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Excluded volume for polydisperse spheroplatelets

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Excluded volume for polydisperse spheroplatelets

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Mulder's derivation of the excluded volume between a pair of identical biaxial spheroplatelets is extended to the case of non-identical particles. This result will be useful in the application of scaled particle theory to the monodisperse spheroplatelet fluid or in the study of a bidisperse spherocylinder—'square' spheroplatelet fluid mixture or a generally polydisperse spheroplatelet fluid.

Mulder recently presented an elegant derivation of the excluded volume between a pair of identical spheroplatelets with fixed arbitrary orientations [1]. A spheroplatelet is the geometrical object swept out by a sphere of radius a whose centre is restricted to a rectangular basis platelet of dimensions $b \times c$, where $c \geqslant b > 0$, and is the only non-axially symmetric convex body for which such a pair excluded volume is known in closed form. As Mulder points out this result is the first step towards a complete study of a fluid of biaxial particles and he suggests scaled particle theory as one possible approach to this problem. (Some information regarding the location of the isotropic–nematic transition in a fluid of monodisperse biaxial spheroplatelets has been determined using bifurcation analysis in the Onsager second virial limit [1, 2] and within a density functional approach [3].)

Application of scaled particle theory to this system of biaxial particles, however, requires knowledge of the pair excluded volume between a 'normal' spheroplatelet of dimensions a, b, c and a scaled version of the same particle, i.e. a spheroplatelet of dimensions $\delta_a a, \delta_b b, \delta_c c$, where $0 \leqslant \delta_a, \delta_b, \delta_c < \infty$ are dimensionless scaling parameters [4]. This pair excluded volume for non-identical spheroplatelets is derived via a straightforward generalization of Mulder's calculation. The excluded volume, $E(a, b, c; a', b', c'; \Omega, \Omega')$, between two spheroplatelets of dimensions a, b, c and a', b', c' whose orientations are given, with respect to a fixed laboratory frame, by the particle principle axes $\Omega = \{\hat{\mathbf{u}}, \hat{\mathbf{v}}, \hat{\mathbf{w}}\}$ and $\Omega' = \{\hat{\mathbf{u}}', \hat{\mathbf{v}}', \hat{\mathbf{w}}'\}$, respectively (where $\hat{\mathbf{u}}$ defines the normal to the basis platelet), is given by the following construction. First we consider just the $b \times c$ and $b' \times c'$ basis platelets of the two particles. From these we generate the convex polyhedron $\mathscr{P}$ by allowing the $b' \times c'$ platelet to move through space (in fixed orientation Ω') with its centre restricted to the $b \times c$ platelet (in fixed orientation Ω). From this polyhedron $\mathscr{P}$ a new geometrical object is generated by allowing a sphere of radius $a + a'$ to move through space with its centre restricted to the surface of $\mathscr{P}$. This defines the parallel body, of radius $a+a'$, of the polyhedron $\mathscr{P}$. The volume of this object is exactly the desired excluded volume $E(a,b,c;\, a',b',c';\Omega,\Omega')$. This volume is given by the Steiner formula in terms of the edge curvature, surface area and volume functionals of the polyhedron $\mathscr{P}$ ($M[\mathscr{P}]$, $S[\mathscr{P}]$ and $V[\mathscr{P}]$, respectively) as follows:

$$\begin{aligned}
E(a,b,c;a',b',c';\Omega,\Omega') &= \frac{4\pi}{3}(a+a')^3+(a+a')^2M[\mathscr{P}]+(a+a')S[\mathscr{P}]+V[\mathscr{P}] \\
&= \frac{4\pi}{3}(a+a')^3+\pi(a+a')^2(b+b')+\pi(a+a')^2(c+c') \\
&\quad +2(a+a')(bc+b'c') \\
&\quad +2(a+a')bc'|\hat{\mathbf{v}}\times\hat{\mathbf{w}}'|+2(a+a')b'c|\hat{\mathbf{w}}\times\hat{\mathbf{v}}'| \\
&\quad 2(a+a')bb'|\hat{\mathbf{v}}\times\hat{\mathbf{v}}'|+2(a+a')cc'|\hat{\mathbf{w}}\times\hat{\mathbf{w}}'| \\
&\quad +bb'\{c|\hat{\mathbf{u}}\cdot\hat{\mathbf{v}}'|+c'|\hat{\mathbf{v}}\cdot\hat{\mathbf{u}}'|\} \\
&\quad +cc'\{b|\hat{\mathbf{u}}\cdot\hat{\mathbf{w}}'|+b'|\hat{\mathbf{w}}\cdot\hat{\mathbf{u}}'|\}.
\end{aligned} \tag{1 a}$$

The specific reference to a laboratory frame can be eliminated by introducing the standard Euler angles α,β,γ ($0\leqslant\alpha,\gamma<2\pi; 0\leqslant\beta<\pi$) to describe the relative orientation between the two non-identical particles. This results in the somewhat less concise expression

$$\begin{aligned}
&E(a,b,c;a',b',c';\alpha,\beta,\gamma) \\
&\quad =\frac{4\pi}{3}(a+a')^3+\pi(a+a')^2(b+b')+\pi(a+a')^2(c+c')+2(a+a')(bc+b'c') \\
&\quad +2(a+a')bc'[\cos^2\alpha\sin^2\beta+\cos^2\beta]^{1/2} \\
&\quad +2(a+a')b'c[\cos^2\gamma\sin^2\beta+\cos^2\beta]^{1/2} \\
&\quad +2(a+a')bb'[\sin^2\alpha\sin^2\beta\sin^2\gamma+\cos^2\alpha\sin^2\gamma+\sin^2\alpha\cos^2\gamma \\
&\quad +2\sin\alpha\cos\alpha\cos\beta\sin\gamma\cos\gamma]^{1/2}+2(a+a')cc'|\sin\beta| \\
&\quad +bb'\{c|\sin\alpha\cos\gamma+\cos\alpha\cos\beta\sin\gamma|+c'|\cos\alpha\sin\gamma+\sin\alpha\cos\beta\cos\gamma|\} \\
&\quad +cc'\{b|\cos\alpha\sin\beta|+b'|\cos\gamma\sin\beta|\}.
\end{aligned} \tag{1 b}$$

Equation (1) is clearly symmetric with respect to particle exchange (noting that in equation (1 b) this requires the interchange of the angles α and γ due to the inversion of the Euler rotation matrix) and its validity can easily be tested for completely orthogonal particle configurations. The above result can also be verified in the limiting cases of identical spheroplatelets (i.e. $a'=a$, $b'=b$, $c'=c$) where we reproduce Mulder's result and non-identical spherocylinders ($b'=b=0$) where we recover Onsager's well-known expression [5].

In addition to its usefulness in the application of scaled particle theory to the spheroplatelet fluid this result can also be used to study a bidisperse spherocylinder—'square' spheroplatelet fluid mixture that is expected to display nematic phase behaviour similar to the biaxial spheroplatelet fluid, including one biaxial and two uniaxial phases [6, 7]. By setting $a'=a$, $c'=b'$ and $b=0$ in equation (1 b) we arrive at the pair excluded volume between a spherocylinder of radius a and cylinder length c and a 'square' spheroplatelet of dimensions a, b', b',

$$E(a, c; a, b', b'; \beta, \gamma) = \frac{32\pi}{3} a^3 + 8\pi a^2 b' + 4\pi a^2 c + 4ab'^2$$

$$+ 4ab'c\{[\cos^2 \gamma \sin^2 \beta + \cos^2 \beta]^{1/2} + |\sin \beta|\}$$

$$+ b'^2 c |\cos \gamma \sin \beta|. \qquad (2)$$

Equation (1) will also be useful in the study of a generally polydisperse spheroplatelet fluid consisting of spheres, spherocylinders and arbitrarily polydisperse biaxial spheroplatelets. Such a model may be useful as a starting point in the description of highly polydisperse colloidal systems such as aqueous solutions of micellar surfactants. A general study of monodisperse and polydisperse spheroplatelet fluids, utilizing the scaled particle theory approximation, is currently in progress. For the monodisperse system, preliminary results on the degree of particle biaxiality at the axial to planar nematic crossover are in agreement with the bifurcation analyses of [2, 3].

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