platelet B moves with its centre over all points of platelet A. The frames of A and B are linked by a cartesian rotation

$$\hat{b}_l = \Omega_{lj}\hat{a}_j. \tag{2.6}$$

We start by determining the volume $V[\mathscr{P}_{AB}]$. This will be done in two stages. (i) Determine the volume of the parallepiped $\tilde{\mathscr{R}}$ that is generated as $\mathscr{R}_B$ is transported over a distance b in the $\hat{a}_2$ direction. (ii) Determine $V[\mathscr{P}_{AB}]$ as the volume swept out by $\tilde{\mathscr{R}}$ as it is transported over a distance c in the $\hat{a}_3$ direction. When a solid body S is transported over a distance d in the direction $\hat{n}$, the volume swept out is given by

$$\tilde{V} = dA(S, \hat{n}) + V[S], \tag{2.7}$$

where $V[S]$ is the volume of S and $A(S, n)$ the area of the projection of S on a plane perpendicular to $\hat{n}$ (cf. figure 3). We find

$$\begin{aligned} V[\tilde{\mathscr{R}}] &= bA(\mathscr{R}_B, \hat{a}_2), \\ &= b|\operatorname{Proj}(b\hat{b}_2; \hat{a}_2) \wedge \operatorname{Proj}(c\hat{b}_3, \hat{a}_2)|, \end{aligned} \tag{2.8}$$

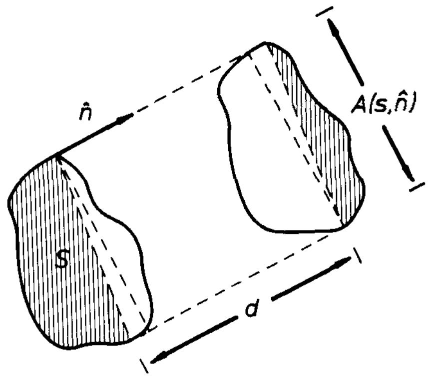

Figure 3. A two-dimensional illustration of the dependence of the volume swept out by a translation of a solid body S in a direction $\hat{n}$, on the volume of the body, the distance of translation and the projection of the body on a plane normal to $\hat{n}$.

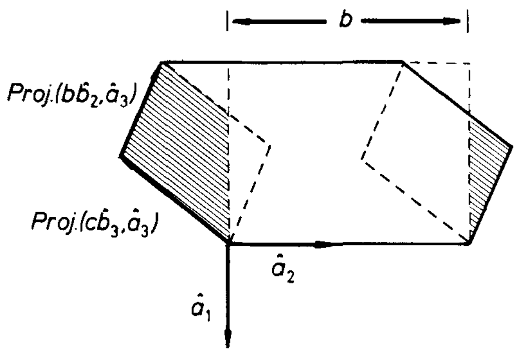

Figure 4. Construction of the projected area $A(\tilde{\mathscr{R}}, \hat{a}_3)$, showing that it is equal to the area of the projection of B on the $(\hat{a}_1, \hat{a}_2)$ plane plus the area of the rectangle formed by the diameter of this projection and the translation over a distance b along $\hat{a}_2$.

where Proj $(\mathbf{v}, \hat{\mathbf{n}})$ denotes the projection of the vector $\mathbf{v}$ on the plane with normal $\hat{\mathbf{n}}$, and $\wedge$ is the vector exterior product. Using equation (2.6) this works out as

$$\begin{aligned} V[\tilde{\mathscr{R}}] &= b^2c|\Omega_{23}\Omega_{31} - \Omega_{21}\Omega_{33}|, \\ &= b^2c|\Omega_{12}|. \end{aligned} \tag{2.9}$$

The second step consists of another application of equation (2.7)

$$V[\mathscr{P}_{AB}] = cA(\tilde{\mathscr{R}}, \hat{a}_3) + V[\tilde{\mathscr{R}}]. \tag{2.10}$$

The computation of $A(\tilde{\mathscr{R}}, \hat{a}_3)$ is illustrated in figure 4;

$$\begin{aligned} A(\tilde{\mathscr{R}}, \hat{a}_3) &= |\mathrm{Proj}\,(b\hat{b}_2,\, \hat{a}_3) \wedge \mathrm{Proj}\,(c\hat{b}_3,\, \hat{a}_3)| + b\{|b\hat{b}_2 \cdot \hat{a}_1| + |c\hat{b}_3 \cdot \hat{a}_1|\} \\ &= bc\{|\Omega_{13}| + |\Omega_{31}|\} + b^2|\Omega_{21}|. \end{aligned} \tag{2.11}$$

Thus

$$V[\mathscr{P}_{AB}] = b^2c\{|\Omega_{12}| + |\Omega_{21}|\} + bc^2\{|\Omega_{13}| + |\Omega_{31}|\}. \tag{2.12}$$

The surface area of $\mathscr{P}_{AB}$ is the sum of the areas of the twelve faces, that are pairwise the same (cf. figure 2). We have

$$\begin{aligned} S[\mathscr{P}_{AB}] &= 2bc|\hat{a}_2 \wedge \hat{a}_3| + 2b^2|\hat{a}_2 \wedge \hat{b}_2| + 2bc|\hat{a}_2 \wedge \hat{b}_3| \\ &\quad + 2bc|\hat{b}_2 \wedge \hat{b}_3| + 2bc|\hat{a}_3 \wedge \hat{b}_2| + 2c^2|\hat{a}_3 \wedge \hat{b}_3| \\ &= 4bc + 2b^2\{\Omega_{21}^2 + \Omega_{23}^2\}^{1/2} + 2bc\{\Omega_{31}^2 + \Omega_{33}^2\}^{1/2} \\ &\quad + 2bc\{\Omega_{21}^2 + \Omega_{22}^2\}^{1/2} + 2c^2\{\Omega_{31}^2 + \Omega_{32}^2\}^{1/2}. \end{aligned} \tag{2.13}$$

The edge curvature of $\mathscr{P}_{AB}$ is easily read off from inspection of figure 2,

$$M[\mathscr{P}_{AB}] = 2\pi b + 2\pi c. \tag{2.14}$$

Combining these results with equation (2.4) yields the explicit form of the excluded volume

$$\begin{aligned} E(A,B) &= \frac{32\pi a^3}{3} + 8\pi a^2 b + 8\pi a^2 c + 8abc + 4abc\{\Omega_{21}^2 + \Omega_{22}^2\}^{1/2} \\ &\quad + 4abc\{\Omega_{31}^2 + \Omega_{33}^2\}^{1/2} + 4ab^2\{\Omega_{21}^2 + \Omega_{23}^2\}^{1/2} + 4ac^2\{\Omega_{31}^2 + \Omega_{32}^2\}^{1/2} \\ &\quad + b^2c\{|\Omega_{21}| + |\Omega_{12}|\} + bc^2\{|\Omega_{31}| + |\Omega_{13}|\}. \end{aligned} \tag{2.15}$$

Inserting the expressions for the rotation matrix elements in terms of the standard Euler angles (α, β, γ) our final result becomes

$$\begin{aligned} E(A,B) &= \frac{32\pi a^3}{3} + 8\pi a^2 b + 8\pi a^2 c + 8abc + 4abc\{(\cos^2\alpha\sin^2\beta + \cos^2\beta)^{1/2} \\ &\quad + (\cos^2\gamma\sin^2\beta + \cos^2\beta)^{1/2}\} + 4ab^2\{(\sin^2\alpha\sin^2\beta\sin^2\gamma + \cos^2\alpha\sin^2\gamma \\ &\quad + \sin^2\alpha\cos^2\gamma + 2\sin\alpha\cos\alpha\cos\beta\sin\gamma\cos\gamma)^{1/2}\} + 4ac^2|\sin\beta| \\ &\quad + b^2c\{|\cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma| + |\sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma|\} \\ &\quad + bc^2\{|\cos\alpha\sin\beta| + |\cos\gamma\sin\beta|\}. \end{aligned} \tag{2.16}$$

As a check on this formula we compute its average over all relative orientations. The integrals involved are of two types

and

$$\left.\begin{aligned} \frac{1}{8\pi^2}\int d\Omega_B|(\hat{a}_k \cdot \hat{b}_l)| &= \tfrac{1}{2} \\ \frac{1}{8\pi^2}\int d\Omega_B|(\hat{a}_k \wedge \hat{b}_l)| &= \frac{\pi}{4}. \end{aligned}\right\} \tag{2.17}$$

We obtain

$$\bar{E}_{A,B} = \frac{32\pi a^3}{3} + 8\pi a^2 b + 8\pi a^2 c + 8abc + 2\pi abc + \pi ab^2 + b^2 c + bc^2. \tag{2.18}$$

Using an elegant integral geometrical formula, the orientation averaged excluded volume can be expressed purely in quantities related to a single sphero-platelet

$$\bar{E}_{A,B} = 2V[A] + 2M[A]S[A]. \tag{2.19}$$

Here $V[A]$ is the volume, $M[A]$ the surface averaged mean curvature and $S[A]$ the surface area. The volume and surface area are

$$\left.\begin{aligned} V[A] &= \frac{4\pi}{3}a^3 + \pi a^2 b + \pi a^2 c + 2abc, \\ S[A] &= 4\pi a^2 + 2\pi ab + 2\pi ac + 2bc. \end{aligned}\right\} \tag{2.20}$$

The surface averaged mean curvature is defined as

$$M[A] = \frac{1}{4\pi}\int dS_A \frac{1}{2}\left\{\frac{1}{R_1} + \frac{1}{R_2}\right\}, \tag{2.21}$$

where R_1, R_2 are the principal radii of curvature, and dS_A an element of surface area. For the sphero-platelet only the spherical and cylindrical parts contribute,

$$\begin{aligned} M[A] &= \frac{1}{4\pi}\left\{4\pi a^2 \frac{1}{a} + (2\pi ab + 2\pi ac)\frac{1}{2a}\right\} \\ &= a + \tfrac{1}{4}b + \tfrac{1}{4}c. \end{aligned} \tag{2.22}$$

Inserting these results in equation (2.19) leads to identity with equation (2.18).

3. Order parameters and distribution functions

In this section we address the definition of order parameters and orientational distribution functions relevant to fluids composed of biaxial particles. This problem has been discussed by several authors [5, 6, 8], mainly concerned with a correct description of biaxial liquid-crystalline phases. Straley was the first to argue, in reference to a specific model he constructed, that a set of four order parameters would be necessary and sufficient [6]. We rederive this observation here, showing how it relates to assumptions about the symmetries of the molecules as well as the symmetries of the phases we wish to describe. Consider particles possessing (like the sphero-platelet) three mutually orthogonal planes of mirror symmetry. The orientation of such a particle with respect to a fixed reference frame can be specified by giving two unit vectors, $\hat{u}$ and $\hat{v}$, chosen orthogonal to two of the mirror planes (cf. figure 5). These unit vectors can be used to build two tensorial second rank order parameters

$$\left.\begin{aligned} \mathbf{U} &= \langle \hat{u} \otimes \hat{u} \rangle, \\ \mathbf{V} &= \langle \hat{v} \otimes \hat{v} \rangle, \end{aligned}\right\} \tag{3.1}$$

and

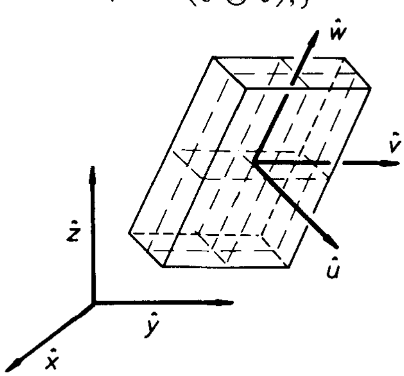

Figure 5. A biaxial particle with three orthogonal mirror planes and the molecular frame $\{\hat{u}, \hat{v}, \hat{w}\}$ associated with it.

where $\otimes$ denotes the direct product and the brackets signify equilibrium averaging. $\mathbf{U}$ and $\mathbf{V}$ are symmetric and have trace unity ($\mathrm{Tr}(\mathbf{U}) = \hat{u}\cdot\hat{u} = 1$), so in principle contain five independent elements each. Due to the orthogonality of $\hat{u}$ and $\hat{v}$, one extra relation exists, leaving nine independent elements in all. Focusing on spatially homogeneous but possibly anisotropic phases, we now inquire into the conditions necessary to be able to diagonalize simultaneously $\mathbf{U}$ and $\mathbf{V}$. Introducing an orientational distribution function $\psi(\Omega)$ describing the phase and a measure on the orientations $d\Omega$, we write the averages in equation (3.1) as integrals, for example

$$\mathbf{U} = \int d\Omega\, \psi(\Omega)\, \hat{u}(\Omega) \otimes \hat{u}(\Omega). \tag{3.2}$$

Forming the commutator of $\mathbf{U}$ and $\mathbf{V}$ we find

$$[\mathbf{U},\mathbf{V}]_{ij} = \varepsilon_{ijl} \int d\Omega \int d\Omega'\, \psi(\Omega)\, \psi(\Omega')(\hat{u}(\Omega)\cdot\hat{v}(\Omega'))\,(\hat{u}(\Omega) \wedge \hat{v}(\Omega'))_l, \tag{3.3}$$

where summation over l is implied. Considering the invariance of the measure under reflections, and the axial nature of the exterior product, we find that $[\mathbf{U},\mathbf{V}]$ will vanish if the distribution described by $\psi(\Omega)$ has three mutually orthogonal mirror symmetry planes. In that case the simultaneous diagonalization can be carried through and we are left with four independent matrix elements. The relatively natural assumption that a spatially homogeneous phase will have a symmetry higher or equal to that of the constituent particles, is the basis of this result. We now turn to the question of which order parameters to use in practice. To this end we define a set of functions to serve as a basis for the expansion of the orientational distribution function, consistent with these conditions on the phase and particle symmetry. We start with an expansion of the distribution function in terms of the standard rotation matrix elements (throughout we employ the conventions of [12])

$$\psi(\Omega) = \sum a_L^{m,n} \mathscr{D}^L_{m,n}(\Omega), \tag{3.4}$$

where the summation runs over L and m, n in their appropriate ranges. The assumption that both phase and particles possess three mutually orthogonal mirror planes leads to the following facts:

(i) only terms with L, m and n even contribute;

(ii) the expansion coefficients satisfy the identities,

$$a_L^{m,n} = a_L^{m,-n} = a_L^{-m,n} = a_L^{-m,-n}.$$

We therefore introduce the functions

$$Q^L_{m,n}(\Omega) = (\tfrac{1}{2}\sqrt{2})^{2+\delta_{m,0}+\delta_{n,0}}\{\mathscr{D}^L_{m,n}(\Omega) + \mathscr{D}^L_{m,-n}(\Omega) + \mathscr{D}^L_{-m,n}(\Omega) + \mathscr{D}^L_{-m,-n}(\Omega)\},$$
$$m, n \geqslant 0 \tag{3.5}$$

and expand

$$\psi(\Omega) = \sum q_L^{m,n} Q^L_{m,n}(\Omega), \tag{3.6}$$

where L takes on only even values and m and n even, non-negative values. The $Q^L_{m,n}$'s are real functions satisfying the orthogonality conditions

$$\int d\Omega\, Q^L_{m,n}(\Omega)\, Q^{L'}_{m',n'}(\Omega) = \frac{8\pi^2}{2L+1}\,\delta_{L,L'}\delta_{m,m'}\delta_{n,n'}. \tag{3.7}$$

They also form a closed set under composition of rotations in the sense that

$$\int d\Omega' \, Q^L_{m,n}(\Omega\Omega') \, Q^{L'}_{m',n'}(\Omega') = \frac{8\pi^2}{2L+1} \delta_{L,L'} \delta_{n,n'} Q^L_{m,m'}(\Omega). \tag{3.8}$$

Specializing to the case $L = 2$, we find the following set of four functions

$$\left.\begin{aligned} Q^2_{0,0}(\Omega) &= \tfrac{1}{2}(3\cos^2\beta - 1), \\ Q^2_{2,0}(\Omega) &= \tfrac{1}{2}\sqrt{3}\sin^2\beta\cos 2\alpha, \\ Q^2_{0,2}(\Omega) &= \tfrac{1}{2}\sqrt{3}\sin^2\beta\cos 2\gamma, \\ Q^2_{2,2}(\Omega) &= \tfrac{1}{2}(1 + \cos^2\beta)\cos 2\alpha\cos 2\gamma - \cos\beta\sin 2\alpha\sin 2\gamma. \end{aligned}\right\} \tag{3.9}$$

These are, apart from some normalization constants, the functions employed by Straley. The associated order parameters are

$$\left.\begin{aligned} q_2^{0,0} &= \langle Q^2_{0,0}\rangle, & q_2^{2,0} &= \langle Q^2_{2,0}\rangle, \\ q_2^{0,2} &= \langle Q^2_{0,2}\rangle, & q_2^{2,2} &= \langle Q^2_{2,2}\rangle. \end{aligned}\right\} \tag{3.10}$$

All four parameters are identically zero in an isotropic phase. If the phase has azimuthal symmetry around the preferred z axis, the parameters $q_2^{2,0}$ and $q_2^{2,2}$ vanish, showing that they signal the appearance of a biaxial phase. $q_2^{0,0}$ and $q_2^{0,2}$ describe uniaxial phases, the first being equal to the Maier–Saupe order parameter $S = \langle P_2(\cos\beta)\rangle$.

4. Onsager theory

Since no truly satisfactory theory for the equation of state of hard particle fluids at finite packing fractions exists at present [13] we shall look at a limiting case where the information on the excluded volume of the sphero-platelets we have obtained can be put to full advantage. We pass to the so-called Onsager limit where we let the length c of the particles tend to infinity, while the average excluded volume, and hence the second virial coefficient B_2, are kept finite. In this limit Onsager was able to show that the third virial coefficient B_3 vanishes as

$$\frac{B_3}{B_2^2} = \left(\frac{k}{c^3}\right)\log\left(\frac{c^3}{k}\right),$$

where k is a constant [3]. Higher order virial coefficients are expected to decrease even more rapidly as function of c, an effect that has been observed in numerical calculations of these quantities [14]. If we now make a density expansion of the free energy functional [15], we need to take into account only terms linear in the density

$$\beta\tilde{f}[\psi] = \int d\Omega\,\psi(\Omega)\log\psi(\Omega) + \varrho\tilde{B}_2[\psi] + \tilde{f}_0(\beta,\varrho), \tag{4.1}$$

where $\tilde{f}$ is the free-energy per particle, β is the inverse temperature, $\tilde{f}_0$ does not depend on the orientational distribution function, and $\tilde{B}_2[\psi]$ is the second virial coefficient defined as

$$\tilde{B}_2[\psi] = \frac{1}{2}\int d\Omega \int d\Omega'\,\psi(\Omega)\,\psi(\Omega')\,\tilde{E}(\Omega,\Omega'). \tag{4.2}$$

$\tilde{E}$ is the excluded volume of two sphero-platelets with fixed orientations in the

Onsager limit, hence

$$\begin{aligned}\tilde{E}(\Omega, \Omega') &= \tilde{E}(\Omega'^{-1}\Omega) \equiv \tilde{E}(\Omega_R), \\ &= \varepsilon\{\sin\beta + \Delta \sin\beta(|\cos\alpha| + |\cos\gamma|)\},\end{aligned} \tag{4.3}$$

where we have introduced the finite quantities $\varepsilon = 4ac^2$, $\Delta = \frac{1}{4}(b/a)$ and the relative orientation $\Omega_R = \Omega'^{-1}\Omega = (\alpha, \beta, \gamma)$. This is easily obtained from equation (2.16) and our definition of the Onsager limit. A necessary requirement for equilibrium is that the free energy be stationary under variations of the orientational distribution function. This leads to the familiar equation for the distribution function

$$\log\psi(\Omega) + \varrho \int d\Omega' \, \psi(\Omega') \, \tilde{E}(\Omega, \Omega') = K, \tag{4.4}$$

where K is a constant related to the normalization of ψ. We shall not attempt to obtain the full solution to equation (4.4) here, but concentrate on the more modest question of finding an upper bound on the density of the stability of the isotropic fluid phase. The method we employ is a bifurcation analysis of the non-linear integral equation (4.4), closely following Kayser and Raveché [16], who were the first to apply this technique to the isotropic–nematic transition of the sphero-cylinder fluid. The essence of the procedure is to linearize equation (4.4) around the isotropic distribution, which is a solution at every density, and then determine the density at which this linearized equation admits solutions corresponding to an ordered phase. The mathematical background to the technique is discussed in Krasnosel'skii [17].

We first introduce a perturbation to the isotropic distribution through

$$\psi(\Omega) = \frac{1}{8\pi^2}[1 + \chi(\Omega)], \tag{4.5}$$

where due to the normalization of the distribution function we have

$$\int d\Omega \, \chi(\Omega) = 0. \tag{4.6}$$

Insertion into equation (4.1) and linearizing then yields

$$\chi(\Omega) = -\frac{\varrho}{8\pi^2} \int d\Omega' \, \tilde{E}(\Omega, \Omega') \, \chi(\Omega'). \tag{4.7}$$

Since non-zero values of the four order parameters introduced in equations (3.9) and (3.10) are a sufficient criterion for ordering, we take the perturbation to be of the form

$$\chi(\Omega) = \sum q_2^{m,n} Q_{m,n}^2(\Omega). \tag{4.8}$$

Since the excluded volume as a function of the relative orientation Ω_R possesses the same symmetries we have assumed for the distribution functions, we can expand

$$\tilde{E}(\Omega, \Omega') = \sum e_L^{m,n} Q_{m,n}^L(\Omega_R). \tag{4.9}$$

We refer to the Appendix for an explicit evaluation of the expansion coefficients $e_L^{m,n}$. Using equations (4.8) and (4.9) the linearized equation (4.7) is turned into a matrix eigenvalue problem,

$$\left\{\frac{8\pi^2}{\varrho}\delta_{s,n} + e_2^{s,n}\right\} q_2^{m,s} = 0. \tag{4.10}$$

Although there are four components $q_2^{m,n}$, the independence of equation (4.10) on the first index shows that the problem factorizes into two identical 2×2 problems, involving the order parameter pairs $(q_2^{0,0}, q_2^{0,2})$ and $(q_2^{2,0}, q_2^{2,2})$ respectively. The matrix $e_2^{s,n}$ has only two independent non-zero elements, that can be evaluated with the help of the Appendix

$$\left.\begin{aligned} e_2^{0,0} &= \varepsilon[A_2 + 2\Delta B_2^0] = -8\pi^2\varepsilon\left[\frac{\pi}{32} + \frac{\Delta}{8}\right] \equiv -8\pi^2\varepsilon\mu, \\ e_2^{2,0} &= e_2^{0,2} = \sqrt{2}\varepsilon\Delta B_2^2 = 8\pi^2\varepsilon\frac{\Delta\sqrt{3}}{16} \equiv 8\pi^2\varepsilon\nu. \end{aligned}\right\} \tag{4.11}$$

Introducing the dimensionless density $d = \varrho\varepsilon$, the bifurcation density d^* is determined by the largest positive root of

$$\begin{vmatrix} \dfrac{1}{d} - \mu & \nu \\ \nu & \dfrac{1}{d} \end{vmatrix} = \frac{1}{d^2} - \frac{\mu}{d} - \nu^2 = 0. \tag{4.12}$$

and so

$$\frac{1}{d^*} = \tfrac{1}{2}\mu + \tfrac{1}{2}[\mu^2 + 4\nu^2]^{1/2}. \tag{4.13}$$

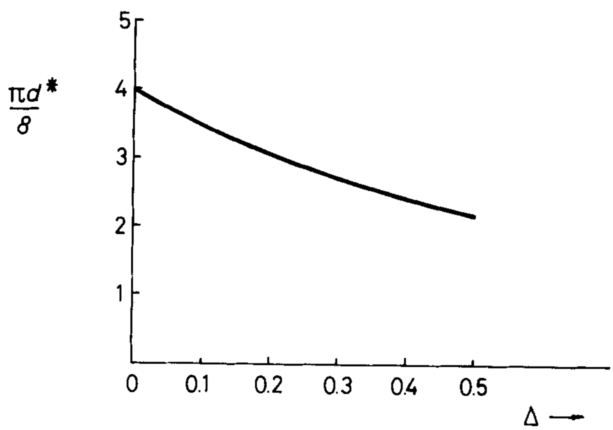

Figure 6. Plot of $\frac{1}{8}\pi d^*$, where d^* is the bifurcation density, as a function of the biaxiality parameter Δ.

In figure 6 we have plotted d^* as a function of the molecular biaxiality parameter Δ. For the case $\Delta = 0$ corresponding to the sphero-cylinder in the Onsager limit we see that

$$\tfrac{1}{8}\pi d^*(\Delta = 0) = \varrho^* B_2(\Delta = 0) = 4, \tag{4.14}$$

which reproduces the result of [16]. We note that ϱ^* decreases as the biaxiality Δ is increased. This is analogous to the increase in the corresponding temperature T^* in Straley's model [6]. Since we are dealing with the isotropic–nematic transition, the information in the subspace spanned by the biaxial order parameters $(q_2^{2,0}, q_2^{2,2})$ is redundant, and consistent solutions to equation (4.10) are obtained by setting them equal to zero.

Experience with other models [6, 8, 10] has shown that at a certain particle biaxiality, marking the cross over from rod-like to plate-like behaviour, the system should show an isotropic-to-biaxial transition of second order, at the meeting point of the first order transition lines to the rod-like and plate-like uniaxial phases. An analysis of the direction of bifurcation as function of the biaxiality should be able to identify this point, where all four order parameters become non-zero simultaneously. Unfortunately this cannot be studied in the context of the present model, as the cross over from rods to plates occurs in a regime where the length and the breadth of the particle are of the same order ($b \sim c$). This is a regime where Onsager's results no long apply, and a more elaborate free energy functional would have to be constructed.

5. Conclusions

The explicit solution of the excluded volume problem of sphero-platelets is a starting point for the study of the role of particle biaxiality in hard particle fluids. The Onsager limit provides a well defined, albeit somewhat unrealistic, case for testing our ideas on these systems. Our preliminary result on the upper bound of the stability of the isotropic phase as a function of particle biaxiality, however, is interesting in its own right. Since the relative distance $(\varrho^* - \varrho_T)/\varrho^*$, where ϱ^* is the bifurcation density and ϱ_T the actual transition density, between the limits of absolute and thermodynamic stability of the isotropic phase is known to be quite small ($\sim$ 10 per cent), we can infer that particle biaxiality lowers the transition density.

As a next step we could study all the solutions to the variational equation for the equilibrium orientational distribution function (cf. equation (4.4)) and thus obtain information on the actual location of the isotropic–nematic transition as well as the expected biaxial phase. Unfortunately this is a somewhat dubious application, as Onsager's argument on the disappearance of higher order virial coefficients is no longer valid for strongly ordered systems, rendering the free energy functional in equation (4.1) inadequate.

The physically more interesting case of systems at finite packing fractions is correspondingly harder to tackle. We could, given our result for the excluded volume of sphero-platelets, apply either scaled particle theory [2] or the y expansion [13] to predict the phase diagram of such systems. Given the state of the art, however, a critical comparison with data obtained by direct simulation seems indispensable. Especially predictions regarding the presence of a biaxial liquid-crystalline phase, merit some caution until more definite evidence of their existence is gathered.

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Appendix

In this Appendix we evaluate the coefficients in the expansion

$$\tilde{E}(\Omega) = \sum \left(\frac{2L+1}{8\pi^2}\right) e_L^{p,q} Q_{p,q}^L(\Omega), \tag{A 1}$$

where $\tilde{E}(\Omega)$ is the excluded volume of two sphero-platelets in the Onsager limit

$$\tilde{E}(\Omega) = \varepsilon[\sin\beta + \Delta\sin\beta\{|\cos\alpha| + |\cos\gamma|\}]. \tag{A 2}$$

The coefficients can be expressed in terms of integrals over rotation matrices

$$e_L^{p,q} = (\sqrt{2})^{2-\delta_{p,0}-\delta_{q,0}} \int d\Omega\, \tilde{E}(\Omega)\, \mathscr{D}_{p,q}^L(\Omega). \tag{A 3}$$

Introducing

$$\left.\begin{aligned} A_L &= \int d\Omega \sin\beta \mathscr{D}_{0,0}^L(\Omega), \\ B_L^m &= \int d\Omega \sin\beta |\cos\alpha| \mathscr{D}_{m,0}^L(\Omega), \end{aligned}\right\} \tag{A 4}$$

the coefficient $e_L^{p,q}$ can be expressed as

$$e_L^{p,q} = \varepsilon(\sqrt{2})^{2-\delta_{p,0}-\delta_{q,0}}\{A_L\delta_{p,0}\delta_{q,0} + \Delta B_L^m\{\delta_{p,m}\delta_{q,0} + \delta_{p,0}\delta_{q,m}\}\}. \tag{A 5}$$

First we evaluate A_L

$$A_L = \int d\Omega \sin\beta \mathscr{D}_{0,0}^L(\Omega) = (2\pi)^2 \int_{-1}^{1} d\xi [1 - \xi^2]^{1/2} P_L(\xi). \tag{A 6}$$

The integral can be found in [18] as formula 7.132 (1)

$$A_L = (2\pi)^2 \frac{\pi}{4} \frac{\Gamma^2(\frac{1}{2})}{(\frac{1}{2}L + 1)\Gamma^2(\frac{1}{2}L + 1)(\frac{1}{2} - \frac{1}{2}L)\Gamma^2(\frac{1}{2} - \frac{1}{2}L)}. \tag{A 7}$$

Using the reflection formula for the Γ function this reduces to

$$A_L = -8\pi^2 \frac{1}{4} \frac{\Gamma^2(\frac{1}{2}L + \frac{1}{2})}{(\frac{1}{2}L + 1)\Gamma^2(\frac{1}{2}L + 1)(L - 1)}. \tag{A 8}$$

Turning to B_L^m we have

$$\begin{aligned} B_L^m &= \int d\Omega \sin\beta |\cos\alpha| \mathscr{D}_{m,0}^L(\Omega), \\ &= 2\pi \int_0^{2\pi} d\alpha \exp(-im\alpha)|\cos\alpha| \int_{-1}^{1} d\xi [1 - \xi^2]^{1/2} d_{m,0}^L(\xi), \\ &= 2\pi I_m \cdot J_L^m, \end{aligned} \tag{A 9}$$

where we have introduced the reduced matrix element

$$d_{m,0}^L(\xi) = \left\{\frac{(L - m)!}{(L + m)!}\right\}^{1/2} P_L^m(\xi). \tag{A 10}$$

The integral I_m is readily evaluated

$$I_m = 4\int_0^{\pi/2} d\alpha \cos m\alpha \cos\alpha = \frac{4(-)^{1/2m+1}}{(m + 1)(m - 1)}. \tag{A 11}$$

We introduce the following integral representation for the associated Legendre polynomial ([19, §4.6.2]; n.b. the formula given in [18] as 8.711.2 lacks the factor i^m)

$$P_L^m(\xi) = i^m \frac{(L + m)!}{L!} \frac{1}{\pi} \int_0^{\pi} d\Phi \cos m\Phi [\xi + (\xi^2 - 1)^{1/2} \cos\Phi]^L, \quad \xi \geq 0. \tag{A 12}$$

Since P_L^m is even for L, m even we have

$$J_L^m = 2i^m \frac{\{(L-m)!(L+m)\}^{1/2}}{L!}$$

$$\times \frac{1}{\pi} \int_0^1 d\xi \int_0^\pi d\Phi [1-\xi^2]^{1/2} \cos m\Phi [\xi + (\xi^2-1)^{1/2}\cos\Phi]^L$$

$$= i^m \frac{\{(L-m)!(L+m)!\}^{1/2}}{L!} \sum_{k=0}^{\frac{1}{2}L} (-)^k \binom{L}{2k}$$

$$\times \frac{B(\frac{1}{2}(L-2k+1), k+\frac{3}{2})}{2^{2k}(2k+1)B(\frac{1}{2}(2k+M+2), \frac{1}{2}(2k-M+2))},$$

where $B(x, y)$ is the Euler Beta function.

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