

## Geometric view on colloidal interactions above the nematic-isotropic phase transition

Holger Stark\*

*Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany*

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Particles dispersed in a liquid crystal above the nematic-isotropic phase transition are surrounded by a surface-induced nematic wetting layer. When the nematic coronas of two particles overlap, they experience a strong attraction since the volume of nematic ordering and therefore the free energy is reduced. For normal anchoring of the liquid-crystal molecules on the particles' surfaces, we demonstrate that the implementation of this geometric view reproduces the Yukawa interaction derived by Galatola and Fournier in a recent paper [Phys. Rev. Lett. **86**, 3915 (2001)], however with half the strength. To understand the factor 2, we rederive the Yukawa potential with the approximation of linear superposition of two one-particle profiles. At the end, we comment on the similarities of our approach to the screened electrostatic interaction of charged colloids.

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In recent years, dispersions of colloidal particles in a nematic liquid crystal have attracted considerable attention, since new and interesting phenomena arise through the combination of colloidal suspensions and anisotropic fluids [1–5]. The one-particle properties, central for the understanding of this new soft-matter system, are determined by the orientational order around a single particle that exhibits topological point and line defects. Three characteristic configurations (dipole, Saturn ring, and surface ring) [6] and their response to external fields [7] were identified theoretically and verified experimentally. With the calculation of the Stokes drag, dynamic properties came into focus [8]. Elastic distortions in the nematic order mediate two-particle interactions of dipolar or quadrupolar type [1,9]. They lead to prominent structure formation involving chaining [10], gel-like ordering with viscoelastic properties [11], and even ordered structures [12]. A numerical method to simulate several particles in a nematic host was developed [13] and cluster formation was predicted [14].

This paper addresses colloidal interactions in a liquid-crystal solvent above the nematic-isotropic phase transition at temperature  $T_c$ . Bounding surfaces induce nematic order that decays to zero in the bulk on a length scale determined by the nematic coherence length  $\xi_N$  [15]. When the surface-induced nematic wetting layers of two parallel plates overlap, they are strongly attracted to each other [16] since the volume of the energetically unfavorable liquid-crystal ordering is reduced. In this paper, we always assume normal anchoring of the liquid crystal molecules on a bounding surface. Applying the mechanism just introduced to the nematic coronas of spherical particles, we obtain a different colloidal interaction (see Fig. 1). It also possesses a repulsive contribution due to the elastic distortions of the director field connecting the particles. Our problem bears analogy to the treatment of interaction potentials in a binary liquid composed of  $A$  and  $B$  components with particles wetted, e.g., by the  $A$ -rich liquid phase [17–19]. Colloidal interactions in a liquid-crystal solvent above  $T_c$  were simultaneously studied by Galatola and Fournier based on a numerical approach [20]

and by Borštnik, Stark, and Žumer who modeled the orientational order between two micron-sized particles with the help of ansatz functions [21]. Borštnik *et al.* demonstrated that the range of the dominating attractive part is easily tunable by temperature. This feature offers the possibility of inducing flocculation close to the nematic-isotropic phase transition in an otherwise stabilized colloidal system [22]. A first experimental verification of the attractive interaction with the help of an atomic force microscope is due to Kočevar *et al.* [23]. Galatola and Fournier, on the other hand, developed a combined analytical and numerical approach with which they predicted that colloidal dispersions of particles whose size is of the order of  $\xi_N$  are solely stabilized by the repulsive component [24]. In addition, they showed by analytical means that the two-particle interaction assumes the form of a Yukawa potential for particle separations much larger than  $\xi_N$  [24,25].

In this paper, we concentrate on particle sizes much larger than  $\xi_N$ . We quantify the geometric view that the overlapping of the nematic coronas of two particles leads to a strong attraction since the total volume of nematic ordering and therefore the free energy is reduced. This idea, which has some resemblance to the origin of depletion forces in conventional colloidal suspensions [27], leads to an interaction potential of Yukawa type, however, with half the strength compared to the result of Ref. [24]. To interpret the factor 2,

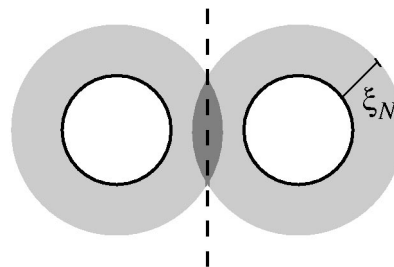


FIG. 1. The overlapping of the two nematic coronas of thickness  $\xi_N$  induces a strong attractive interaction between the particles (the liquid-crystal molecules are normally anchored on the particles' surfaces). In the geometric view, the negative of the free energy of the excess orientational order in the dark shaded region is the interaction energy. For an exact definition, see Eq. (12).

\*Email address: Holger.Stark@uni-konstanz.de

we rederive the Yukawa potential with the help of the approximation of linear superposition well known in connection with the Debye-Hückel approximation for electrostatically stabilized colloids on which we shortly comment at the end [26].

We describe the orientational order of the constituent rod-like organic molecules of a liquid-crystal by the symmetric and traceless second-rank alignment tensor  $\mathbf{Q}$ . In the uniaxial case, i.e., when all molecules align on average along the unit vector  $\mathbf{n}$  called director, the alignment tensor takes the form

$$Q_{ij} = \frac{3}{2} S \left( n_i n_j - \frac{1}{3} \delta_{ij} \right), \quad (1)$$

where  $\delta_{ij}$  is the Kronecker delta. We have introduced the Maier-Saupe order parameter  $S$  to signify the degree of orientational order. For weak surface-induced nematic ordering in the isotropic phase, it is sufficient to employ the Landau-de Gennes free energy density in the harmonic approximation,

$$f_b = [a_0(T - T^*)Q_{ij}^2 + L(\nabla_k Q_{ij})^2]/2, \quad (2)$$

where  $\nabla_k$  indicates partial derivative with regard to  $x_k$ , and Einstein's summation convention over repeated indices is employed. In the isotropic phase,  $T > T^*$ , and the first and second term on the right-hand side quantify, respectively, the free energy to create or distort the orientational order. For simplicity, we assume the one-constant approximation for the elastic terms. To model the anchoring of the liquid-crystal molecules at the surface of a particle, we use the surface free energy density [28],

$$f_s = W(Q_{ij} - Q_{ij}^{(0)})^2/2. \quad (3)$$

In the following we assume that the particles favor uniaxial order along the surface normal  $\hat{\mathbf{v}}$ , i.e.,  $Q_{ij}^{(0)} = \frac{3}{2} S_0 (\hat{v}_i \hat{v}_j - \frac{1}{3} \delta_{ij})$ . If we write all lengths in units of the nematic coherence length  $\xi_N = \sqrt{L/[a_0(T - T^*)]}$  and introduce the surface coupling parameter  $\gamma = L/(W\xi_N)$ , the reduced free energy in units of  $L\xi_N/2$  reads

$$F[\mathbf{Q}(\mathbf{r})] = \int [Q_{ij}^2 + (\nabla_k Q_{ij})^2] d^3r + \frac{1}{\gamma} \int (Q_{ij} - Q_{ij}^{(0)})^2 d^2r. \quad (4)$$

Its variation leads to the Euler-Lagrange equation in the bulk,

$$\nabla^2 Q_{ij} = Q_{ij} \quad (5)$$

and to the mixed boundary condition

$$\hat{\mathbf{v}} \cdot \nabla Q_{ij} + \frac{1}{\gamma} (Q_{ij} - Q_{ij}^{(0)}) = 0, \quad (6)$$

where  $\hat{\mathbf{v}}$  points towards the center of a spherical particle. In performing the variation, we implied that  $\mathbf{Q}$  is already chosen symmetric and traceless.

One spherical particle of radius  $R$  carries a corona of surface-induced nematic order. In accordance with the

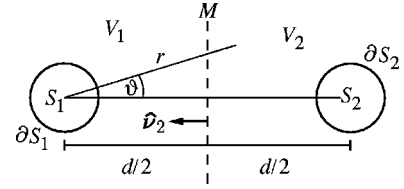


FIG. 2. Explanation of the geometry. Two spherical particles 1 and 2 with a separation  $d$  occupy regions  $S_i$  ( $i=1,2$ ) with surfaces  $\partial S_i$ . The region bounded by the midplane  $M$  and the surface  $S_i$  is denoted  $V_i$ . The unit vector  $\hat{\mathbf{v}}_2$  is normal to  $M$ . The spherical coordinates  $r$  and  $\vartheta$  are chosen relative to the center of  $S_1$  and the line connecting  $S_1$  and  $S_2$ .

boundary condition and the symmetry of the system, we choose the uniaxial alignment tensor of Eq. (1) with  $S = S(r)$  and  $\mathbf{n} = \mathbf{e}_r$ , where  $r$  is the distance from the center of the particle and  $\mathbf{e}_r$  is a unit vector pointing along the radial direction. With such an alignment tensor, the total free energy is

$$\frac{F}{4\pi} = \frac{1}{2} \int \left[ \left( 1 + \frac{6}{r^2} \right) S^2 + \left( \frac{\partial S}{\partial r} \right)^2 \right] r^2 dr + \frac{R^2}{2\gamma} [S(R) - S_0]^2, \quad (7)$$

where the factor  $4\pi$  comes from the integration over the unit sphere. Variation of energy (7) results in the Euler-Lagrange equation for  $S(r)$  in the bulk,

$$\frac{\partial^2 S}{\partial r^2} + \frac{2}{r} \frac{\partial S}{\partial r} - \left( 1 + \frac{6}{r^2} \right) S = 0, \quad (8)$$

and in the mixed boundary condition

$$\frac{\partial S}{\partial r} \Big|_{r=R} - \frac{1}{\gamma} [S(R) - S_0] = 0. \quad (9)$$

These equations are also directly derivable from Eqs. (5) and (6). The solution of the bulk equation (8) can be given in closed form:

$$S(r) = S_0 A^{-1}(R, \gamma) \frac{\exp[-(r-R)]}{r} \left( 1 + \frac{3}{r} + \frac{3}{r^2} \right), \quad (10)$$

where the factor

$$A(R, \gamma) = \frac{\gamma+1}{R} + \frac{4\gamma+3}{R^2} + \frac{9\gamma+3}{R^3} + \frac{9\gamma}{R^4} \quad (11)$$

is determined by the boundary condition (9).

We are prepared to implement our geometric view on the two-particle interaction. It does not try to find a smooth alignment tensor field between two particles but rather employs the one-particle properties. When the coronas of two particles overlap, the orientational order from particle 1 in the half space  $V_2 + S_2$  on the right of the midplane  $M$  (see Fig. 2) is removed. The equivalent is valid for particle 2. An

approximation to the interaction energy is then the free energy of the removed orientational order which amounts to

$$F_{int}^{(1)} = -2 \int_{V_2+S_2} [(Q_{ij}^{(1)})^2 + (\nabla_k Q_{ij}^{(1)})^2] d^3r, \quad (12)$$

where  $\mathbf{Q}^{(1)}(\mathbf{r})$  is the alignment tensor field of particle 1. Transforming  $(Q_{ij}^{(1)})^2$  with the help of the bulk Euler-Lagrange equation (5) into  $Q_{ij}^{(1)} \nabla^2 Q_{ij}^{(1)}$  and performing a partial integration (Green's first identity [29]), we arrive at an equivalent expression which involves a surface integration over the midplane:

$$F_{int}^{(1)} = -2 \int_M Q_{ij}^{(1)} \hat{\mathbf{v}}_2 \cdot \nabla Q_{ij}^{(1)} d^2r. \quad (13)$$

The unit vector  $\hat{\mathbf{v}}_2$  is illustrated in Fig. 2. To calculate the interaction energy from Eq. (12), we insert the uniaxial alignment tensor of Eq. (1) with the specifications for one particle [ $\mathbf{n} = \mathbf{e}_r$  and  $S = S(r)$ ] and arrive at the same free energy density as Eq. (7). However, the integration limits have to be adjusted to the half space  $V_2 + S_2$ , i.e.,  $r \in [d/2 \cos \vartheta, \infty)$  and  $\vartheta \in [0, \pi/2]$ . For the scalar order parameter profile  $S(r)$  of Eq. (10), the integration can be done analytically with the final result,

$$\frac{F_{int}^{(1)}}{6\pi} = - \left( \frac{S_0}{A} \right)^2 \frac{\exp[-(d-2R)]}{d} \left( 1 + \frac{6}{d} + \frac{12}{d^2} \right). \quad (14)$$

For particle radii much larger than  $\xi_N$  ( $R \gg 1$ ) which implies  $d \gg 1$ , the interaction energy is of the Yukawa type:

$$\frac{F_{int}^{(1)}}{6\pi} \approx - \left( \frac{S_0}{A} \right)^2 \frac{\exp[-(d-2R)]}{d}. \quad (15)$$

This form agrees with the exact result of Galatola and Fournier derived in the limit of  $d-2R \gg 1$  [24]. The strength of our interaction, however, is smaller, by a factor of 2 which is due to the choice of the alignment tensor field consisting of one-particle fields clued together at the midplane. Nevertheless, the advantage of our approach consists in its simplicity and its semiquantitative agreement, which implies that the idea of removing the overlapping parts of the nematic coronas describes the main feature of this interaction even for distances to contact of  $d-2R \approx \xi_N$ . Note that in Ref. [25], the Yukawa interaction was demonstrated to be a good approximation down to  $d-2R \approx \xi_N$  for particle radii of  $R \gg 1$ .

To achieve a better understanding of the factor 2, we have performed an alternative derivation of the interaction potential by approximating the alignment tensor field around two particles by a linear superposition of the two one-particle solutions  $\mathbf{Q}^{(i)}(\mathbf{r})$  centered on particles 1 and 2,

$$\mathbf{Q}(\mathbf{r}) = \mathbf{Q}^{(1)}(\mathbf{r}) + \mathbf{Q}^{(2)}(\mathbf{r}). \quad (16)$$

The field  $\mathbf{Q}(\mathbf{r})$  solves the bulk Euler-Lagrange equation (5). The boundary condition (6), however, is satisfactorily fulfilled only in the limit of  $d-2R \gg 1$  since then, e.g.,  $\mathbf{Q}^{(1)}(\mathbf{r})$

has nearly decayed to zero at the location of particle 2. As usual, the interaction energy is defined by

$$F_{int}^{(2)} = F[\mathbf{Q}^{(1)}(\mathbf{r}) + \mathbf{Q}^{(2)}(\mathbf{r})] - 2F_S[\mathbf{Q}^{(i)}(\mathbf{r})], \quad (17)$$

where  $F_S$  denotes the self-energy of one particle. To evaluate  $F_{int}^{(2)}$ , we can also integrate twice over the volume  $V_2$  (see Fig. 2) due to the symmetry of the problem. Applying the Euler-Lagrange equations (5) and (6) and performing a partial integration (Green's first identity [29]), we arrive at

$$F_{int}^{(2)} = -4 \int_M Q_{ij}^{(2)} \hat{\mathbf{v}}_2 \cdot \nabla Q_{ij}^{(1)} d^2r + 2 \int_{\partial S_2} \left[ \frac{1}{\gamma} (Q_{ij}^{(1)})^2 - Q_{ij}^{(1)} \hat{\mathbf{v}} \cdot \nabla Q_{ij}^{(1)} \right] d^2r. \quad (18)$$

The second integral over the surface  $\partial S_2$  of sphere 2 gives a higher-order correction to the Yukawa potential and can be neglected. The first surface integral is similar to Eq. (13), however, the factor 2 is replaced by 4 and instead of  $Q_{ij}^{(1)} \hat{\mathbf{v}}_2 \cdot \nabla Q_{ij}^{(1)}$  the integrand contains both  $Q_{ij}^{(1)}$  and  $Q_{ij}^{(2)}$ . If our order parameter were just a scalar field  $\Phi(\mathbf{r})$ , then, by definition,  $\Phi^{(1)}(\mathbf{r}) = \Phi^{(2)}(\mathbf{r})$  on the midplane  $M$ , and the approximation of linear superposition reproduces exactly twice the interaction energy of our geometric view. For a tensorial order parameter, however,  $\mathbf{Q}^{(1)}(\mathbf{r}) \neq \mathbf{Q}^{(2)}(\mathbf{r})$  on the midplane since the alignment tensor possesses an orientation in space that differs from particle 1 to 2. To verify the factor 2 in this case, all we can do is to evaluate the first integral in Eq. (18) explicitly, which needs some effort since several delicate steps including the application of differential geometry have to be performed. After performing the integration, one arrives at an analytic expression which contains the exponential integral function  $E_1(d)$  [30]. Using its Laurent expansion [30]

$$E_1(d) e^d d = \sum_{n=0}^{\infty} (-1)^n n! / d^n, \quad (19)$$

we finally derive the relation  $F_{int}^{(2)} = 2F_{int}^{(1)}$  [for  $F_{int}^{(1)}$ , see Eq. (15)] which reproduces the result of Galatola and Fournier [24] and which we already predicted in the scalar case.

In the end, we note that the two-particle interaction for electrostatically stabilized colloids in the Debye-Hückel approximation with the Debye screening length  $\kappa^{-1}$  as the characteristic length scale can be investigated by the same type of bulk free energy as in Eq. (4). However,  $\mathbf{Q}(\mathbf{r})$  is replaced by the scalar field  $\Phi(\mathbf{r})$  of the electrostatic potential, and the surface free energy now reads  $2\sigma \int \Phi d^2r$ , where  $\sigma$  is a reduced surface charge density [31]. Variation of such a free energy reproduces the linearized Poisson-Boltzmann equation for a 1:1 electrolyte together with the von Neumann boundary condition. The two-particle interaction energy can be written in analogy to Eq. (18). It contains an additional surface term due to the different boundary condition which renders the two particle interaction repulsive.

In conclusion, we have demonstrated that the geometric view of removing the overlapping parts of nematic coronas around particles reproduces the Yukawa type two-particle interaction in a semiquantitative manner. This idea thus highlights the main feature of the new colloidal interaction mediated by surface-induced nematic order. In addition, we derived the exact form of the Yukawa interaction on the basis of the approximation of linear superposition reproducing in an alternative manner the result by Galatola and Fournier [24]. The advantage of our geometric view lies in its simplic-

ity. Using a type of Voronoi cell construction, it is extensible to multibody interactions which are important in the study of particle aggregation and the formation of ordered crystalline structures. Phase ordering studies due to particle interactions mediated by the scalar order parameter field of binary liquids were already presented by Löwen [17] and Netz [18].

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