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Calculating the helical twisting power of dopants in a liquid crystal by computer simulation

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The helical twisting power determines the pitch of the helical structure produced by introducing a given concentration of chiral dopant molecules to a nematic liquid-crystal phase. By using alternative, twisted, periodic boundary conditions, and measuring the relative chemical potentials of right- and left-handed dopants in a twisted nematic phase, we have succeeded in measuring this property by computer simulation of a simple molecular model. The technique should be generally applicable.

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In the simplest liquid-crystal phase, the *nematic*, molecular orientations are ordered, in the sense that there is a preferred direction in space, the *director* $\mathbf{n}$. Suppose we take the undistorted director field $\mathbf{n}(\mathbf{r})$, where $\mathbf{r}$ is the spatial position, to lie in the x direction, $\mathbf{n}(\mathbf{r}) = (1,0,0)$. Splay, twist, or bend deformations are resisted by the Frank elastic constants K_1, K_2, and K_3, respectively. A helical, or uniformly twisted, nematic state

$$\mathbf{n}(\mathbf{r}) = (\cos\phi(z), \sin\phi(z), 0), \quad \frac{d\phi}{dz} = k = \text{const},$$

characterized by its pitch λ or wave number $k = 2\pi/\lambda$, has an elastic free energy relative to the undistorted state [1,2]

$$\Delta\mathcal{F} = \frac{1}{2} V K_2 k^2, \tag{1}$$

where V is the volume of the system. Such a deformation may be induced by mechanical torques applied at the surface of the sample, or by applied fields. Alternatively, such a twisted director field results when small concentrations of chiral (left- or right-handed) dopant molecules are added to a nematic phase; the result is termed a *chiral nematic* or *cholesteric* phase. At low dopant concentrations there is a linear relation between concentration and equilibrium wave number k_0, which we write conventionally [2] as

$$k_0 = 2\pi/\lambda_0 = 4\pi\beta\rho, \tag{2}$$

where $\rho = N/V$ is the number density of dopant molecules. The constant of proportionality β has the dimensions of area and is termed the *helical twisting power.* The sign of β, and hence k_0, determines the sense of the twist. In the presence of such dopants, the twist contribution to the elastic free energy becomes [2]

$$\Delta\mathcal{F} = \frac{1}{2} V K_2 (k - k_0)^2, \tag{3}$$

and this resists deviations from the uniformly twisted state with $k = k_0$.

The two parameters in these equations, K_2 and β, are of great importance in determining the behavior of liquid-crystal systems in optical devices. It is of great interest to investigate the relationship between these quantities and the structures of both the solvent and dopant molecules, using theoretical methods and by computer simulation. Recently, we obtained estimates of the elastic constants by observing k-dependent orientational fluctuations in computer simulations [3] and by measuring the internal torque density present in a uniformly twisted nematic phase [4]. At first sight, the calculation of β seems a much more difficult task. The requirement to avoid unphysical surface effects by using periodic boundary conditions means that the helix pitch must be commensurate with the simulation box length. Typical values of λ_0, for dopant concentrations of a few percent, are comparable with the wavelength of visible light: far larger than accessible system sizes in molecular simulations, using ~ 1000 particles. High concentrations of dopant would be needed to produce much smaller values of λ_0, but Eq. (2) is only valid in the dilute regime. Clearly, the properties of a nearly pure liquid of chiral molecules will be quite different from those of a dilute solution. In experiment, more exotic phases (the "blue" phases) may be formed as the dopant concentration increases, so it may not be at all relevant to study a small, highly concentrated sample. Moreover, we anticipate that very long simulation time scales would be needed to establish the equilibrium helix pitch for a given composition of liquid.

In this paper, we demonstrate that the helical twisting power β can, in fact, be measured in a simulation, and we illustrate this by calculating it for chiral molecules composed of two hard-ellipsoidal units, in a scissors arrangement, dissolved in a nematic phase of ellipsoidal monomers. In this particular case we are able to investigate a range of geometries for the chiral dimer, and relate the structure to the value of β, using the results of a single simulation of ellipsoids at each state point. The chiral dimer is representative of a class of molecules actually synthesized and studied experimentally, and known to have very high values of β [5]. The method is not restricted to this case, however, and we indicate later how it may be applied to more general dopants. The only requirement is that a method be found to measure the chemical potential difference between mirror-image left- and right-handed forms of a dopant molecule, in a uniformly twisted nematic phase of fixed pitch. There is no need to adjust the pitch to the equilibrium value consistent with any particular dopant concentration: we simply use thermodynamic relationships to deduce values of β.

Consider a twisted nematic phase of pitch $\lambda = 2\pi/k$, containing small numbers of molecules N_+ and N_- of mirror-image forms of a dopant, having equal and opposite values of the helical twisting power $\beta_\pm = \pm\beta$. Then, from Eq. (3), the elastic part of the free energy is

$$\Delta\mathcal{F} = \frac{1}{2}VK_2\left(k - \frac{4\pi\beta}{V}[N_+ - N_-]\right)^2. \tag{4}$$

Assuming that this elastic term is solely responsible for any *difference* in the chemical potentials between mirror-image forms, we have, in the limit $N_+, N_- \to 0$,

$$\mu_- - \mu_+ = \frac{\partial\mathcal{F}}{\partial N_-} - \frac{\partial\mathcal{F}}{\partial N_+} = 8\pi\beta K_2 k,$$

so

$$\beta = \frac{\mu_- - \mu_+}{8\pi K_2 k}. \tag{5}$$

Hence a measurement of the chemical potential difference $\mu_- - \mu_+$ in a twisted nematic phase, with a simultaneous determination of the elastic constant K_2, should be sufficient to determine β. We assume that k is sufficiently low that the expression for the elastic free energy is correct; also the measurements must be made at vanishingly low dopant concentrations.

The twisted nematic phase is stabilized by conducting the simulation in twisted periodic boundary conditions, using a cuboidal box containing exactly one-quarter of a turn of the director helix. The box has dimensions $L_x = L_y \neq L_z$. It is surrounded by periodic replicas in all directions. However, we adopt the convention that the x and y components of the center-of-mass vectors $\mathbf{r}_i$, the molecular axis vectors $\mathbf{e}_i$, and all associated velocity and angular velocity vectors, of image particles in the neighboring box in the $+z$ direction are rotated by $\pi/2$ about the z axis with respect to those in the original box. Those in the neighboring box in the $-z$ direction are rotated by $-\pi/2$. Particle coordinates $\mathbf{r}_i$ are measured with respect to the center of the box for convenience. This convention is implemented whenever a particle leaves the box through one of the faces at $z = \pm L_z/2$: it is replaced by the incoming particle at the opposite face, which has (x, y) coordinates rotated by $\mp\pi/2$ as appropriate. The convention is also applied to the calculation of all pairwise vectors crossing the faces at $z = \pm L_z/2$.

The effect of this is to impose a helical structure with a pitch equal to $4L_z$ on the orientational distribution in the system. The consequences of such a twist on the translational distribution in a solid would be dramatic: enormous stresses would result from the perturbation of the positional distribution. The same applies to any phase for which the twist couples with long-range translational ordering (for example, smectic phases in certain circumstances). However, the nematic phase lacks translational order, and so there are no undesirable consequences of perturbing the center-of-mass positions in this way: these fluids are stress-free by definition. Because the twist is exactly $\pm\pi/2$, all the simulation boxes in a given xy layer match up exactly with appropriately rotated periodic image boxes in the layers above and below. This would not be possible if the rotation angle were made an arbitrary parameter. These boundary conditions are discussed in more detail elsewhere [4].

Apart from these boundary conditions, our simulation techniques are standard [6]. We conduct molecular dynamics simulations of hard prolate ellipsoids of axial ratio $e = a/b$, a being half the length of the symmetry axis and b half the length of each of the two perpendicular axes. The molecules move in free flight, with constant linear and angular momenta, in between impulsive collisions. They are treated kinematically as linear rotors, having unit mass m and a moment of inertia I (about the nonsymmetry axes) chosen on the basis of uniform mass distribution within the ellipsoid. The moment of collision between each pair is determined by using two equivalent, exact, criteria due to Vieillard-Baron [7] and Perram and Wertheim [8]. The colliding surfaces are smooth, with the impulse directed normal to the surfaces, and the magnitude of the impulse determined by the laws of conservation of energy, linear momentum, and angular momentum. Units of length are chosen so that $8ab^2 = 1$ and we set $k_BT = 1$ to determine velocity and time scales.

Here we report results for ellipsoids of axial ratio $e = 5$, at densities ρ/ρ_{cp} between 0.5 and 0.6, where ρ_{cp} is the close-packed density. The lower end of this range is close to the nematic-isotropic phase transition, while the upper end is safely below the estimated freezing density. We use a box length $L_z = 2L_x = 2L_y \sim 15$ units at the densities employed here, so the helix pitch is $\lambda = 4L_z \sim 60$.

The chemical potential difference $\mu_- - \mu_+$ is measured as follows. We restrict our interest to dopant molecules composed of pairs of ellipsoids in surface-surface contact. The contact pair geometry is defined by three quantities: two parameters χ_1 and χ_2 determining the location of the contact points on the surface of each ellipsoid and a twist angle ϕ between the unit axis vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ (see Fig. 1). The χ_1 parameter can be defined as the angle between $\mathbf{e}_1$ and the vector joining the center of molecule 1 with the point of contact on its surface, and similarly for molecule 2. The excess chemical potential of such a dimer $\mu^{\text{ex}}_{\text{dimer}}(\chi_1, \chi_2, \phi)$, dissolved at infinite dilution in the ellipsoid fluid, is related to the monomer excess chemical potential $\mu^{\text{ex}}_{\text{monomer}}$ [9]:

$$\mu^{\text{ex}}_{\text{dimer}}(\chi_1, \chi_2, \phi) = 2\mu^{\text{ex}}_{\text{monomer}} - k_BT \ln y(\chi_1, \chi_2, \phi), \tag{6}$$

where $y(\chi_1, \chi_2, \phi)$ is the background pair-correlation function for monomer ellipsoids. Provided the ellipsoids do not overlap, y is identical with the equilibrium pair distribution function $g(\chi_1, \chi_2, \phi)$. Thus the desired quantities, for all dimer configurations that arise in a simula-

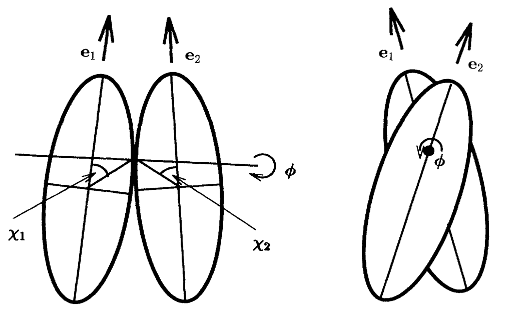

FIG. 1. Two views of the chiral dimer molecule, illustrating the angles χ_1, χ_2, and ϕ defined in the text. χ_1 and χ_2 are the colatitude angles locating the contact points on each ellipsoid surface. ϕ is the twist angle between the symmetry axes of the ellipsoids $\mathbf{e}_1$ and $\mathbf{e}_2$, about the line normal to both surfaces at the point of contact.

tion of the monomer solvent, can be measured at once. For every collision we simply increment the appropriate counter in a three-dimensional histogram of χ_1, χ_2, ϕ values. For given χ_1 and χ_2, switching $\phi \to -\phi$ corresponds to transforming between mirror-image configurations. Thus

$$\mu_- - \mu_+ = -k_B T[\ln y(\chi_1, \chi_2, -\phi) - \ln y(\chi_1, \chi_2, \phi)]. \quad (7)$$

The functions $\ln y(\chi_1, \chi_2, \pm\phi)$ are illustrated in Fig. 2, as functions of ϕ, for values of $\chi_1 \approx \chi_2 \approx \pi/2$ corresponding to collisions near the "equator" of both ellipsoids. The dimer is thus an X shape, with one arm of the X displaced above the other, and with ϕ corresponding to the twist angle between the arms. The small, systematic effect of the applied twist on $y(\chi_1, \chi_2, \phi)$ is clearly visible in the figure. The values of β obtained from Eqs. (7) and (5), with the known values of K_2 [4], are plotted as functions of ϕ, for $\chi_1 \approx \chi_2 \approx \pi/2$, at various densities, in Fig. 3. For this family of molecules, both $\phi = 0$ and $\phi = \pm\pi/2$ correspond to dimer molecules possessing a mirror plane; for other values of χ_1 and χ_2, $\phi = \pm\pi/2$ will not have this symmetry. We can see that $|\beta|$ reaches a maximum near, but not exactly at, $\phi = \pm\pi/4, \pm 3\pi/4$, and that the helical twisting power generally increases as the system density goes up. Results for other dimer geometries will be reported elsewhere. From Fig. 3, we see that a typical value of β is ~ 0.1 in our units. This means that a 1% solution of the dopant would produce a helix pitch of $\lambda = 1/2\beta\rho \sim 500$ units. In our units, the ellipsoid width is $2b \approx 0.6$ and the length is $2a \approx 3$. Thus the pitch would be of the order of hundreds of molecular lengths, as observed in experiment. It is worth re-emphasizing that direct simulations of systems of this scale would be very expensive.

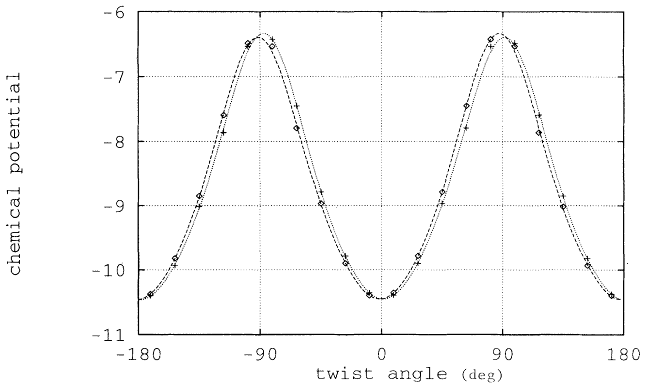

FIG. 2. The function $-\ln y(\chi_1, \chi_2, \phi)$ (dashed line) and its mirror image $-\ln y(\chi_1, \chi_2, -\phi)$ (dotted line), as functions of twist angle ϕ, for contact pairs of hard ellipsoids with $e = 5$ in a twisted nematic phase with density $\rho/\rho_{cp} = 0.55$. Here χ_1 and χ_2 are both in a narrow range around $\pi/2$, $k_B T = 1$, and the absolute position of the vertical scale is arbitrary. The points are simulation results. Statistical errors were calculated by assuming a normal distribution of sub-block averages, each sub-block being 1000 Monte Carlo sweeps, but the error bars are too small to see on this scale. The lines are least-squares fits to the data using a Fourier series in ϕ up to and including the sixth-order term.

This illustration has been for a specific case of dopant molecule structure, which was advantageous because of the good statistics obtained by recording pair collisions in the hard-particle monomer solvent and because the hard-ellipsoid system has already been well studied. This type of model is, admittedly, idealized. Although the importance of entropic, packing effects in condensed-matter physics is widely recognized, there are theoretical predictions that long-range attractive forces may be at least as important in determining elastic constants and related properties. Indeed there is scope for comparison with a range of theories both of the Maier-Saupe kind [10,11] and of the Van der Waals–Onsager–density-functional type [12–14], which are more directly applicable to hard particles (for reviews in this context see [15,16]). The ba-

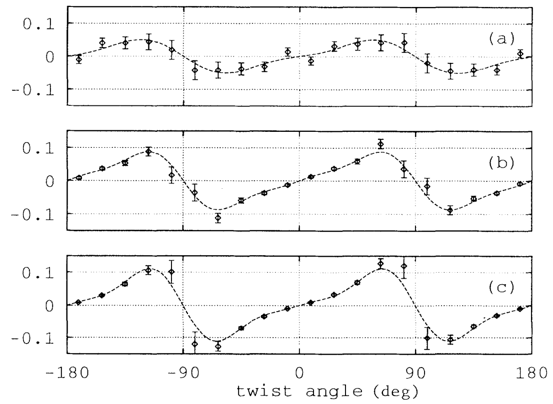

FIG. 3. The helical twisting power β for hard ellipsoid dimers with $\chi_1 \approx \chi_2 \approx \pi/2$ as functions of twist angle ϕ, at densities (a) $\rho/\rho_{cp} = 0.50$, (b) $\rho/\rho_{cp} = 0.55$, and (c) $\rho/\rho_{cp} = 0.60$. Error bars and fitting curves calculated as in Fig. 2.

sic simulation technique described here is not restricted to hard particles, nor to dopants of this kind. A simulation of a single dopant molecule, of any kind (whether a dimer or not), in the twisted nematic solvent, would suffice. It is only necessary to measure the chemical potential *difference* between such a molecule and its mirror-image form. This may be achieved by a variety of Monte Carlo techniques, involving progressive mutation of one structure into the other, determining the free-energy difference by overlapping distribution methods, and possibly using umbrella sampling [17]. We anticipate that this will be a useful general technique for determining the helical twisting powers for more realistic models of liquid crystals.

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