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Colloidal interactions in nematic fluids

T. G. Sokolovska,[1,2] R. O. Sokolovskii,[1,2] and G. N. Patey[1]
[1]*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6 T 1Z1*
[2]*Institute for Condensed Matter Physics, 1 Svientsitskii, Lviv 79011, Ukraine*

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Microscopic theory is used to obtain effective interactions between colloidal particles in nematic fluids subjected to an external orienting field. It is shown that the field can dramatically change the effective intercolloidal interactions without altering the symmetry of the director configuration around a single particle. Our calculations suggest that a rich variety of colloidal structures can be promoted by varying the external field.

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Nematic-colloid dispersions have unique physical properties and exhibit a variety of structures, such as colloid chains [1,2], periodic lattices [3], and cellular forms [4]. A colloidal particle interacts with molecules of the fluid and can orient them with respect to its surface. Each colloidal particle creates a nematic "coat," altering the local density, the degree of orientational order, and the director field of the bulk nematic. The coats interact with each other creating effective interactions among the colloidal particles. Since in orientationally ordered fluids the nematic coats do not have spherical symmetry, the effective colloid-colloid pair interaction depends on the orientation of the center-center vector with respect to the bulk director, as well as on the interparticle separation.

A growing number of experimental [5] and phenomenological [6–8] approaches have been employed to investigate effective colloidal interactions and related structures. Most theoretical studies are consistent in that the particular symmetry of the director field configuration (the defect) around a single colloidal particle defines the effective intercolloidal interaction. Defects with dipole symmetry result in the formation of colloidal chains along the bulk director. In contrast, so-called quadrupole defects lead to repulsive forces both along and perpendicular to the bulk director, with the maximum attraction occuring when the intercolloidal vector is at an angle of 49° with respect to the director. In this Rapid Communication we argue that this picture is significantly oversimplified. We show that an aligning field can change the sign of effective intercolloidal forces in a given direction without changing the defect symmetry. This is relevant and significant because external fields of different origins (e.g., magnetic, surface induced) are frequently present in experimental situations. We employ a statistical mechanical theory that begins with the particle pair interactions and takes into account orientational and density fluctuations. It is based on an integral equation method and allows all relevant short- and long-range correlations to be calculated.

Our model [9–11] consists of a system of uniaxial particles [nematogens (N)] interacting through a pair potential taken to be the sum of a hard-sphere interaction (sphere diameter σ) and an anisotropic part defined by

$$v(1,2)=v_2(R_{12})P_2(\hat{\boldsymbol{\omega}}_1\cdot\hat{\boldsymbol{\omega}}_2), \tag{1}$$

where $P_2(\hat{\boldsymbol{\omega}}_1\cdot\hat{\boldsymbol{\omega}}_2)$ is the second-order Legendre polynomial, R_{12} is the center-center distance, the unit vector $\hat{\boldsymbol{\omega}}_i$ denotes the orientation of particle i, and

$$v_2(R_{12})=-A_N(z_N\sigma)^2\frac{\exp(-z_NR_{12})}{R_{12}/\sigma}. \tag{2}$$

Here, A_N and z_N are the energy and the length parameters characterizing the interaction. The nematogen interaction with the external field is given by

$$v_N(1)=-W\sqrt{5}P_2(\hat{\boldsymbol{\omega}}_1\cdot\hat{\mathbf{n}}),\quad W>0, \tag{3}$$

where W is the field strength. This interaction orders the bulk director $\hat{\mathbf{n}}$ parallel to the field.

Colloidal particles (C) interact as hard spheres of diameter Σ. The interaction of nematogens with the surface of a colloidal particle (anchoring) is modeled as [11,12]

$$v_{NC}(1,2)=\begin{cases}\infty, & \text{if } s_{12}<\sigma/2,\\ -A_C\exp[-z_C(s_{12}-\sigma/2)]P_2(\hat{\boldsymbol{\omega}}_1\cdot\hat{\mathbf{s}}_{12}), & \text{if } s_{12}>\sigma/2,\end{cases} \tag{4}$$

where $\mathbf{s}_{12}$ is a vector connecting the nearest point of the surface of colloid 2 with the center of nematogen 1, and $\hat{\mathbf{s}}_{12}=\mathbf{s}_{12}/s_{12}$. A_C and z_C are energy and length parameters. Note that positive and negative values of A_C favor, respectively, perpendicular and parallel orientations of nematogen molecules with respect to the surface.

The calculation of effective colloid-colloid pair potentials in a nematic medium requires a solution of the Ornstein-Zernike (OZ) equations for the nematogen-colloid mixture at infinite dilution of colloidal particles [13]. These equations are

$$h_{NN}(1,2)=c_{NN}(1,2)+S_{NN}(1,2), \tag{5}$$

$$h_{NC}(1,2)=c_{NC}(1,2)+S_{NC}(1,2), \tag{6}$$

$$h_{CC}(1,2)=c_{CC}(1,2)+S_{CC}(1,2), \tag{7}$$

where

$$S_{\alpha\beta}(1,2)=\int c_{\alpha N}(1,3)\rho_N(3)h_{N\beta}(3,2)d(3), \tag{8}$$

$c_{\alpha\beta}$ and $h_{\alpha\beta}$ are the direct and total correlation functions, and $\rho_N(3)$ is the density distribution function of the bulk nematic. Also, for a nematogen, the label 1 denotes the coordinates $(\mathbf{R}_1,\hat{\boldsymbol{\omega}}_1)$; for a colloid $1\equiv(\mathbf{R}_1)$,

The bulk functions can be found by employing Eq. (5)

together with the exact Lovett relation and an appropriate closure. For the present model, this problem has been solved analytically in the mean spherical approximation (MSA) [9,10]. The function $\rho_N(1)$ gives the density-orientational distribution in the pure nematic, and $\rho_N(1)[1+h_{NC}(1,2)]$ gives the complete distribution of nematic fluid about a colloidal particle (labeled 2). This takes into account all effects induced by the colloidal particle. Maps of the nematic distribution about colloidal particles have been given for a range of parameters [12]. It should be noted that all director fields around a single colloidal particle obtained for our model possess up-down symmetry with respect to the external field.

The effective potential between two hard colloidal spheres has a very simple form within the hypernetted-chain (HNC) approximation [13],

$$\phi_{CC}(1,2) = k_B T[c_{CC}(1,2) - h_{CC}(1,2)], \tag{9}$$

and can be determined through Eq. (7). Here, as in Ref. [12], $h_{NC}(1,2)$ is calculated directly from Eq. (6) using the nematogen-wall direct correlation function as an approximation for $c_{NC}(1,2)$. Our calculations show that for *sufficiently large* colloidal particles this approximation agrees with an exact condition resulting from the inpenetrability of hard cores. It gives a valid MSA solution to Eq. (6) for all sets of model parameters considered in this paper. This is very convenient because within the MSA the nematogen-wall direct correlation function for the present model can be obtained analytically for different orientations of the wall with respect to the field [11]. Calculation details will be published elsewhere. Here we simply note that the effective HNC potential can be expressed in the spherical harmonic expansion

$$\phi_{CC}(1,2) = \sum_{l=0,2,4} \phi_l(R_{12}) Y_{l0}(\hat{\mathbf{R}}_{12}), \tag{10}$$

where the unit vector $\hat{\mathbf{R}}_{12}$ denotes the orientation of $\mathbf{R}_{12}$ with respect to the field.

We have calculated interactions between pairs of identical colloidal particles at different field strengths ($W/A_N = 10^{-5}, \ldots, 1$) and for $\Sigma = 50\sigma, \ldots, 1000\sigma$. All results presented are for the fixed temperature $k_B T/A_N = 1$ and the nematic interaction length parameter $z_N\sigma = 1$. Systems with both long-range ($z_C\sigma = 0.2$) and short-range ($z_C\sigma = 1$) anchoring are investigated. This paper focuses on perpendicular anchoring ($A_C/A_N = 2$). The theory can be solved for planar anchoring ($A_C/A_N = -2$) as well, and these results will be given elsewhere.

All calculated effective potentials are "nonpolar" and cylindrically symmetric about the field direction. Therefore, we plot only a quarter of the two-dimensional slice that passes through the centers of colloidal particles (Figs. 1–3). One colloidal particle is shown as a white circle of radius $\Sigma/2$ and the gray stripe of width $\Sigma/2$ surrounding it denotes the region inaccessible to the center of the other colloidal particle due to the hard-core repulsion. Note that in all plots σ is the unit of length and the external field is directed along the vertical axis. The effective potential $\phi_{CC}/k_B T$ as a function of $\mathbf{R}_{12}$ is shown by different colors; the blue regions indicate the lowest values and are the most attractive.

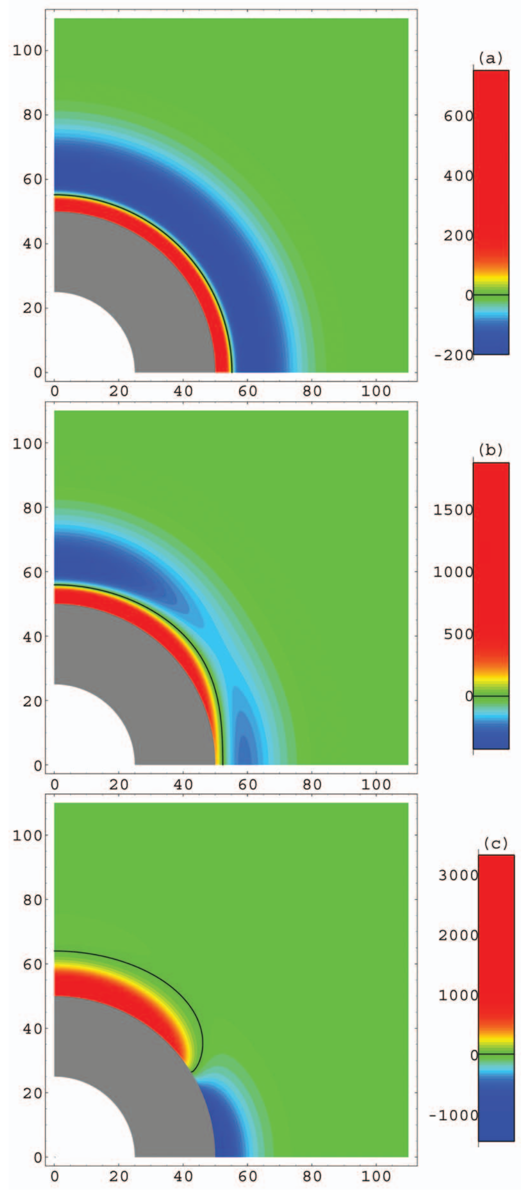

FIG. 1. (Color) $\phi_{CC}(1,2)/k_B T$ for $z_C\sigma = 0.2$, $A_C/A_N = 2$, $\Sigma = 50\sigma$, $\eta = 0.2$, $k_B T/A_N = 1$, and different external fields: (a) $W/A_N = 0.001$, (b) $W/A_N = 0.1$, and (c) $W/A_N = 1$. Distances in units of σ are indicated on both axes, and the color code is shown for each plot. The positions where the potential changes sign ($\phi_{CC} = 0$) are shown by solid black lines.

Figures 1 and 2 illustrate the potential landscapes for colloids of diameter 50σ with perpendicular anchoring. The results strongly depend on the reduced density $\eta = \pi\rho_N\sigma^3/6$ of the bulk fluid. Note that at the given temperature and zero external field, $\eta = 0.2$ (Fig. 1) corresponds to a bulk isotropic state near the isotropic-nematic phase transition, whereas $\eta = 0.35$ (Fig. 2) is a stable nematic ($S_2 = 0.714$) [14]. First we consider the low-density case where the orientational order in the bulk is induced by the external field. For $W/A_N = 0.001$, the effective potential is almost spherically symmetric; a strong repulsion ($\sim 600 k_B T$) at contact becomes a strong attraction for distances larger than 5σ. The strong attraction likely indicates nematic bridge formation in confined

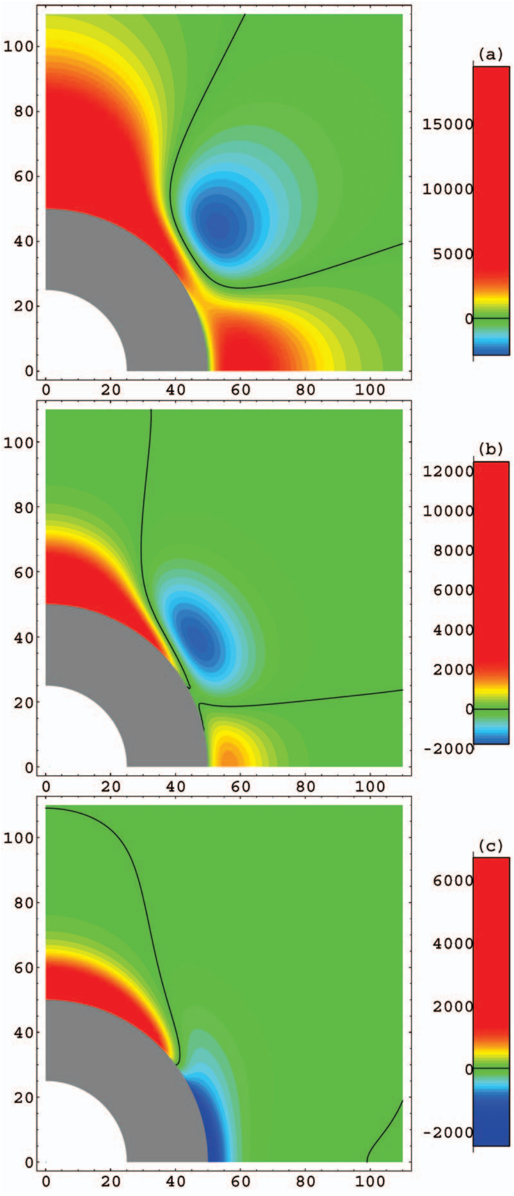

FIG. 2. (Color) As in Fig. 1, but for $\eta=0.35$.

geometry. The strong repulsion is connected with the fact that the director field between the two colloids undergoes elastic deformation as the spheres approach each other. We would expect this repulsion to decrease for larger colloids, because surfaces with lower curvature will impose weaker deformations of the nematic bridge. Indeed, the landscapes calculated for $\Sigma=100\sigma$ and larger have no red halo, and the potential remains negative at contact.

These observations are consistent with conclusions of Ref. [6], where colloidal interactions in the isotropic phase were studied phenomenologically without any specification of the colloid-nematogen interactions. We have found that the anchoring length parameter, z_C, plays a crucial role in defining how the colloidal interactions behave. If two sets of anchoring parameters (A_C, z_C) produce the same nematic distribution on the colloidal surfaces, the resulting pair interaction is longer ranged and stronger for the smaller z_C. Generally, as z_C increases, the equilibrium distance between a colloidal pair decreases. For example, colloidal particles of diameter 50σ with $z_C\sigma=1$ and all other parameters as in Fig. 1(a) attract each other at contact.

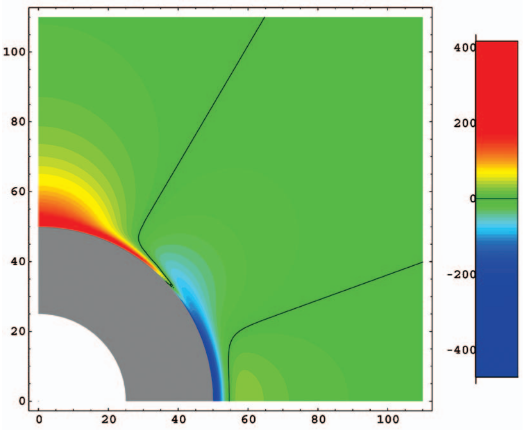

FIG. 3. (Color) As in Fig. 1, with $z_C\sigma=1$, $A_C/A_N=2$, $\Sigma=50\sigma$, $\eta=0.35$, and $W/A_N=10^{-5}$.

As the field increases, the nematic phase transition in confined geometry (probably complemented by condensation) is promoted in the vicinity of the poles, so in this case the strongest attraction can appear in the field direction [Fig. 1(b)]. These effects can be better understood by considering maps of the nematic distribution, which are given for the same parameters in Ref. [12]. The situation is different for stronger fields [Fig. 1(c)]. Now the induced order in the bulk is significant [see Fig. 3(c) of Ref. [12]], and the nematic phase transition in confined geometry is less beneficial. The strongest attraction occurs at contact at the equator. In this region the field and anchoring interactions strongly compete, creating depleted zones with a lower orientational order [12]. The resulting attraction can be viewed as a depletion interaction, although the interaction is stronger, longer ranged, and grows more rapidly with particle size than in isotropic fluids.

In the stable nematic region ($\eta=0.35$), phase transitions induced by confined geometry are supressed, and at strong fields depletion interactions are most important [Fig. 2(c)]. For weaker fields [Figs. 2(a) and 2(b)] the situation is qualitatively different. The colloidal interactions are now both long range and strong [Fig. 2(a)]. The strongest repulsions appear at 0° and 90° to the field, whereas the strongest attraction occurs at ~45° latitude. Qualitatively, this behavior agrees with the predictions of elastic theory [7]. From a microscopic point of view, the attraction at weak fields can be understood by considering reorientation phenomena in tilted geometry. At $\eta=0.35$, the liquid is less compressible and has more saturated orientational order than at $\eta=0.2$, but the susceptibility of the bulk director to reorientation by very weak fields tends to infinity [15]. Therefore colloidal particles create significant, long-range changes in the bulk nematic. The strongest reorientation, driven by the so-called flip effect [11], is induced by regions on the colloid surfaces that are tilted at ~45° to the field.

The $l=4$ (quadrupole) term in Eq. (10) dominates

$\phi_{CC}(1,2)$ as $W \to 0$ and $R \to \infty$, and numerically we find that $\phi_{CC}(1,2)$ behaves as Σ^6/R^5 in this limit. This is consistent with results of Ref. [7(b)]. However, for small R the $l=0$ and $l=2$ terms are important and the Σ^6 scaling does not apply even at zero field. For example, at the point of strongest attraction, the effective potential scales somewhere between Σ and Σ^3. Note also that the attractive well at ~45° is spatially localized and does not extend into the contact separation. However, it must be emphasized that the equilibrium position decreases in distance and changes direction (varying from ~45° to the equator) with increasing field (Fig. 2). With shorter range anchoring depletion dominates at much weaker fields; compare Fig. 3 ($z_C\sigma=1$, $W/A_N=10^{-5}$) with Fig. 2(c) ($z_C\sigma=0.2$, $W/A_N=1$). The same behavior is observed for much larger colloids; e.g., for $\Sigma=1000\sigma$, $z_c\sigma=1$, and $W/A_N=10^{-5}$, the maximum attraction ($\sim 8000 k_BT$) occurs at the equator.

It is interesting to ask how our model can be mapped onto real experimental situations. If we take as an example $k_BT/A_N=1$, $\eta=0.35$, and $W=10^{-5}k_BT$, then in our model the correlation length of the director fluctuation is $\xi/\sigma = 1.61\sqrt{k_BT/W}$. Note that ξ is analogous to the magnetic (electric) coherence length [15]. At $T=300$ K and $\sigma=2$ nm, these give $\xi=1.02$ μm. This is comparable with the values found for the nematogen 5CB, i.e., $\xi \approx 1$ μm at the magnetic flux density $B=4.7$ T [17]. Further, for a nonpolar nematogen, W and the local electric field intensity, E, are related by $\Delta\alpha E^2 = 3\sqrt{5}W$. For 5CB, $\Delta\alpha = (4\pi\epsilon_0)40$ Å^3 [16], which gives $E=7.9$ V/μm. It is worth noting that this value represents a crude upper limit on the external field. Since we do not take account of the fields due to molecular polarization, the actual applied field could be considerably smaller than our estimate. Note that for larger nematogens the same ξ could be produced by weaker fields. The influence of surface effects is more difficult to estimate. The direct influence of interfaces on ξ has not been systematically studied. However, it is known that rubbed surfaces can pinch the director and supress fluctuations, such that the effective fields associated with surfaces could be rather large.

Next consider a pair of colloidal particles with $\Sigma = 1000\sigma = 2$ μm, $A_C/A_N=2$, and $z_C\sigma=1$ immersed in the system discussed above. Note that for this example the nematogen-colloid interaction range is of the order of the nematogen "length." The strength of the nematogen-colloid interaction is determined by A_C; the sign of this parameter will vary for different surfactants, and its magnitude depends on the surfactant concentration on the colloidal surfaces. For the example we are considering, the potential at 0° increases from $\sim 28k_BT$ at $R=2\Sigma$ to $\sim 705k_BT$ at $R=1.2\Sigma$, which gives an average force of $\sim 2.0pN$ over the interval. In the zero field limit, $\phi_4(R=1.5\Sigma)=216k_BT$, and from this we estimate the anchoring energy as defined by Eq. (7) of Ref. [7(a)] to be of order 10^{-5} J/m^2.

In conclusion, we have employed a microscopic theory to calculate effective colloidal pair interactions in nematic fluids. The model includes an external orienting field. Our results indicate that colloidal interactions in orientationally ordered fluids are influenced by three main factors: phase transitions in confined geometry, depletion effects, and elastic interactions between the nematic coats surrounding colloidal particles. Changing the external field shifts the relative importance of these factors, and significantly alters the effective colloid-colloid interaction. A rich variety of equilibrium colloidal structures can be promoted by different orienting fields, without changing the composition of the system.

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