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Chiral dipole induced by azimuthal anchoring on the surface of a planar elastic quadrupole

V. A. Uzunova[1] and V. M. Pergamenshchik[1,2,*]

[1]*Institute of Physics, prospect Nauki, 46, Kiev 03039, Ukraine*

[2]*Korea University, Display & Semiconductor Physics, Jochiwon-eup, Yeongi-gun, Chungnam 339-700, Republic of Korea 03039*

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A spherical colloid with the tangential surface nematic director, aligned along the surface meridians, is known as a planar elastic quadrupole. The azimuthal anchoring, however, can induce a deviation of the planar director from the meridional lines. We show that a helical component of the planar surface director at the spherical surface of a planar quadrupole removes all the reflection symmetry planes and gives rise to a chiral elastic dipolar component. Using an ansatz approach, we consider the interplay between the quadrupole and anchoring-induced chiral dipole components. The chirality is enhanced by the bend-twist anisotropy. The interaction of the chiral components changes the attraction directions of two such colloids. In particular, a point appears at which the quadrupolar repulsion is balanced by the dipolar attraction.

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I. INTRODUCTION

Interaction of foreign particles mediated by the nematic director is long range and has a similarity to the electrostatic multipole interaction, which is the origin of the so-called electrostatic analogy [1–12] . The area of nematic colloids has been greatly guided by this analogy. A powerful method of laser tweezers has been developed to manipulate colloids and study their interaction effects in a nematic liquid crystal (NLC) [13–19]. Particular colloids whose director-mediated interaction as a function of their separation R scales as R^{-3} were called elastic dipoles, and other colloids whose interaction potential scales as R^{-5} were called elastic quadrupoles.

Actually, however, the elastic multipoles have an extra tensorial index compared to their electrostatic counterparts [7,8,10,20,21], and many of them have no electrostatic analogs [22]. The colloid shape, which along with the surface anchoring determines the colloid-induced director perturbations, is a major colloid parameter [22]. The simplest spherical shape gives rise to the best-known colloids, the so-called topological dipole, Saturn ring quadrupole, and planar quadrupole (PQ) [7]. In spite of their nontrivial topological structure, these spherical colloids are simple to fabricate, which has given them a great experimental advantage, and highly symmetric (uniaxial), which made them attractive for theorists. However, an expected strong shape dependence prompts one to experiment with colloids of a more and more complex shape [18]. The colloid shape is a major factor in the mobility in a field-induced motion of colloids [23,24] and motility of self-propelled particles (e.g., bacteria [25]).

So far, a colloid type has been associated with its form and polar surface anchoring, which is determined by its easy directions with respect to the surface normals. For instance, for the strong polar anchoring with normal-to-surface easy axes, a spherical particle can be either a topological dipole or a Saturn ring quadrupole (in confined geometries), while for tangential easy axes along the sphere's meridians passing through the poles it becomes a PQ [26–29]. Recently, however, we demonstrated the unique role an azimuthal anchoring can play in the colloidal nematostatics [22]. The type of a particle's elastic multipole is determined by the symmetry of the director distortions induced by this particle in its close vicinity. It is well known that vector fields with a finite vorticity cannot be described by a system of surfaces with the scalar potential assigned to them. In our recent paper [22], we showed that for the same reason, the full symmetry of the director distortions and hence the multipole type cannot be uniquely determined by the colloid shape and polar anchoring. In particular, an azimuthal anchoring can convert a PQ into a chiral dipole (CD) by adding a helicoidal tangential director component on a colloid surface while the shape and polar anchoring remain the same. According to the classification of elastic dipoles presented in Ref. [22], such a dipole is a uniaxial helicoid of a pure chiral type, which is fully characterized by its chiral strength C. In this paper we consider the effect of the azimuthal-anchoring-induced chiral dipole component in a PQ colloid quantitatively and show that it might result in well-observable effects. Namely, in a NLC with the usual elastic anisotropy, the balance of the dipole-dipole and quadrupole-quadrupole interactions can manifest itself in attraction directions along and across the director in which two PQs repel one another. The distance of the balance in this directions is calculated. The anchoring-induced CD is larger for a larger elastic bend/twist ratio; hence its effect is expected to strengthen at a NLC-smectic A transition.

II. QUADRUPOLAR SYMMETRY BREAKING BY A HELICAL DIRECTOR COMPONENT AND CHIRAL ELASTIC DIPOLE

In terms of the spherical coordinates, the director on the surface of a PQ has only the polar component n_θ and, very close to the poles, also the radial component n_r, while the azimuthal component $n_\phi = 0$ [Fig. 1(a)]. The point symmetry group of this field is $D_{\infty h}$, which comprises any rotations about the undistorted director, the mirror reflection in any vertical plane passing through the vertical axis along the undistorted director $\mathbf{n}_\infty$, the mirror reflection in the horizontal equatorial plane, and the rotations by an angle π about any horizontal axis. A uniaxial helicoid [Fig. 1(b)] has a nonzero azimuthal component n_ϕ and is also azimuthally symmetric, but has

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[*] victorpergam@yahoo.com

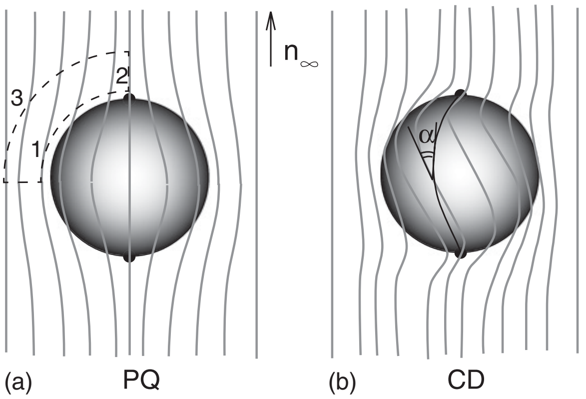

FIG. 1. (a) If the director lines on the spherical colloid surface lie in the vertical meridional planes passing through the poles, then this is a bipolar planar quadrupole. (b) If the surface director makes a nonzero angle α with the vertical meridional planes, the helical component, proportional to $\sin\alpha$, in addition gives rise to a chiral dipole component.

a lower symmetry group D_∞ with the same rotations but without any reflection plane. This symmetry D_∞ is chiral [22]. From the physical point of view, the mirror reflection planes can be eliminated, and, at the same time, chirality can be induced by an azimuthal anchoring with the helical alignment of its easy axes [Fig. 1(b)]. The lowest-order elastic multipole moment of such a colloid is no longer a quadrupole: The symmetry-breaking azimuthal component n_ϕ gives rise to a dipolar moment. It is worth stressing that, in contrast to an electrostatic dipole, a chiral elastic dipole does not have any mirror reflection plane. This property stems from the difference between the vector nature of the nematostatics and scalar nature of the electrostatics and demonstrates that elastic multipoles might have no electrostatic analogs. Chiral elastic deformation sources were first identified with elastic dipoles by de Gennes, who considered the cholesteric spiral as a superposition of the dipolar director distortions induced by chiral molecules in a NLC [30]. Thus, a finite helical component n_ϕ makes a CD of the otherwise quadrupolar colloid. Before considering this effect quantitatively, it is necessary to make the following general statement concerning the actual status of the theory in the area of nematic colloids.

The isotropic approximation, $K_{11} = K_{22} = K_{33} = K$, usually called a one-constant approximation, plays the key role in the very idea of elastic multipoles: In this approximation, the linearized Euler-Lagrange equations of the nematostatics reduce to Laplace's equation, whose asymptotic solutions can be associated with the elastic multipoles by analogy to the electrostatics. However, NLC is a highly anisotropic medium, and its elastic free energy depends on five different elastic constants: K_{11}, K_{22}, K_{33}, K_{24}, and K_{13}. The first three are the coefficients of the elastic splay, twist, and bend terms, and the last two are the coefficient of the two divergence terms. The fundamental problem of the theory of nematic colloids lies in solving the bulk Euler-Lagrange equations. The two divergence terms do not contribute to these equations, and their role can be considered in each configuration individually. However, even far from colloids where the deformations are weak, the linearized Euler-Lagrange equations with different K_{11}, K_{22}, and K_{33} do not reduce to Laplace's equation; their Green functions, exact solutions, and, in particular, asymptotic far distance solutions have not been obtained. Thus, on the one hand, strictly speaking, so far there has been no consistent theoretical justification of the existence, functional form, and widely used interaction potentials of what we call elastic multipoles. On the other hand, the numerous comprehensive and versatile experimental data accumulated over the last two decades in the area of nematic colloids have shown that the prediction of the theory, based on the one-constant approximation, does successfully describe the colloidal interaction in real anisotropic NLCs. At present, theorists working in this area have to admit that it is this experimental fact that makes their approximate theories of "isotropic" NLC meaningful and viable. Under these circumstances, the known expressions for the elastic multipoles, obtained in the one-constant approximation, have to be viewed as ansatzes whose form is expectedly close to the exact asymptotic solutions of the anisotropic Euler-Lagrange equations in the sense that the predicted director-mediated interaction is well justified experimentally. As in many cases the elastic anisotropy plays a crucial role, it is in order to emphasize here the following well-known general relation between the ansatz-based and exact formulas. An ansatz is a function with certain numbers of free parameters that is used as an approximate minimizer of a given functional. Whatever the origin of the ansatz is, its parameters must be found from the exact functional. In our case this implies that the elastic multipoles, which satisfy the Laplace's equation derived from the one-constant free energy, in the exact theory have the status of ansatz fields, and their coefficients must be found from the exact free energy with different elastic constants. Our consideration below, which goes in terms of the elastic multipoles, is to be understood in this context: We use the expressions for the chiral dipole and planar multipole (i.e., the minimizers of the isotropic free energy) and find their magnitudes from the exact anisotropic free energy. As for the divergence terms, their free-energy contribution is shown to be quadratic in the polar anchoring extrapolation length, which makes them practically negligible even if the polar anchoring is finite (Appendix B).

Let the uniform unperturbed director at infinity be parallel to the z axis, $\mathbf{n}_\infty = (0,0,1)$. Assume that at each point of the spherical colloid surface with the radius $r_0 = 1$, the tangential director makes an angle α with the vertical meridional plane passing through this point (Fig. 1): The director lines on the surface are thus loxodromes (lines that intersect the meridians at a constant angle). Clearly, $\alpha = 0$ and $\alpha > 0$ correspond, respectively, to a pure PQ and modified PQ with a constant azimuthal surface director component. The colloid-induced perturbation $\mathbf{n}_\perp$ sufficiently far is weak and transverse to $\mathbf{n}_\infty$, $\mathbf{n}_\perp = (n_x,n_y,0)$. In the one-constant approximation and in the axisymmetric case we deal with, the exact form of the transverse director perturbation, induced by a colloid with the considered surface director field, at a large distance r from the center is the sum of the form

$$\mathbf{n}_\perp = \frac{3C\sin\theta}{r^2}(-\sin\phi,\cos\phi,0) + \frac{5Q\sin 2\theta}{r^3}(\cos\phi,\sin\phi,0), \tag{1}$$

where r, θ, and ϕ are spherical coordinates of a spatial point $\mathbf{r}$. The first term is identified as the field of a CD of the uniaxial helicoid type with the chiral strength C [22] (the ϕ dependence is peculiar for just this dipole; other dipolar types have different ϕ dependence); the second term is the field of a PQ with the quadrupole moment Q [12]. Let $\mathbf{R}$ be the separation vector of particles 1 and 2, and Ψ be the angle made by $\mathbf{R}$ and the z axis. The interaction potential of two hybrid PQ and CD colloids is the sum $U = U_{CC} + U_{QQ} + U_{C_1Q_2} + U_{C_2Q_1}$ of the dipole-dipole interaction of the two CD components, quadrupole-quadrupole interaction of the two PQ components, and dipole-quadrupole interaction of the CD and PQ components. The dipole-quadrupole interaction between a pure CD dipole and any uniaxial quadrupole identically vanishes, $U_{CQ} = U_{QC} = 0$ (Appendix A). The other two potentials have, respectively, the form

$$U_{CC} = \frac{12\pi K C_1 C_2}{R^3}(1 - 3\cos^2\Psi), \tag{2}$$

$$U_{QQ} = \frac{80\pi K}{9R^5} Q_1 Q_2 (9 - 90\cos^2\Psi + 105\cos^4\Psi). \tag{3}$$

We choose the following parametrization of the director's components in the spherical coordinates:

$$(n_r, n_\theta, n_\phi) = [\cos(\Theta - \theta)\cos\Phi, \sin(\Theta - \theta)\cos\Phi, \sin\Phi], \tag{4}$$

where the angles Θ and Φ depend only on r and θ. The Cartesian components of the same director are

$$\begin{aligned}(n_x, n_y, n_z) &= (\sin\Theta\cos\Phi\cos\phi - \sin\Phi\sin\phi, \sin\Theta\cos\Phi\sin\phi \\ &\quad + \sin\Phi\cos\phi, \cos\Phi\cos\Theta).\end{aligned} \tag{5}$$

If $\Phi = 0$, this goes over into the familiar expression $(n_x, n_y, n_z) = (\sin\Theta\cos\phi, \sin\Theta\sin\phi, \cos\Theta)$. Now the conditions, which must be imposed on the director field at the three smooth boundaries shown by dashed lines in Fig. 1(a), can be formulated as follows. The boundary condition on the sphere surface, $r = 1$ [boundary 1 in Fig. 1(a)], reads $n_r = 0$, $n_\theta = -\cos\alpha$, $n_\phi = \sin\alpha$, which implies $\Theta = \theta - \pi/2$ and $\Phi = \alpha$. At the vertical line passing through the poles, but off the surface [boundary 2 in Fig. 1(a)], where $\theta \to 0$ and $r > 1$, $\mathbf{n}$ must be along the z axis; hence $\Theta \to 0$ and $\Phi \to 0$. Far from the colloid [boundary 3 in Fig. 1(a)], for $r \gg 1$, $\mathbf{n}$ must be a superposition (1) of the quadrupole and dipole terms. The director field with these conditions can be obtained precisely only by purely numerical methods. In the absence of such results, we are left to resort to the ansatz approach in the spirit of Ref. [7]. The following ansatz satisfies the above conditions:

$$\Theta = \arctan(\tan\widetilde{\Theta}),$$

$$\widetilde{\Theta} = 2\theta - \arctan\left(\frac{r^{3/2}\sin\theta}{r^{3/2}\cos\theta - 1}\right) - \arctan\left(\frac{r^{3/2}\sin\theta}{r^{3/2}\cos\theta + 1}\right), \tag{6}$$

$$\Phi = \left[\frac{r}{\alpha} + \frac{(r-1)^2}{3c\sin\theta}\right]^{-1}. \tag{7}$$

The auxiliary variable $\widetilde{\Theta}$ is discontinuous and can take values larger than π, whereas the angle Θ is continuous and takes values in the segment $[-\pi/2, \pi/2]$. For $r = 1$ and $\theta > 0$, one has exactly $\Theta \to \theta - \pi/2$ and $\Phi \to \alpha$ (boundary 1); when $\theta \to 0$, but $r^{3/2}\cos\theta > 1$, $\Theta \to 0$ and $\Phi \to 3c\sin\theta/(r-1)^2 \to 0$ as required (boundary 2); finally, when $r \gg 1$, $\Theta \to -\sin 2\theta/r^3$ and $\Phi \to 3c\sin\theta/r^2$ (boundary 3). Thus, the large r asymptotics of the ansatz director is of the form (1) with $Q = -0.2$ and $C = c$ (in the standard units, $Q = -0.2{r_0}^3$ and $C = c{r_0}^2$).

We see that a colloid described by the ansatz (Θ, Φ) has the fixed quadrupole component and CD component determined by the variational parameter c. There are four reasons to justify this approach. First, we failed to invent a robust ansatz parametrization of the quadrupole component, which would result in a lower quadrupole energy than that of the ansatz field (6); second, the values of $|Q|$ for PQ that can be extracted from the experimental data of Refs. [27] and [28] are, respectively, 0.17 and 0.2, in good agreement with the above value 0.2 (note, however, that the data of Refs. [26,29] suggest a notably larger $|Q| \sim 0.66$ and 0.4, respectively); third, the effect consists in an emergence of a dipole component whose contribution to the energy is considerably larger than the expectedly fixed quadrupole contribution, and hence it is the dipole energy that should be optimized as a function of the angle α; fourth, the ansatz approach can give only a qualitative result of the correct order of magnitude [22], and it is reasonable to keep it as simple as possible.

III. RESULTS AND DISCUSSION

The parameter c was found by numerical minimization of the elastic free energy for the field (Θ, Φ). This ansatz was substituted in the standard Frank free energy with the fixed elastic constants K_{11}, K_{22}, and K_{33} and then minimized for a given α. The minimizer $c(\alpha)$ is found to strongly depend on the bend/twist anisotropy $b = K_{33}/K_{22}$, while its dependence on the splay/twist anisotropy $s = K_{11}/K_{22}$ is relatively weak (Fig. 2). The maximum value of the curve $c(\alpha)$ strongly depends on b: For $b = 2 - 3$, $c_{\max}$ is ~0.2; for $b = 5$, $c_{\max} \sim 0.5$; for $b = 7$, $c_{\max}$ is already ~1, while for $K_{33}/K_{22} = 10$, $c_{\max}$ jumps to the value ~4. The reason is that the anchoring-imposed azimuthal component at the surface relaxes through all the three deformation modes, not only through the twist. Close to the colloid these deformations cost high energy, the bend deformation contributing the most as, in particular, K_{33} is the largest elastic constant. Hence saving the bend energy is possible if the imposed director components vary faster at large distances and as slow as possible at small distances. Then the deformational coat of the φ component expands, its effective radius increases, and thus the dipole strength becomes higher. In other words, the bend energy is saved at the expense of a larger twist and hence a stronger CD component. Clearly, this effect is stronger for larger K_{33}/K_{22}. The dependence $c_{\max}(b)$ can be approximated by the function $c_{\max} \approx 0.1\exp(b/2.7)$.

The dipole-dipole interaction of colloids with a finite α can considerably alter the quadrupole-quadrupole interaction of pure PQs. The fields of the force directions acting between the two PQs and two hybrid colloids with the CD components of the like and unlike handedness are shown in Fig. 3 [the left screw corresponds to $C > 0$; the right screw corresponds

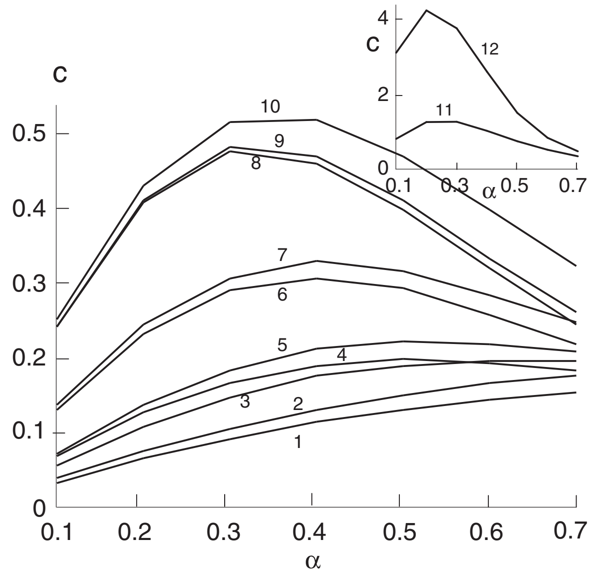

FIG. 2. Numerical value of the dipole coefficient c vs α for different elastic anisotropy $s = K_{11}/K_{22}$ and $b = K_{33}/K_{22}$. 1: $s = 1, b = 2$; 2: $s = 2, b = 2$; 3: $s = 2, b = 2.6$; 4: $s = 1, b = 3$; 5: $s = 2, b = 3$; 6: $s = 1, b = 4$; 7: $s = 2, b = 4$; 8: $s = 0.5, b = 5$; 9: $s = 1, b = 5$; 10: $s = 3.33, b = 5$; 11: $s = 0.5, b = 7$; 12: $s = 0.5, b = 10$.

to $C < 0$ [22]; for instance, the CD in Fig. 1(b) has $C > 0$]. The maximum attraction of PQs is along the line $\Psi \simeq 49^\circ$ [Fig. 3(a)], while the maximum repulsion is along, $\Psi = 0$, and across, $\Psi = 90^\circ$, the unperturbed director [Eq. (3)]. At the same time, the maximum attraction of two CDs is along the director for $C_1C_2 > 0$ (both CDs have like handedness) [Fig. 3(b)] and across the director otherwise [Fig. 3(c)] [22]. In particular, the quadrupole repulsion can be balanced by the dipole attraction along the director, for $C_1C_2 > 0$ [Fig. 3(b)], and across the director, for $C_1C_2 < 0$ [Fig. 3(c)]. The correspondent distances $R_\parallel$ and $R_\perp$ between two identical colloids are

$$R_\parallel/r_0 = \frac{20\sqrt{3}Q}{9c(\alpha)}, \quad R_\perp/r_0 = \frac{10Q}{3c(\alpha)}, \tag{8}$$

where $Q = -0.2$ is the quadrupole moment of a pure PQ. Both distances are inverse proportional to $c(\alpha)$: For small c the balance is possible for very large distances, which means that the dipole component is negligible. Even for a modest $b = 2.6$ pertinent to the standard $5CB$ liquid crystal, these distances can be small: For $\alpha \simeq 0.7$, $R_\parallel \simeq 3.8r_0$ (Fig. 4) and $R_\perp \simeq 3.3r_0$; hence the effect is strong and observable. An even stronger effect is expected close to a nematic-smectic A transition temperature where b can be very large (see Ref. [31] for the recent discussion of possible values of K_{33}/K_{22} for $8CB$ liquid crystal at this transition).

Because of the high viscosity of a NLC, the force direction coincides with the velocity direction of a colloid. Then Fig. 3 can also be used to find the trajectories of a hybrid PQ&CD colloid in the field of another such colloid placed at the origin. It is seen that the CD components make it possible an attractive trajectory along the director, for $C_1C_2 > 0$, and across the director, for $C_1C_2 < 0$. None of them is possible without a CD component: Two pure PQs repel one another in both directions. The existence of these two attractive trajectories is the qualitative effect of the azimuthal-anchoring-induced CD component, which should be observed without force measurements.

For completeness, we studied a possibility that the azimuthal director component with nonzero α appears spontaneously provided the azimuthal anchoring is degenerate and the director can rotate on the colloid surface without energy loss. Such an instability is known to be possible inside a spherical nematic droplet if

$$K_{33}/K_{11} \leqslant 2.32(1 - K_{22}/K_{11}), \tag{9}$$

i.e., when K_{33}/K_{11} and K_{22}/K_{11} are sufficiently small [32]. This condition is not exotic and can be fulfilled in the standard $8CB$ compound sufficiently far from the NLC-SmA transition [33]. In our case, however, when the NLC is outside the sphere, the instability turns out to be practically impossible. The onset of nonzero α is determined by the condition that the lowest order, the α^2 term in the energy expansion, vanishes. Using the ansatz (6, 7), expanding analytically the energy in the powers

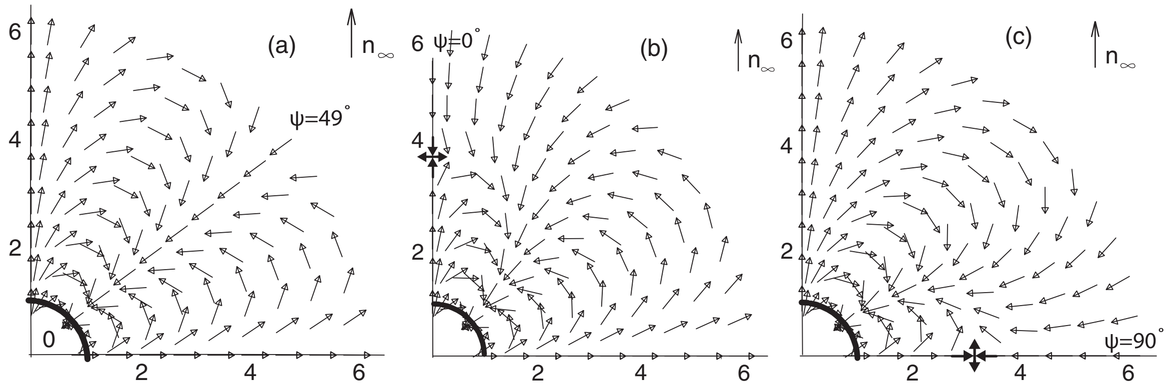

FIG. 3. Directions of the force a colloid at the center exerts on another similar colloid; the spatial scale (indicated by integers along and across the director) is in units r_0. (a) Both colloids are pure PQs, the attraction direction is at $\Psi \simeq 49^\circ$. (b) Two quadrupoles with PQ and CD components of like handedness, $C_1C_2 > 0$, the attraction direction is at $\Psi = 0^\circ$. (c) Two quadrupoles with PQ and CD components of opposite handedness, $C_1C_2 < 0$, the attraction direction is at $\Psi = 90^\circ$. The saddle balance point is shown by crossed arrows. The fields in panels b and c correspond to curve 3 in Figs. 2 and 4: $s = 2$, $b = 2.6$. Because of very different scales, the force magnitude is not indicated.

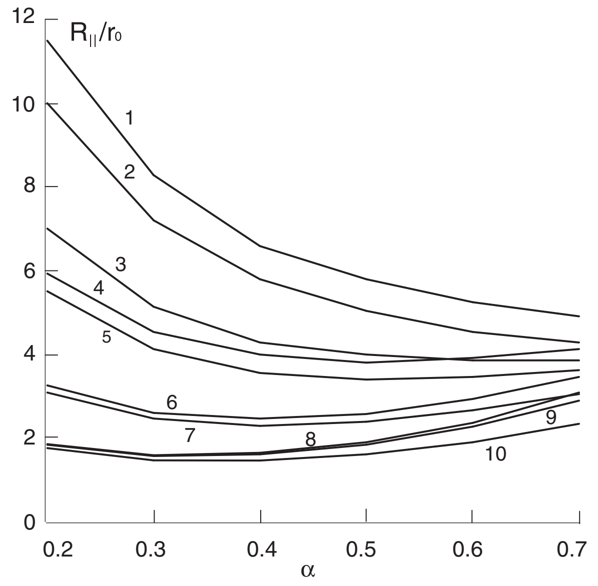

FIG. 4. Numerical values of the balance distance $R_{||}$ (in units r_0) vs angle α. The curves with the same numbers in this figure and Fig. 2 correspond to the same anistropies s and b.

of α and numerically calculating the coefficient of α^2, we found this condition in the form

$$K_{11} = 2.3K_{33} + 19.6K_{22}. \tag{10}$$

This requires that $K_{11} \gg K_{22}, K_{33}$. We do not know NLCs with such anisotropy. In this regard we note that a spontaneous twist is possible outside a spherical colloid with a strong normal surface anchoring, which induces a hyperbolic point defect (hedgehog) in its proximity and gives rise to the so-called topological dipole. For a sufficiently small K_{22}/K_{11}, the strong splay and bend deformations around the hyperbolic hedgehog can be reduced at the expense of spontaneous twist mode with an azimuthal director component [9,34]. This twist, however, adds a small CD component to the large nonchiral uniaxial dipole, and the effect of CD itself cannot be sharp.

Thus, the considered effect can be induced only by an azimuthal anchoring. An important question is what the appropriate colloid size and azimuthal anchoring strength have to be for the effect to be realistic. Reportedly, spherical bids of a 3–4 μm diameter with a strong tangential polar anchoring resulting in bipolar PQs are readily accessible experimentally [26–29] (the polar anchoring reported in Ref. [26] is less than 10^{-4}J/m^2). The problem is that the azimuthal anchoring W_{az} can be considered strong and the azimuthal angle α fixed if the colloid radius r_0 is considerably larger than the anchoring extrapolation length L_{az}, which, in the case of interest, is related to the twist elastic constant, i.e., $L_{\text{az}} = K_{22}/W_{\text{az}}$. A weak azimuthal anchoring is in the range 10^{-6}–10^{-5}J/m^2, the standard value of the twist elastic constant $K_{22} \approx 5 \times 10^{-12}$N, which gives $L_{\text{az}} = 0.5$–5μm. Thus, the colloid radius should be a few micrometers, for $W_{\text{az}} = 10^{-5}$J/m^2, and about or more than 10μm, for $W_{\text{az}} = 10^{-6}$J/m^2. Close to a NLC-smectic A transition K_{22} increases, L_{az} is expected to be larger; hence the colloid has to be larger, too.

We would like to conclude the paper by suggesting possible ways of making colloids with a helical surface anisotropy (although the subject is admittedly beyond our competence as theorists). A polymer NLCs considered in Ref. [35] has an extremely low ratio $K_{22}/K_{11} \sim 6 \times 10^{-2}$ and $K_{33}/K_{11} \approx 2$. Imagine that an interface between this polymer NLC and some isotropic liquid imposes a degenerate tangential boundary conditions on the surface director. Then droplets of the polymer NLC suspended in this isotropic liquid will certainly be twisted as the criterion of the spontaneous twist transition (9) is readily satisfied. As predicted in Ref. [32], the lines of the surface director in such droplets will be very close to loxodroms. On polymerizing, the droplets will become solid bids of a spherical form with helical surface patterns. Thus, one can expect that such bids immersed in a NLC can have a helical component in their azimuthal surface anchoring. Another possibility is that a bunch of long fibers are stretched and then twisted. The surface pattern in the resulting string will have a helical structure. Then the string's temperature is raised very close to the melting point so that the material of the string partially liquidizes and starts to form droplet-like bulges. As the bulges have developed sufficiently, the material is cooled and then cut into individual bulges. If the helical pattern will at least partially sustain the liquidizing, then the bulges can serve as colloids with the helical surface patterns [36]. It is important that a spherical shape was chosen in this paper just as an example, and actually an elongated nonspherical colloid with a helical component of the azimuthal anchoring would be even more effective as far as the CD component is concerned: Clearly, a larger lateral surface does not increase the quadrupole moment but does increase a CD component. In any case one should not forget that even molecular chiral dipoles give rise to the macroscopic cholesteric spiral. Why would not one try to experiment with manmade micrometer-size chiral dipoles?

APPENDIX A: UNCOUPLING OF THE CD AND PQ COMPONENTS

Assume that index t takes values x and y, indexes α, β, γ take values x, y, z, and there is a summation over the repeating indexes. Then the dipole-quadrupole interaction potential can be written as the following sum of the two scalars:

$$U_{dQ} = \frac{16\pi K}{R^5}\left[5Q^{(2)}_{t,\alpha\beta}d^{(1)}_{t,\gamma}u_\alpha u_\beta u_\gamma - 2Q^{(2)}_{t,\alpha\beta}d^{(1)}_{t,\alpha}u_\beta\right],$$

where $Q_{t,\alpha\beta}$ and $d_{t,\alpha}$ are the elastic quadrupole and dipole dyads [12,20,21], and u_α is the unit vector in the separation direction, $\mathbf{u} = \mathbf{R}/R$. In the case of a PQ and CD, the nonzero components of the dyads are $Q_{x,xz} = Q_{x,zx} = Q_{y,yz} = Q_{y,zy} = Q$ [12] and $d_{x,y} = -d_{y,x} = C$ [22]. Substituting these components in the above U_{dQ} gives zero: The CD and PQ components do not interact.

APPENDIX B: THE FREE-ENERGY CONTRIBUTION OF THE DIVERGENCE TERMS IS NEGLIGIBLE

The free energy of the divergence K_{24} and K_{13} terms can be converted to the surface integrals of the form

$$\int dS(-K_{24}f_{24} + K_{13}f_{13}), \tag{B1}$$

where

$$f_{24} = \nu[\mathbf{n}(\nabla\mathbf{n}) - (\mathbf{n}\nabla)\mathbf{n}], \quad f_{13} = (\nu\mathbf{n})(\nabla\mathbf{n}), \tag{B2}$$

and ν is the unit outer surface normal. To consider an arbitrary curved surface of an NLC it is convenient to introduce the following curvilinear orthogonal coordinate system (x_1,x_2,x_3) with metric tensor g_{ij}: The boundary S coincides with the coordinate surface $x_3 = \text{const}$, x_1 and x_2 are the orthogonal coordinates on S, and the outer normal to S is directed along the coordinate line x_3, i.e., $\nu = (0,0,1)$; the differential of the surface area is $dS = \sqrt{g_{11}g_{22}}dx_1dx_2$. Then the integrand in Eq. (B1) can be rewritten in the following form [37]:

$$-K_{24}f_{24} + K_{13}f_{13} = f_{||} + f_{\perp}, \tag{B3}$$

where

$$f_{||} = -K_{24}J + \frac{K_{13}-K_{24}}{\sqrt{g}}\left[n_3^2\partial_3\sqrt{g_{11}g_{22}} + n_3\partial_1\left(n_1\sqrt{\frac{g}{g_{11}}}\right) + n_3\partial_2\left(n_2\sqrt{\frac{g}{g_{22}}}\right)\right], \tag{B4}$$

$$f_{\perp} = K_{13}\frac{n_3\partial_3 n_3}{\sqrt{g_{33}}}. \tag{B5}$$

Here $g = g_{11}g_{22}g_{33}$, $\partial_i = \partial/\partial x_i$, and J is given by the formula

$$\sqrt{g}J = n_1^2\sqrt{g_{22}}\partial_3\sqrt{g_{11}} + n_2^2\sqrt{g_{11}}\partial_3\sqrt{g_{22}} - (n_2\sqrt{g_{11}}\partial_2 + n_1\sqrt{g_{22}}\partial_1)(\sqrt{g_{33}}n_3). \tag{B6}$$

If S is a sphere, the above coordinate system is a spherical one where $(x_1,x_2,x_3) = (\theta,\phi,r)$ and $(n_1,n_2,n_3) = (n_\theta,n_\phi,n_r)$; the order of the coordinates is obtained from its standard form (r,θ,ϕ) by the clockwise permutation to fulfill the requirement that the coordinate line $x_3 = r$ is normal to S. Then S is given by $r = r_0$, and the metric tensor components are $g_{11} = g_{\theta\theta} = r^2$, $g_{22} = g_{\phi\phi} = r^2\sin^2\theta$, $g_{33} = g_{rr} = 1$, $\sqrt{g} = \sqrt{g_{11}g_{22}} = r^2\sin\theta$. Making use of these expressions in the formulas (B4)–(B6), one obtains

$$\int dSf_{||} = 2\pi r_0\int_0^\pi d\theta\sin\theta\big[-K_{24}\big(\sqrt{1-n_r^2} - n_\theta\partial_\theta n_r\big) + (K_{13}-K_{24})\left(2n_r^2 + n_rn_\theta\cos\theta + n_r\partial_\theta n_\theta\right)\big],$$

$$\int dSf_{\perp} = K_{13}\pi r_0^2\int_0^\pi d\theta\sin\theta\partial_r n_r^2, \tag{B7}$$

where the calculations are performed at $r = r_0$. The geometry considered implies that the functions n_θ, n_r, and $\sin\theta$ are symmetric with respect to the plane $\theta = \pi/2$, whereas $\partial_\theta n_r$, $\partial_\theta n_\theta$, and $\cos\theta$ are antisymmetric. We see that by virtue of this symmetry, the nonvanishing director-dependent terms in the above surface integrals are of the order n_r^2. These terms are negligible. Indeed, if the polar anchoring is infinite, then $n_r \neq 0$ only in the small vicinity of the poles where $\sin\theta \ll 1$; if the polar anchoring is finite, but its extrapolation length L_{pol} is small compared to the colloid size r_0 (the assumption which makes the study meaningful), then the additional contribution of the divergence terms is negligible since outside the polar caps $n_r^2 \sim (L_{\text{pol}}/r_0)^2$.

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