Long-range elastic-mediated interaction between nanoparticles adsorbed on free-standing smectic films

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We determine the elastic-mediated interaction between colloidal nanoparticles adsorbed on the surface of free-standing smectic films. In contrast with the short-range character of the elastic-mediated force between particles adsorbed on smectic films supported by a solid substrate, the effective force acquires a long-range character in free-standing films, decaying with the particles distance R as slow as $1/R$. We also discuss the dependence of the effective interaction potential on the surface tension γ and film thickness. We show that it decays as $1/\gamma$ in the regime of large surface tensions and becomes independent of the film thickness at a characteristic surface tension.

Long-range interactions emerge in correlated liquid crystal systems when their fluctuation modes are modified by the imposition of boundary conditions [1]. In particular, fluctuation-induced interactions are assumed to play an important role in a great variety of phenomena, such as wetting transitions [2], aggregation of guest particles [3], and thin film stability [4,5]. However, a distinct interaction takes place in these systems as a response to elastic distortions in the liquid-crystalline order when colloidal particles are immersed in them. These elastic-mediated interactions between colloidal particles have been identified as the main mechanism to the formation of several self-assembly organized structures, such as periodic lattices and anisotropic clusters [6–9].

The effective interaction between guest particles in liquid crystal hosts has been extensively investigated by different experimental [10–14] and theoretical techniques [15–19]. In nematic samples, the addition of spherical colloidal particles induces the formation of topological defects in the nematic order that depend on the strength and direction of the anchoring at the colloid surface [12,16]. For a strong homeotropic anchoring, a guest particle behaves itself as a radial hedgehog defect. An additional hyperbolic hedgehog defect emerges in order to annihilate the topological charge in the nematic environment [12]. Such pair of particle-defect constitutes an elastic-dipole which minimizes the elastic energy associated with the nematic order distortions. As a consequence, an effective dipolelike interaction takes place between colloidal particles. Its attractive or repulsive nature depends on the distance and the relative direction of the elastic dipoles [12]. On the other hand, an effective quadrupolarlike interaction arises between immersed particles when the colloidal liquid crystal dispersions are confined in a planar cell [14], as well as when a strong tangential anchoring is induced at the colloid surface [11]. Colloidal interactions at the nematic-air interface have been shown to be of a new type as compared to the bulk interaction. In this case, the director deformations caused by the particles lead to distortions of the interface and thus to capillary attraction [20].

In free-standing smectic films, experimental investigations have revealed that soft and hard colloids modify the smectic layer structure around them [21–23]. In particular, it was observed the formation of a decorated meniscus surrounding the adsorbed colloids and an effective attractive interaction emerges as the menisci overlap [21]. Such effective interaction has been associated with smectic layer undulations. Further, the addition of guest particles affects other physical properties of smectic films, such as the transition temperature [24] and photonic response [25]. In ferroelectric smectic membranes, the interaction between the inclusions is influenced by the rearrangement of topological defects and anchoring on the inclusion boundary [26]. Theoretical studies have predicted that pointlike deformations of smectic layers promote an elastic-mediated interaction between colloid particles in bulk samples [27], as well as in membranes and in thin films supported by a solid substrate [28,29]. In the last case, the predicted effective force decays exponentially with the separation between the colloids.

In this work, we determine the effective elastic-mediated interaction between colloidal nanoparticles adsorbed on the surface of a free-standing smectic film. We will be particularly interested in analyzing the dependence of the interaction on the film thickness l and on the distance R between the colloidal nanoparticles. Films under distinct surface tension regimes will be considered. We will reveal the long-range character of the elastic-mediated force which contrasts with the short-range nature of this force in smectic films supported by a solid substrate. Such force shall play a key role in the formation of self-assembled colloidal structures in the surface of free-standing films.

Free-standing smectic films can be described as a stacking of two-dimensional equidistant liquid layers surrounded by a gas. The coupling between the film and the gas environment is represented by a surface tension which reduces the smectic fluctuations close to the film surface, providing a quasi-long-range order. In the harmonic approximation, the free energy associated with the deformation of the smectic layers is given by [30]

$$\mathcal{H}_S = \frac{1}{2} \int d^3r \left\{ B\left[\frac{\partial u(\mathbf{r})}{\partial z}\right]^2 + K[\Delta u(\mathbf{r})]^2 \right\}$$
$$+ \frac{\gamma}{2} \int d^2r [|\nabla_\perp u(r_\perp, 0)|^2 + |\nabla_\perp u(r_\perp, l)|^2]. \quad (1)$$

The first term in Eq. (1) represents the energy cost associated with bulk deformations of the smectic order while the second term is the surface contribution. Here, $u(\mathbf{r} = r_\perp, z)$ is the layer displacement at the point $\mathbf{r}$ and l is the film thickness. K and B are the elastic constants associated with the bending and the compression of smectic layers, respectively. γ is the surface tension which penalizes variations in the area of the film surface. A characteristic surface tension can be defined from the elastic constants of the smectic phase, $\gamma_c = \sqrt{KB}$, which delimits the regimes of large ($\gamma > \gamma_c$) and small ($\gamma < \gamma_c$) surface tensions.

In order to investigate the effects associated with the adsorption of colloidal particles on free-standing smectic films, an additional term in the free energy is included to represent the energy cost associated with deformations in the smectic order due to colloids adsorbed on the film surface

$$\mathcal{H}_A = -\int_{a_0}^L d^2r f(r_\perp) u(r_\perp, l), \quad (2)$$

with the total free energy being $\mathcal{H}_T = \mathcal{H}_S + \mathcal{H}_A$. f is the colloid load that represents the normal stress at the film surface due to the colloid adsorption. In particular, f is assumed to present an action radius of a few nanometers, with a magnitude that overcomes the energy cost to undulate the surface layer [28]. L is the transverse size of the film and a_0 is a cutoff length of the order of the molecular diameter.

Actually, there are additional contributions to the film free energy associated with the presence of the adsorbed colloids. One of them is related to fact that a colloid disturbs the homogeneous distribution of the liquid crystal molecules in its surrounding. When two colloids are close enough, the superposition of these disturbed regions leads to the reduction of the free energy in the interface which can be interpreted as an effective interaction between the particles. Another physical mechanism which leads to an effective interaction between the colloids is due to the topological defects they induce in the nematic order that usually result in a dipole-dipole-like coupling. Although the coupling of the colloids with the interface can possible involve additional terms, such as capillary deformations and induced smectic-C order, we will restrict our following analysis to the effective interaction between the colloids resulting from the pressure field they exert on the film surface.

The additional pressure field on the film surface due to the colloids adsorption disturbs the smectic order. Therefore the layer displacement that minimizes the elastic free energy has to be obtained from the Euler-Lagrange equation

$$B\frac{\partial^2 u}{\partial z^2} = K\Delta^2 u, \quad (3)$$

which must satisfy the following boundary conditions

$$\gamma\Delta u(z=l) - B\left(\frac{\partial u}{\partial z}\right)_{z=l} = -f(r_\perp), \quad (4)$$

$$\gamma\Delta u(z=0) + B(\partial u/\partial z)_{z=0} = 0. \quad (5)$$

Performing some partial integrations and assuming that the layer deformations are null at the film holder, the total free energy can be expressed as [28]

$$\mathcal{H}_T = -\frac{1}{2}\int_{a_0}^L d^2r[f(r_\perp)u(r_\perp, l)]. \quad (6)$$

The elastic free energy depends on the deformation induced by the colloidal particles at the film surface, which is represented by the load f. In fact, the layer displacement $u(\mathbf{r})$ is distorted by the adsorbed particles at $z = l$. Using the Green's function formalism, we can define the smectic layer displacement as

$$u(r_\perp, z) = \int_{a_0}^L d^2\bar{r}[f(\bar{r}_\perp)G(|r_\perp - \bar{r}_\perp|, z)]. \quad (7)$$

It is straightforward to show that the Green's function in Fourier space is given by

$$G_q(z) = \frac{1}{q^2\gamma_c}\left[\frac{\cosh(q^2\lambda_c z) + \alpha \sinh(q^2\lambda_c z)}{2\alpha \cosh(q^2\lambda_c l) + (1+\alpha^2)\sinh(q^2\lambda_c l)}\right], \quad (8)$$

where $\alpha = (\gamma/\gamma_c)$ and $\lambda_c = \sqrt{K/B}$. The inverse transform results in

$$G(R, z) = \int_{2\pi/L}^{2\pi/a_0} \frac{qdq}{2\pi} G_q(z) J_0(qR). \quad (9)$$

Here, $R = |r_\perp - \bar{r}_\perp|$ and $J_0(qR)$ is the Bessel function of zeroth order. The total elastic free energy can then be expressed as $\mathcal{H}_T = \frac{1}{2}[U_{1,1} + U_{2,2}] + U_{1,2}$, where

$$U_{ij} = -\int d^2r d^2\bar{r} f_i(r_\perp) f_j(\bar{r}_\perp) G(|r_\perp - \bar{r}_\perp|, l). \quad (10)$$

U_{ii} is the self-energy associated with the ith colloid ($i = 1, 2$), while $U_{1,2}$ represents the elastic-mediated interaction energy between the adsorbed colloids which is a function of the film thickness and the distance between the particles. The colloid load was written as $f(r_\perp) = f_1(r_\perp) + f_2(r_\perp)$, with f_i presenting a small action radius. It can be represented as $f_i(r_\perp) = p_i(|r_\perp - r_\perp^i|)$, where p_i is non-null for distances smaller than a cutoff length a_i of the order of a few nanometers and $r_\perp^i$ is the position of the ith colloid. As the Green's function does not change significantly over distances smaller than a_i, one can write the elastic-mediated interaction energy as $U_{1,2} = -P_1 P_2 G(R, z=l)$, where $P_i = \int_0^{a_i} p_i(r)2\pi rdr$ represents the effective load of the ith colloid particle adsorbed on the film surface and R is the distance between the colloids. The problem of computing the elastic-mediated interaction is reduced to the problem of finding the Green's function in real space. Such formalism was previously used to investigate the interaction between colloidal particles adsorbed on a smectic film deposited in a solid substrate which suppresses the smectic layer displacement close to it [28]. In such case the Green's function reads

$$G_q^s(z) = \frac{\sinh(q^2\lambda_c z)}{q^2[\gamma_c \cosh(q^2\lambda_c l) + \gamma \sinh(q^2\lambda_c l)]}, \quad (11)$$

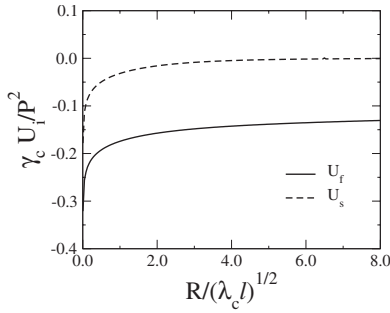and it leads to an elastic-mediated force that decays exponentially with the distance between the colloids. However,

FIG. 1. The elastic-mediated interaction potential versus their scaled distance. Both cases of a film anchored by a solid substrate (U_s—dashed line) and a free-standing film (U_f—solid line) are shown. Physical parameters used were $\gamma = 25 \times 10^{-3}$ N/m and $l = 300$ nm. The fast asymptotic exponential decay of U_s contrasts with the slow logarithmic convergence of U_f which is typically of the order of $10 k_B T$ at room temperature.

one should notice that the presence of a solid substrate makes the Green's function regular in the regime of small wave vector ondulations. It is such regular behavior at small q that is responsible for the exponential decay of the interaction energy at large interparticle distances. For free-standing films the picture is quite distinct. The Green's function is singular at small wave vectors, diverging as $1/q^2$. Such singularity has a strong impact on the elastic-mediated interaction, as we will describe below.

In what follows we use typical experimental parameters: $K = 10^{-11}$ N, $B = 2.5 \times 10^6$ N/m^2 ($\gamma_c = \sqrt{KB} = 5 \times 10^{-3}$ N/m). Also, we consider identical colloidal particles ($P_1 = P_2 = P$), with an effective load $P = 5$ K, a cutoff length of the order of the molecular diameter of $a_0 = 4$ Å, layer spacing $d = 30$ Å and a typical film diameter of $L = 4$ mm. In Fig. 1 we plot the effective elastic-mediated interaction energy as a function of the distance between the particles, for fixed film thickness and surface tension. Both cases of a film deposited on a solid substrate U_s and a free-standing film U_f are shown. The distance between the particles is scaled by a typical distance given by $\sqrt{l\lambda_c}$. The interaction is mainly attractive in both cases, except by an oscillatory character of U_s at large distances that is not visible in the scale shown [28]. Notice that the exponential decay of the interaction on films supported by a solid substrate contrasts with the very slow decay of the interaction energy on a free-standing film. The effective force between the particles is reported in Fig. 2 for the same set of parameters given above. For small interparticles distances, the interaction force depicts a similar $1/R$ decay for both surface tension regimes. For a film supported by a solid substrate, the interaction crosses over to an exponentially decaying force in the regime of large interparticle distances. This crossover takes place at larger force values for thinner films and weker surface tension. On the other hand, the slow $1/R$ decay persists in free-standing films. Actually, the asymptotic form of the interaction force can be analytically computed by noticing that its long distance behavior is determined by the singular form of the Green's function at small wave vectors. A straightforward calculation results in $|F| = P_1 P_2 / (4 \pi \gamma R)$. This asymptotic form is shown in Fig. 2 as a solid line.
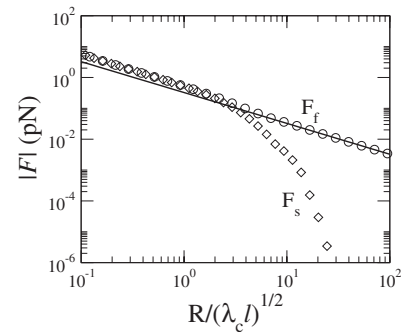

FIG. 2. The amplitude of the elastic-mediated force as a function of the scaled interparticle distance. The force in the film anchored by a solid substrate (F_s—diamonds) crosses over from a $1/R$ decay at small distances to an exponential decay at large distances. The force in free-standing films (F_f—circles) keeps the slow $1/R$ decay at large distances. The solid line represents the analytical asymptotic form $|F_f| = P_1 P_2 / (4 \pi \gamma R)$.

We also analyze the dependence of the effective interaction potential on the film thickness. The main results are shown in Fig. 3. It slowly converges to a constant value that is proportional to $1/(\gamma + \gamma_c)$. The potential is strictly thickness independent at the characteristic surface tension $\gamma = \gamma_c$, exhibiting opposite trends for large and small surface tensions. Finally, we report the dependence of the interaction potential on the surface tension. Figure 4 shows the typical $1/\gamma$ decay at large surface tensions which holds for different interparticle distances and film thicknesses. In particular, a single $1/\gamma$ law holds for large interparticle distances irrespective to the surface tension regime.

In conclusion, we determined the elastic-mediated interaction between colloidal nanoparticles adsorbed on the surface of a free-standing smectic film. We demonstrated that this interaction has an attractive long-range character, with the force decaying asymptotically as slow as $1/R$. Such long-range character contrasts with the exponentially decaying force mediated by the smectic elastic deformations of a film supported by a solid substrate. These opposite scenarios were shown to be related to the role played by the long wavelength elastic deformations on films under distinct surface
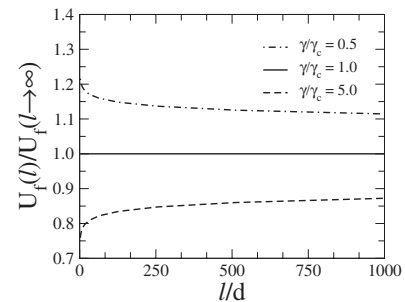

FIG. 3. The elastic-mediated interaction potential in free-standing smectic films as a function of the normalized film thickness for three representative surface tensions and $R = 5a_0$. The physical parameters are the same as in the previous figures. It slowly converges to a constant value proportional to $1/(\gamma + \gamma_c)$, with distinct convergence trends for large and small surface tensions.
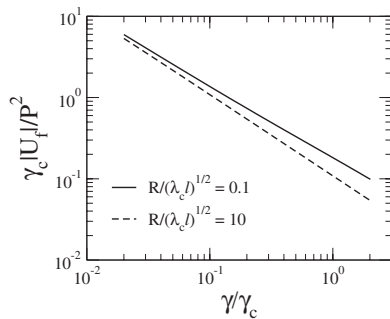
FIG. 4. The elastic-mediated interaction potential in free-standing smectic films as a function of the surface tension for two representative interparticle distances and film thicknesses. It typically decays as $1/\gamma$. Physical parameters are the same as in the previous figures.

tension conditions. A solid substrate regularizes the characteristic Green's function in this regime, thus leading to a short-ranged interaction energy. On the other hand, the surface tension term acting on both surfaces of a free-standing film leaves a singular contribution of long wavelength elastic modes which is responsible for the long-range nature of the effective interaction between the nanoparticles. This elastic-mediated force is longer ranged than the Coulomb force between charged nanoparticles. Therefore, it shall be the predominant long distance interaction between nanoparticles adsorbed in the surface of free-standing smectic films, thus playing an important role in the formation of self-assembly structures in these systems. The here reported force can, in principle, be directly measured experimentally using laser tweezers [11,31] or combined magneto-optical techniques [10,32]. It would be interesting to have such measurements performed in order to probe the long-range character of this elastic-mediated interaction.

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