

## Long-range forces and aggregation of colloid particles in a nematic liquid crystal

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We calculate the long-range pair potential between spherical colloid particles suspended in a uniform liquid crystal. At weak director anchoring on the particle surface the director distortions decay as  $\delta n \sim r^{-3} \sin 2\theta$  away from its center. This leads to an anisotropic interaction potential of the form  $U \sim d^{-5}$  with  $d$  the distance between two colloid particles. This interaction also depends on the particle position with respect to the nematic director, giving strong repulsion for particles along the director axis and for particles located in the perpendicular plane, and attraction at oblique angles. We also analyze the system behavior in an external field, when the director decays exponentially away from the particle and, hence, interaction forces are short range. [S1063-651X(97)02603-2]

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Colloid suspensions are characteristically mesoscopic systems with structure and time scales such that typical shear rates can bring them out of equilibrium and into some exotic states. Even without a flow the structure and properties of colloids pose a number of theoretical and experimental challenges [1,2]. Of much interest are various novel interactions, for instance, hydrodynamic and polymeric solvent-mediated forces. Many obvious practical applications of colloid systems add to the fundamental interest of this class of objects.

Colloid suspensions in a liquid crystal matrix are qualitatively different from their isotropic analogues due to the long-range deformation field  $\mathbf{n}(\mathbf{r})$  created by particles in the liquid crystal [3]. Perhaps one of the most important applications of liquid crystal colloids is the moulding processing of filled liquid crystalline polymers and the suspension of abrasive particles in lyotropic mesophases. Recently the phase equilibrium of a nematic colloid has been examined experimentally [4]. In that work the authors also explore the theoretical model, accounting for the steric interaction between particles and the concept of "distortion" of nematic order by individual particles.

Obviously, the effect of a suspended particle on the orientational order in its surrounding will depend on the strength and type of director anchoring on its surface. Colloids with extremely weak anchoring will disturb the static director field very little, although in the flow one must expect a significant effect due to the Leslie-Ericksen coupling [5]. Particles with very strong anchoring create a topological mismatch with the otherwise uniform director field and develop singularities. The resulting director texture can have a quadrupolar symmetry, such as that of the nematic matrix itself. In this case one obtains a pair of polar boojums for planar anchoring, or a  $(-1/2)$  disclination ring for radial (homeotropic) anchoring. The equilibrium quadrupolar director field around a single spherical particle has been analyzed theoretically [3], where it has been shown that in all cases the director distortions decay as  $r^{-3}$  away from the particle. It is possible that large particles with an accompanying topological defect have a director texture of different symmetry. A dipolar arrangement with a single companion monopole may occur [6]. Higher multipoles will appear in the director field for soft deformable particles, capable of

adjusting their shape. Such long-range deformation fields must have a strong effect on interaction forces in the resulting colloid system.

This paper describes a calculation of the pair interaction potential between quadrupolar spherical colloid particles in a uniform liquid crystal matrix. This is possible only for the case of weak director anchoring, when the linearized equilibrium conditions can be solved exactly. In the low-density colloid (i.e., large particle separation  $d$ ) we show that the pair interaction potential  $U \sim d^{-5}$  and is very anisotropic [these results correct the previous analysis [7], where an oversimplified ansatz for  $\mathbf{n}(\mathbf{r})$  has been used]. It will turn out that this regime may, in fact, span over colloid concentrations up to the crystallization point and thus is important in the analysis of the phase behavior. In the end we briefly look at the situation, where the nematic director is made more rigid by the application of an external electric or magnetic field. In this case the director distortions decay exponentially and the particles become essentially decoupled at large distances.

This paper has a qualitative nature and we, therefore, use the one-constant Frank elastic energy

$$F = \int \frac{1}{2} K [(\operatorname{div} \mathbf{n})^2 + (\operatorname{curl} \mathbf{n})^2] d^3 r - \oint \frac{1}{2} W (\mathbf{n} \cdot \hat{\mathbf{v}})^2 dS, \quad (1)$$

and neglect the  $K_{13} - K_{24}$  terms (see [3] for the discussion of surface terms in a system with singularities and inner boundaries). The anchoring contribution in Eq. (1) is chosen to be radial, with  $W$  the anchoring energy and  $\hat{\mathbf{v}}$  the unit vector normal to the surface of the spherical particle with radius  $R$ . Planar anchoring corresponds to the reversal sign of  $W$ .

In the given geometry, Fig. 1, it is convenient to describe the director field by two principal angles of a spherical coordinate system:  $n_z = \cos \beta(\mathbf{r})$ ;  $n_x = \sin \beta(\mathbf{r}) \cos \phi$ ;  $n_y = \sin \beta(\mathbf{r}) \sin \phi$ , where  $\phi$  is the azimuthal angle, thus respecting an obvious azimuthal symmetry of the problem. At small anchoring,  $WR/K \ll 1$  (see [3] for details and discussion), or sufficiently far away from any particle, the differential equation for the minimum of the Frank free energy can be linearized:

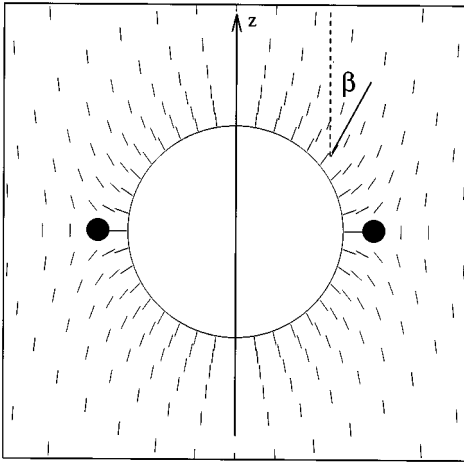


FIG. 1. Particle with rigid radial boundary conditions and a disclination ring of radius  $a$  in the plane perpendicular to  $\mathbf{n}_0$ . The rotationally symmetric director field is determined by the angle  $\beta(\mathbf{r})$ .

$$\nabla^2 \beta - \frac{\beta}{r^2 \sin^2 \theta} = 0, \quad \left( \frac{\partial \beta}{\partial r} + \frac{\beta}{r} \right)_{r=R} = -\frac{W}{2K} \sin 2\theta. \quad (2)$$

The general solution of Eq. (2), decaying at infinity and satisfying the boundary conditions, is

$$\beta = \frac{WR}{4K} \left( \frac{R}{r} \right)^3 \sin 2\theta. \quad (3)$$

Obviously, the approximation leading to this expression is satisfied when  $WR/K \ll 4$ . The convention of “weak anchoring” usually corresponds to values  $W \leq 10^{-7} \text{ J/m}^2$ . Taking the typical value for Frank elastic constants,  $K \sim 10^{-11} \text{ J/m}$ , this approximation is valid for particle sizes  $R \ll 0.4 \text{ mm}$ . Even for the conventionally “strong anchoring,”  $W \geq 10^{-5} \text{ J/m}^2$ , colloid particles smaller than  $R \sim 3-4 \mu\text{m}$  will satisfy the linearization approximation and the director field around them will be fully described by Eq. (3). The same asymptotic expression will be valid for particles with planar anchoring, which corresponds to the  $W$  sign reversal in Eq. (1), but preserves the basic quadrupolar symmetry responsible for this type of behavior. It has been shown [3] that a very good interpolation into the region of strong deformations very near the particle is achieved by the expression

$$\beta_a = \theta - \frac{1}{2} \arctan \frac{\sin 2\theta}{(a/r)^3 + \cos 2\theta}, \quad (4)$$

or with the substitution  $a^3 \rightarrow WR^4/4K$  for weak anchoring.

When two such colloid particles are not directly approaching each other, but are separated by a distance  $d \gg a$  (or, in fact, any distance at  $WR/4K \ll 1$ ), one can use the superposition principle, because in this regime the problem for the director equilibrium is linear. We denote director fields, corresponding to each particle, as  $\mathbf{n}_1 \approx (\beta_1 \cos \phi_1; \beta_1 \sin \phi_1; 1 - \frac{1}{2} \beta_1^2)$  and  $\mathbf{n}_2 \approx (\beta_2 \cos \phi_2; \beta_2 \sin \phi_2; 1 - \frac{1}{2} \beta_2^2)$  where  $\beta_{1,2}$  are the polar angles of each director distribution, given by Eq. (3) in respective spherical coordinates

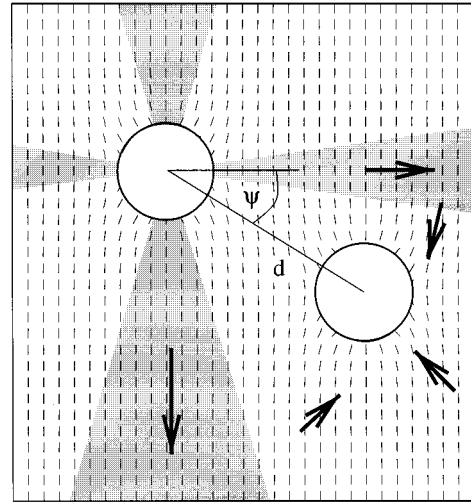


FIG. 2. Configurations of the two particles, interacting via the liquid crystalline matrix distortions. Arrows show the direction of the force, shaded sectors represent the repelling regions.

( $r_{1,2}, \theta_{1,2}, \phi_{1,2}$ ) based on each particle's center. For the aggregate superimposed director field we take the spherical coordinate system with the origin in the particle No. 1 and substitute for the other particle:

$$\begin{aligned} \beta_2 &= \frac{w^3}{r_2^3} \sin 2\theta_2, \quad \text{with } r_2^2 = (x - d \cos \psi)^2 + y^2 \\ &\quad + (z - d \sin \psi)^2; \\ \tan \theta_2 &= \frac{z - d \sin \psi}{\sqrt{(x - d \cos \psi)^2 + y^2}}, \quad \tan \phi_2 = \frac{y}{x - d \cos \psi}, \end{aligned} \quad (5)$$

where the parameter  $w$  takes the form  $w = WR^4/4K$  for weak anchoring conditions and  $\psi$  denotes the angle of the connecting line of the particle centers with the  $x$  axis (see Fig. 2).

Now all that is required is to calculate the total elastic free energy (1) using this superimposed director field. During this calculation some care should be taken in evaluating the contribution on the particle surface, which is altered by the effect of the other particle. An additional “polarization” effect is also present, but has a much higher power of  $(1/d)$ . The result will contain the energy of an individual particle distortion field ( $F \approx 6.7KW^2/R^5$ , obtained in the limit  $d \rightarrow \infty$ ) and the pair interaction potential  $U(d, \psi)$ . Since  $d/R \gg 1$  we can look for the leading term in the expansion of this potential in powers of  $R/d$  only, which turns out to be  $\sim d^{-5}$  (this can be expected from the direct power counting in the Frank free energy with  $\delta n \sim r^{-3}$ ). This analytical calculation involves quite heavy algebraic manipulations, which have been carried out with the help of the MATHEMATICA program package. However, in spite of all the complexity, it is possible to obtain the analytical result. The pair interaction potential is

$$U(d, \psi) = \frac{\pi W^2 R^8}{30Kd^5} \left( 1 - \frac{WR}{56K} \right) [9 - 20 \cos 2\psi + 35 \cos 4\psi]. \quad (6)$$

The two contributions to this potential, one from the bulk Frank energy (the second term in the brackets) and the other one from the anchoring energy (the first term in the brackets) have different signs. However, there is no possibility of changing the sense of this interaction, as long as we remain in the weak anchoring regime where the quadrupolar solution Eq. (3) is exact. Therefore, at  $WR/K \ll 1$  (which is always true for small enough particles) we have

$$U(d, \psi) \approx \frac{W^2 R^8}{K d^5} [1 - 2.2 \cos 2\psi + 3.9 \cos 4\psi]. \quad (7)$$

It is most interesting to examine the angular dependence of this pair potential and its consequence to the distribution of actual forces acting on colloid particles. Obviously,  $U(d, \psi)$  is a noncentral potential and the force on the particle (indicated by arrows in Fig. 2) has both radial and polar components, determined by the gradient of  $U$  in spherical coordinates. The dependence of  $U(d, \psi)$  on the angle  $\psi$  of the particle separation vector in the frame, based on the uniform nematic director, indicates that particles repel quite strongly, when they are aligned along  $\mathbf{n}$ . They also repel, but about 3 times weaker, when they are located in the perpendicular plane ( $\psi=0$  in Fig. 2). Particles attract each other when placed at oblique angles  $\psi$ . The conclusion of this is that in a real colloid system, when there are many particles interacting with each other in many different directions, as well as the element of Brownian motion, these particles will always find a route towards the global angular minimum of  $U(\psi)$  and will aggregate under the action of the attractive part of  $U(d, \psi)$ .

It would be interesting to see the effect of this anisotropic noncentral long-range pair interaction on the equilibrium structure of more dense colloids. As mentioned above, sufficiently small particles will always satisfy the condition  $WR/K \ll 1$  and their pair interaction will be given by Eq. (7) for all, including very small, separations—thus substantially modifying the other, traditional colloid interactions. We can estimate the order of magnitude of this liquid crystalline potential: for a typical moderate anchoring in thermotropic nematic liquid crystal,  $W \sim 10^{-6} \text{ J/m}^2$ ,  $K \sim 10^{-11} \text{ N}$  and particles with  $R \sim d \sim 1 \text{ } \mu\text{m}$ , we obtain  $U \sim 10^{-19} \text{ J} \gg k_B T$ . Note the very strong dependence on the particle size and  $W$  in Eq. (7), which can change this estimate within a wide range of values, to add to the striking effect of force anisotropy.

The time scale for the colloid particle aggregation due to the elastic liquid crystal-mediated attraction (7) is also controlled by their friction drag. The friction force  $f_d$  acting on a sphere moving through the liquid crystal has been studied theoretically [5,8] (the second paper takes into account the actual director distribution around the particle). This force is also noncentral, with the ‘lift’ component perpendicular to the line of motion and, therefore, nondissipative. Although the particle motion trajectory could be quite curious under the action of two such anisotropic forces, the order of magnitude of the aggregation time is crudely determined by the simple  $f_d \sim 6\pi\eta R v$  with  $\eta$  the characteristic viscosity. The distance between particles,  $d$ , depends on the colloid concentration  $c$ :  $d_0 \sim c^{-1/3} R$ . This leads to an estimate for time required for two particles to move towards each other (as-

suming that the long-range interaction (7) prevails over other contributions, i.e., hydrodynamic interactions being screened in a sufficiently dense system). We have

$$\tau = \int_{d_0}^d \frac{6\pi\eta R}{f(x)} dx \approx 0.5 \frac{K\eta}{W^2} \left( \frac{1}{c^{7/3}} - \frac{1}{c_m^{7/3}} \right), \quad (8)$$

where  $c_m$  is the maximal close-packing volume fraction of a given type of colloid. Using the same values for parameters of a thermotropic nematic liquid crystal as above and a typical viscosity  $\eta \sim 10^{-1} \text{ Pa s}$ , we obtain the value  $\tau \sim c^{-7/3} \times (0.5 \text{ s}) \sim 120 \text{ s}$  for a volume fraction of  $c \sim 0.1$ . Note that the Frank constants are proportional to the square of the nematic order parameter  $Q$  ( $K \sim Q^2$ ) whereas the anchoring energy  $W$  is linear in the lowest order of  $Q$ . Therefore, the aggregation time  $\tau$  is virtually independent of the temperature in the nematic phase.

An interesting turn of the above theory is obtained in the presence of an external electric or magnetic field, which makes the nematic order more rigid. In this case Eq. (2) gets an additional term,

$$\nabla^2 \beta - \left( \frac{1}{r^2 \sin^2 \theta} + \frac{\chi_a H^2}{K} \right) \beta = 0, \quad (9)$$

the solution of which decays exponentially at large distances:

$$\beta(\mathbf{r}) = \frac{1}{9\sqrt{2}\pi} \frac{WR^4}{K} \frac{1}{\xi_H^{5/2}} \frac{1}{\sqrt{r}} \mathcal{K}_{5/2}(r/\xi_H) \sin 2\theta \sim \frac{1}{r} e^{-r/\xi_H}, \quad (10)$$

with the magnetic coherence length  $\xi_H = \sqrt{K/\chi_a} H^{-1}$  [9] and  $\mathcal{K}_{5/2}(x) = \sqrt{\pi/2} e^{-x} (x^{1/2} + 3x^{2/3} + 3x^{-5/2})$  the modified Bessel function of the second kind. For moderate values of magnetic field (or electric field in the analogous setup) this characteristic length  $\xi_H$  is of the order of a few micrometers. The corresponding interaction potential will also decay exponentially. Therefore, in an external field colloid particles of suspension with a sufficiently low concentration (so that  $d \gg \xi_H$ ) will decouple and behave as in the isotropic system. Switching the field off will restore the long-range nature of this pair interaction, Eq. (7).

The pair potential  $U(d, \psi)$  between colloid particles with quadrupolar director alignment has also been obtained by the authors of [10]. That work used a different, less rigorous but more qualitatively transparent method and their conclusion is identical to our Eq. (7). This result is somewhat disappointing, because experimentally it is quite well known that foreign objects in a nematic matrix align in ‘strings’ along the director—where our  $U(d, \psi)$  indicates the repulsion region. Two possible conclusions seem to follow: (i) At strong radial anchoring,  $WR/K \gg 1$ , the quadrupolar director texture is not the optimal case. The dipolar case with a companion  $(-1)$  monopole has been examined recently [11] and, indeed, shown a possibility of forming ‘strings.’ (ii) In the case of weak anchoring (where the director field is obtained exactly) and in the case of planar anchoring (leading to a bipolar texture) the director field around the particle remains quadrupolar. Therefore, in these cases one should not expect particles to aggregate in strings along  $\mathbf{n}$ . Because the effective anchoring strength is controlled by the particle size  $R$ , we

may predict that only large radial particles (or emulsion droplets, as often used in experiments [12]) would aggregate in such a way. Smaller particles, or particles with planar anchoring would also aggregate due to the attraction at oblique angles  $\psi$ , but they would not form any distinct aggre-

gate shapes.

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