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Molecular surface and order parameters in liquid crystals

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The surface model for solute ordering in nematics, which is based on the decomposition of the orientational potential according to the contributions of surface elements, leads to a simple procedure for the calculation of both orientational properties and the cholesteric order induced by a chiral compound. However, a realistic representation of the molecular surface accessible to the solvent is required. The rolling sphere algorithm, applied to the ensemble of atomic van der Waals spheres of a molecule, provides a natural determination of such a surface, since it smoothes away the small scale details. The surface ordering model implemented with the rolling sphere smoothing of the surface is described and applied to several molecular systems. It is shown that the orientational order parameters are substantially independent of the rolling sphere radius identified with the average curvature of the solvent molecular surface. On the contrary, a sensible dependence on such a parameter emerges for the chirality order parameter, this behaviour pointing out the role of the shape of solvent molecules in the chirality recognition of solutes. A fair agreement is obtained in the comparison with experimental data.

1. Introduction

If one imagines a nematic liquid crystal as an ensemble of long molecules which are anisotropically distributed, then the orientational order induced on a solute with elementary shape (say, for instance, a rod or a disk) can be easily understood on the basis of the interactions with solvent molecules which favour particular solute configurations. The quantitative modelling of such an effect, however, is not so simple since description of solute–solvent interactions requires knowledge of their dependence upon the local distribution of the solvent molecules. Even the prediction of the preferential orientation might be difficult in the case of a solute with complex molecular structure. In order to circumvent these difficulties, several theories have been proposed on the basis of simplified models for solute–solvent interactions. Burnell and coworkers were the first to investigate in detail the relation between order and shape of solutes [1]. They have proposed some models with the nematic solvent assimilated to an elastic medium which tends to minimize the area projected by the solute in a plane orthogonal to the director. Alternatively, the volume excluded by the solute to a representative molecule of the solvent can be used to parameterize the orientational potential acting on the solute, as done by Terzis *et al.* [2]. Some of us have contributed to the elaboration of a method based on the additivity of surface contributions to account for solute–solvent interactions [3]. The underlying hypothesis is that each surface element contributes independently to the orientational potential according to the standard form assumed for the anchoring free energy of macroscopic surfaces [4]. The resulting orientational potential is then parameterized in terms of a surface tensor determined by the solute shape and the strength of the order induced by the solvent on the planar surface of unit area.

It is evident that a rather crude approximation is employed for solute–solvent interactions in the surface model. On the other hand, one should consider that the full order matrix (i.e. its principal components and the corresponding directions) can be easily calculated on the basis of the solute shape only, once the solvent ordering strength is fixed. The minimal requirement of availability of the molecular surface is certainly the most appealing feature of the model which allows the comparison of the order parameters of different solutes in the same nematic solvent. Moreover it can be applied to the calculation of other properties of liquid crystals, like the cholesteric order induced by chiral solutes [5]. In this case one considers the pitch dependence of the free energy which includes both the elastic contribution

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of the solvent and the distortion term due to the interactions with the chiral solute [6]. From the minimum of the free energy, the equilibrium pitch is derived with a substantial agreement with the experimental data. The analysis of the corresponding orientational potential leads to a helicity tensor which allows the definition of the chirality order parameter of the solute [7]. As a further application we should mention the analysis of phase transitions of liquid crystals in a mean field framework, where the surface model is employed to estimate the required order parameters [8]. By considering that ordinary nematogenic molecules have a rather complex structure with distinct conformational states, the utility of the surface model emerges as a convenient procedure to account for the effects of different molecular architectures.

A reliable choice of molecular surface is the prerequisite of the method. In previous applications having the objective of understanding the major effects of the molecular shape, the issue of surface determination was not examined in detail, and an elementary procedure was employed by considering a molecule as an ensemble of overlapping van der Waals spheres centred on the atoms, with a united atom representation for CH_3, CH_2 and CH groups [3, 5–8]. However, the crucial role of the surface determination clearly emerges from the results reported in a recent work by Tarroni and Zannoni [9] where the predictions of different theories have been tested against the experimental order parameters measured on anthracene and related molecules. They have performed calculations with the surface method both by using the united atoms representation, and by explicit inclusion of van der Waals spheres also for hydrogen atoms, with a change of up to 50% for the order parameters in the two cases. These findings point out the need for precise rules for the determination of the molecular surface in order to eliminate any ambiguity in the surface model calculations.

The optimal choice of molecular surface is specifically examined in the present work. The surface effectively in contact with the solvent provides the natural guideline for the analysis of solute–solvent interactions. A similar problem has been considered in relation to other physico-chemical properties of a solute, notably friction coefficients [10] and solvation free energies [11], in which cases the rolling sphere procedure has been applied. Given the rolling sphere representing a solvent molecule and the solute assimilated to an ensemble of van der Waals spheres, one determines the volume excluded by the solute under the constraint that the rolling sphere cannot overlap with the van der Waals spheres. The boundary of such an excluded volume determines the solute surface exposed to the solvent. As a pictorial representation one can imagine the solvent sphere rolling on such a surface and being always in contact with the van der Waals spheres of the solute. Numerical algorithms have been specifically developed for the surface determination according to the rolling sphere method [12–14]. We shall analyse their application to the calculation of both chirality and orientational order parameters according to the surface method.

The rolling sphere determination of the molecular surface is not simply a technical improvement of the original surface method [3], because it introduces a new parameter for the solvent: the radius R of the rolling sphere. An obvious relation exists with the size of solvent molecules only if these can be approximated to spherical objects. On a more general ground one can interpret such a parameter according to the capability of solvent molecules to probe by contact the cavities of the solute surface. In fact the rolling sphere procedure produces a smoothing of the molecular surface by eliminating details characterized by a length scale much shorter than R. Then a more meaningful assignment to R would be the average local curvature of the solvent molecular surface when properly smoothed.

Once a physical interpretation is provided to R, it becomes important to rationalize its effects on the order parameters. Correspondingly, a range of reasonable values of this parameter is required. The lower limit $R \geqslant 2.5$ Å can be chosen in relation to the size of typical substituents such as the methyl group. Even if the variability of the molecular structures of nematogens prevents a definite estimate of the upper bound, values of R greater than 5 Å can be excluded even in the case of large solvent molecules by considering that the overall shape always includes parts with comparatively small local curvatures. It should be noticed that in the limit for $R \to 0$ one recovers the molecular surface without any smoothing.

The paper is organized as follows. In the next section the surface model for order parameter calculations is summarized and the implementation of the rolling sphere method is described. In §3, applications to several molecular systems are presented and the effects of the rolling sphere radius are discussed. Comparison with available experimental order parameters is also made. The general conclusions of this work are reported in the last section.

2. Model and computational procedure

2.1. *Surface and helicity tensors*

The surface model is based on the assumption that each infinitesimal element dS of the molecular surface tends to be aligned with respect to the mesophase director $\mathbf{n}$ according to the anchoring free energy of a nematic to a planar surface [4]. The whole molecule then experiences the following orientational potential due to the cumulative effects of these elementary contributions

$$U(\Omega) = k_B T \varepsilon \int_S P_2(\mathbf{n}\;\;\mathbf{s})\,\mathrm{d}S \tag{1}$$

where integration is performed over all the molecular surface S, $\mathbf{s}$ is a unit vector along the outer normal to the surface element $\mathrm{d}S$, P_2 is the second Legendre polynomial, and ε is a parameter describing the strength of the orienting interactions. The explicit dependence of $U(\Omega)$ on the molecular orientation Ω is derived by applying the addition theorem for spherical harmonics [3]:

$$U(\Omega) = -k_B T \varepsilon \sum_m T^{(2,m)*} \mathscr{D}^{2}_{0,m}(\Omega) \tag{2}$$

where $\mathscr{D}^{2}_{0,m}(\Omega)$ are Wigner functions having as argument the Euler angles Ω for the rotation from the laboratory to the molecular frame, the Z axis of the former being parallel to the nematic director. $T^{(2,m)}$ are irreducible spherical components of the following molecular tensor $\mathbf{T}$ of second rank, denoted as surface tensor:

$$\mathbf{T} = -\int_S \frac{3\mathbf{s}\otimes\mathbf{s} - \mathbf{1}}{\sqrt{6}}\,\mathrm{d}S. \tag{3}$$

This depends on the orientational distribution of surface elements, as appears more clearly by rewriting equation (3) in the form of an integral over the polar angles ω_s describing the orientation of $\mathbf{s}$ in the molecular frame:

$$\mathbf{T} = -\int \rho_s(\omega_s) \frac{3\mathbf{s}\otimes\mathbf{s} - \mathbf{1}}{\sqrt{6}}\,\mathrm{d}\omega_s \tag{4}$$

where $\rho_s(\omega_s)$ is the density of surface elements with orientation ω_s. The angular dependence of $\rho_s(\omega_s)$ characterizes the molecular surface anisotropy within the following two limits: ρ_s is constant for the spherical surface (in which case $\mathbf{T} = 0$) and becomes the Dirac delta function in the case of a plane. Since the largest principal elements of $\mathbf{T}$ for fixed area of the molecular surface are recovered in the latter case, one can conclude that the magnitude of the surface tensor elements measures the anisotropy of the surface element distribution. Once the surface tensor is determined one can calculate the order matrix $\mathbf{S}$ from the relation

$$\mathbf{S} = \frac{\displaystyle\int \frac{1}{2}(3\mathbf{n}\otimes\mathbf{n} - \mathbf{1}) \exp[-U(\Omega)/k_B T]\,\mathrm{d}\Omega}{\displaystyle\int \exp[-U(\Omega)/k_B T]\,\mathrm{d}\Omega} \tag{5}$$

with the components of the unit vector $\mathbf{n}$ expressed in the molecular frame. This procedure requires the specification of the parameter ε for the ordering strength of the solvent, which should be independent of the type of of solute according to our model. This has been verified in [3] by demonstrating that the surface model, with a suitable value of ε, accounts for the changes of experimental order parameters when different solutes are examined in the same solvent (for a fixed temperature). Moreover, one can interpret the orientational potential (1) according to the mean field treatment of intermolecular interactions, in which case a direct proportionality is expected between ε and the orientational order parameter P_2 of the solvent [3].

The orienting potential in equation (1) can be employed to describe the anisotropic interactions in the cholesteric phase too, by introducing a position dependent director field $\mathbf{n}(\mathbf{R})$, corresponding to a helical structure characterized by its handedness and pitch p, or by the wavevector $\mathbf{q}$ of magnitude $q = 2\pi/p$ [5–7]. In the limit $q \to 0$ the orientational potential acting on a molecule in the laboratory frame with the Z axis along the local director at $\mathbf{R}$ can be approximated by the following expression:

$$U(\Omega) = -k_B T \varepsilon \sum_m [T^{(2,m)*} - qQ^{(2,m)*}] \mathscr{D}^{2}_{0,m}(\Omega) \tag{6}$$

where $Q^{(2,m)}$ are irreducible spherical components of the second rank pseudo-tensor $\mathbf{Q}$ called the helicity tensor (its diagonal elements describe the helicities of the molecular surface along the coordinate axes) and to be calculated by integration on the molecular surface as in equation (4)

$$\mathbf{Q} = \left(\frac{3}{8}\right)^{1/2} \int_S [\mathbf{s}\otimes(\mathbf{s}\times\mathbf{r}) + (\mathbf{s}\times\mathbf{r})\otimes\mathbf{s}]\,\mathrm{d}S \tag{7}$$

where $\mathbf{r}$ is the vector position of the surface element $\mathrm{d}S$ in the molecular frame. The helical twisting power β of nematic solvents due to chiral solutes is obtained by minimization of the q-dependent free energy which includes a bulk elastic contribution and the chiral distortion term derived from the orientational average of equation (6) [5–7]

$$\beta = \frac{\mathscr{R} T \varepsilon Q}{2\pi K_{22} v_m} \tag{8}$$

where $\mathscr{R}$ is the gas constant and T is the temperature, while K_{22} and v_m are the elastic constant and molar volume of the solvent, respectively. The chirality order parameter Q measures the chiral effects of the molecular surface and it is determined by both the orientational order matrix $\mathbf{S}$ and the helicity tensor $\mathbf{Q}$ according to the relation

$$Q = -\left(\frac{2}{3}\right)^{1/2} \mathbf{Q}\;\;\mathbf{S}. \tag{9}$$

2.2. *Computations based on the rolling sphere algorithm*

Calculation of surface and helicity tensor components requires knowledge of the molecular structure, which can be taken from experimental data or from computations such as energy minimizations using force field calculations (for the examples of the next section we have employed the semi-empirical method PM3 included in the GAMESS package [15]). Starting from the structure, a molecular surface can be defined in different ways. The easiest choice is that of the outer surface of an assembly of van der Waals spheres centred at the atom positions [3]. A more realistic definition is that of the surface enclosing the volume excluded to the solvent by such an ensemble. According to the rolling sphere algorithm proposed by Connolly [12, 13, 16], this is defined as the smooth outer surface contour generated by rolling a probe sphere, mimicking the solvent, over the van der Waals sphere assembly. This surface can be decomposed in pieces which in the original formulation of the algorithm [12] belong to three different classes: sphere fragments, concave quadrilaterals (torus fragments) and concave triangles. The three classes correspond to regions in which the probe touches one, two or three van der Waals spheres, respectively. However, the original algorithm cannot describe regions where the probe sphere comes into contact with more than three atoms, a situation which is not uncommon in flat systems like aromatic rings, because it tries to describe the surface as a set of spherical triangles, but it fails to handle properly a possible overlap of these triangles. Thus, we have modified the algorithm in such a way that it uses large n-edge concave polygons instead, so that handling triangle overlap is avoided. Throughout the paper, unless otherwise stated, the atomic van der Waals radii of [17] are employed as the standard for the calculations.

Once the pieces of analytical surface are defined, each of them is sliced down to strips [13]. Points are uniformly distributed, at a distance equal to the strip width, on the central line of each strip, which is then split further into spherical quadrilaterals. In this way a dense and irregular point set is generated. The surface can be made arbitrarily close to the analytical surface by increasing the number of surface elements. Each point i is defined by its coordinates in a molecular frame and associated with a quadrilateral characterized by its surface area S_i and its outer normal $\mathbf{s}_i$. With these ingredients the surface and helicity tensor components are calculated by summing over the elementary contributions, according to equations (3) and (7). Details of the computational derivation will not be discussed here, because they have already been reported [18].

The molecular surface obtained for a given probe radius can be visualized using the VRL software [19] in connection with the program MSMS vers. 2.3.1 [20], which computes the triangulated solvent accessible surface [16].

3. Results

Changes of the molecular surface lead to modifications of both principal directions and principal values of the orientational order matrix $\mathbf{S}$ of the solute. In order to characterize in simple terms the effects of different determinations of the molecular surface, we shall confine the analysis mainly to solutes whose principal axes are determined by symmetry, so that only changes of the principal order parameters need be examined.

The anthracene molecule is the first solute we consider in order to analyse the dependence of the orientational order parameters on the molecular surface determination. In figure 1 the molecular surface of anthracene is drawn under two conditions: (i) by representing the non-overlapping parts of the van der Waals spheres centred on the atoms, and (ii) by using a rolling sphere of radius $R = 3$ Å. The first case is also the limit for a vanishing radius of the rolling sphere, $R = 0$. Clearly, the surface without any smoothing includes cavities or re-entrant parts which are not accessible to solvent molecules of realistic size. This is even more evident in alkyl chains (see figure 3 below). Only with the rolling sphere procedure can one derive a reasonable representation of the solute surface in contact with the solvent.

Figure 2 illustrates how the principal order parameters change with different determinations of the molecular surface for a fixed ordering strength $\varepsilon = 0.05$ Å^{-2} of the solvent. This value corresponds to typical ordering strengths of nematic phases, as shown in previous publications [3, 8]. Following [9], the principal axes

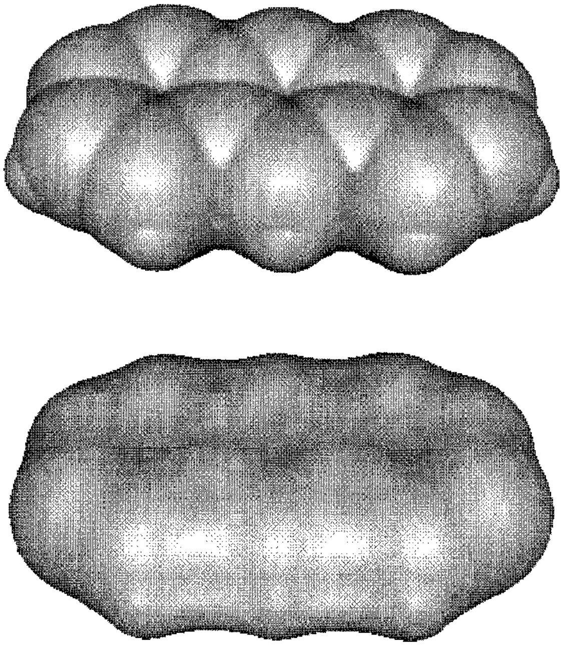

Figure 1. Anthracene surfaces generated with rolling sphere radii $R = 0$ (top) and $R = 3$ Å (bottom).

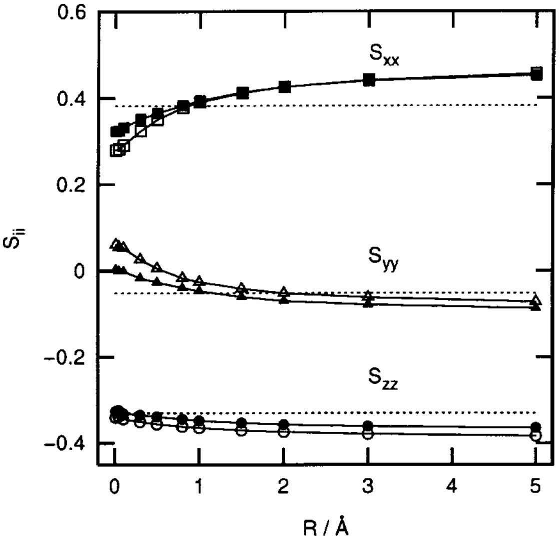

Figure 2. Orientational order parameters S_{ii} of anthracene as a function of the radius R of the rolling sphere for the fixed ordering strength $\varepsilon = 0.05\,\text{Å}^{-2}$ of the solvent. Filled symbols refer to the standard set of van der Waals radii [17], while open symbols describe the change due to the increase from 1.0 to 1.2 Å of the hydrogen van der Waals radius. The dotted lines are drawn to correspond with the order parameters calculated from the united atom representation of the surface without rolling sphere smoothing.

of **S** are labelled by assigning the x direction to the molecular long axis, while the z direction is taken orthogonal to the molecular plane. Let us first discuss the dependence on the rolling sphere radius when the standard set of van der Waals radii is employed (filled symbols in figure 2). A significant dependence on R is evident only if one considers very small values of the rolling sphere radius in the range $0 \leqslant R \leqslant 1.5$ Å, which have to be considered unrealistic according to the estimates given in §1. On the contrary, the order parameters have a rather weak dependence on R when it is in the range $2.5\,\text{Å} \leqslant R \leqslant 5\,\text{Å}$ which is appropriate to typical nematic solvents. One can conclude that the orientational properties predicted by the surface model are substantially independent of the size of the rolling sphere, when this has a physically meaningful value.

In order to explain the decrease of order parameter by approaching the limit $R \to 0$, one should analyse the corresponding changes of the orientational distribution $\rho_S(\omega_S)$ of surface elements. For non-overlapping van der Waals spheres, the surface elements have an isotropic distribution $\rho_S =$ constant. On the other hand, when anthracene is represented by a smooth surface, one obtains a highly anisotropic distribution of surface elements, which reflects the non-spherical shape of the overall molecule. By lowering the rolling sphere radius, a more intricate surface is obtained with a decrease in the anisotropy of surface element distribution towards the limit of non-overlapping spheres. Correspondingly, the orientational potential (2) decreases in strength together with the orientational order parameters, since according to equation (4) the surface tensor mirrors the anisotropy of the surface element distribution. One should notice that the range of R with a significant change of order parameters has an upper bound of the order of the distance between adjacent atoms. In fact a rolling sphere of this size in contact with two or more van der Waals spheres of neighbouring atoms leads to a nearly planar contribution, and the major contributions to the anisotropy of $\rho_S(\omega_S)$ mainly derive from such a type of surface elements.

The choice of the van der Waals radius of hydrogen is somehow problematic since this is not considered as an intrinsic property of the atom, but depends also on the chemical surrounding. Thus, in [17] two distinct radii were introduced: 1.0 Å for hydrogens of aromatic groups, and 1.2 Å in alkyl chains. It is then important to assess the stability of the results with respect to changes of this parameter. The open symbols of figure 2 denote the results for anthracene when the hydrogen van der Waals radius for an alkyl chain is employed. In the absence of surface smoothing, this leads to significant modifications of order parameters (see in particular S_{yy}). On the contrary, rather small variations are found when a rolling sphere of physically acceptable size is employed. The stability of the orientational order parameters with respect to small changes of hydrogen van der Waals radius is another reason supporting the rolling sphere determination of the molecular surface.

In previous applications of the surface model without the rolling sphere smoothing [3, 5, 8], a united atom representation with a single sphere for CH, CH_2 and CH_3 groups was employed. This choice was justified for computational reasons, but also in an effort to provide in a simplified manner the molecular surface exposed to the solvent by collapsing the carbon and hydrogen spheres into a unique van der Waals sphere. When this method is applied to anthracene (dotted lines of figure 2), a recognizable but not exceedingly large reduction in the order parameters is recovered with respect to the more reasonable values calculated with rolling spheres of proper size. Larger changes are obtained by using separate van der Waals spheres for all atoms, hydrogen included, without surface smoothing (see the values for $R = 0$ in figure 2). Thus, if one does not intend to apply the rolling sphere smoothing because of its computational complexity, then the united atom representation should be preferred.

An important issue concerns the order parameters of alkyl chains which very often are constituents of nematogenic molecules. In the past, different parameterizations were proposed to interpret the chain alignment in nematics on the basis of group contributions [21]. More realistic estimates are supplied by the surface model since it takes into account the overall shape of the molecule [3]. As a typical system we consider here *n*-heptane in the all-*trans*-conformation as shown in figure 3. Of course, the calculation of observable order parameters would require the average over all the conformations weighted by their populations [3, 8], but our interest is here confined specifically to the optimization of the molecular surface, and so only one conformer will be analysed.

Figure 4 illustrates the results of the same type of calculations previously reported for anthracene, by using the same value $\varepsilon = 0.05\,\text{Å}^{-2}$ for the solvent ordering strength. Also in this case the principal axes are fixed by the molecular symmetry (C_{2v}), the z direction being assigned to the molecular long axis, while the y direction is taken orthogonal to the plane of carbon atoms. Larger variations of the order parameters with the size R of the rolling sphere are obtained for *n*-heptane than for anthracene, but again the results are substantially independent of this parameter when confined to a physically meaningful range of R. It is also evident that by using the non-overlapping surfaces of the van der Waals spheres (i.e. the limit for $R \rightarrow 0$), one largely underestimates the order parameters. This effect is partially compensated by using the united atom representation (dotted lines in figure 4). In conclusion, the general trends found with anthracene appear even more clearly in alkyl chain systems. It should be emphasized that similar results are obtained for other conformers of *n*-heptane, or for other linear alkyl chains.

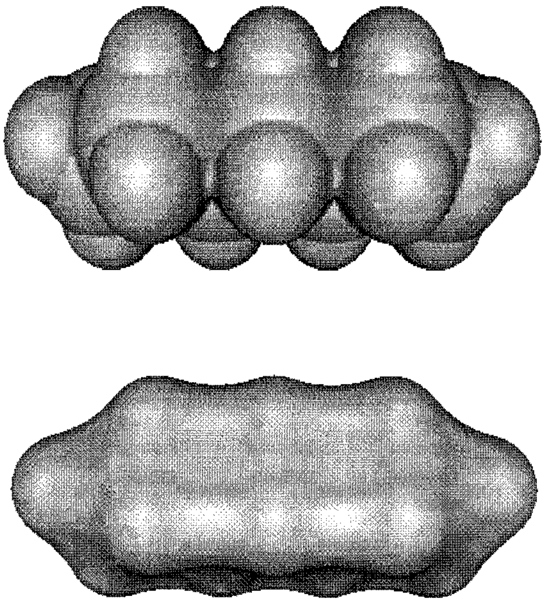

Figure 3. Surfaces of the *n*-heptane molecule in the all-*trans*-conformation for rolling sphere radii $R = 0$ (top) and $R = 3$ Å (bottom).

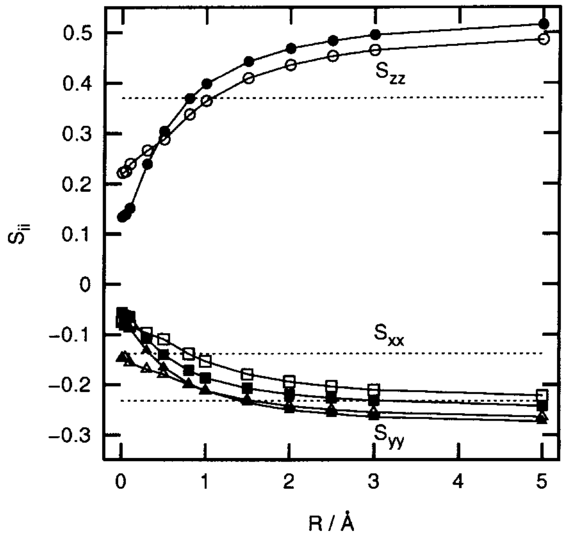

Figure 4. Orientational order parameters S_{ii} of all-*trans*-*n*-heptane as a function of the radius R of the rolling sphere under the same conditions as Fig. 2. The standard set of van der Waals radii [17] has been used for filled symbols, while for the open symbols the hydrogen van der Waals radius of the aliphatic hydrogens has been decreased from 1.2 to 1.0 Å. The dotted lines are drawn to correspond to the order parameters calculated from the united atom representation of the surface without rolling sphere smoothing.

In order to make a comparison with experimental data, we shall employ the order parameters of anthracene and 9,10-dibromoanthracene dissolved in the ZLI-1167 liquid crystal, which are reported in [9, 22]. Since all the principal order parameters are available, the comparison is conveniently performed with the diagram of biaxiality $\langle D^2_{02} \rangle = (S_{xx} - S_{yy})/\sqrt{6}$ as a function of the order parameter $\langle D^2_{00} \rangle = S_{zz}$ along the chosen z direction, since this allows the elimination of the parameter ε for the solvent ordering strength (each value of ε corresponds to a unique point in this type of diagram). The experimental values and the theoretical results obtained with a rolling sphere of radius $R = 3$ Å are reported in figure 5 for anthracene and in figure 6 for 9,10-dibromoanthracene. For a meaningful comparison with the theoretical results, one should take into account that the surface model is based on a simplified treatment of solute–solvent interaction. Very accurate predictions are certainly beyond the possibilities of the model which is aimed in the first instance at providing estimates easily derivable on the basis of the molecular structure. In this framework, the predictions for anthracene might be considered even

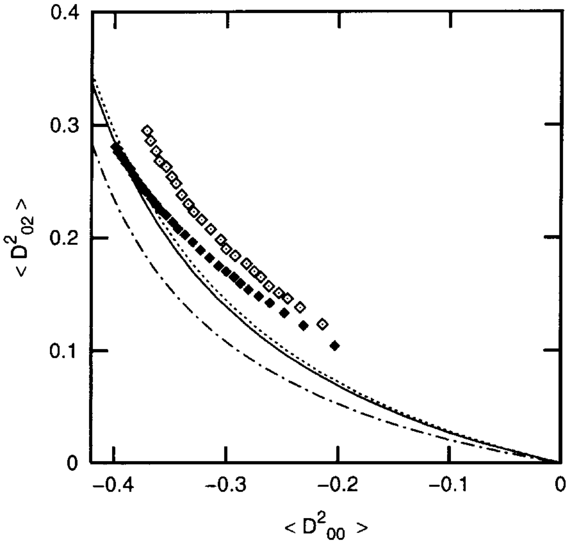

Figure 5. Biaxiality order parameter $\langle D^2_{02}\rangle$ as function of $\langle D^2_{00}\rangle$ for anthracene. Open and filled symbols represent experimental data from ^{13}C NMR [9] and D NMR [22], respectively. The lines denote the surface model results with rolling sphere radius $R = 3$ Å (continuous line), $R = 0$ Å (dot-dashed line), and with the united atom representation without rolling sphere smoothing (dotted line).

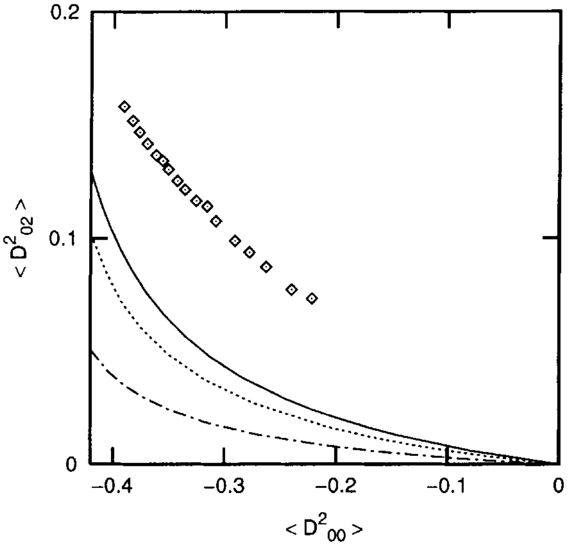

Figure 6. Biaxiality order parameter $\langle D^2_{02}\rangle$ plotted as a function of $\langle D^2_{00}\rangle$ for 9,10-dibromoanthracene. The symbols represent experimental data from ^{13}C NMR [9], while the lines denote the surface model results under the same conditions as Figure 5.

more accurate than expected. Much larger deviations emerge with dibromoanthracene. Even if they could be attributed to the intrinsic limits of the model, we conjecture a specific electrostatic origin for them. The substitution of a hydrogen by a bromine gives rise to a local electric dipole along the C–Br bond which strongly interacts with a polar solvent such as ZLI-1167 containing a mixture of cyanobiphenyls. Evidence of significant electrostatic contributions to the orientational potential has been found by Chandrakumar and Burnell in the case of 1,3,5-trichlorobenzene by comparing the temperature dependence of its orientational order parameters in nematic solvents with different dielectric properties (see figure 2 in [23]). To model such an effect within a continuum representation of the solvent, one should describe the coupling of the solute charge distribution (possibly by taking into account also the solute polarizability) with the solvent polarization, which can modify the orientational distribution if the dielectric tensor is anisotropic. Calculations of this type have been implemented by Tomasi and coworkers in the framework of the quantum mechanical treatment of molecular properties [24]. They have found a significant orientational dependence for the electrostatic part of the solvation free energy in the case of dipolar solutes in cyanobiphenyl solvents. In principle the same method can be applied with our surface model by decomposing the mean field potential in the part of equation (1) due to short range interactions scaled by the contact surface with the solvent, and the contribution deriving from the solvent polarization [25].

In figures 5 and and 6, besides the results obtained with the rolling sphere method, the order parameters calculated from the non-overlapping surface of van der Waals spheres are also reported for the sake of comparison. If one chooses the latter method as a simpler algorithm for the surface determination, then the united atom representation should be preferred to the all-atom representation, because it leads to estimates closer to the rolling sphere method and also to the experimental results.

Liquid crystal mixtures with an isotropic dielectric tensor would be the optimal nematic solvents for the assessment of the surface model without electrostatic contributions. We are not aware of measurements in these specific conditions. Somewhat close systems are the 'zero-electric field gradient (EFG)-mixtures' selected by Burnell and coworkers on the basis of vanishing NMR splittings of dideuterium D_2 solute [26]. If surface effects are neglected for such a small solute, all the orientational effects can be attributed to the coupling between the molecular quadrupolar moment and the induced polarization of the solvent considered as a continuum. Correspondingly the absence of orientational order in the solute D_2 as detected from NMR splittings might be attributed to a negligible dielectric anisotropy of the solvent. This justifies the neglect of orientational effects due to electrostatic interactions in 'zero-EFG-mixtures'. In figure 7 we have reported the orientational

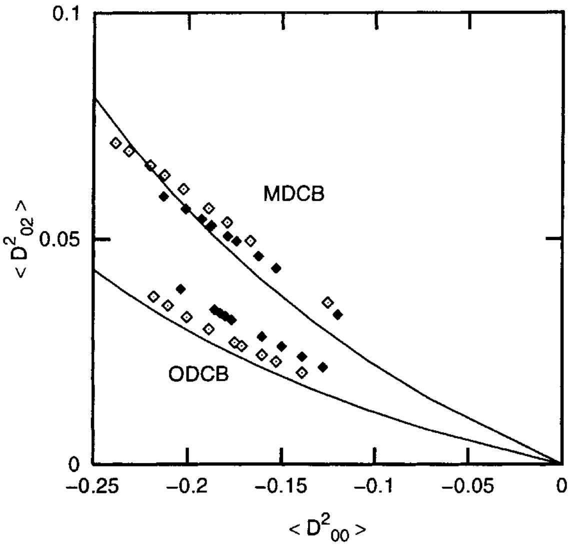

Figure 7. Biaxiality order parameter $\langle D^2_{02}\rangle$ plotted as a function of $\langle D^2_{00}\rangle$ for *ortho*-dichlorobenzene (ODCB) and *meta*-dichlorobenzene (MDCB). Open and filled squares denote experimental values reported in [23] for two 'zero-EFG-mixtures'. The continuous lines represent the surface model results for a rolling sphere radius of 3 Å.

order parameters taken from [23] for two solutes, *ortho*-dichlorobenzene (ODCB) and *meta*-dichlorobenzene (MDCB), in two 'zero-EFG-mixtures', together with the corresponding theoretical results from the surface model with a rolling sphere of 3 Å radius (the same axis labelling of [23] has been adopted). Deviations from the experimental results are much smaller than those displayed in figure 6 for 9,10-dibromoanthracene in a cyanobiphenyl solvent, in spite of the presence of strongly polar bonds between carbon–halogen atoms in both cases. On the other hand, the relative deviations in figure 7 are of the same order of magnitude as those found for anthracene (see figure 5), that is a molecule without strongly polarized bonds. This confirms that orientational effects of electrostatic interactions are minimized in 'zero-EFG-mixtures', and that they may generate significant contributions in cyanobiphenyl solvents. In [23] (see figure 3 therein) Chandrakumar and Burnell have analyzed the same data for ODCB and MDCB according to their one-parameter model [1] with an agreement comparable to that of figure 7. Also their model accounts for the short range interactions between solute and solvent, but by employing a completely different method based on the surface projections orthogonal to the director. On the other hand, it has been shown in [25*b*] that the results of such a model are roughly equivalent to those of the surface model in the limit of an infinite radius of the rolling sphere, and this explains why the two models lead to a comparable agreement with experimental data. It should be mentioned that Burnell and coworkers [1] have improved their models, but at the cost of incrementing the number of parameters for the solvent to be optimized.

Finally we examine the influence of the rolling sphere determination of the molecular surface on the chirality order parameter defined by equation (9). The binaphthyl molecule has been chosen as a model system by computing the chirality order parameter $Q(\vartheta)$ as a function of the torsional angle ϑ between the two molecular planes (see the inset of figure 8). Actual observations of chirality effects (i.e. induced cholesteric phases with a measurable pitch) need to constrain the torsional angle ϑ by inserting rigid bridge groups between the two naphthyl moieties [27, 28]. In figure 8 we have represented the ϑ-dependent chirality order parameter obtained from the surface model with several values of the rolling sphere radius R for a fixed ordering strength of the solvent $\varepsilon = 0.05\,\text{Å}^{-2}$. Clearly, changes of the Q order parameter are not confined to the range of low R values, but they extend also to the domain of physically acceptable values of R. For instance, the change of R from 3 to 5 Å leads to an average 30% reduction of Q. This suggests that not only the ordering strength ε of the nematic solvent, but also the shape of its molecules, as taken into account by the radius R of the rolling sphere, has a role in probing the chirality of the solute.

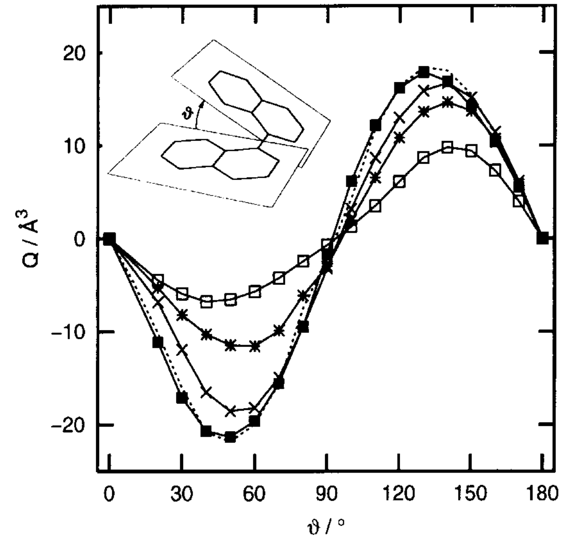

Figure 8. Chirality order parameter Q of P-binaphthyl plotted as a function of the dihedral angle between the naphthyl moieties, for the following values of the rolling sphere radius: $R = 0$ (filled squares), $R = 1$ Å (crosses), $R = 3$ Å (asterisks) and $R = 5$ Å (open squares). The results obtained from the united atom representation without rolling sphere smoothing are denoted by the dotted line.

As shown in a previous work [7], the balance of different components of **S** and **Q** tensors with opposite sign has a critical role in determining the value of the chirality order parameter. This prevents a direct and simple explanation of the R-dependence of Q by disentangling the contribution of the two tensors. However, the general trend can be easily understood by considering an infinite chain molecule in a helical structure with periodicity length λ. A sphere probing its surface would not recognize the helical structure (and also therefore its chirality) if its radius R is much larger than λ. Only for $R \lesssim \lambda$ can the helicity of the chain be effectively probed by the sphere, with larger chirality effects arising by lowering R because of the inclusion of contributions at shorter scale lengths. A similar behaviour is expected for binaphthyl molecules since they can be considered as part of a larger helical structure. As a matter of fact, a further decrease of chirality order parameters shown in figure 8 is obtained by using radii R greater than 5 Å. However, as emphasized in the introduction, these values have to be considered unrealistic by taking into account that the rolling sphere radius should be identified with the average curvature of solvent molecules, as a measure of their capability to probe by contact the cavities and the foldings of the solute surface. Even for large nematogens like cyanobiphenyls with long alkyl chains, it is justified to assume a radius $R \simeq 3$ Å corresponding to the typical dimensions of the phenyl ring considered as the molecular segment in contact with the solute surface.

A direct comparison between chirality order parameter and experimental twisting power according to equation (8) requires knowledge of the solvent elastic constant K_{22}, besides the ordering strength parameter ε. Previous evaluations based on the united atom representation without rolling sphere smoothing have shown that the surface model predicts the correct order of magnitude of the twisting power [5–7]. The present calculations do not modify such a conclusion, because the surface smoothing with a realistic radius $R = 3$ Å of the rolling sphere decreases at most by 50% the results obtained with the united atom representation (dotted line in figure 8). It is clear, however, that the shape of the solvent molecules, as taken into account by the radius R of the rolling sphere, has a crucial role in the precise determination of Q and of the solute twisting power. In order to eliminate the dependence on the solvent properties, one can analyse the ratio of twisting powers of structurally similar compounds in the same nematic liquid crystal, as in [7, 28]. In this case the size of the rolling sphere should play a secondary role, since the data of figure 8 show that the increase of R has proportionally the same effect on Q at the different twist angles, which can be associated to distinct rigid solutes.

4. Conclusions

The solute surface exposed to solvent molecules is the basic ingredient of the surface ordering model of a solute in nematics. The rolling sphere method appears to be the natural way of determining such a surface since it eliminates from the atomic van der Waals sphere representation of a molecule, the small size cavities which are inaccessible to the solvent. This procedure, however, introduces the rolling sphere radius as a new parameter characterizing the solvent. Reasonable estimates of its values can be determined by identifying it with the average curvature of the surface of solvent molecules. On the other hand, calculations for typical molecular systems show that the orientational order parameters are substantially independent of the rolling sphere radius when confined to a physically plausible range. A rather different behaviour is displayed by the chirality order parameter for the cholesteric pitch. A sensible dependence on the rolling sphere radius is found in this case, and this points out the important role of the solvent molecular shape in the chirality recognition of a solute. Accurate descriptions of this effect would require a more general treatment of the orientational order in a nematic solvent by taking explicitly into account the specific shape of its molecules, as done by Terzis *et al.* within a hard-body representation of molecular interactions [2].

A fair agreement is found in the comparison with experimental order parameters only in the absence of orientational effects due to electrostatic interactions between polar groups and a solvent with anisotropic dielectric properties. Actually, the surface model is suitable to account for the orientational effects of short range interactions only. In the presence of relevant electrostatic contributions, the mean field potential should include the orientational effects due to the anisotropic polarization of the solvent [25]. Alternatively, one can choose solvents like ‘zero-EFG-mixtures’ [23], which minimize the orientational effects of electrostatic interactions.

In conclusion the rolling sphere determination of the molecular surface should be considered as the standard method for the implementation of the surface ordering model.

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