

Interaction of spherical particles dispersed in a liquid crystal above the nematic-isotropic phase transition

A. Borštnik,¹ H. Stark,² and S. Žumer¹

¹*Department of Physics, University of Ljubljana, 1000 Ljubljana, Slovenia*

²*Institut für Theoretische und Angewandte Physik, Universität Stuttgart, D-70550, Germany*

(Received 11 September 1998; revised manuscript received 30 November 1998)

The effective interaction of micron-size particles immersed in a nematic liquid crystal at temperatures above the nematic-isotropic phase transition is examined. Using the Landau–de Gennes theory we describe the surface-induced ordering of the liquid crystal. Modeling a spherical particle by a sequence of conical surfaces enables us to draw an analogy with the partial ordering in a thin nematic film and to obtain an analytical expression for the two-particle interaction. Special attention is paid to the dependence of the effective interaction on temperature and on the interfacial coupling parameters, which are chosen in agreement with recent experiments. We show that the interaction as a function of the interparticle distance exhibits a potential barrier of the order of kT . The height of the barrier decreases exponentially with increasing temperature while it grows linearly with the interfacial coupling parameters. [S1063-651X(99)02810-X]

PACS number(s): 61.30.Cz, 82.70.Dd

I. INTRODUCTION

The first observations of forces mediated by a nematic liquid crystal were performed by Horn *et al.* [1] more than fifteen years ago. Interest in an experimental analysis of such interactions has been renewed recently when Muševič *et al.* [2] have used an atomic force microscope (AFM) to probe forces due to a surface-induced nematic order above the nematic-isotropic phase transition while Poulin *et al.* [3] measured interactions between water droplets immersed into a liquid crystal deep in the nematic phase. Theoretically, the problem of forces in nematic liquid crystals was discussed by Poniewierski and Sluckin [4] who studied partially ordered nematic films using the Landau–de Gennes approach. More efforts were devoted to completely ordered nematic phases. In particular, fluctuation (Casimir) forces in thin nematic films [5,6] and long-range interactions between colloidal particles caused by the deformation of the surrounding nematic director field [7–10] were studied. Interest in partially ordered nematic films has been renewed recently. Borštnik and Žumer [11] investigated forces between two parallel plates immersed into a liquid crystal slightly above the bulk nematic-isotropic phase transition.

The motivation for performing a study of two-particle interactions in a partially ordered liquid crystal above the bulk nematic-isotropic phase transition temperature T_{NI} results from an enormous interest in colloidal dispersions among condensed-matter physicists. Especially, “exotic” effects in colloidal interactions, like fluctuation-induced Casimir forces [12,13] and depletion forces [14–17] have attracted a lot of attention recently. So far, only the interaction of particles immersed into a liquid crystal deep in the nematic phase has been studied rather extensively, e.g., many efforts were devoted to the suspension of micron-size water droplets in a nematic liquid crystal [18,19]. However, besides a few examples [20], the behavior of the system when heated into the isotropic phase is practically unknown. We have, therefore, started a theoretical study of the interaction between two

spherical particles immersed into a partially ordered nematic liquid crystal above T_{NI} [21]. A similar situation has also been investigated by Galatola and Fournier [22]. However, we would like to point out that their numerical study is focused on nanometer-size particles with a rigid surface anchoring of liquid crystal molecules while our analytical study deals with particles of micron size with a finite surface anchoring strength and is therefore closer to the experimentally investigated systems [19]. In this paper, we explore this type of colloidal interactions mediated by the surface-induced nematic order above T_{NI} , for which we develop an analytical expression. It serves as a necessary background for the study of pretransitional stability of liquid-crystal dispersions. An investigation of the possible temperature-induced flocculation transition reminiscent to a similar effect in colloidal dispersions with polymeric stabilization [14] will be presented elsewhere.

In our previous study of the mean-field contribution to forces between two parallel plates immersed into a partially ordered liquid crystal [11] it was shown that in the case of homeotropic surface alignment, which results in a nondistorted director field, there is always an attraction between the plates. Since above the transition point an orientationally ordered phase costs more free energy than an isotropic phase, it is favorable for the system to reduce the interplate distance and thus also the amount of the material with nonzero liquid crystalline order. For large interplate distances d the interaction decays exponentially with increasing d . The characteristic length scale of this decay is given by a correlation length, which for a typical liquid-crystal material close to the temperature of the nematic-isotropic phase transition is of the order of 10 nm. In curved geometries like the one formed by dispersed spherical particles the director field is no longer undistorted, and its contribution to the interaction has to be taken into account as well. Such a contribution is expected to be repulsive since with decreasing interparticle distance the distortion of the director field increases. We notice that a nematic ordering exists only close to the surfaces; therefore, no defects of the director field are expected to appear in the

liquid crystal. Since the effective volume of nematic ordering is reduced when the particles approach each other, we also expect an attractive component of the interaction. Both attractive and repulsive contributions decay exponentially with increasing distance between particles. In this paper we will show that the sum of both components yields an interaction exhibiting a potential barrier. Our treatment aims to be fully analytic. We therefore replace the two spheres by simple geometrical objects and approximate the director field and the order-parameter profile by properly chosen ansatz functions.

The paper is organized as follows. In Sec. II we first present our model structure, which approximates two spherical particles. Further, we introduce the free energy consisting of the bulk and the surface coupling term. The approximations for the order-parameter profile and the director field are described in Sec. III. Section IV is devoted to the analytical expression for the liquid-crystal mediated interaction of two particles. The interaction as a function of the interparticle distance, surface coupling parameters, and temperature is studied in Sec. V. Finally, in Sec. VI, we discuss our results.

II. DESCRIPTION OF THE MODEL

In a spatially restricted liquid crystal, confining surfaces enforce certain orientation of molecules in the interfacial layer. In a nontrivial geometry below T_{NI} this leads to a spatially dependent director field. The presence of the surface influences also orientational fluctuations of molecules and thus modifies the degree of order and biaxiality. It also reduces molecular exchange in the surface layer [23–25]. A flat substrate promotes a formation of several smectic layers even at temperatures above the smectic-nematic phase transition [26,27]. Above T_{NI} , i.e., in the isotropic phase the most significant effect of the substrate is the induction of orientational order extending beyond the surface layer. Since this ordering is weaker than in the nematic phase and is also localized to the vicinity of the interfaces, the effect of deformed director fields and smectic layering is less pronounced.

In our study we concentrate on temperatures above T_{NI} . Like in the study of forces between two parallel plates [11] we limit our discussion to surfaces that prefer homeotropic, i.e., perpendicular anchoring of molecules. We further assume that no smectic layers are formed in the film. This assumption seems to be appropriate for the isotropic phase of 5CB where rarely surface layers are found in contrast to 8CB or 12CB where pretransitional smectic layering is often observed [26,27]. Studies of the surface-induced ordering in confined liquid crystals with a film thickness larger than 10 nm [28–30] indicate that a combination of a phenomenological continuum approximation and an extra surface layer of molecular thickness and constant order gives a good description of the liquid-crystal ordering. We therefore leave the properties of the surface layer aside, and we simply consider the surface layer as a part of the substrate. We stress that our analysis is performed within a mean-field approximation neglecting order fluctuations. An estimate of liquid-crystalline order fluctuations between two parallel plates immersed into an isotropic liquid crystal performed by Zihelr *et al.* [31] shows that the fluctuation-induced forces usually yield only a

minor correction to the mean-field values and will be therefore left for further considerations.

The aim of our study is to estimate the liquid-crystal mediated interaction of micron-size spheres immersed into a liquid crystal at temperatures slightly above the nematic-isotropic phase transition. We concentrate on particle separations ranging from 10 to 70 nm. Namely, above the nematic-isotropic phase transition nematic ordering decays exponentially with increasing distance from the particle surface that renders the liquid-crystal interaction almost negligible if the particle separation exceeds some correlation lengths, e.g., 70 nm. Furthermore, distances examined in our study correspond to the relevant range of particle interactions in colloidal science [14].

Since we deal with homeotropic anchoring and rather weak deformations of the director field, we neglect any biaxiality in the liquid-crystal ordering. We, therefore, describe the nematic ordering with a simplified tensor order-parameter Q_{ij} , which only contains the information about the degree of orientational order $Q(\mathbf{r})$ and about the preferred axis, called the director $\hat{\mathbf{n}}(\mathbf{r})$ [32],

$$Q_{ij} = \frac{1}{2} Q(\mathbf{r}) [3n_i(\mathbf{r})n_j(\mathbf{r}) - \delta_{ij}]. \quad (1)$$

Here n_i stands for the i th component of the director.

By using the Landau–de Gennes phenomenological approach we calculate the free energy of the system and determine the spatial dependence of Q_{ij} . The approach assumes that Q_{ij} changes slowly across the sample, so that the first spatial derivatives of Q_{ij} are small quantities. Then the free-energy density of a liquid crystal is expanded into a series of Q_{ij} and its derivatives, $Q_{ij,k} = \partial Q_{ij} / \partial x_k$, in the following way [33–35]:

$$f = f_b + L_1 Q_{ij,k} Q_{ij,k}, \quad (2)$$

where a summation over repeated indexes is assumed. The coefficient L_1 is a material-dependent “elastic parameter.” In writing down Eq. (2) we use an one-constant approximation as introduced in Refs. [33,34], which corresponds to $L_2 = L_3 = L_5 = L_6 = 0$ in Ref. [35]. As was explained by de Gennes [36] and repeated by Pristely, Wojtowicz, and Sheng [33], choosing $L_2 \neq 0$ merely introduces some anisotropy in the coherence length with which the nematic order decays in different spatial directions above T_{NI} [37].

The term f_b is the free-energy density of an undistorted bulk liquid crystal, $f_b = \frac{1}{2} a (T - T^*) Q^2 + \frac{1}{3} b Q^3 + \frac{1}{4} c Q^4$, with a , b , c , and T^* as temperature-independent constants. For temperatures close to T_{NI} the value of Q at the surface is not small so that the $\frac{1}{3} b Q^3$ and $\frac{1}{4} c Q^4$ terms cannot be neglected. If the surface coupling is very strong, which is not the case in our study, these terms can even yield a nematic wetting layer on the surface of the particles. However, the effect of these third- and fourth-order terms becomes negligible if the temperature is about a kelvin above T_{NI} and if the particle separation is more than the correlation length. This is the case in the major part of our study. Nevertheless, we performed an estimate of the neglected terms by calculating the interaction energy of two parallel plates with homeotropic boundary conditions for the two cases $b, c \neq 0$ and $b = c = 0$. Like in our analytical study we modeled the surfaces of the spherical

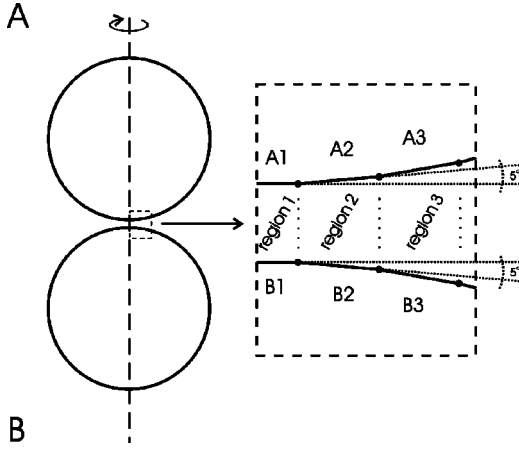


FIG. 1. Modeling of the two particles (A and B) by conical segments. As a result, the space between the particles is divided into several regions: 1, 2,

particles by a sequence of parallel plates. Omitting the contribution of the distorted director field and using the same surface coupling constant as in the rest of our study we found out that for temperature $T_{NI} + 0.2$ K and particle separations larger than 10 nm the effect of the third- and fourth-order terms is almost unnoticeable. Therefore, these terms are neglected and f_b is reduced to $\frac{1}{2}a\Delta TQ^2$ where ΔT stands for $T - T^*$.

Inserting expression (1) into Eq. (2), the following expression for the free-energy density is obtained [33]:

$$f = \frac{1}{2}a\Delta TQ^2 + \frac{3}{2}L_1(\nabla Q)^2 + \frac{9}{2}L_1Q^2|\text{grad } \hat{\mathbf{n}}|^2. \quad (3)$$

Taking into account that the geometry of our system shown in Fig. 1 exhibits cylindrical symmetry and assuming that no twist deformations in the director field are present we see that the director $\hat{\mathbf{n}}$ is coplanar with the plane containing the axis of symmetry. Its direction in this plane is described by the polar angle α between $\hat{\mathbf{n}}$ and the axis of symmetry [see Fig. 2(a)]. Introducing cylindrical coordinates r , φ , and z , the components of $\hat{\mathbf{n}}$ assume the following form, $\hat{\mathbf{n}} = (n_r, n_\varphi, n_z) = (\sin \alpha, 0, \cos \alpha)$, and the free energy of Eq. (3) can be written as

$$f = \frac{1}{2}a\Delta TQ^2 + \frac{3}{2}L_1(\nabla Q)^2 + \frac{9}{2}L_1Q^2 \left[\frac{\sin^2 \alpha}{r^2} + \left(\frac{\partial \alpha}{\partial r} \right)^2 + \left(\frac{\partial \alpha}{\partial z} \right)^2 \right]. \quad (4)$$

Dispersed particles influence the ordering of the liquid crystal by an interfacial coupling. To describe this *surface coupling* we add to the bulk free-energy density a commonly used extra surface term in Q_{ij} [38]. Introducing two surface-coupling constants G_Q and G_n our surface free energy yields a generalization of the expression $G(Q_{ij} - Q_{sij})^2$ in Ref. [39]:

$$f_s = [G_Q(Q - Q_s)^2 + 3G_nQQ_s \sin^2(\alpha - \beta)] \delta(|\mathbf{r} - \mathbf{R}_s|). \quad (5)$$

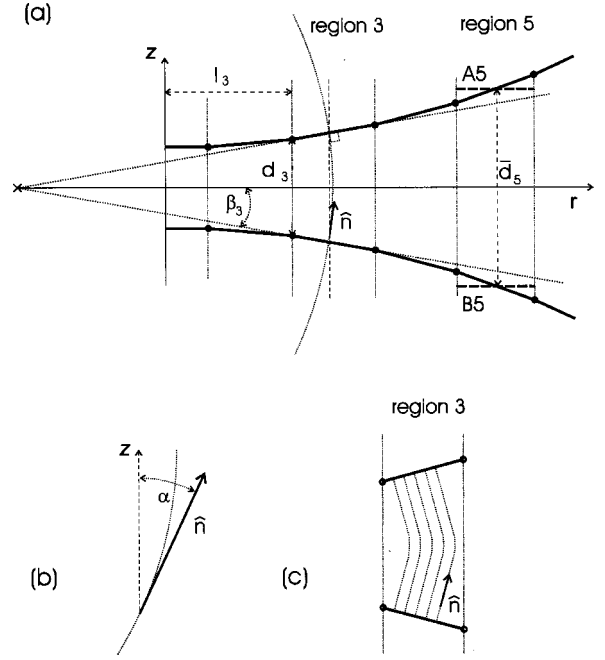


FIG. 2. Introduction of the relevant notation. (a) In region 3 the relevant lengths l_i , d_i , and angle β_i , are introduced. For small interparticle distances the director $\hat{\mathbf{n}}$ is modeled as the tangent vector to a circle as illustrated for rigid surface anchoring. In region 5 the average distance \bar{d}_5 between the surface elements A_5 and B_5 is defined. (b) The polar angle α of the director $\hat{\mathbf{n}}$ is illustrated. (c) Illustration of the ansatz for the director field at large interparticle distances.

The quantity β is the angle between the surface normal and the z axis, and \mathbf{R}_s is the position vector, describing the surface of the particles. The coupling term tends to equalize the scalar order-parameter Q of the liquid crystal with the value Q_s , preferred by the surface, and to rotate the director $\hat{\mathbf{n}}$ parallel to the surface normal. The constants G_Q and G_n determine the strength of the coupling.

In order to obtain the effective interaction of particles dispersed in a liquid crystal we assume that the medium is in a quasiequilibrium state characterized by a spatial dependence of Q and $\hat{\mathbf{n}}$. This state can thus be determined by a minimization of the free-energy functional $F = \int (f + f_s) dV$. Taking into account Eqs. (4) and (5) this minimization yields two second-order differential equations for Q and α in the bulk,

$$\nabla^2 Q - \frac{a\Delta T}{3L_1}Q - 3 \left[\frac{\sin^2 \alpha}{r^2} + \left(\frac{\partial \alpha}{\partial r} \right)^2 + \left(\frac{\partial \alpha}{\partial z} \right)^2 \right] Q = 0, \quad (6)$$

$$\nabla^2 \alpha - \frac{\sin \alpha \cos \alpha}{r^2} = 0, \quad (7)$$

and the corresponding boundary conditions are

$$\nabla_\perp Q = \frac{2G_Q}{3L_1}(Q - Q_s) - \frac{G_n}{L_1}Q_s \sin^2(\alpha - \beta), \quad (8)$$

$$\nabla_{\perp} \alpha = \frac{G_n}{3L_1} \frac{Q_s}{Q} \sin 2(\alpha - \beta). \quad (9)$$

Here ∇^2 stands for the Laplacian in cylindrical coordinates while ∇_{\perp} stands for the directional derivative along the surface normal.

Since for the geometry of Fig. 1 differential equations (6) and (7) are too complicated to be solved analytically we simplify our problem. We choose a simplification, which enables us to draw an analogy with the partial ordering in a thin nematic film. In the first step the two spheres are approximated by several conical areas whose cross sections in any plane containing the axis of symmetry are polygons of n equally long line segments (see Fig. 1). We choose $n=72$ since this number of lines corresponds to a suitable value of 5° for the angle between two neighboring segments. If we assume the diameter of the object to be $0.5 \mu\text{m}$ the length of each polygon line is equal to 22 nm.

In the second step of our simplification we construct suitable ansatz functions for the order-parameter profile and director field rather than solving differential equations (6) and (7) by a straightforward method. When choosing the ansatz functions we will use the analogy with the problem of two parallel plates immersed into a liquid crystal. Namely, as it was shown in the study of pretransitional forces between two plates [11] the interaction is only noticeable if the distance between the plates does not exceed a few nematic correlation lengths, i.e., 60 nm. Therefore the interval of our interest will be 10–100 nm. Taking into account that the diameter of our particles is an order of magnitude larger than such distances one can see that the relevant parts of the surfaces are almost flat, which encourages the use of the analogy with the planar geometry.

III. ANALYTICAL EXPRESSIONS FOR THE ORDER-PARAMETER PROFILE AND DIRECTOR FIELD

Approximate order-parameter profile. In order to determine the order-parameter profile, $Q(\mathbf{r})$, of a liquid crystal between two particles, we divide the space between the objects into several regions (see Fig. 1). Each region is bounded by surface elements A_i and B_i , and by the two neighboring regions. Since we are determining interactions we only have to calculate the order-parameter profile for those regions where the ordering of the liquid crystal is influenced by the surfaces of both particles. As we will discuss below, only the regions 1–9 (see Fig. 1) are relevant. Especially, the liquid-crystalline order in the area on the “far sides” of the spheres (i.e., opposite the region between the two spheres) does not depend on the particle separation. Therefore, this area does not contribute to the interaction energy, and we will not take it into account in our calculations.

As illustrated in Fig. 1 the surface elements A_1 and B_1 are parallel to each other, and we choose the order-parameter profile in this region to be equal to the one obtained for two infinite parallel plates immersed into an isotropic liquid crystal [11]. Furthermore, we approximate the order-parameter profile between the surface elements A_2 and B_2 by the one obtained for two infinite parallel plates whose interplate distance is taken to be the average distance between A_2 and

B_2 , $\bar{d}_2 = \frac{1}{2}(d_2 + d_3)$. The order-parameter profiles for regions that are further away from the axis of symmetry are obtained in the same way [see region 5 of Fig. 2(a)].

In region 1 (parallel plates) the free energy is minimized by a director field pointing everywhere along the z axes, i.e., the direction perpendicular to the surfaces. Therefore there is no contribution from the second term of surface energy (5) and also the elastic part in the polar angle α of bulk free energy (4) is zero. The order-parameter profile between the two plates A_1 and B_1 situated at $z = \pm \frac{1}{2}d_1$, respectively, follows from simplified differential equation (6) $(\partial^2/\partial z^2)Q - (a\Delta T/3L_1)Q = 0$ and boundary condition (8) $(\partial/\partial z)Q = 2G_Q/3L_1(Q - Q_s)$. Their solution has the form $Q = Q_s \cosh(z/\xi)/(\cosh d_1/2\xi + \gamma_Q \sinh d_1/2\xi)$. Here, $\xi = \sqrt{3}L_1/a\Delta T$ is the nematic correlation length while L_1/G_Q is the surface extrapolation length [32]. We introduce the ratio of the two lengths as a parameter, $\gamma_Q = \frac{3}{2}(L_1/G_Q)(1/\xi)$.

In the regions 2,3,4, . . . , the segments A_i and B_i are not parallel to each other, and the director field can, therefore, not fulfill Eqs. (7) and (9) by pointing everywhere in the region in the same direction. But the contribution of the director field distortion is small. We neglect the $\hat{\mathbf{n}}$ -dependent terms in Eqs. (6) and (8) and describe the order-parameter profile by the same expression as in region 1. In this case, d_1 is replaced by the average distance \bar{d}_i between the surface elements A_i and B_i

$$Q = Q_s \frac{\cosh z/\xi}{\cosh \bar{d}_i/2\xi + \gamma_Q \sinh \bar{d}_i/2\xi}, \quad (10)$$

where $\gamma_Q = 3L_1/(2G_Q\xi)$. Note that Q contains a term, which crucially depends on the strength of the surface coupling $\gamma_Q^{-1} \propto G_Q$.

Approximate director field. When constructing an ansatz for the director field configuration we must pay special attention to the magnitude of the terms describing the contribution of the director field to the free-energy densities in Eqs. (4) and (5). The bulk terms are proportional to Q^2 while the surface terms include also terms proportional to Q . Since Q decreases exponentially with increasing distance from the surface [see Eq. 10] the free-energy terms, which are $\hat{\mathbf{n}}$ -dependent, contribute significantly only in the vicinity of the surfaces. For $\hat{\mathbf{n}}$ we therefore choose an ansatz that fulfills the boundary condition of Eq. (9) while it does not completely fulfill differential equation (7) in the whole space. When choosing the ansatz for the director field we distinguish between two limiting cases. In the limit of small distances between the plates, i.e., $d \approx \xi$, Q is noticeable everywhere in the region, and we describe the director $\hat{\mathbf{n}}$ by a tangent vector to a circle lying in the plane, which includes the axis of symmetry. We choose the origin of the circle in such a way that $\hat{\mathbf{n}}$ fulfills boundary condition (9). Then the components of $\hat{\mathbf{n}}_o$, where the index o indicates the limit of small distances, have the following spatial dependence:

$$\hat{\mathbf{n}}_o = (n_r, n_\varphi, n_z) = (\sin \alpha, 0, \cos \alpha) = \left(\frac{-z}{\sqrt{\rho_i^2 + z^2}}, 0, \frac{\rho_i}{\sqrt{\rho_i^2 + z^2}} \right). \quad (11)$$

Here, $\sqrt{\rho_i^2 + z^2}$ is the radius of the circle with $\rho_i = r - l_i + \frac{1}{2}d_i \cot \beta_i + \Delta R_i$, where ΔR_i stands for $\gamma_n \xi (1 + \gamma_Q \tanh \bar{d}_i / 2\xi)^{-1} (\sin \beta_i)^{-1}$ and becomes negligible in the limit of strong surface coupling G_n , i.e., $\gamma_n = \frac{3}{2}(L_1 / G_n)(1/\xi) \rightarrow 0$. Like in Eq. (5), $\beta_i > 0$ is the tilt angle of the surface elements A_i and B_i against the mirror plane, l_i is their closest distance from the symmetry axes at $r=0$, and d_i is the closest distance between surface elements A_i and B_i [see Fig. 2(a)]. A director field configuration for a very strong surface coupling G_n , which forces $\hat{\mathbf{n}}$ to be perpendicular to the surface, is schematically shown in region 3 of Fig. 2(a).

In the limit of large d ($d \gg \xi$) the two spheres do not interact. Q is negligible in the middle of the zone, and the contribution of the director field to the free energy is the least, if around each sphere the director field $\hat{\mathbf{n}}_\infty$, where index ∞ indicates the limit of large distances, points radially outward. Close to the $z=0$ plane the director fields of the two spheres are matched together by choosing $\hat{\mathbf{n}}_\infty$ as the tangent vector of a circle with radius $R_o/2 \sin \beta_i$ [see Fig. 2(c)]. The parameter R_o is chosen in such a way that the diameter of the area close to $z=0$ where the director field is distorted is small in comparison to d while the radius of the circle should be large enough to stay within the validity of the Landau–de Gennes approach. These limitations are fulfilled if R_o is of the order of a few nanometers.

Increasing the distance d between the two particles the director field should change continuously from the ansatz $\hat{\mathbf{n}}_o$ at small d to the field $\hat{\mathbf{n}}_\infty$ at large d . For medium values of d we therefore choose the director field $\hat{\mathbf{n}}$ as a weighted superposition of $\hat{\mathbf{n}}_o$ and $\hat{\mathbf{n}}_\infty$:

$$\hat{\mathbf{n}} = \epsilon_i \hat{\mathbf{n}}_o + (1 - \epsilon_i) \hat{\mathbf{n}}_\infty. \quad (12)$$

The free parameter ϵ_i is determined minimizing the free energy in region i , i.e., $\partial F / \partial \epsilon_i = 0$.

IV. EFFECTIVE INTERACTION OF TWO PARTICLES

In order to obtain the effective interaction between the two particles that is mediated by the surrounding liquid-crystal we have to calculate the free energy $F(d)$ of the liquid-crystal ordering as a function of the interparticle distance d . We also need $F(d \rightarrow \infty)$ where $d \rightarrow \infty$ corresponds to interparticle separations much larger than the correlation length. The interaction is then defined as the difference between these two quantities, $\text{Int}(d) = F(d) - F(\infty)$.

We were not able to obtain analytically the volume integral of the last term of expression (4) without making the following simplifications of the free-energy expression. We have neglected z^2/r^2 in comparison to 1 in those regions where the director field distortion is different from zero, i.e., in regions 2–9. This condition is not completely true for region 2 but is well justified for all further regions. We have, in addition, approximated the expression $\rho_i(r)^2 + z^2$, which originates in ansatz function (11), by $\rho_i(r)^2$ evaluated at $r = \frac{1}{2}(l_i + l_{i+1})$. Here $\rho_i(r)$ equals $\rho_i(r) = r - l_i + \frac{1}{2}d_i \cot \beta_i + \Delta R_i$. The validity of this approximation can be demonstrated by evaluating ρ_i for different regions. We stress that we have checked the validity of our simplifications by com-

paring the analytically obtained integral with the numerically integrated nonsimplified expression (4). We have observed a good agreement between both methods.

In the following we divide the interaction into its attractive part resulting from the scalar order-parameter Q and its repulsive part originating in the elastic distortion of the director field.

The attractive interaction Int_i^a corresponds to the volume integral of the terms $\frac{1}{2}a\Delta T Q^2$ and $\frac{3}{2}L_1(\nabla Q)^2$ in Eq. (4) and the surface term $G_Q(Q - Q_s)^2$ in Eq. (5):

$$\text{Int}_i^a = 3\pi \frac{L_1}{\xi} Q_s^2 (l_{i+1}^2 - l_i^2) \left[\frac{\tanh \frac{\bar{d}_i}{2\xi}}{1 + \gamma_Q \tanh \frac{\bar{d}_i}{2\xi}} - \frac{1}{1 + \gamma_Q} \right]. \quad (13)$$

The parameters l_i , β_i , γ_Q , and \bar{d}_i are introduced via Eqs. (10) and (11), and in Fig. 2. For large d , i.e., $d \gg \xi$, the potential Int_i^a decays exponentially, $\text{Int}_i^a = -6\pi(L_1/\xi)Q_s^2(l_{i+1}^2 - l_i^2)e^{-\bar{d}_i/\xi}/(1 + \gamma_Q)^2$.

The repulsive interaction Int_i^r corresponds to the integral of the bulk term $\frac{9}{2}L_1Q^2[\sin^2\alpha/r^2 + (\partial\alpha/\partial r)^2 + (\partial\alpha/\partial z)^2]$ in Eq. (4) and the surface term $3G_nQQ_s \sin^2(\alpha - \beta)$ in Eq. (5). These two terms yield a repulsion of the following form:

$$\begin{aligned} \text{Int}_i^r = & \frac{9}{2}\pi L_1 Q_s^2 \frac{l_{i+1}^2 - l_i^2}{\cosh^2 \frac{\bar{d}_i}{2\xi} \left(1 + \gamma_Q \tanh \frac{\bar{d}_i}{2\xi}\right)^2} \\ & \times \left[(1 - \epsilon_i)^2 \frac{4 \sin^2 \beta_i}{R_o^2} \Phi(R_o) + 2\epsilon_i(1 - \epsilon_i) \frac{4 \sin \beta_i}{R_o \kappa_i} \right. \\ & \left. \times \Phi(R_o) + \epsilon_i^2 \left(\frac{4}{\kappa_i^2} \Phi(\bar{d}_i) + \frac{4\gamma_n \xi}{\kappa_i^2} \frac{\cosh^2 \frac{\bar{d}_i}{2\xi}}{1 + \gamma_Q \tanh \frac{\bar{d}_i}{2\xi}} \right) \right]. \quad (14) \end{aligned}$$

Here, $\Phi(x) = \xi \sinh x / 2\xi \cosh x / 2\xi + x/2$, $\kappa_i = \eta_i + 2\Delta R_i$, and $\eta_i = l_{i+1} - l_i + d_i / \tan \beta_i$. The parameter ϵ_i , defined in Eq. (12), follows after minimizing Eq. (14) with respect to ϵ_i :

$$\begin{aligned} \epsilon_i = & \left(1 - \frac{R_o}{\eta_i \sin \beta_i} \right) \left(1 - 2 \frac{R_o}{\eta_i \sin \beta_i} \right. \\ & \left. + \frac{\Phi(\bar{d}_i)}{\Phi(R_o)} \frac{R_o^2}{(\eta_i \sin \beta_i)^2} \right)^{-1}. \quad (15) \end{aligned}$$

The parameters l_i , d_i , β_i , and ΔR_i are introduced in Eq. (11) and in Fig. 2. In the limit of large d , i.e., $d \gg \xi$, expression (14) reduces to the contribution of the far-field $\hat{\mathbf{n}}_\infty$ only and yields an exponentially decaying function of d : $\text{Int}_i^r = 72\pi L_1 Q_s^2 (l_{i+1}^2 - l_i^2) \sin^2 \beta_i \Phi(R_o) R_o^{-2} e^{-\bar{d}_i/\xi} / (1 + \gamma_Q)^2$.

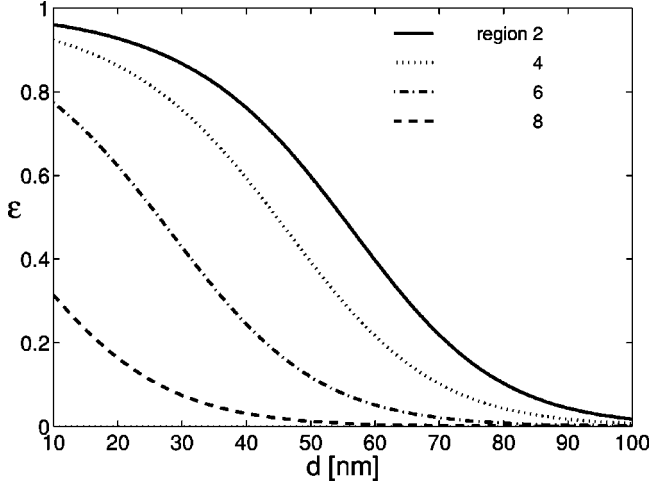


FIG. 3. Coefficients ϵ_i [see Eq. (15)] for different regions as a function of the interparticle distance. The surface coupling constants G_Q and G_n are 1×10^{-3} J/m² and 5×10^{-3} J/m², respectively, and $\Delta T = 2$ K.

V. RESULTS

To obtain a feeling for the magnitude of the interaction we use the following constants: $a = 0.18 \times 10^6$ J/m³ K, $b = -2.3 \times 10^6$ J/m³, $c = 5.02 \times 10^6$ J/m³, $L_1 = 9 \times 10^{-12}$ J/m, and $T^* = 313.5$ K, characteristic for a typical nematic liquid crystal [40]. According to the Landau–de Gennes approach, the temperature T_{NI} of the nematic–isotropic phase transition is then equal to $T_{NI} = T^* + 2b^2/9ac \approx T^* + 1.3$ K, and the corresponding correlation length $\xi = \sqrt{3L_1/[a(T-T^*)]}$, at T_{NI} is ≈ 10 nm. In the following we discuss our results in terms of $\Delta T = T - T^* \geq 1.3$ K. We set the surface-ordering parameter Q_s to 0.3 while G_Q and G_n , according to some recent experimental data [29,30], vary between 1×10^{-4} J/m² and 5×10^{-3} J/m², with the ratio G_n/G_Q not being larger than 5.

Director field configuration. In Fig. 3 we present the coefficients ϵ_i of Eq. (15) as functions of the interparticle distance d for relatively large values of the surface-coupling parameters, i.e., $G_Q = 1 \times 10^{-3}$ J/m² and $G_n = 5 \times 10^{-3}$ J/m². We choose $\Delta T = 2$ K, which is 0.7 K above T_{NI} . Examining the curve corresponding to the region $i=2$ one realizes that for small d , $d \sim \xi$, ϵ_2 is nearly 1, i.e., $\hat{\mathbf{n}} \approx \hat{\mathbf{n}}_o$. It decreases with growing d , and for large d , $d \gg \xi$; it is close to 0, i.e., $\hat{\mathbf{n}} \approx \hat{\mathbf{n}}_\infty$. These results agree with our expectations about the director field configuration in the limits of small and large d . We stress that in region $i=8$ ϵ_i is substantially smaller than 1, even for $d \approx \xi$. Its contribution to the interaction is of the order of 10%. The contribution of region 9 is even smaller, 5% or less. Therefore, no further regions have to be taken into account.

Repulsive and attractive interaction. In order to convince the reader that expressions (13) and (14) indeed represent an attractive and repulsive interaction, respectively, we plot in Fig. 4 Int_i^a and Int_i^r for region 5. As our parameters we choose $G_Q = 1 \times 10^{-3}$ J/m², $G_n = 5 \times 10^{-3}$ J/m², and $\Delta T = 1.3$ K. It is interesting to note that for small d the absolute value of Int_i^a is larger than Int_i^r , which results in an attractive interaction. With increasing distance the interaction in-

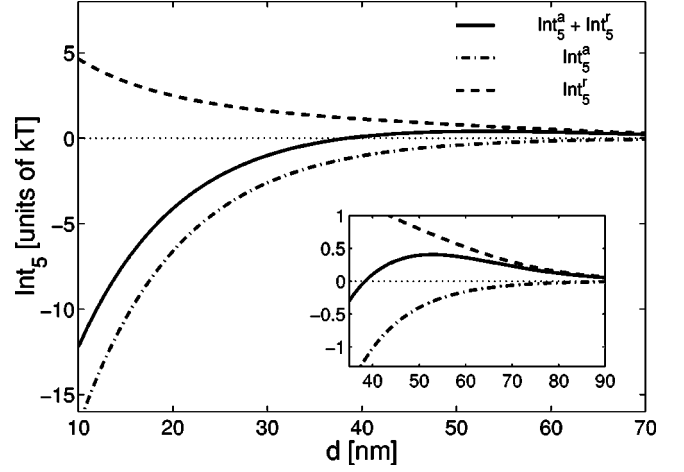


FIG. 4. Attractive and repulsive part of the interaction [see Eqs. (13) and (14)] and their sum as a function of the interparticle distance in region 5. The surface-coupling constants G_Q and G_n are 1×10^{-3} J/m² and 5×10^{-3} J/m², respectively, while $\Delta T = 1.3$ K. A magnified part of the figure is shown as the inset.

creases, reaches a maximum at $d = 53$ nm (see inset of Fig. 4), beyond which it becomes repulsive. In the limit of large d , i.e., $d \gg \xi_{NI} \approx 10$ nm the interaction decays exponentially, $\text{Int}_i^a + \text{Int}_i^r \propto e^{-d_i/\xi}$, as is shown in Eqs. (13) and (14) (see inset of Fig. 4).

Contributions of different regions to the interaction. In Fig. 5 we present the contributions ($\text{Int}_i = \text{Int}_i^a + \text{Int}_i^r$) from the regions 2, 3, 5, and 7 and compare them to the total liquid-crystal mediated interaction, i.e., the sum over regions 1–9: $\text{Int} = \sum_{i=1}^9 \text{Int}_i^a + \text{Int}_i^r$. As expected, the contribution of regions close to the axis of symmetry is crucial while the regions further apart do not contribute significantly. We would like to point out that the contribution of region 3 is larger than the contribution of region 2. This can be easily understood if one takes into account that for small i the increase of the interaction due to an increase in volume over

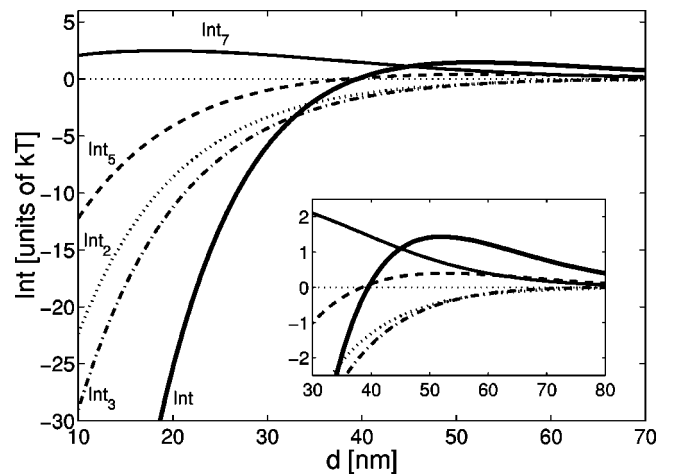


FIG. 5. Contributions Int_i of different regions to the total two-particle interaction ($\text{Int} = \sum_{i=1}^9 \text{Int}_i^a + \text{Int}_i^r$) as a function of d . The surface-coupling constants G_Q and G_n are 1×10^{-3} J/m² and 5×10^{-3} J/m², respectively, while $\Delta T = 1.3$ K. A magnified part of the figure is shown as the inset.

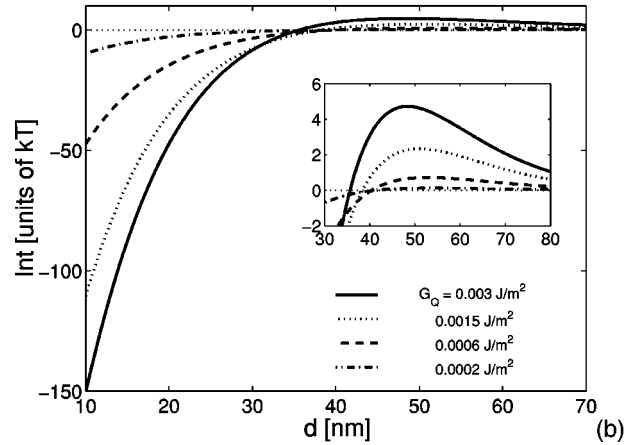
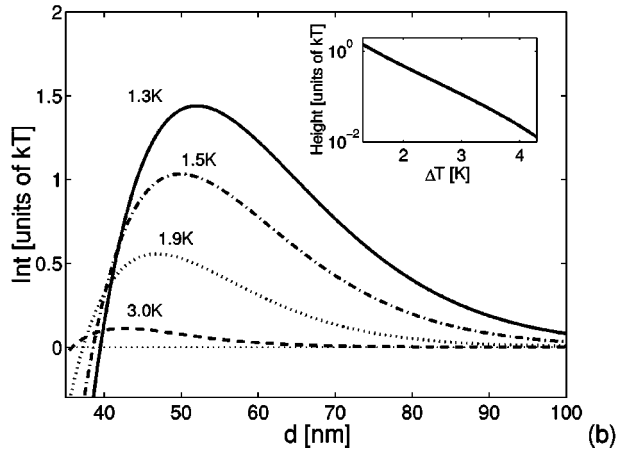
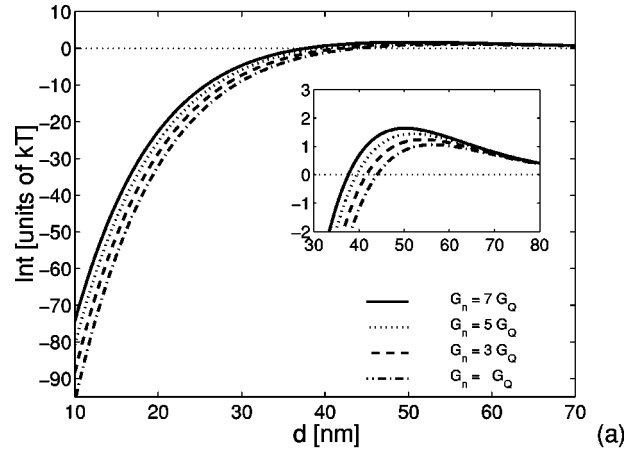
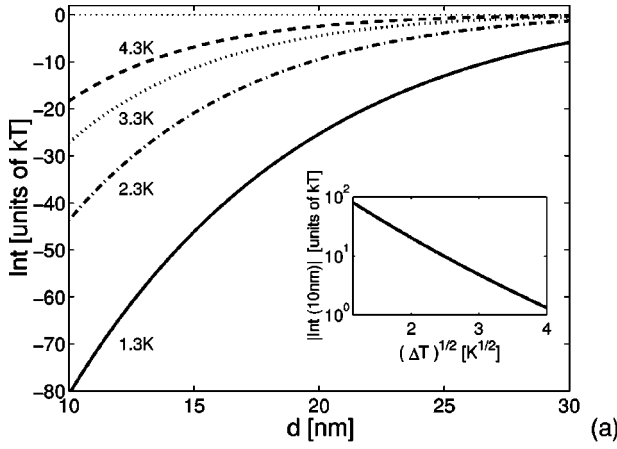


FIG. 6. Two-particle interaction Int as a function of distance d between the particles at various temperatures ΔT . (a) In the range $10 \text{ nm} < d < 30 \text{ nm}$ a strong attraction occurs. Inset: The absolute value of the interaction at $d = 10 \text{ nm}$ is plotted in a logarithmic scale versus $\sqrt{\Delta T}$. (b) $\text{Int}(d)$ in the range of the repulsion barrier, i.e., $35 \text{ nm} < d < 100 \text{ nm}$. Inset: The height of the repulsion barrier is plotted in a logarithmic scale versus ΔT . The surface-coupling constants G_Q and G_n are $1 \times 10^{-3} \text{ J/m}^2$ and $5 \times 10^{-3} \text{ J/m}^2$, respectively.

comes the effect of the diminished order parameter as one moves from the region i to the region $i + 1$.

Interaction at various temperatures. In Figs. 6(a) and 6(b) we show the total inter-particle interaction Int as a function of d for various temperatures. The surface-coupling strengths are $G_Q = 1 \times 10^{-3} \text{ J/m}^2$ and $G_n = 5 \times 10^{-3} \text{ J/m}^2$. In Fig. 6(a) we concentrate on the range of relatively strong attraction between particles, i.e., $10 \text{ nm} < d < 30 \text{ nm}$ while Fig. 6(b) presents larger distances, i.e., $35 \text{ nm} < d < 100 \text{ nm}$ where the interaction exhibits a repulsion barrier.

We would like to point out that the magnitude of the interaction strongly decreases with increasing temperature for all distances d . A closer look at the inset of Fig. 6(a) where the absolute value of the interaction at $d = 10 \text{ nm}$ is plotted in a logarithmic scale versus $\sqrt{\Delta T}$ reveals that the interaction at $d = 10 \text{ nm}$ is proportional to $e^{-\sqrt{\Delta T}/\Delta T_\alpha}$, where $\Delta T_\alpha = 0.4 \text{ K}$ is a fitted parameter. We introduce an effective distance $d_\alpha \approx 20 \text{ nm}$ via $\Delta T_\alpha = 3L_1/ad_\alpha^2$, so that the exponential decrease is described by $e^{-d_\alpha/\xi(\Delta T)}$, where $\xi(\Delta T) = \sqrt{3L_1/a\Delta T}$ is the correlation length at ΔT . On the other hand, for $\Delta T < 3.5 \text{ K}$, the magnitude of the repulsion barrier

FIG. 7. Two-particle interaction as a function of distance d for different values of the surface-coupling constants G_Q and G_n , $\Delta T = 1.3 \text{ K}$. (a) G_Q is $1 \times 10^{-3} \text{ J/m}^2$ while G_n is the curve parameter. (b) The ratio G_n/G_Q is fixed while G_Q is varied. Magnified parts of the figures are shown as insets.

is proportional to $e^{-\Delta T/\Delta T_\beta}$, where $\Delta T_\beta = 0.67 \text{ K}$ is again a fitting parameter. This can be seen from the inset of Fig. 6(b) where the magnitude of the peak is plotted in a logarithmic scale versus temperature. For larger ΔT the temperature dependence of the potential barrier height is more complicated. Because of the relatively strong dependence of the liquid-crystal mediated interaction on temperature, already a couple of K above the bulk nematic-isotropic phase transition the attraction between our approximated particles is decreased considerably, and the repulsive barrier becomes much smaller than kT .

Influence of surface coupling parameters G_Q and G_n . In Figs. 7(a) and 7(b) we show how the magnitude of the interaction is influenced by the surface-coupling constants G_Q and G_n . In Fig. 7(a) we present the interaction of particles as a function of d for various ratios G_n/G_Q . G_Q is fixed to $1 \times 10^{-3} \text{ J/m}^2$ and $\Delta T = 1.3 \text{ K}$. The magnitude of the interaction increases with the ratio G_n/G_Q but there is no significant change in the shape of the interaction curve. We, therefore, choose the ratio G_n/G_Q to be 5 and focus our attention on the effect of G_Q [see Fig. 7(b)]. We find that the magnitude of the interaction decreases considerably with G_Q . A more detailed investigation reveals that the magnitude of the repulsion barrier is approximately linear in G_Q .

VI. DISCUSSION AND CONCLUSIONS

We have shown that the interaction of two spherical particles immersed into an isotropic liquid crystal depends on the interparticle distance d , on surface-coupling parameters G_Q and G_n , and on temperature ΔT . Concentrating on the spatial dependence of the interaction we show that the particles strongly attract each other in the regime characterized by $d \sim \xi$, in full analogy to the interaction between two parallel plates. At larger d a repulsion barrier appears. Its height can be several kT at the nematic-isotropic phase transition. In the limit of large d , $d \gg \xi$, the repulsion decays exponentially with increasing d . The shape of the interaction curve is a consequence of the sum of repulsive and attractive contributions. The repulsive one originates in a distortion of $\hat{\mathbf{n}}$ while the attractive one is due to changes in the scalar order-parameter Q .

The magnitude of the interaction depends on the surface-coupling parameters G_Q and G_n as well as on temperature. Generally, the magnitude of the interaction is rather insensitive to the ratio G_n/G_Q but it increases linearly with G_Q . The most crucial is the dependence of the interaction on temperature. With increasing ΔT the strong attractive interaction at smaller interparticle distances decreases as $e^{-\sqrt{\Delta T/\Delta T_a}}$ while the height of the repulsion barrier decreases approximately as $e^{-\Delta T/\Delta T_b}$. The parameters ΔT_a and ΔT_b are of the order of 1 K. Therefore, even a small increase of temperature reduces the magnitude of the interaction so that the repulsion barrier drops well below kT .

While obtaining the analytical expression for the interaction we have performed some simplifications. Although we have checked the validity of all simplifications one may still suspect that the shape of the interaction curve might originate in our approximations. However, numerical calculations of the interparticle interaction, which are in progress [41], show the same behavior of the interaction as our analytical approach.

We stress that in this paper we have concentrated on the pretransitional liquid-crystal mediated interaction of two

spherical particles. We have derived the mean-field part to this interaction while an estimate of the contribution due to fluctuations shows that in most cases the latter represents a tiny correction [31]. According to our knowledge direct measurements of the two-particle interaction in the isotropic phase have not been performed so far. However, some indirect investigations do exist. In the experimental study performed by Poulin *et al.* [19] it was shown that colloidal water droplets remained stable for weeks if the system was cooled deep into the nematic phase. However, the droplets coalesced in less than an hour after the system was heated to the isotropic phase. Using results of our study this phenomenon can be explained in the following way. The liquid-crystal interaction exhibits a strong attraction at small particle separations, which is followed by a weak repulsive barrier of the order of kT if the particles are moved further apart. Since the repulsive barrier is decreased by the van der Waals attraction [42] typically down to a few tenths of kT , it can not prevent the droplets from coalescing and the dispersion collapses.

To be able to predict the behavior of spherical particles in an experiment, one has to consider all possible two-particle potentials. Besides the one already mentioned, these include electrostatic and steric interactions. The combined effect of all the relevant interactions in an electrostatically stabilized colloidal dispersion will be published elsewhere.

ACKNOWLEDGMENTS

One of the authors (A.B.) would like to thank T. C. Lubensky, R. Kamien, and T. Bellini for stimulating discussions. Financial support from the Ministry of Science and Technology of Slovenia (Grant No. J1-0595/1554-98) and European Community (Grant No. EC IC15-CT96-0744) are gratefully acknowledged. A.B. also gratefully acknowledges financial support from the Institut für Theoretische und Angewandte Physik, Universität Stuttgart, where part of this work was done.

-
- [1] R. G. Horn, J. N. Israelachvili, and E. Perez, *J. Phys.* **42**, 39 (1981).
- [2] I. Muševič, G. Slak, and R. Blinc (unpublished).
- [3] P. Poulin, V. Cabuil, and D. A. Weitz, *Phys. Rev. Lett.* **79**, 4862 (1997).
- [4] A. Poniewierski and T. J. Sluckin, *Liq. Cryst.* **2**, 281 (1987).
- [5] A. Adjari, L. Peliti, and J. Prost, *Phys. Rev. Lett.* **66**, 1481 (1991).
- [6] B. D. Swanson and L. B. Sorensen, *Phys. Rev. Lett.* **75**, 3293 (1995).
- [7] S. Ramaswamy, R. Nityananda, V. Raghunathan, and J. Prost, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **288**, 175 (1996).
- [8] R. W. Ruhwandl and E. M. Terentjev, *Phys. Rev. E* **55**, 2958 (1997).
- [9] T. C. Lubensky, D. Petey, N. Currier, and H. Stark, *Phys. Rev. E* **57**, 610 (1998).
- [10] O. V. Kksenok, R. W. Ruhwandl, S. V. Shiyonovskii, and E. M. Terentjev, *Phys. Rev. E* **54**, 5198 (1996).
- [11] A. Borštnik and S. Žumer, *Phys. Rev. E* **56**, 3021 (1997).
- [12] M. Krech, *The Casimir Effect in Critical Systems* (World Scientific, Singapore, 1994).
- [13] V. M. Mostepanenko and N. N. Trunov, *The Casimir Effect and its Application* (Clarendon Press, Oxford, 1997).
- [14] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1995).
- [15] A. D. Dinsmore, A. G. Yodh, and D. J. Pine, *Nature (London)* **383**, 259 (1996).
- [16] A. D. Dinsmore, D. T. Wong, P. Nelson, and A. G. Yodh, *Phys. Rev. Lett.* **80**, 409 (1998).
- [17] D. Rudhardt, C. Bechinger, and P. Leiderer, *Phys. Rev. Lett.* **81**, 1330 (1998).
- [18] P. Poulin and D. A. Weitz, *Phys. Rev. E* **57**, 626 (1998).
- [19] P. Poulin, H. Stark, T. Lubensky, and D. Weitz, *Science* **275**, 1770 (1997).
- [20] A. Böttger, D. Frenkel, E. van de Riet, and R. Zijlstra, *Liq. Cryst.* **2**, 539 (1987).
- [21] A. Borštnik, H. Stark, and S. Žumer (unpublished).
- [22] P. Galatola and J. B. Fournier (unpublished).

- [23] N. Vrbančič, M. Vilfan, R. Blinc, J. Dolinšek, G. P. Crawford, and J. W. Doane, *J. Chem. Phys.* **103**, 8726 (1993).
- [24] J. Dolinšek, O. Jarh, M. Vilfan, S. Žumer, R. Blinc, J. W. Doane, and G. P. Crawford, *J. Chem. Phys.* **95**, 2154 (1991).
- [25] G. P. Crawford, D. K. Yang, S. Žumer, D. Finotello, and J. W. Doane, *Phys. Rev. Lett.* **66**, 723 (1991).
- [26] B. M. Ocko, *Phys. Rev. Lett.* **64**, 2160 (1990).
- [27] G. S. Iannacchione, J. T. Mang, S. Kumar, and D. Finotello, *Phys. Rev. Lett.* **73**, 2708 (1994).
- [28] Y. K. Fung, A. Borštnik, S. Žumer, D.-K. Yang, and J. W. Doane, *Phys. Rev. E* **55**, 1637 (1997).
- [29] G. P. Crawford, R. J. Ondris-Crawford, J. W. Doane, and S. Žumer, *Phys. Rev. E* **53**, 3647 (1996).
- [30] G. P. Crawford, R. Ondris-Crawford, S. Žumer, and J. W. Doane, *Phys. Rev. Lett.* **70**, 1838 (1993).
- [31] P. Zihlerl, R. Podgornik, and S. Žumer, *Chem. Phys. Lett.* **295**, 99 (1998).
- [32] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).
- [33] E. B. Priestely, P. J. Wojtowicz, and P. Sheng, *Introduction to Liquid Crystals* (Plenum, New York, 1974), p. 156.
- [34] E. G. Virga, *Variational Theories for Liquid Crystals* (Chapman & Hall, London, 1994), p. 129.
- [35] S. Kralj and S. Žumer, *Phys. Rev. A* **45**, 2461 (1992).
- [36] P. G. de Gennes, *Mol. Cryst. Liq. Cryst.* **12**, 193 (1971).
- [37] To be sure that setting $L_2=0$ indeed does not affect the qualitative behavior of our system we have checked the influence of the L_2 term, using the ansatz function of this paper [see Eqs. (10) and (11)]. We found that the curves of the interaction energy versus particle separation, which we present below, are shifted to larger distances in agreement with the changing coherence length. However, the main features of the interaction are not affected.
- [38] A. K. Sen and D. E. Sullivan, *Phys. Rev. A* **35**, 1391 (1987).
- [39] M. Nobili and G. Durand, *Phys. Rev. A* **46**, R6174 (1992).
- [40] H. J. Coles, *Mol. Cryst. Liq. Cryst. Lett.* **49**, 67 (1978).
- [41] M. Ambrožič (private communication).
- [42] J. Israelachvili, *Intermolecular & Surface Forces* (Academic, London, 1992), p. 184.