Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

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First published on: 13 July 2010

To cite this Article Bisi, Fulvio , Longa, Lech , Pajk, Grzegorz and Rosso, Riccardo(2010) 'Excluded-Volume Short-Range Repulsive Potential for Tetrahedral Molecules', Molecular Crystals and Liquid Crystals, 525: 1, 12 — 28
To link to this Article: DOI: 10.1080/15421401003795670
URL: http://dx.doi.org/10.1080/15421401003795670

Mol. Cryst. Liq. Cryst., Vol. 525: pp. 12–28, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421401003795670

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Excluded-Volume Short-Range Repulsive Potential for Tetrahedral Molecules

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Tetrahedral symmetry in nematic liquid crystals has been studied for several years, since the seminal paper by Fel [1]. Amongst statistical theories of nematic liquid crystals, a molecular mean-field model has proven to be quite effective in predicting phase sequences for thermotropic biaxial nematic molecules endowed with D_{2h} symmetry, as a function of the parameters entering their interaction potential [2,3]. This model has highlighted the role of a partially repulsive quadrupolar potential of mean torque in promoting condensed phases. It has been shown that the quadrupolar approximation to the excluded-volume interaction between hard spherocuboids can be written precisely as the superposition of two London interactions: one repulsive and one attractive [4]; furthermore, polar steric interactions have been shown to be capable of inducing orientationally ordered states possibly unexpected [5]. By adapting a numerical code available to the scientific community, we evaluate the analytical excluded volume function for non-convex tetrahedral molecules, modelled as chains of tangent hard spheres. Since this function is overly complicated, we expand it over a suitable set of Symmetry Adapted Wigner Functions (SAWFs).

Keywords Excluded volume; nematic liquid crystal; symmetry adapted; tetrahedral symmetry; Wigner rotation functions

1. Introduction

Tetrahedral symmetry in nematogenic molecules was studied in a series of pioneering papers by Fel [1,6] who drew attention on the fact that their treatment requires, at the lowest order of approximation, a third-rank order tensor rather than a second-rank order tensor, as in ordinary nematics. Fel developed a Maier-Saupe theory for such molecules and he discussed the peculiarities of Fréedericksz transition in

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compounds formed by achiral molecules. More recently, the coupling between biaxial and tetrahedral order has been advocated as a possible explanation for the uncommon behaviour of achiral banana liquid crystals that exhibit coexistence of left- and right-handed domains and a field-induced anisotropy of large magnitude [7,8]. Besides Fel's analysis of tetrahedral order, a general theory of banana liquid-crystals that resorts to a vector order parameter together with both a second- and a third-rank tensor order parameter was proposed in [9]. Computer simulations based on a lattice model consistent with tetrahedral symmetry have been recently performed too [10]. Here, we try to understand steric interactions between molecules with tetrahedral symmetry by determining the main qualitative features of the excluded volume for a pair of equal molecules. Since Onsager's well known paper [11], there has been a long quest for explicit expressions of the excluded volume for nematogenic molecules and, as a result, analytic formulae are known mostly for *convex* molecules with $D_{\infty h}$ symmetry—ellipsoids of revolution, spherocylinders—D_{2h} symmetry—biaxial ellipsoids, speheroplateles [12], spherocuboids [13]—and a few other cases embraced by the family of sphero-zonotopes [13]. For non-convex molecules, the excluded *area* has been computed explicitly for two-dimensional V-shaped molecules whose shape is obtained through a kinematic construction [14].

In a genuine three-dimensional environment, Teixeira *et al.* [15] considered a V-shaped molecule whose arms are formed by equal parallelepipeds and they computed the excluded volume for a pair of molecules at particular values of the relative orientation. They employed these values to *interpolate* the excluded volume, by expanding it on a set of Wigner rotation functions adapted to the symmetry of the arms. In this way, however, the absolute minimum of the excluded volume, which is attained when the molecules are *antiparallel*, was missed. The main quantitative features of the excluded volume for V-shaped molecules have been captured in [5]. In this paper, the excluded volume has been computed *analytically* by resorting to a model in which the molecules are conceived as aggregates of mutually tangent spheres. Here, we follow a similar avenue to compute the excluded volume for a pair of tetrahedral molecules, each formed by four arms which, in turn, are formed by a certain number of tangent spheres. We adapt the analytic procedure proposed in [16] that relies on stereographic projection. In principle, for many purposes such as simulations and assessment of the minimum value of the excluded volume, we need to know the excluded volume for *any* relative orientation; however, its analytic expression is too intricate, therefore we resort to an expansion on a set of symmetry-adapted Wigner rotation functions (SAWFs), whose expression is obtained by applying the format proposed, for instance, in [17–19]. To build such an expansion we need to evaluate the excluded volume for some selected configurations. We then conclude that the essential properties of the excluded volume V are captured by four coefficients of the expansion. In particular, it turns out that V fails to attain its absolute minimum when the molecules are parallel to one another, indicating that steric interaction could promote unexpected molecular packings.

2. Analytic Computation of the Excluded Volume

We compute the excluded volume for a pair of equal molecules endowed with tetrahedral symmetry T_d built by spherical units of radius r: for basic elements of group theory and for the notations and conventions adopted here, we refer the reader to Chapt. 3 of McWeeny's book [20]. The simplest arrangement is shown in Figure 1

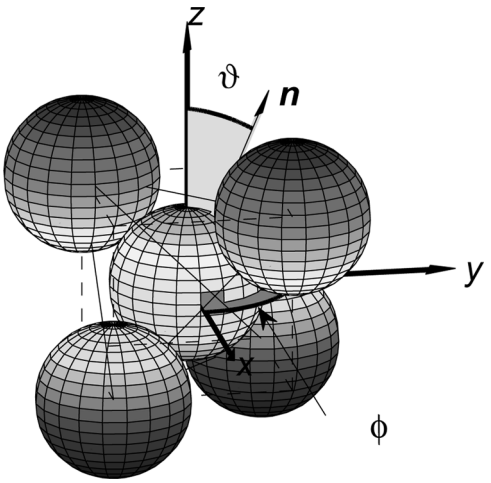

Figure 1. The reference molecule M_0 endowed with tetrahedral symmetry. It consists of five equal hard spheres. Precisely, there is a central sphere centred at the origin (0, 0, 0) and four peripheral spheres placed at $\left(\frac{\ell}{2},\frac{\ell}{2},\frac{\ell}{2}\right)$, $\left(-\frac{\ell}{2},-\frac{\ell}{2},\frac{\ell}{2}\right)$, $\left(-\frac{\ell}{2},\frac{\ell}{2},-\frac{\ell}{2}\right)$, and $\left(\frac{\ell}{2},-\frac{\ell}{2},-\frac{\ell}{2}\right)$. The molecule is placed so that the generators of the basic tetrahedral group are C_2^z, a π -rotation about the e_z-axis, and C_3^{xyz}, a rotation by $2\pi/3$ about the unit vector $3^{-1/2}(e_x+e_y+e_z)$. For any configuration, the positions of the two molecules $\mathcal{M}$ and $\mathcal{M}'$ are obtained upon rotating $\mathcal{M}_0$ of an angle $\psi/2$ about the direction **n**, defined by the angles ϑ and φ.

where a *central* sphere is placed at the origin of a set of Cartesian, orthogonal coordinates (x,y,z) and other four spheres are placed at four vertices of a cube with sides of length $\ell = \frac{4r}{\sqrt{3}}$. To fix the ideas, the occupied vertices have coordinates $\left(\frac{\ell}{2},\frac{\ell}{2},\frac{\ell}{2}\right)$, $\left(-\frac{\ell}{2},-\frac{\ell}{2},\frac{\ell}{2}\right)$, $\left(-\frac{\ell}{2},\frac{\ell}{2},-\frac{\ell}{2}\right)$, and $\left(\frac{\ell}{2},-\frac{\ell}{2},-\frac{\ell}{2}\right)$. Larger molecules with the same symmetry can be obtained by adding spheres along the diagonals of the cube directed as the unit vectors

$$\begin{aligned} \boldsymbol{e}_1^0 &:= \frac{1}{\sqrt{3}}(\boldsymbol{e}_x+\boldsymbol{e}_y+\boldsymbol{e}_z), \qquad \boldsymbol{e}_2^0 := \frac{1}{\sqrt{3}}(-\boldsymbol{e}_x-\boldsymbol{e}_y+\boldsymbol{e}_z), \\ \boldsymbol{e}_3^0 &:= \frac{1}{\sqrt{3}}(-\boldsymbol{e}_x+\boldsymbol{e}_y-\boldsymbol{e}_z), \qquad \boldsymbol{e}_4^0 := \frac{1}{\sqrt{3}}(\boldsymbol{e}_x-\boldsymbol{e}_y-\boldsymbol{e}_z). \end{aligned} \tag{1}$$

In [17], a procedure was proposed to compute *analytically* the volume and the surface area of aggregates consisting of spheres that could be either tangent or mutually intersecting. While we refer the reader to [16] for details, we outline here the basic steps of the method. Let us suppose that an aggregate $\mathcal{A}$ is formed by n intersecting spheres $\mathcal{S}_i$ $(i=1,\ldots,n)$. By the divergence theorem, the volume of $\mathcal{A}$ can be reduced to n surface integrals on $\partial\mathcal{A}_i$, the part of $\partial\mathcal{S}_i$ that lies outside *all* its neighbours. Taking a point on $\partial\mathcal{A}_i$ as the North Pole, the sphere S_i is projected stereographically onto its tangent plane Π at the South Pole. Hence, the circles along which $\mathcal{S}_i$ is cut by other spheres of the family are mapped into circles of Π and the surface integrals on $\partial\mathcal{A}_i$ become integrals on a *planar* domain bounded by circles. Application of the Gauss-Green formula reduces these latter integrals into *line* integrals along circular arcs that can be computed *analytically*. The crucial point is the determination

of the integration domain which depends ultimately on the original intersections of $\mathcal{S}_i$ with its neighbours.

This method is suited for our scopes since the excluded region of two molecules formed by spherical units is *still* the union of spheres that generally intersect themselves even if the spheres forming the molecules are tangent. To prove this, let us select a reference point O bound to molecule $\mathcal{M}$ and a point O' bound to $\mathcal{M}'$. For a given fixed relative orientation, the boundary of the excluded region is obtained by tracking the position of O' with respect to O when $\mathcal{M}'$ *glides* along the contour of $\mathcal{M}$. Now, when $\mathcal{M}$ and $\mathcal{M}'$ are in contact, there is at least a sphere of $\mathcal{M}$ that touches a sphere of $\mathcal{M}'$, while all the other spheres of $\mathcal{M}$ and $\mathcal{M}'$ do not intersect themselves. Let us suppose that $\mathcal{M}$ consists of n spheres $\mathcal{S}_i$ centred at $C_i \equiv (x_i, y_i, z_i)$, with radius r_i whereas $\mathcal{M}'$ consists of m spheres $\mathcal{S}'_j$ centred at $C'_j \equiv (x'_j, y'_j, z'_j)$ and with radius r'_j. When $\mathcal{S}_i$ and S'_j are in contact, the reference point O' of $\mathcal{M}'$ obeys

$$O' - O = (O' - C'_j) + (C'_j - C_i) + (C_i - O)$$

that can clearly be recast as

$$O' - O = (x_i - x'_j)\boldsymbol{e}_x + (y_i - y'_j)\boldsymbol{e}_y + (z_i - z'_j)\boldsymbol{e}_z + (r_i + r'_j)\boldsymbol{e}_r \tag{2}$$

where $\boldsymbol{e}_r$ is the unit vector joining the centres of the tangent spheres $\mathcal{S}_i$ and S'_j. By introducing the point K_{ij} such that

$$K_{ij} - O := (x_i - x'_j)\boldsymbol{e}_x + (y_i - y'_j)\boldsymbol{e}_y + (z_i - z'_j)\boldsymbol{e}_z$$

and setting $r_{ij} = r_i + r'_j$, we can write (2) as

$$O' - K_{ij} = r_{ij}\boldsymbol{e}_r$$

which states that, when the molecules are in contact with the spheres (C_i, r_i) and (C'_j, r'_j) mutually tangent, then the reference point O' of $\mathcal{M}'$ will move on the surface of a sphere with radius r_{ij} centred at the point K_{ij}. When $\mathcal{M}'$ explores all possible configurations that keep it in contact with $\mathcal{M}$ at a fixed relative orientation, O' will move on a certain set of these spheres (K_{ij}, r_{ij}). Moreover, points that lie on the boundary of the spheres (K_{ij}, r_{ij}) either belong to the boundary of the excluded region of $\mathcal{M}$ and $\mathcal{M}'$, or lie in the interior of this region. Thus, by intersecting all possible spheres (K_{ij}, r_{ij}) we obtain the whole excluded region, which generally consists of $n \times m$ spheres, a number that can decrease for particular values of the relative orientations at which some of the spheres coalesce together. Here we will consider the case $n = m$ and $r_i = r'_j = r$, so that the excluded region consists of spheres with radius $R = 2r$, to which all lengths of the problem are scaled. To exploit the symmetry of the problem, we introduce a *reference* molecule $\mathcal{M}_0$ placed as shown in Figure 1. Let us suppose that the rotation $\mathbf{Q}(\mathbf{n}, \psi)$ by an angle ψ about a unit vector $\mathbf{n}$ maps $\mathcal{M}$ into $\mathcal{M}'$, and let ϑ, ϕ be the polar angles of $\mathbf{n}$, defined according to Figure 1. It is clear that we can always obtain $\mathcal{M}'$ from $\mathcal{M}_0$ by a rotation $\mathbf{Q}(\mathbf{n}, \psi/2)$ and $\mathcal{M}$ from $\mathcal{M}_0$ by a rotation $\mathbf{Q}(\mathbf{n}, -\psi/2)$. By this device, the excluded region has the same symmetry as the referential molecule $\mathcal{M}_0$. If we suppose that, besides the sphere centred at the origin, $\mathcal{M}_0$ possesses N spheres along each arm, the centres C_k^{01} of the k-th sphere

placed along $\boldsymbol{e}_1^0$ are given by

$$C_k^{01} - O = 2kr\boldsymbol{e}_1^0 =: 2kr\mathbf{f}(\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z)$$

or, in dimensionless units,

$$C_k^{01} - O = k\mathbf{f}(\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z).$$

Hence, by looking at (1), we conclude that

$$C_k^{02} - O = k\mathbf{f}(-\boldsymbol{e}_x, -\boldsymbol{e}_y, \boldsymbol{e}_z), \tag{3a}$$
$$C_k^{03} - O = k\mathbf{f}(-\boldsymbol{e}_x, \boldsymbol{e}_y, -\boldsymbol{e}_z), \tag{3b}$$
$$C_k^{04} - O = k\mathbf{f}(\boldsymbol{e}_x, -\boldsymbol{e}_y, -\boldsymbol{e}_z). \tag{3c}$$

The positions of the centres C_k^1 of the spheres pertaining to the molecule $\mathcal{M}$ are then given by

$$C_k^1 - O = k\mathbf{Q}\left(\mathbf{n}, \frac{\psi}{2}\right)\boldsymbol{e}_1^0 = k\mathbf{f}_T(\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z, \mathbf{n}, \psi)$$

where it is expedient to adopt an intrinsic representation of the rotation $\mathbf{Q}\left(\mathbf{n}, \frac{\psi}{2}\right)$ as

$$\mathbf{Q}\left(\mathbf{n}, \frac{\psi}{2}\right) = \mathbf{I} + \sin\frac{\psi}{2}\mathbf{W}(\mathbf{n}) - \left(1 - \cos\frac{\psi}{2}\right)\mathbf{P}(\mathbf{n}), \tag{4}$$

where $\mathbf{I}$ is the identity tensor, $\mathbf{W}(\mathbf{n})$ is the skew-symmetric tensor associated with $\mathbf{n}$, whose action on an arbitrary vector $\mathbf{v}$ is given by $\mathbf{W}(\mathbf{n})\mathbf{v} = \mathbf{n} \times \mathbf{v}$, and $\mathbf{P}(\mathbf{n}) := \mathbf{I} - \mathbf{n} \otimes \mathbf{n}$ is the projector onto the plane orthogonal to $\mathbf{n}$. Finally, the spheres of $\mathcal{M}$ along the remaining arms are centred at

$$C_k^2 - O = k\mathbf{f}_T(-\boldsymbol{e}_x, -\boldsymbol{e}_y, \boldsymbol{e}_z, \mathbf{n}, \psi) \tag{5a}$$
$$C_k^3 - O = k\mathbf{f}_T(-\boldsymbol{e}_x, \boldsymbol{e}_y, -\boldsymbol{e}_z, \mathbf{n}, \psi) \tag{5b}$$
$$C_k^4 - O = k\mathbf{f}_T(\boldsymbol{e}_x, -\boldsymbol{e}_y, -\boldsymbol{e}_z, \mathbf{n}, \psi). \tag{5c}$$

Similarly, we conclude that the centres of the spheres that form the arms of $\mathcal{M}'$ are placed at

$$C_k^{1\prime} - O = k\mathbf{f}_T(\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z, \mathbf{n}, -\psi) \tag{6a}$$
$$C_k^{2\prime} - O = k\mathbf{f}_T(-\boldsymbol{e}_x, -\boldsymbol{e}_y, \boldsymbol{e}_z, \mathbf{n}, -\psi) \tag{6b}$$
$$C_k^{3\prime} - O = k\mathbf{f}_T(-\boldsymbol{e}_x, \boldsymbol{e}_y, -\boldsymbol{e}_z, \mathbf{n}, -\psi) \tag{6c}$$
$$C_k^{4\prime} - O = k\mathbf{f}_T(\boldsymbol{e}_x, -\boldsymbol{e}_y, -\boldsymbol{e}_z, \mathbf{n}, -\psi). \tag{6d}$$

Unlike the case of its original formulation, where the analytical method introduced in [17] is applied to the computation of the volume of molecules, i.e., of aggregates of

spheres with a certain known configuration, in our case in principle the excluded region has to be computed for any relative orientation of the molecules $\mathcal{M}$ and $\mathcal{M}'$. Then it is not surprising that, though obtained analytically, the excluded volume has an intricate expression to find which we should track the intersections of the circles obtained through stereographic projection as a function of the relative orientation: a prohibitive, if useful at all, task.

Hence, we followed a different strategy that amounts at expanding the excluded volume on a basis of symmetry-adapted Wigner rotation functions (SAWFs), and that can be summarised as follows:

1. We determine the set of SAWFs consistent with tetrahedral symmetry. This task is easier to perform if the group of rotations is parameterised in term of Euler angles.
2. The coefficients $a_{\ell mn}$ of the expansion of the excluded volume V on the set of SAWFs require the numerical evaluation of integrals involving the product of V with Wigner functions. We implement a Gauss-Legendre quadrature to compute these integrals; to do this we need to know V on a three-dimensional grid characterised by Euler angles $(\alpha_i, \beta_j, \gamma_k)$.
3. This in turn requires conversion from the intrinsic representation (4) of **Q** to that in terms of Euler angles.
4. Once the set $(\vartheta_i, \phi_j, \psi_k)$ corresponding to $(\alpha_i, \beta_j, \gamma_k)$ is obtained, we compute the excluded volume $f(\alpha_i, \beta_j, \gamma_k)$ by using the analytic procedure described above, together with the computer program ARVO associated with [16].
5. Thus, we can approximate the excluded volume $V(\alpha, \beta, \gamma)$ by computing a set of coefficients $a_{\ell mn}$ up to a certain value of ℓ.

2.1. *Symmetry-Adapted Wigner Functions*

The choice of the axes in Figure 1 ensures us that the excluded volume V, defined on the rotation group $SO(3)$, is symmetric under the basic tetrahedral group T with generators $\{C_2^z, C_3^{xyz}\}$, where C_2^z is a π-rotation about the $\boldsymbol{e}_z$-axis and C_3^{xyz} is a rotation by $2\pi/3$ about the axis $\mathbf{n} := \frac{1}{\sqrt{3}}(\boldsymbol{e}_x + \boldsymbol{e}_y + \boldsymbol{e}_z)$. Wigner D-functions form a basic set of functions on $SO(3)$. They are defined according to

$$D^{\ell}_{mn}(\alpha, \beta, \gamma) := \mathrm{e}^{-\imath(m\alpha + n\gamma)} d^{\ell}_{mn}(\beta) \tag{7}$$

where $\imath$ is the imaginary unit,

$$d^{\ell}_{mn}(\beta) := \sum_{t=t_m}^{t_M} (-1)^t \frac{[(\ell+m)!(\ell-m)!(\ell+n)!(\ell-n)!]^{1/2}}{(\ell+m-t)!(\ell-n-t)!t!(t+n-m)!} \times \left(\cos\frac{\beta}{2}\right)^{2\ell+m-n-2t} \left(\sin\frac{\beta}{2}\right)^{2t+n-m} \tag{8}$$

is a reduced Wigner function, and $\{\alpha, \beta, \gamma\}$ are the Euler angles parameterizing the relative rotation between the two molecules, defined according to the y-convention (*see*, e.g., pp. 50–52 of [21]). In (8), the summation is restricted to the integers t that make the factorials well defined, namely

$$t_m \le t \le t_M, \quad t_m := \max\{0, m-n\}, \quad t_M := \min\{\ell+m, \ell-n\}.$$

As a consequence of the Peter-Weyl theorem, Wigner D-functions form an orthogonal basis of $L^2(SO(3))$, the space of square-integrable functions defined on $SO(3)$, that is,

$$\langle D^{\ell_1}_{m_1 n_1}, D^{\ell_2}_{m_2 n_2} \rangle = \frac{8\pi^2}{2\ell_1 + 1} \delta_{\ell_1 \ell_2} \delta_{m_1 m_2} \delta_{n_1 n_2}, \tag{9}$$

where the scalar product $\langle f, g \rangle$ between two functions in $L^2(SO(3))$ is defined as

$$\begin{aligned} \langle f, g \rangle &:= \int_{SO(3)} f(\Omega) g^*(\Omega) \mathrm{d}\Omega \\ &= \int_0^{2\pi} \mathrm{d}\alpha \int_0^{\pi} \mathrm{d}\beta \sin\beta \int_0^{2\pi} \mathrm{d}\gamma f(\alpha, \beta, \gamma) g^*(\alpha, \beta, \gamma), \end{aligned} \tag{10}$$

where Ω is the invariant measure on $SO(3)$, parameterised by Euler angles and $*$ denotes complex conjugation. Hence, any function $f \in L^2(SO(3))$ can be expanded as

$$f(\alpha, \beta, \gamma) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \sum_{n=-\ell}^{\ell} a_{\ell m n} D^{\ell}_{mn}(\alpha, \beta, \gamma), \tag{11}$$

for a uniquely defined set of complex-valued coefficients $a^*_{\ell m n}$. It is not restrictive to assume that the excluded volume $V(\alpha, \beta, \gamma) \in L^2(SO(3))$ and then extend it as explained. Since

$$(D^{\ell}_{mn})^* = (-1)^{m-n} D^{\ell}_{\bar{m}\bar{n}} \tag{12}$$

where, for notational simplicity, we set $\bar{m} = -m$ [22], we conclude that the coefficients $a_{\ell m n}$ associated with a real-valued function like V obey the reality condition

$$a^*_{\ell \bar{m} \bar{n}} = (-1)^{m-n} a_{\ell m n} \tag{13}$$

in particular, the coefficients $a_{\ell 00}$ are real. Moreover, the excluded volume is symmetric against molecular exchange. This requirement amounts at saying that using a rotation or its inverse to go from a molecule to the other is irrelevant, and so $V(\alpha, \beta, \gamma) = V(-\gamma, -\beta, -\alpha)$. Now, since it can be proved that (*see* Eq. (4.21), p. 54 of [21])

$$D^{\ell}_{mn}{}^*(\alpha, \beta, \gamma) = D^{\ell}_{nm}(-\gamma, -\beta, -\alpha)$$

it is not difficult to check that swapping indices m and n yields the complex conjugate of the corresponding coefficients. In other words

$$a^*_{\ell m n} = a_{\ell n m}. \tag{14}$$

This expansion can be extended to improper rotations in $O(3) \backslash SO(3)$ by replacing $a_{\ell m n}$ with independent coefficients $(-1)^{\ell} b_{\ell m n}$. As remarked before, when two equal molecules have a certain symmetry, only SAWFs enter the expansion of V. These

SAWFs are closely related to symmetry-adapted spherical harmonics that have been obtained by resort to group-representation theory: [23,24]. In particular, the authors of [24] use Gaussian integration to obtain the coefficients that determine the linear combinations of symmetry-adapted spherical harmonics.

The relation between SAWFs and symmetry-adapted spherical harmonics is not surprising since (*see* p. 60 of [21])

$$D^{\ell}_{m0}(\alpha, \beta, 0) = \sqrt{\frac{4\pi}{2\ell + 1}} Y^{*}_{\ell m}(\beta, \alpha)$$

where $Y_{\ell m}$ is a spherical harmonic function.

To obtain the expression of SAWFs for the tetrahedral group T_d, we apply the method employed in [17] for D_{2h} molecules and in [19] for LO_h molecules. Compared with other methods employed for spherical harmonics, it requires a minimum knowledge of group-representation theory. A precise statement of symmetry for a function f is the following. Given a *real-valued* function f defined on the orthogonal group $O(3)$ and a symmetry point group $\mathcal{G} \subset O(3)$, f is invariant under the operations of $\mathcal{G}$ if, for any $g \in O(3)$ and $h \in \mathcal{G}$ [18]

$$f(g) = f(gh) = f(hg) \quad \forall g \in O(3), \quad \forall h \in \mathcal{G}. \tag{15}$$

To handle this requirement, we need only a basic result from representation theory, namely that, for a given ℓ the Wigner D-functions form an ℓ-dimensional representation of $SO(3)$ (*see* e.g., Chapt. 4 of [25]) and so, if g_1 and g_2 are any two elements of $SO(3)$, we have

$$D^{\ell}_{mn}(g_1 g_2) = \sum_{k=-\ell}^{\ell} D^{\ell}_{mk}(g_1) D^{\ell}_{kn}(g_2). \tag{16}$$

Clearly, it is sufficient to enforce the requirements (16) only on the *generators* of any symmetry group $\mathcal{G}$.

First, we show that invariance under C_2^z selects even values of both m and n, but does not constrain ℓ. In fact, the Euler angles (α, β, γ) associated with this rotation are $\alpha + \gamma = \pi$, $\beta = 0$ and so, (*see* Eq. (28) of [23])

$$D^{\ell}_{mn}(C_q) = \mathrm{e}^{\imath \pi m} \delta_{mn}.$$

By use of Eqs. (15) and (16) we conclude that $f(g) = f(gC_2^z)$ is equivalent to

$$\begin{aligned} &\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \sum_{n=-\ell}^{\ell} a_{\ell mn} D^{l}_{mn}(g) \\ &\quad = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \sum_{n=-\ell}^{\ell} a_{\ell mn} \sum_{k=-\ell}^{\ell} D^{l}_{mk}(g) D^{l}_{kn}(C_q) \\ &\quad = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \sum_{n=-\ell}^{\ell} a_{\ell mn} D^{l}_{mn}(g) \mathrm{e}^{\imath \pi n} \end{aligned} \tag{17}$$

and equality occurs for any $g \in SO(3)$ if and only if

$$e^{\imath\pi n} = 1,$$

that is, if and only if n is even. Similarly, by imposing $f(g) = f(C_q g)$ we conclude that m is even too. When g$\in O(3)\backslash SO(3)$, we obtain the same restrictions on $b_{\ell mn}$, this is true also for the following analysis.

To discuss the restrictions imposed by C_3^{xyz}, we first determine its Euler angles. Using Eqs. (4–10) in Sect. 3–4 of [26] we readily obtain $\alpha = 0$, $\beta = \frac{\pi}{2}$, and $\gamma = \frac{\pi}{2}$, and so

$$D^{\ell}_{mn}(C_3^{xyz}) = e^{-\imath\pi\frac{n}{2}} d^{\ell}_{mn}\left(\frac{\pi}{2}\right).$$

The reduced Wigner functions have a simpler expression when their argument is $\pi/2$ since the terms containing $\sin\frac{\beta}{2}$ and $\cos\frac{\beta}{2}$ boil down to a constant factor $2^{-\ell}$. These functions played an important rôle in the expansion of the excluded volume on a set of SAWFs for spheroplatelets [17] and spherocuboids [4]. They were employed in [27] to also convert expansions on Wigner D-functions into ordinary three-dimensional Fourier expansions. Their essential property, first noted by Wigner and published by Edmonds in [28], is that they can transform a rotation by an angle β about e_y into a rotation by β about e_z since

$$\mathbf{R}(0,\beta,0) = \mathbf{R}\left(-\frac{\pi}{2},0,0\right)\mathbf{R}\left(0,-\frac{\pi}{2},0\right)\mathbf{R}(\beta,0,0)\mathbf{R}(0,\frac{\pi}{2},0)\mathbf{R}\left(\frac{\pi}{2},0,0\right).$$

For future use, we record here the expression of $d^{\ell}_{mn}\left(\frac{\pi}{2}\right)$:

$$d^{\ell}_{mn}\left(\frac{\pi}{2}\right) = \sum_{t=t_m}^{t_M} (-1)^t 2^{-\ell} \frac{[(\ell+m)!(\ell-m)!(\ell+n)!(\ell-n)!]^{1/2}}{(\ell+m-t)!(\ell-n-t)!t!(t+n-m)!}, \tag{18}$$

where t_m and t^M have the same meaning as in Eq. (8). We now impose the invariance requirement $f(g) = f(gC_3^{xyz})$ obtaining

$$\begin{aligned} f(gC_3^{xyz}) &= \sum_{\ell,m,n} a_{\ell mn} \sum_{k=-\ell}^{\ell} {}^{e}D^{\ell}_{mk}(g) D^{\ell}_{kn}(C_3^{xyz}) \\ &= \sum_{\ell,m,n} a_{\ell mn} \sum_{k=-\ell}^{\ell} {}^{e}D^{\ell}_{mk}(g) e^{-\imath n\frac{\pi}{2}} d^{\ell}_{kn}\left(\frac{\pi}{2}\right) \\ &= \sum_{\ell,m,n} a_{\ell mn} D^{\ell}_{mn}(g) = f(g), \end{aligned} \tag{19}$$

where $\sum_k^{\ell} = -\ell^e$ means that only *even* values of k are selected, and summations on m and n are restricted to *even* values. By taking the scalar product with the D-function $D^{\ell_0}_{m_0 n_0}$ and using the orthogonality conditions (9) we arrive at

$$a_{\ell mn} = \sum_{k=-\ell}^{\ell} {}^{e}a_{\ell mk} (-1)^{\frac{k}{2}} d^{\ell}_{nk}\left(\frac{\pi}{2}\right), \tag{20}$$

where we replaced ℓ_0, m_0 and n_0 with ℓ, m, and n, we reintroduced k to denote the dummy index, and we observed that only even values of k are allowed by the presence of the generator C_2^z. We note that Equations (20) are unaffected by m so that if a condition holds on $a_{\ell mn}$ for a given m, it holds on all the admissible values of m. Similarly, by imposing the requirement $f(g) = f(C_3^{xyz} g)$, we obtain the system of equations

$$a_{\ell mn} = \sum_{k=-\ell}^{\ell} {}^{e}a_{\ell kn}(-1)^{\frac{m}{2}} d^{\ell}_{km}\left(\frac{\pi}{2}\right). \tag{21}$$

Due to the symmetry properties of the reduced functions $d^{\ell}_{mn}(\frac{\pi}{2})$ [30], we have

$$d^{\ell}_{mn}\left(\frac{\pi}{2}\right) = (-1)^{\ell+m} d^{\ell}_{m\bar{n}}\left(\frac{\pi}{2}\right)$$

to check it, it is sufficient to multiply (18) by $(-1)^{-(\ell+m)}$, set $t' = \ell + m - t$ in the summation and compare with the expression of $d^{\ell}_{m\bar{n}}$. By recalling the general property (*see* Eq. (4.19) of [21])

$$d^{\ell}_{mn}(\beta) = (-1)^{m-n} d^{\ell}_{\bar{m}\bar{n}}(\beta)$$

we conclude that in (20)

$$d^{\ell}_{nk}\left(\frac{\pi}{2}\right) = (-1)^{\ell} d^{\ell}_{\bar{n}k}\left(\frac{\pi}{2}\right)$$

since m and k are even numbers. Thus, $a_{\ell mn} = a_{\ell m\bar{n}}$, when $n \neq 0$ and ℓ is even, while $a_{\ell m\bar{n}} = a_{\ell mn}$ if ℓ is odd: in particular, $a_{\ell m0} = 0$ in this case. Moreover, since k and $-k$ have the same parity, we can rewrite (20) by considering only the terms with non-negative k and doubling the coefficients, that is

$$a_{\ell mn} = a_{\ell m0} d^{\ell}_{n0}\left(\frac{\pi}{2}\right) + 2\sum_{k=2}^{\ell} {}^{e}a_{\ell mk}(-1)^{\frac{k}{2}} d^{\ell}_{nk}\left(\frac{\pi}{2}\right), \tag{22}$$

with the stipulation that $a_{\ell m0} = 0$, if ℓ is odd. When ℓ is even we can recast (22) in the compact form

$$\mathbf{Ma} = \mathbf{0} \tag{23}$$

where the $\frac{\ell}{2}+1$-dimensional vector $\mathbf{a}$ is such that $(\mathbf{a})_j := a_{\ell m[\ell-2(j-1)]}$ while the $\left(\frac{\ell}{2}+1\right) \times \left(\frac{\ell}{2}+1\right)$ matrix $\mathbf{M}$ is such that

$$M_{ij} := (-1)^{\frac{\ell}{2}-(j-1)}[2 - \delta_{(\frac{\ell}{2}-(j-1)),0}] d^{\ell}_{\ell-2(i-1),\ell-2(j-1)} - \delta_{ij},$$

where δ_{ij} is the Kronecker delta. When ℓ is odd, $\mathbf{a}$ is a $\frac{\ell-1}{2}$-dimensional vector such that $(\mathbf{a})_j := a_{\ell m[\ell-1-2(j-1)]}$ and the entries of the $\frac{\ell-1}{2} \times \frac{\ell-1}{2}$ matrix $\mathbf{M}$ are now given by

$$M_{ij} = 2(-1)^{\frac{\ell-1}{2}-(j-1)} d^{\ell}_{\ell-1-2(i-1),\ell-1-2(j-1)}\left(\frac{\pi}{2}\right) - \delta_{ij}.$$

As to Eq. (21), it is the index n that plays an ancillary rôle now, so that, if a restriction holds on $a_{\ell mn}$ for a given value of n, it also holds for all admissible values of n. We still have $a_{\ell mn} = (-1)^{\ell} a_{\ell \bar{m} n}$ and by setting $(\mathbf{a})_j := a_{\ell[\ell-2(j-1)]n}$ it is possible to give (21) the structure $\mathbf{M}'\mathbf{a} = \mathbf{0}$ where

$$M'_{ij} := (-1)^{\frac{\ell}{2}-(i-1)}[2 - \delta_{(\frac{\ell}{2}-(i-1)),0}] d^{\ell}_{\ell-2(j-1),\ell-2(i-1)}\left(\frac{\pi}{2}\right) - \delta_{ij},$$

if ℓ is even, and

$$M'_{ij} = 2(-1)^{\frac{\ell-1}{2}-(i-1)} d^{\ell}_{\ell-1-2(j-1),\ell-1-2(i-1)}\left(\frac{\pi}{2}\right) - \delta_{ij},$$

if ℓ is odd. Since $d^{\ell}_{mn}(\vartheta) = (-1)^{m-n} d^{\ell}_{nm}(\vartheta)$ (p. 54 of [22]), it is possible to check that if we multiply $\mathbf{M}$ by the matrix $\mathbf{A}$ such that $(\mathbf{A})_{ij} := (-1)^{i+1}\delta_{ij}$, the Equations $\mathbf{AMa} = \mathbf{0}$ and $\mathbf{M}'\mathbf{a} = \mathbf{0}$ are equivalent. Since $\mathbf{A} = \pm\mathbf{A}^{-1}$, a vector $\mathbf{a}$ belongs to the kernel of $\mathbf{M}$ if and only if it belongs to the kernel of $\mathbf{M}'$. Hence, if certain restrictions are placed on the values of n, the same restrictions hold for the values of m.

The solution of Equation (23) can be obtained with the help of any computer program that performs symbolic computations. By using MAPLE® LinearAlgebra package we were able to characterise the non-trivial bases of the kernel of $\mathbf{M}$ up to $\ell = 16$: this bound was chosen to compare our results with those of [26]. As a result, Eq. (23) had only trivial solutions when $\ell = 1$, 2, and 5. To normalise the SAWFs to 1, we introduce the normalisation factor

$$\lambda_{\ell} := \sqrt{\frac{2\ell+1}{8\pi^2}}. \tag{24}$$

When $\ell = 0$, we clearly have the SAWF

$$\Delta^0_{00} = \lambda_0 D^0_{00}.$$

In general, the building blocks to obtain SAWFs are

$$\Delta^{\ell}_{mn} := \frac{\lambda_{\ell}}{2}\left(\frac{\sqrt{2}}{2}\right)^{\delta_{m0}+\delta_{n0}} \sum_{\sigma,\tau\in\{-1,1\}} D^{\ell}_{\sigma m,\tau n}, \tag{25}$$

when ℓ is even, and

$$\Delta^{\ell}_{mn} := \frac{\lambda_{\ell}}{2}\left(\frac{\sqrt{2}}{2}\right)^{\delta_{m0}+\delta_{n0}} \sum_{\sigma,\tau\in\{-1,1\}} (-1)^{(\sigma-\tau)/2} D^{\ell}_{\sigma m,\tau n} \tag{26}$$

when ℓ is odd. For instance, when $\ell = 3$ the kernel of $\mathbf{M}$ is spanned by

$$\mathbf{a} = a_{3m2}(1)$$

and so, since ℓ is odd, only the combination

$$a_{3m2}(D^3_{m2} - D^3_{m\bar{2}})$$

enters the expansion. By repeating the analysis for m we conclude that $m=0$ is ruled out from the expansion and that $a_{32n} = -a_{3\bar{2}n}$ so that the only admissible SAWF is

$$\Delta^3_{22} = \frac{\lambda_3}{2}[D^3_{22} - D^3_{2\bar{2}} - D^3_{\bar{2}2} + D^3_{\bar{2}\bar{2}}]$$

as given by (26). We point out that, the choice of a different frame for the reference molecule $\mathcal{M}_0$ would end up in a different set of SAWFs (for a different choice, *see* [10]).

When $\ell=4$, the kernel of $\mathbf{M}$ is spanned by

$$\mathbf{a} = a_{4m0}\begin{pmatrix} \sqrt{\frac{5}{14}} \\ 0 \\ 1 \end{pmatrix}$$

so that the following combination is allowed

$$a_{4m0}[D^4_{m0} + \sqrt{\frac{5}{14}}(D^4_{m4} + D^4_{m\bar{4}})],$$

since now ℓ is even and so $a_{4m4} = a_{4m\bar{4}}$. The parallel analysis on m rules out $m=\pm 2$ and imposes the restriction $a_{440} = a_{4\bar{4}0} = \sqrt{\frac{5}{14}}a_{400}$. Hence, a symmetric, real-valued function f has in its expansion only a term proportional to

$$\Delta^4_{00} + \sqrt{\frac{5}{7}}(\Delta^4_{40} + \Delta^4_{04}) + \frac{5}{7}\Delta^4_{44}.$$

When $\ell=6$ the kernel of $\mathbf{M}$ is two-dimensional and it is spanned by

$$\mathbf{a}_1 = a_{6m0}\begin{pmatrix} 0 \\ -\sqrt{\frac{7}{2}} \\ 0 \\ 1 \end{pmatrix} \quad \text{and} \quad \mathbf{a}_2 = a_{6m2}\begin{pmatrix} -\sqrt{\frac{5}{11}} \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

in particular, $\mathbf{a}_1$ rules out the coefficients a_{6m2} and a_{6m6}, while $\mathbf{a}_2$ rules out coefficients $a_{\ell m0}$ and $a_{\ell m4}$: equivalently, the pairs $n=2,\ 6$ $n=0,\ 4$ can never be mixed. A similar analysis holds for m and so coefficients like a_{6mn} vanish identically unless $m = n \pmod 4$. After normalisation, two terms are allowed, proportional to

$$\left[\Delta^6_{00} - \sqrt{7}(\Delta^6_{04} + \Delta^6_{40}) + 7\Delta^6_{44}\right], \quad \text{and} \tag{27a}$$

$$\left[\Delta^6_{22} - \sqrt{\frac{5}{11}}(\Delta^6_{26} + \Delta^6_{62}) + \frac{5}{11}\Delta^6_{66}\right], \tag{27b}$$

respectively. Hence, only two integrals are to be computed at this level, namely those expressing the coefficients a_{600} and a_{622}. (Up here we would have analysed group T to

complete the analysis for group T_d, we have to add the rotary inversion $S_4^{-2} = JC_4^2$ to the generators. This would yield $a_{\ell mn} = (-1)^{\ell+n/2}\ b_{\ell mn} = (-1)b_{\ell mn}$ which relates to the coefficients $a_{\ell mn}$ to their counterparts $b_{\ell mn}$. We can focus on the former to represent as a function on rotations.)

2.2. *Parameterisations of a Rotation*

While the parametrisation of **Q**, and hence of the excluded volume, in terms of **n** and ψ is extremely useful for computations, we have just seen that Wigner D-functions are naturally expressed in terms of the Euler angles (α, β, γ). Thus, we have to express the intrinsic representation (4) in terms of the Euler angles associated with **Q**. This goal is conceptually straightforward [26], as it requires only some care in inverting trigonometric functions. Details about our approach are reported elsewhere [30].

2.3. *Gaussian Quadrature*

To compute the coefficients

$$\alpha_{\ell mn} := \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma \int_0^{\pi} \sin\beta V(\alpha,\beta,\gamma)\Delta^{\ell}_{mn}(\alpha,\beta,\gamma)\mathrm{d}\beta \tag{28}$$

in the expansion of the excluded volume on a set of SAWFs we resorted to Gauss-Legendre integration. Since the integration domain in the (α, β, γ)-space is the full toroidal manifold $[0, 2\pi] \times [0, \pi] \times [0, 2\pi]$, we can compute the set of nodes and weights for a given integer N and for a normalised range $[-1, 1]$, where the nodes are the roots of Legendre polynomials, in one variable. By rescaling we obtain the integration mesh G_α along α, G_β along β, and G_γ along γ; subsequently, we build the three-dimensional mesh by taking $G_\alpha \times G_\beta \times G_\gamma$ [31]. In particular, to compute the terms to be added in the numerical quadrature expression, this procedure requires the knowledge of the integrand at certain specific nodes $(\alpha_i, \beta_j, \gamma_k)$. For any required set $(\alpha_i, \beta_j, \gamma_k)$, we compute the parameters $(\vartheta_i, \phi_j, \psi_k)$ that enter in (4). Through these value, and using the general procedure described in Sec. 2, we compute the centres of the spheres forming the excluded region that ARVO needs to compute the excluded volume $V(\vartheta_i, \phi_j, \psi_k) = V(\alpha_i, \beta_j, \gamma_k)$. Finally, through Gaussian integration we can evaluate numerically the coefficients $a_{\ell mn}$. By truncating the expansion we obtain an approximation of the excluded volume V. In Table 1 we

Table 1. Table reporting the values of the coefficient for approximation of the excluded volume function based on a truncation of its expansion. The coefficients α_{lmn} in Eq. (28) are used with the SAWFs (symmetry-adapted Wigner rotation functions); see Eq. (29)

l	m	n	α_{lmn}
0	0	0	400
3	2	2	12.7
4	0	0	−0.549
6	0	0	−0.300
6	2	2	0.627

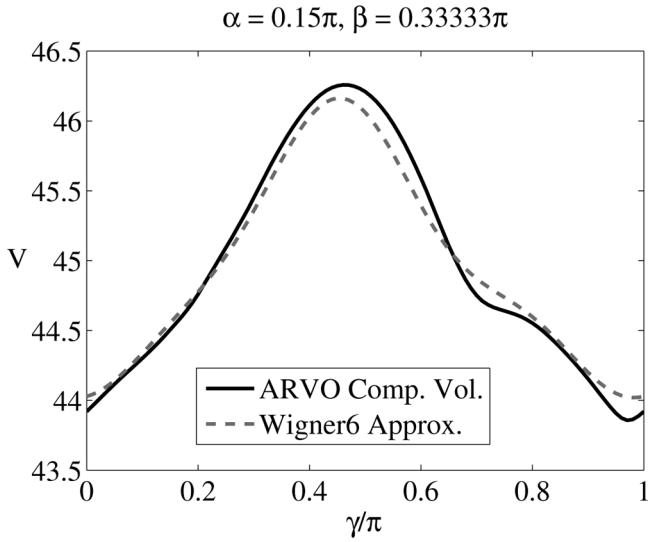

Figure 2. Plot of the excluded volume V against the angle of proper rotation γ, normalised to π, for $\alpha = 0.15\pi$ and $\beta = \pi/3$. V has been normalised to $4\pi/3$, i.e., the volume of a sphere of unit radius. The continuous line shows the actual profile of the excluded volume computed through stereographic projection with ARVO [16]; the dashed line is the approximation of V given by (29), with the coefficients $\alpha_{\ell mn}$ obtained using Gaussian integration, as explained in the text (see Table 1).

report the coefficients obtained with a number of nodes per dimension $N = 22$; these values are in fair agreement with an estimation of the coefficients obtained by computing the excluded volume on a regular linearly spaced lattice in the angles

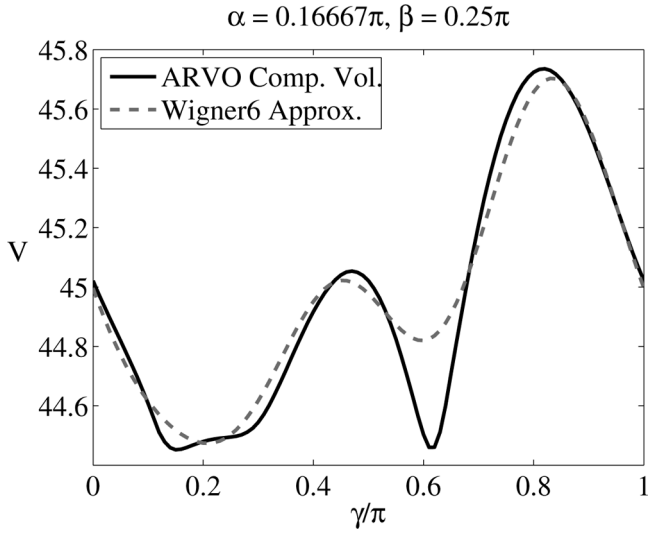

Figure 3. Plot of the excluded volume V against the angle of proper rotation γ, normalised to π, for $\alpha = \pi/6$ and $\beta = \pi/4$. Details as in Figure 2.

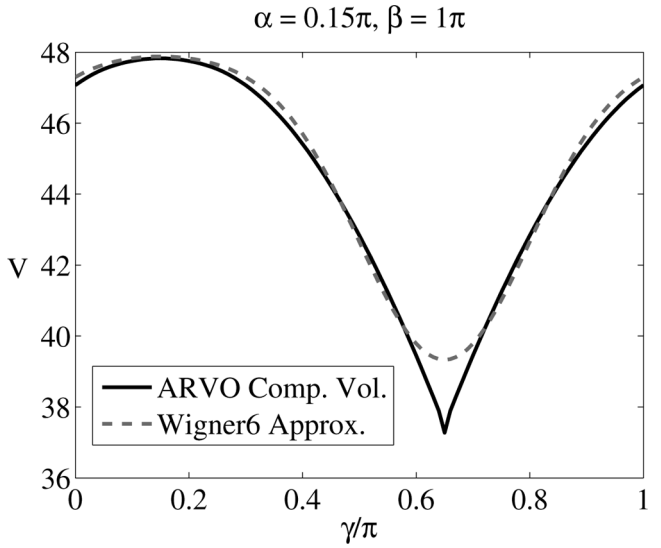

Figure 4. Plot of the excluded volume V against the angle of proper rotation γ, normalised to π, for $\alpha = 0.15\pi$ and $\beta = \pi$. Details as in Figure 2.

$(\varphi, \vartheta, \psi)$ and performing a fitting procedure on oscillating functions adapted to the tetrahedral symmetry

$$\cos(i\psi) \quad \cos(2j\vartheta) \quad \cos(4k\varphi),$$

where i, j, k are integer numbers; the procedure has been carried out with the aid of Mathematica 6, and for a few different angular steps.

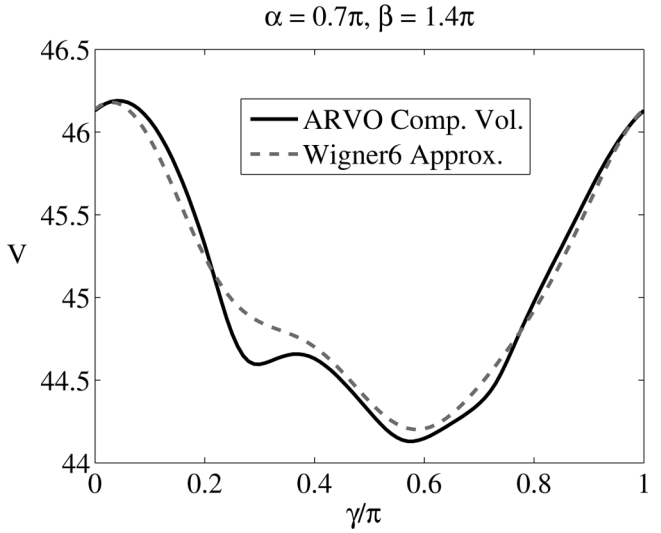

Figure 5. Plot of the excluded volume V against the angle of proper rotation γ, normalised to π, for $\alpha = 0.7\pi$ and $\beta = 1.4\pi$. Details as in Figure 2.

Figures 2–5 show some comparisons between the *actual* value of the excluded volume directly computed by the aid of ARVO and and its approximation

$$\begin{aligned} V^a(\alpha,\beta,\gamma) := {} & \alpha_{000}\Delta^0_{00} + \alpha_{322}\Delta^3_{22} \\ & + \alpha_{400}\left[\Delta^4_{00} + \sqrt{\frac{5}{7}}(\Delta^4_{40}+\Delta^4_{04}) + \frac{5}{7}\Delta^4_{44}\right] \\ & + \alpha_{600}\left[\Delta^6_{00} - \sqrt{7}(\Delta^6_{04}+\Delta^6_{40}) + 7\Delta^6_{44}\right] \\ & + \alpha_{622}\left[\Delta^6_{22} - \sqrt{\frac{5}{11}}(\Delta^6_{26}+\Delta^6_{62}) + \frac{5}{11}\Delta^6_{66}\right] \end{aligned} \tag{29}$$

truncated at $\ell = 6$. The graphs are plotted by fixing two Euler angles and keeping γ free to vary.

The plots reveal the complex structure of the excluded volume. The truncation based on (28) is quite accurate, at least away from points where V fails to be differentiable. A more accurate study reveals that the configuration at which the tetrahedral molecules are parallel fails to be the absolute minimum of V, suggesting that steric interaction could promote aggregates in which the molecules are not aligned, as one could intuitively expect. This in turn is in accordance with the unexpected arrangements of zigzag molecules observed in computer simulations [32]: though the geometry is different, the common feature is the presence of a *shape polarity* that could induce counter intuitive arrangements, potentially conflicting with other tendencies as due, for instance, to the presence of electric multipoles.

Acknowledgments

This work was partly supported by a Grant for Progetto Giovani 2008 by the GNFM (Gruppo Nazionale per la Fisica Matematica), Italy and supported in part under Grant N202 169 31/3455 of the Polish Ministry of Science and Higher Education.

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