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Orientational ordering of solutes in confined nematic solvents: A possible way to probe director distributions

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We propose a method to study the director distribution in a nematic liquid crystal confined in a slab geometry. It is based on the measurement, by NMR spectroscopy, of the Saupe ordering matrices of a collection of biaxial solute molecules dissolved in the confined nematic liquid crystal of interest. Due to the combined action of the surface anchoring and magnetic field interactions, the director is generally not uniformly aligned within the cell. Consequently, the resulting Saupe ordering matrices may be considered as weighted sums of the corresponding Saupe ordering matrices measured in the bulk nematic phase, and modulated by the director distribution. The determined Saupe ordering matrices may then be taken as the set of data in a fitting process where the fitting function, whose form is deduced from molecular mean field and continuum theories, is dependent on the director distribution; the angle that the director forms with the plain surfaces and the corresponding derivative at the surfaces are taken as fitting parameters. The methodology is preliminarily tested on the virtual nematic phase formed by the Lebwohl-Lasher lattice model, confined between two plain surfaces favoring planar anchoring, and where a number of model cuboidal solutes has been dissolved. We comment on the implemention of the method when applied to real experimental systems.

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Liquid crystals encompass a number of complex fluid systems of both fundamental and applicative interest. In particular, research on thermotropic nematic liquid crystals has been stimulated since the second half of the 20th Century by the usage that such materials have met in optoelectronic devices. The basic unit of the latter is a cell in which a nematic liquid crystal is kept between two solid surfaces and subject to external applied fields. Because the latter are generally competing with surface anchoring interactions, the director orientation at the interior of the cell is inhomogeneously distributed. It becomes of interest to determine such a distribution experimentally. One method involves the combined application of continuum theory [1] and deuterium NMR spectroscopy [2], as shown in Ref. [3].

A possible alternative method, also suitable to be used in a mutually synergistic fashion with respect to the approach of Ref. [3], can be in principle conceived to treat the problem. It is based on that well established [4] area of liquid crystal research that concerns the study of the orientational ordering of solutes in nematic solvents [2]. In an experiment of this type, the Saupe ordering matrix, **S**, of a solute dissolved in a nematic liquid is determined through the analysis of its NMR spectrum. In a bulk phase, the elements of **S** are defined as follows:

$$S_{\alpha\beta}=\left\langle \frac{3}{2}\cos\vartheta_\alpha\cos\vartheta_\beta-\frac{\delta_{\alpha\beta}}{2}\right\rangle =\int d\Omega P(\Omega|\hat{\mathbf{n}})\left[\frac{3}{2}\cos\vartheta_\alpha\cos\vartheta_\beta-\frac{\delta_{\alpha\beta}}{2}\right]. \quad (1)$$

In the above expression, $\cos\vartheta_\alpha$ is the direction cosine that the α axis of the molecular reference frame forms with the direction of the magnetic field, **B**, $\delta_{\alpha\beta}$ is the Krönecker symbol, and $\langle\rangle$ indicate a statistical average. $P(\Omega|\hat{\mathbf{n}})$ is the probability density to find a solute molecule in the orientational state defined by the set of Euler angles Ω, with respect to the laboratory reference frame. $P(\Omega|\hat{\mathbf{n}})$ depends on the affinity between the solute and the orienting nematic field, the latter being described by the director $\hat{\mathbf{n}}$. In a bulk phase, the direction of **B** coincides with the nematic phase director $\hat{\mathbf{n}}$, or it is perpendicular to the latter, depending on whether the sample is of positive or negative diamagnetic anisotropy, $\Delta\chi$, respectively. In a nematic liquid confined between two plates, however, the angle θ formed by the direction of **B** with $\hat{\mathbf{n}}$ is, in general, not the same across the cell, but rather a function of z [$\theta\equiv\theta(z)$]. The experimentally determined **S** is expected to reflect this situation. In fact, its elements should be the following average:

$$\bar{S}_{\alpha\beta}=\int_0^L dz\rho(z)S_{\alpha\beta}(z), \quad (2)$$

where L is the thickness of the cell, $\rho(z)$ is the probability density to find the solute molecule at a position comprised between z and $z+dz$ along the direction perpendicular to the

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two surfaces, and $S_{\alpha\beta}(z)$ is the $\alpha\beta$ element of the corresponding local Saupe ordering matrix. If we make the reasonable assumptions that the solute molecule explores homogeneously all the confined sample and that the local Saupe ordering matrix depends solely on the affinity between the solute molecule and the local director $\hat{\mathbf{n}}(z)$, we may write

$$\begin{aligned}\bar{S}_{\alpha\beta} &= \frac{1}{L}\int_0^L dz S_{\alpha\beta}(z)\\ &= \frac{1}{L}\int_0^L dz \int d\Omega P[\Omega|\hat{\mathbf{n}}(z)]\left[\frac{3}{2}\cos\vartheta_\alpha \cos\vartheta_\beta - \frac{\delta_{\alpha\beta}}{2}\right].\end{aligned} \tag{3}$$

Furthermore, we may assume that the shape of $P[\Omega|\hat{\mathbf{n}}(z)]$ is unaffected by the confinement, and therefore it can be taken equal to that determined in the bulk phase at the same temperature T. Exploiting Eq. (1) and rotational transformation properties, Eq. (3) can be made explicit in the following form:

$$\begin{aligned}\bar{S}_{\alpha\beta} = \frac{1}{L}\int_0^L dz \int d\Omega \sum_{i=1}^{3}\sum_{j=1}^{3} R_{i\alpha}[\theta(z)]\Bigg\{ P(\Omega|\hat{\mathbf{n}})\\ \times\left[\frac{3}{2}\cos\vartheta_i \cos\vartheta_j - \frac{\delta_{ij}}{2}\right]\Bigg\} R_{j\beta}[\theta(z)],\end{aligned} \tag{4}$$

where $R_{i\alpha}[\theta(z)]$ is the $i\alpha$ element of the $\mathbf{R}$ rotation matrix depending on $\theta(z)$. Without loss of generality, we can take

$$P(\Omega|\hat{\mathbf{n}}) \propto \exp\left[-\frac{U(\Omega|\hat{\mathbf{n}})}{k_B T}\right], \tag{5}$$

where k_B is the Boltzmann constant and $U(\Omega|\hat{\mathbf{n}})$ is an effective potential. It has been shown by several authors [2] that, in the particular nematic phase called magic mixture (MM), $U(\Omega|\hat{\mathbf{n}})$ can be described as effectively depending only on the size and shape of the solute. It has turned out [5] that a simple yet very effective description of the ordering of a biaxial solute in the MM solvent is achieved by modeling the solute as a parallelepiped of dimensions l, w, and b, respectively lying along the directions z', x', and y' of the solute frame of reference (see Fig. 1 in Ref. [5]), and taking $U[(\Omega|\hat{\mathbf{n}})]$ as follows:

$$U(\Omega|\hat{\mathbf{n}}) = -q\sum_{r=1}^{6} \lambda_r P_2(\hat{\mathbf{k}}_r \cdot \hat{\mathbf{n}}); \tag{6}$$

q is a positive solute-solvent coupling parameter dependent on temperature, and whose physical dimensions are those of an energy per length, λ_r is the length of the dimension r, and $\hat{\mathbf{k}}_r$ its direction. Basically, the set of the geometrical ratios between two solute dimensions dictates the shape of the curve $S_{x'x'}$-$S_{y'y'}$ versus $S_{z'z'}$, $S_{\alpha\beta}$ being the $\alpha\beta$ element of the solute Saupe ordering matrix measured in the bulk nematic phase. The actual position along this curve depends peculiarly on the temperature and on the nature of the solute-solvent pair; these three variables are effectively condensed in the parameter q. Deviations from a MM behavior can be effectively accounted for by including additional (e.g., electrostatic) interactions in the effective potential, as described, e.g., in Ref. [6]. On the basis of the results presented in Ref. [7], it is plausible that Eq. (6) holds also for magic solutes (i.e., relatively inert molecules like cycloalkanes) dissolved in any nematic solvents.

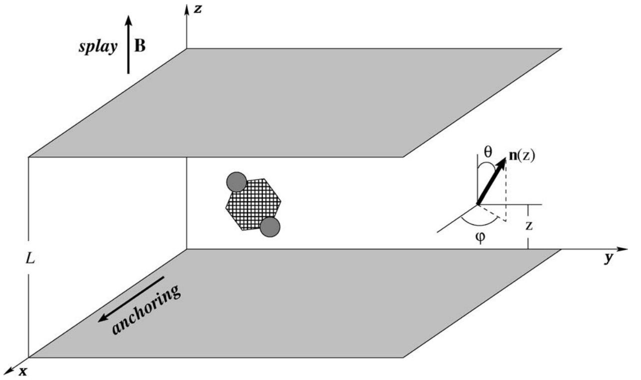

FIG. 1. The nematic liquid crystal solution considered in this work: it consists of a nematic solvent confined between two parallel surfaces, subject to both anchoring and magnetic field interactions, and that hosts solute molecules (e.g., an idealized para-dichlorobenzene). Because of the competition between anchoring and magnetic field interactions, the director is expected to be inhomogeneously aligned at the interior of the cell.

By combining Eqs. (5) and (6) with Eqs. (3) and (4), we obtain an expression of $\bar{S}_{\alpha\beta}$ that depends functionally on $\hat{\mathbf{n}}(z)$. Therefore, we may think to use the experimentally determined Saupe ordering matrices of a collection of biaxial solute molecules dissolved in a confined nematic solvents as a set of data to determine $\hat{\mathbf{n}}(z)$ by a fitting process. This could be achieved if an analytical expression for $\hat{\mathbf{n}}(z)$ is available that contains a few fitting parameters. To this end, we can resort to continuum theory [1]. In the case of the splay geometry of Fig. 1, for which the director $\hat{\mathbf{n}}(z)$ can be written as $(\cos\phi(z), 0, \sin\phi(z))$, continuum theory states that the director profile at the interior of the cell is determined by integrating the following differential equation [1]:

$$\begin{aligned}&[K_1\cos^2\phi(z) + K_3\sin^2\phi(z)]\frac{d^2\phi(z)}{dz^2}\\ &\quad+\frac{1}{2}(K_3-K_1)\sin 2\phi(z)\frac{d\phi(z)}{dz} - \frac{\Delta\chi}{2\mu_0}B^2\sin 2\phi(z) = 0,\end{aligned} \tag{7}$$

with K_1 and K_3 the splay and bend elastic constants, together with the two boundary conditions

$$\phi(0) = \phi(L) = \phi_0 \tag{8}$$

and

$$\left.\frac{d\phi}{dz}\right|_{z=0} = -\left.\frac{d\phi}{dz}\right|_{z=L} = \dot{\phi}_0. \tag{9}$$

We may take as the sought expression for $\hat{\mathbf{n}}(z)$ that obtained by integrating Eq. (7) with Eqs. (8) and (9) as boundary conditions, ϕ_0 and $\dot{\phi}_0$ playing the role of fitting parameters.

Before embarking on a series of measurements on real biaxial solutes dissolved in confined nematic solvents, we have decided to test the above-described methodology on a virtual system. We have considered $\ell_x \times \ell_y \times \ell_z$ rotors at the sites of a cubic lattice and interacting through the Lebwohl-Lasher pair potential [8]. This system is confined between two plain surfaces that preferentially orient the rotors at the surfaces along the x direction of the laboratory reference frame. In addition, each rotor interacts with a magnetic field $\mathbf{B}$ applied along the z axis. The total potential energy of the system can thus be written

$$U = -\sum_{i=1}^{N-1} \left\{ \left[\sum_{j>i}^{N} \epsilon_{ij} P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j) \right] + V_0 \Theta(z) P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{x}}) + \frac{\Delta\chi}{3\mu_0} B^2 P_2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{z}}) \right\}. \tag{10}$$

N is the number of rotors; $\epsilon_{ij} = \epsilon > 0$ if i and j are nearest neighbors, whereas $\epsilon_{ij} = 0$ otherwise. $P_2()$ indicates the second-rank Legendre polynomial and $\hat{\mathbf{u}}_i$ is the unit vector that defines the orientation of rotor i in the laboratory reference frame. V_0 is the anchoring strength and $\Theta(z)$ a step function such that $\Theta = 1$ if $z = 1$ or $z = \ell_z$, and $\Theta = 0$ otherwise. Each rotor of the system can be considered the nematic director of the microdomain of dimensions Λ^3, located at the corresponding site of the lattice. The assumption that the interaction among the nematic directors is regulated by the Lebwohl-Lasher pair potential amounts to taking $K_1 = K_2 = K_3 = K$ and $\epsilon = \Lambda K$ [9] while it is worth noting that the term describing the interaction of each rotor at one of the two surfaces with it is of the Rapini-Papoular form [10]. In such a special confined nematic liquid crystal solvent, we may think to dissolve a number of model cuboidal solutes whose orientation is determined by Eq. (6).

The behavior of the virtual nematic solvent at a specific temperature can be simulated through the Metropolis Monte Carlo technique [11], with periodic boundary conditions in the x and y directions only. The Saupe ordering matrices are obtained as averages over the run, through Eqs. (3) and (4). This is what we have done employing the following typical parameters: $T = 300$ K, $\Lambda = 1$ μm [9], $K = 4 \times 10^{-12}$ N [3], $V_0 = 10^{-4}$ J/m^2 [3], $\Delta\chi = 10^{-6}$ [3], and $B = 10$ T [3], with $\ell_x = \ell_y = 10$ and $\ell_z = 20$. Four types of solutes have been taken into account, each one with $b = 3$ Å and $w = 6$ Å, while $l = 9$, 12, 15, and 18 Å, respectively; that is, the four types of solutes have $b:w:l$ ratios, respectively, equal to 1:2:3, 1:2:4, 1:2:5, and 1:2:6. For each type of solute, a number of q values has been considered in the range [0–100] k_B (J/Å). In light of the above remarks on the role of the solute-solvent coupling parameter q, it is fair to point out here that the various values of q we have used in the simulations are to be intended as referred to different solutes sharing circa the same geometrical ratios but exhibiting a sort of intrinsically different orientational affinity toward the solvent, rather than the same solute at different temperatures.

In Fig. 2 we show the simulation results obtained. For each type of solute, the set of data $\{(S_{x'x'} - S_{y'y'})(q), S_{z'z'}(q)\}$ has then been used separately to determine the director profile according to the procedure outlined above. Figure 3 shows the director distributions obtained, each one to be compared with the exactly known distribution determined through the Monte Carlo runs. The latter is consistent with the directors at the surfaces aligned along x ($\phi = 0$), while those in the bulk are aligned with the magnetic field ($\phi = 90°$).

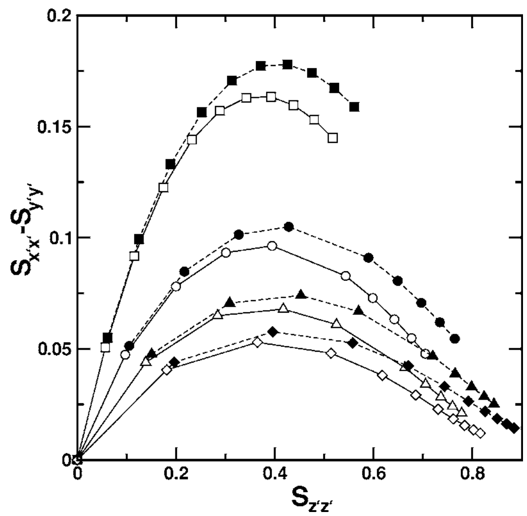

FIG. 2. $S_{x'x'}$-$S_{y'y'}$ versus $S_{z'z'}$ in bulk (black symbols), and averaged (white symbols) for the following type of solutes: 1:2:3 (squares), 1:2:4 (circles), 1:2:5 (triangles), 1:2:6 (diamonds).

For solutes that have dimensions in the ratio 1:2:3, it has been proven quite important to include in the fitting process data for the higher values of q, that is those corresponding to a solute with a high orientational order. Otherwise, the optimized value of ϕ_0 turned out to be too high, as is seen in

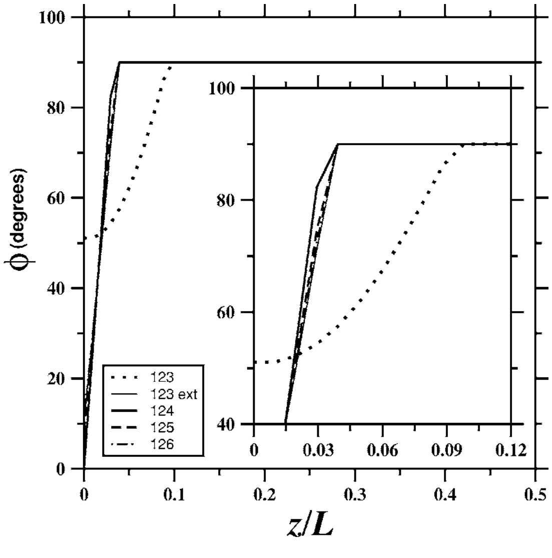

FIG. 3. The director profile at the interior of the cell obtained by the fitting process described in the text applied to the different types of solutes. "123 ext" means that we have included in the fitting process Saupe ordering matrix data for the 1:2:3 type of solutes with high values (up to 300 k_B) of the quantity q. The inset shows details for smaller values of z/L.

Fig. 3 (confront the curve labeled "123" with that labeled "123 ext"). This can be understood since, as can be seen in Fig. 2, the difference between the corresponding averaged and bulk results increases with the orientational order of the solute. Figure 3 suggests to restrict the experimental applicability of the method to longer solutes, where realistic director distributions have been obtained even employing sufficiently low values of q. One interesting possibility could be offered by dissolving long stiff polymers in nematic liquid crystals. In fact, theories predict that long solutes are much more orientationally ordered than the shorter molecules of the nematic solvent [12]. Recent experiments [13] have confirmed these predictions, finding that a stiff long polymer is essentially aligned with the director of the nematic medium. NMR experiments are currently underway to test the proposed methodology on real systems.

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