Nematic-Wetted Colloids in the Isotropic Phase: Pairwise Interaction, Biaxiality and Defects

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We calculate the interaction between two spherical colloidal particles embedded in the isotropic phase of a nematogenic liquid. The surface of the particles induces wetting nematic coronas that mediate an elastic interaction. In the weak wetting regime, we obtain exact results for the interaction energy and the texture, showing that defects and biaxiality arise, although they are not topologically required. We evidence rich behaviors, including the possibility of reversible colloidal aggregation and dispersion. Complex anisotropic self-assembled phases might be formed in dense suspensions.

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Dispersions of small particles or liquid droplets in a host fluid, namely colloidal suspensions, are a widespread and important state of matter [1]. They are long-lived metastable states, of fundamental interest from the point of view of collective interactions in complex matter. They also have considerable technological importance, e.g., in paints, coatings, foods and drugs. To prevent coagulation due to attractive van der Waals forces, usually the particles are treated in order to produce Coulombic or steric repulsive interactions. Recently, a novel source of repulsion has been reported: the elastic distortion of a liquid crystal host [2], i.e., a fluid phase with long-range orientational order of the molecules. The repulsion arises from the competition between the surface aligning property, which favors, e.g., a radial orientation of the nematic molecules, and the bulk elasticity, which favors a uniform nematic orientation [3]. This effect was shown to arise also in other anisotropic fluid hosts, e.g., lyotropic solutions of anisotropic micelles [4], and in different liquid crystal phases, e.g., cholesterics [5]. Lately, such systems were shown to form liquid or solid composite materials with unusual properties [6].

It is well known that solid surfaces influence not only the orientation of liquid crystals, but also, in general, the degree of order of their constituent molecules. In particular, a surface can induce a wetting nematic layer even above the transition temperature at which the nematic becomes an ordinary isotropic liquid [6] [10]. Therefore, an elastic colloidal stabilization could be achieved also above the nematic–isotropic transition. In addition, the vicinity of a phase transition may give a critical character to the stabilization mechanism and yield rich phase-separation behaviors, as predicted in [11] for a simpler system with a scalar order-parameter.

To understand these complex collective effects, it is essential to calculate the interaction between the particles precisely. An attempt, based on a quasi-planar approximation and assuming uniaxiality of the nematic tensorial order, has been proposed in Ref. [12]. Here, we give the first exact solution to the problem, including biaxiality. Our calculation, based on a multipolar expansion, is valid for weak surface ordering. We obtain numerically the texture between two spherical particles imposing normal boundary conditions: unexpectedly, we find a defect line that is not topologically required and a strong biaxiality around it. We give an analytical expression for the interaction energy at large distances, which we find always attractive. At short distances, comparable to the nematic coherence length, we find either attraction or repulsion, depending critically on the distance to the nematic-isotropic transition. Collective behaviors could thus be critically tuned in such systems, in analogy with, e.g., the switchable tackiness or wettability of liquid crystal polymers [13].

Nematic liquid crystals are anisotropic liquid phases, in which elongated molecules display a long-range orientational order. Since nematics are non-polar, this order is described by a symmetric traceless tensorial order-parameter $Q_{ij}$ ($i, j = 1, 2, 3$). The eigenvectors of $Q_{ij}$ represent the axes of main molecular orientation and its eigenvalues describe the amount of ordering and biaxiality [6]. Usually, nematics are uniaxial phases, however biaxiality naturally arises in inhomogeneous situations, e.g., in the vicinity of defects [15]. For a weak induced nematic order in the isotropic phase, the quadratic Landau-de Gennes expansion of the bulk free-energy density [14] has the form

$$f = \frac{1}{2} a Q_{ij} Q_{ij} + \frac{1}{2} L Q_{ijk} Q_{ijk},$$

where $a > 0$ (resp. $L > 0$) quantifies the cost of creating (resp. distorting) the nematic phase. For simplicity, we take a one-constant approximation for the gradient terms. We consider spher-
tical colloidal particles dispersed in the isotropic phase of the nematic. They favor a uniaxial nematic order \( Q_{ij}^{(0)} = S_0 (\nu_i \nu_j - \frac{1}{3} \delta_{ij}) \) on their surface, of outward normal \( \nu \). Here, \( 0 \leq S_0 \leq 1 \) is the preferred surface scalar order parameter and \( \delta_{ij} \) the Kronecker delta. At quadratic order, the corresponding surface free-energy density is

\[
fs = \frac{1}{2} W \left( Q_{ij} - Q_{ij}^{(0)} \right) \left( Q_{ij} - Q_{ij}^{(0)} \right), \quad (2)
\]

where \( W \) measures the anchoring strength.

Scaling lengths to the nematic correlation length \( \xi = (L/a)^{1/2} \) and energies to \( F_0 = a \xi^3 S_0^2 \), the total free-energy can be written as

\[
F = \sum_{i=0}^{4} \frac{c_i}{r} \int \left[ \left( \nabla q_i \right)^2 \right] d^3r + \frac{w}{S} \int \left( q_i - q_i^{(0)} \right)^2 d^3r \label{eq:free_energy}
\]

where \( q_0 = (Q_{xx} - Q_{yy})/S_0 \), \( q_1 = Q_{yz}/S_0 \), \( q_2 = Q_{zx}/S_0 \), \( q_3 = Q_{xy}/S_0 \), \( q_4 = Q_{zz}/S_0 \), \( c_0 = 1/4 \), \( c_1 = c_2 = c_3 = 1 \), \( c_4 = 3/4 \), and \( w = W/(a \xi) \) is a normalized anchoring strength. The corresponding equilibrium equations are

\[
\nabla^2 q_i = q_i, \quad (4)
\]

in the bulk, and

\[
\nu \cdot \nabla q_i = w \left( q_i - q_i^{(0)} \right), \quad (5)
\]

on the surface of each colloidal particle. In spherical coordinates \((r_p, \theta_p, \phi_p)\) centered on colloidal particle \( p \), the general solution of Eq. \((4)\) that is regular everywhere but in \( r_p = 0 \) can be written as a multipolar expansion:

\[
q_i = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} q_i^{\ell m} u_{\ell}(r_p) Y_{\ell m}(\theta_p, \phi_p), \quad (6)
\]

where \( Y_{\ell m}(\theta_p, \phi_p) \) are spherical harmonics and \( u_{\ell}(r_p) = \sqrt{2/(\pi r_p)} K_{\ell+1/2}(r_p) \), in terms of half-integer modified Bessel functions. The solution to Eqs. \((4)\) and \((6)\) can be written as a superposition of a multipolar expansion \((6)\) for each particle, the coefficients of which can be adjusted by imposing the boundary conditions \((4)\) for each spherical harmonic.

In the following, we consider the case of two identical particles, with reduced radius \( R = 2 \) and centers in \( z = \pm d/2 \). Then, by symmetry,

\[
q_0 = \alpha(r, \theta) \cos 2\phi, \quad (7a)
\]

\[
q_1 = \beta(r, \theta) \sin \phi, \quad (7b)
\]

\[
q_2 = \beta(r, \theta) \cos \phi, \quad (7c)
\]

\[
q_3 = \frac{1}{2} \alpha(r, \theta) \sin 2\phi, \quad (7d)
\]

\[
q_4 = \gamma(r, \theta), \quad (7e)
\]

FIG. 1. Order-parameter profile between two spheres of reduced radius \( R = 2 \) with normalized anchoring strength \( w = 4 \). The profile has cylindrical symmetry about the axis joining the centers of the two spheres. Top: field lines of the nematic director \( \nu \); Middle: contour lines of the uniaxial order parameter \( S \); Bottom: contour lines of the biaxial order parameter \( B \). The dots indicate the center of the core (the biaxial region) of the \( -\frac{1}{2} \) defect Saturn ring.

where \((r, \theta, \phi)\) are spherical coordinates relative to the origin, and

\[
\alpha(r, \theta) = \sum_{\ell=2}^{\infty} \sum_{p=1}^{2} \alpha_{\ell p} u_{\ell}(r_p) P_{\ell}^2(\cos \theta_p), \quad (8a)
\]

\[
\beta(r, \theta) = \sum_{\ell=1}^{\infty} \sum_{p=1}^{2} (-1)^p \beta_{\ell p} u_{\ell}(r_p) P_{\ell}^1(\cos \theta_p), \quad (8b)
\]

\[
\gamma(r, \theta) = \sum_{\ell=0}^{\infty} \sum_{p=1}^{2} \gamma_{\ell p} u_{\ell}(r_p) P_{\ell}^0(\cos \theta_p), \quad (8c)
\]

in which the \( P_{\ell m}^m \) are the modified Legendre functions appearing in the spherical harmonics \( Y_{\ell m} \).

Solving for \( \alpha_{\ell}, \beta_{\ell}, \gamma_{\ell} \) at leading order in the reduced separation \( d \), we obtain the asymptotic interaction free-
energy (subtracted of the self-energy of each particle):  
\[ F \sim \frac{-8\pi w^2 R^8 \exp(-d + 2R)}{3d [9 + 3(3 + w) R + (4 + 3w) R^2 + (1 + w) R^3]^2}. \]

Hence, the interaction is always asymptotically attractive, in disagreement with the estimation of Ref. [12].

At arbitrary distance \( d \), we solve numerically the linear system giving \( \alpha, \beta, \gamma \) by truncating the expansions \( \mathcal{Q} \) at some order \( \ell_{\text{max}} \) and checking for convergence. From the three eigenvalues \( \lambda_1 > \lambda_2 > \lambda_3 \) (with \( \lambda_1 + \lambda_2 + \lambda_3 = 0 \)) we obtain the scalar order-parameter \( S = \frac{3}{2} \lambda_1 \) and the biaxiality \( B = \frac{1}{2} (\lambda_2 - \lambda_3) \). We call nematic director \( \mathbf{n} \) the direction corresponding to the largest eigenvalue \( \lambda_1 \).

Typical profiles of \( \mathbf{n}, S \) and \( B \) are shown in Fig. 4. The tensor \( \mathcal{Q} \) is everywhere continuous, however, a defect (discontinuity) of \( \mathbf{n} \) appears, in the form of a “Saturn ring” of strength \(-\frac{1}{4}\). This defect is not topologically required: one can expand it to infinity, where it would disappear since \( \mathcal{Q} \) vanishes. Thus, it arises spontaneously to minimize the energy, similarly to focal conic defects in smectic-\( \Delta \) “batonnets” [16]. Note that our calculation does include the defect’s core energy, since it resolves the gradients of \( \mathcal{Q} \) also within the core. Our only approximation is the neglect of higher-order gradient terms in Eq. (8): this is however justified as long as \( \xi \) is much larger than the range of molecular interactions. Biaxiality develops within the Saturn ring. Again, this is surprising, since both the bulk and the surface favor uniaxiality. Thus, any modeling of similar systems assuming uniaxiality might miss important features. The behavior of the eigenvalues of \( \mathcal{Q} \) along a diameter of the defect is shown in Fig. 2. On the ring’s center, \( \lambda_1 = \lambda_2 \): the nematic is locally uniaxial in the direction of the ring, however with a discotic-like ordering, since the ring axis corresponds to the smallest eigenvalue.

The behavior of the interaction energy as a function of the separation \( d \) exhibits many detailed features. At large \( d \)’s, it is always attractive, in agreement with the asymptotic expression (9). Then, we distinguish six scenarios, depending on the value of \( R \) and \( w \) (Fig. 3). In case 0, the interaction is monotonically attractive. In case 1a (resp. 1b), a minimum develops, the interaction energy at contact being negative (resp. positive), as shown in Fig. 4. In case 2a, 2b and 2c, the interaction energy displays first a minimum then a maximum, as \( d \) decreases. In case 2a, both the maximum and the contact energy are negative; in case 2b, the maximum is positive while the contact energy is negative; finally, in case 2c both the maximum and the contact energy are positive (Fig. 3).

To understand the collective behavior of such colloids, one needs to compare the amplitudes of the barriers and of the wells of the interaction energy with \( k_B T \). To simplify, let us assume that the colloids are treated, e.g., with surfactants or polymer coatings, such as to prevent aggregation due to van der Waals attraction. Qualitatively, we distinguish three different cases. Whenever the interaction energy displays a minimum deeper than \( k_B T \), attraction occurs, yielding aggregation either at contact or at a finite distance. Otherwise, two cases are possible. If a maximum is present with a height larger than \( k_B T \),...
short-range repulsion occurs: the nematic alone could stabilize the colloidal dispersion. If, on the other hand, the energy is everywhere smaller than $k_B T$, the interaction is indifferent. Figure 6 displays the phase behavior of colloidal particles of fixed radius when changing the distance to the nematic transition. Here we have assumed $L \simeq k_B T/m$, $S^2 \simeq 0.5$, and $W \simeq k_B T/m^2$, where $m$ is a molecular or a micellar length. Note that $W$ is a microscopic anchoring, stronger than the corresponding coarse-grained anchoring that would be measured at a macroscopic scale $\xi$.

In conclusion, we have investigated the interaction between colloidal particles dispersed in the isotropic phase of a nematogenic liquid. Our calculations show that small particles, of size ranging from a few to several hundreds nematic correlation lengths, could be reversibly dispersed or aggregated by tuning the vicinity to the nematic transition, e.g., by changing the temperature. Interesting effects might occur when more than two particles are brought together. Standard aggregation favors three-dimensional close packing. Here, however, the onset of extra defects might produce anisotropic self-assembled structures, although both the embedding fluid and the particles are isotropic. Indeed, while it is obvious that three particles in a line will create two Saturn rings, it is not easy to picture the defects, and the associated energy, in the case of three particles forming a triangle, or four forming a tetrahedra. Our method allows to calculate the textures and free-energies of arbitrary arrangements of colloidal particles. Such detailed studies are however beyond the scope of this paper, since they require heavy numerical simulations: further analyses are required to investigate whether gel-like structures (when linear aggregates are favored) or smectic-like structures (when two-dimensional close-packing is favored) could arise.

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\[ F = \frac{\xi}{m} \times 10^{-3} \]

\[ \xi/m \]

\[ R \]

\[ 1 \]

\[ A \]

\[ \mathcal{R} \]

\[ 10 \]

\[ 100 \]

\[ I \]

\[ 10 \]

\[ 100 \]

FIG. 5. Dimensionless interaction energy $F$ as a function of $d$ for $R = 0.7$ and $w = 2$ (continuous line: case 0), $w = 2.6$ (dashed line: case 2a), $w = 3.2$ (dash-dotted line: case 2b), $w = 3.6$ (dotted line: case 2c). Different scales for $F$ are used on the two sides of the vertical line.

FIG. 6. Different regimes of the interaction between two colloidal particles, as gauged by $k_B T$: I indifferent, R repulsive, A attractive. $\mathcal{R}$ is the particle radius in molecular or micellar units $m$, and $\xi$ is the nematic coherence length.