PHYSICAL REVIEW E **70**, 050702(R) (2004)

Field-driven crossover from attractive-to-repulsive Casimir-like force in smectic films

I. N. de Oliveira and M. L. Lyra
Departamento de Física, Universidade Federal de Alagoas, 57072-970 Maceió-AL, Brazil
(Received 4 June 2004; published 30 November 2004)

External fields have a profound effect on the fluctuations of strongly correlated fluids, such as a liquid crystal. Within a harmonic functional integral approach, we compute the fluctuation-induced force between the surfaces of a smectic liquid-crystal film under the presence of an ordering field. In particular, we show that for asymmetrically anchored films, the thermal Casimir interaction energy can be collapsed into a universal form crossing over from a repulsive to an attractive interaction as the film thickness is increased. We discuss the possible relevance of this field effect in nematic-smectic wetting transitions.

DOI: 10.1103/PhysRevE.70.050702 PACS number(s): 61.30.Hn, 61.30.Dk, 64.70.Md

The fluctuation modes of a correlated system are known to be modified by the presence of surfaces and/or external bodies. The most prominent example of such a phenomenon is the suppression of fluctuation modes of the electromagnetic vacuum field between conducting grounded parallel plates. As a consequence, it gives rise to an effective and attractive interaction between the plates, namely the Casimir force [1]. Similar fluctuation-induced interactions also emerge in classical systems exhibiting thermal fluctuations. They are particularly important in liquid crystals [2–6], where the long-range character of this interaction has been shown to be relevant to several interesting phenomena, such as wetting and unbinding of fluid membranes.

Liquid crystals are characterized by the presence of orientational order of the constituent molecules which may coexist with some degree of positional order [7,8]. In the nematic phase, with pure molecular orientational order, the thermal Casimir-like force between the surfaces of a slab of thickness l decays as $1/l^3$ [3]. It has an attractive character for likely boundaries and a repulsive one for mixed boundary conditions. In the smectic phase, the liquid crystal develops an additional layered structure. Layer fluctuations, described by the displacement field $u(\mathbf{r})$, induce an effective surface-surface interaction force decaying as $1/l^2$. Similar fluctuation-induced forces have also been identified for the columnar [3,9], chiral smectic [10], and hexatic [11] phases, as well as for liquid crystals with rough surfaces [4,12] and nematic films frustrated by external fields [13]. In this latter case, the competition between bulk and surface fields gives rise to a crossover of the surface-surface interaction from attraction to repulsion as the film thickness increases.

In smectic liquid-crystal films, the decay of the thermal Casimir force is slower than the usual van der Waals interaction and, therefore, it plays a relevant role on wetting transitions of smectic films [2]. Most experimental set ups result in smectic films with strong anchoring of their surfaces, thus leading to an attractive surface-surface interaction. This attraction leads to incomplete wetting by the smectic phase, i.e., the wetted phase can grow only up to a finite thickness. A possible exception was pointed out in the case of a smectic film bordered by a nematic liquid crystal. In this case, the weak nematic-smectic boundary provides the mixed anchoring condition needed for the emergence of a repulsive interaction and would promote complete wetting.

External fields that couple to a long-range correlated order parameter are also able to promote profound modifications in their fluctuation modes [7,8]. The influence of an applied magnetic field on the critical behavior of liquid crystals has been extensively investigated [14–17]. Theoretical and experimental studies showed that several effects can be associated with the field influence on the smectic fluctuations [15–17], which was recently shown to be nonmonotonic with the average following a universal behavior [18]. Analogous effects can also be observed for films under an external electric field once it couples similarly to the smectic layer displacement. In chiral liquid crystals, an electric field applied in the smectic layer plane can further induce a molecular tilt (the electroclinic effect), which has been explored in the development of electro-optic devices [19,20].

In this Rapid Communication, we will compute the fluctuation-induced interaction in free-standing smectic liquid-crystal films under the influence of an ordering field. Within a quadratic functional approach we will provide the scaling correction to the free energy as obtained from both discrete and continuous models of a smectic film. We will be particularly interested in analyzing the field effect in films under mixed boundary conditions. In this case, the repulsive thermal Casimir interaction can be driven to an attractive one as the field is increased. We will characterize the scaling properties governing this crossover and discuss the possible relevance and predictions which can be drawn from these findings to experimental investigations of the field effect on nematic-smectic wetting transitions.

In free-standing smectic liquid-crystal films, the interplay between surface, field ordering, and finite-size effects can be investigated in great detail. The coupling between the film and the surrounding fluid is usually represented by a surface-tension term, which reduces fluctuations in the smectic order and promotes quasi-long-range order with logarithmically diverging fluctuations. For strongly anchored films, the reduced fluctuations near the film surface are related to several anomalous phenomena, such as the existence of smectic films at high temperatures as compared with bulk samples [21,22], surface-enhanced ordering, and layer-thinning transitions [23–26]. Within the harmonic approximation, the Hamiltonian describing the small layer deformations of a film with N layers can be written as $H=H_B+H_S+H_F$, where

$$H_B = \int_a^L d^2r \left[\sum_{i=1}^{N} \frac{dK}{2} [\Delta u_i(\mathbf{r})]^2 + \sum_{i=1}^{N-1} \frac{B}{2d} [u_{i+1}(\mathbf{r}) - u_i(\mathbf{r})]^2 \right], \tag{1}$$

$$H_S = \int_a^L d^2r \left[\frac{\gamma_1}{2} |\nabla u_1(\mathbf{r})|^2 + \frac{\gamma_N}{2} |\nabla u_N(\mathbf{r})|^2 \right], \tag{2}$$

$$H_F = \int_a^L d^2r \left[\sum_{i=1}^{N} \frac{d\chi_a H^2}{2} |\nabla u_i(\mathbf{r})|^2 \right], \tag{3}$$

are the bulk, surface, and external field contributions, respectively, and $u_i(\mathbf{r})$ represents the small displacement of the ith smectic layer from its original equilibrium position $z=id$ at point $\mathbf{r}$, with d being the mean layer spacing. The upper integration limit L is the transversal size of the film and the lower limit a is a cut-off length of the order of the molecular diameter. K and B are, respectively, the layer bending and layer coupling constants. γ_i $(i=1,N)$ is the surface tension which penalizes variations in the area of the surface layers [27]. A characteristic surface tension, $\gamma_c=\sqrt{KB}$, delimits the regimes of weak $(\gamma<\gamma_c)$ and strong $(\gamma>\gamma_c)$ anchoring. The above model was introduced by Holyst to compute the x-ray diffraction pattern for thin smectic-A liquid-crystal films [28], and further extended by Mirantsev to allow for nonflat profiles of the elastic constants [29] and the presence of a solid substrate [30]. The anisotropy χ_a is usually positive and therefore an external field H (magnetic or electric) applied perpendicularly to the layer's plane reinforces the smectic order by penalizing any in-plane gradient of smectic fluctuations.

The quadratic form of the total Hamiltonian allows for a direct computation of several thermodynamic properties of free-standing smectic films in Fourier space. In particular, the Helmholtz free energy per unit area can be written as

$$f = \frac{k_B T}{2} \int_{2\pi/L}^{2\pi/a} \frac{d^2q}{(2\pi)^2} \ln \det M, \tag{4}$$

from which trivial extensive contributions were neglected. In the above expression, M is the dimensionless interaction matrix of the system whose only nonzero elements are

$$M_{i,i} = \left[\left(\frac{\gamma_i}{\gamma_c} \right) + \left(\frac{H}{H_c} \right)^2 \left(\frac{d}{a} \right) \right] d^2q^2 + \lambda_c d^3 q^4 + \left(\frac{d}{\lambda_c} \right); \quad i = 1 \text{ and } N, \tag{5}$$

$$M_{i,i} = \left(\frac{H}{H_c} \right)^2 \left(\frac{d}{a} \right) d^2q^2 + \lambda_c d^3 q^4 + 2\left(\frac{d}{\lambda_c} \right); \quad i = 2, N-1, \tag{6}$$

$$M_{i,i+1} = M_{i+1,i} = -\left(\frac{d}{\lambda_c} \right); \quad i = 1, N-1, \tag{7}$$

where $H_c=\sqrt{\gamma_c/a\chi_a}$ is a characteristic field and $\lambda_c=\sqrt{K/B}$ is a characteristic length scale. For a film of thickness l with open boundaries, the total free energy is expected to have the following functional thickness dependence:

$$f = l f_B + f_S + \Delta f(l), \tag{8}$$

where f_B represents the bulk contribution to the free energy, f_S is the surface contribution, and $\Delta f(l)$ is the effective fluctuation-induced (Casimir-like) interaction energy. The Casimir-like contribution to the total free energy can be extracted by a subtraction scheme within the above discrete formulation.

In the limit where the number of smectic layers $N\to\infty$ but with $l=(N-1)d$ finite, a simple expression for the interaction energy can be obtained from the continuous version of the model [2]. The eigenmodes are obtained from the differential equation

$$dKq^4 u(z) + d\chi_a H^2 q^2 u(z) - dB \frac{d^2u}{dz^2} = \lambda u(z), \tag{9}$$

where z runs from 0 to l. By imposing appropriated boundary conditions, the eigenmodes can be obtained and the scaling correction to the free energy can be extracted after the splitting of the surface and volume contributions [2,6,11]. After some algebra, it results in

$$\frac{2\Delta f(l)}{k_B T} = \int_{2\pi/L}^{2\pi/a} \frac{d^2q}{(2\pi)^2} \ln[1 - e^{-2l\lambda_c q^2 \kappa(q)} G_1 G_N], \tag{10}$$

where $\kappa(q)=\sqrt{1+1/a\lambda_c q^2 (H/H_c)^2}$ and

$$G_i = \frac{2(\kappa(q) - \gamma_i/\gamma_c) - d\lambda_c q^2 - (d/a)(H/H_c)^2}{2(\kappa(q) + \gamma_i/\gamma_c) + d\lambda_c q^2 + (d/a)(H/H_c)^2}, \tag{11}$$

In the absence of an applied external field, the fluctuation-induced interaction energy between the film surfaces is attractive for likely boundary conditions [2,3], decaying as $1/l$. Strong anchoring configuration on both film surfaces is the most commonly obtained in experimental set ups where the smectic film surfaces are in contact with the surrounding gas, or confined by isotropic liquid or solid phases. The action of an external field in this case will further reduce smectic fluctuations, but the fluctuation profile remains symmetric and the attractive nature of the fluctuation-induced interaction remains, although it decays faster as $1/l^2$ due to the field-ordering effect [31]. This attractive interaction favors the incomplete wetting of the smectic film.

An experimental set up for generating mixed boundary conditions would result in a repulsive long-range interaction between the film surfaces. This configuration may be obtained in a smectic film bordered on one side by a nematic liquid crystal once the surface tension at a nematic-smectic interface is small [2]. In this case, the fluctuation profile can be quite asymmetric in the absence of an external field and the fluctuation-induced interaction becomes repulsive. Such a condition would favor the complete wetting of the smectic film with its thickness growing continuously as the bulk transition temperature is approached. The presence of an external field under this condition strongly affects the fluctuation-induced interaction once it acts by reducing the fluctuation profile asymmetry, thus restoring its attractive character. In

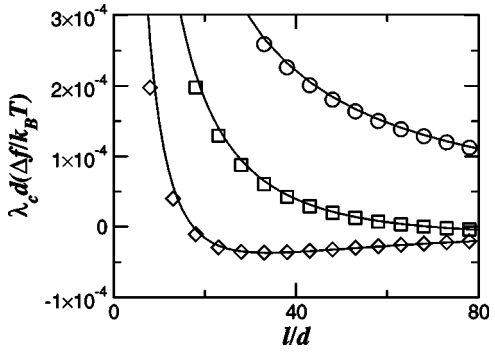

FIG. 1. The fluctuation-induced interaction energy vs film thickness for films under mixed boundary conditions. The external fields are: $H=0$ (circles), $H=0.05H_c$ (square), and $H=0.1H_c$ (diamonds). In all cases, surface tensions are $\gamma_1=0$ and $\gamma_N=3\gamma_c$. We used as typical smectic parameters $K=10^{-6}$ dyn/cm, $B=2.5\times10^7$ dyn/cm^2, $a=4$ Å, and $d=30$ Å. Solid lines were obtained from the continuous model. Quantities are in dimensionless units.

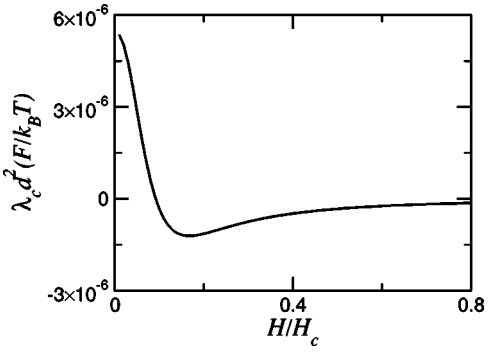

FIG. 3. Normalized Casimir-like force vs normalized external field for a 40-layer film. The surface tensions are the same as those of Fig. 1. Notice that the nature of fluctuation-induced force changes from repulsive to attractive with growth of the external field.

what follows, we will restrict our analysis to this mixed boundary conditions case in order to fully characterize the crossover from a repulsive to an attractive interaction.

In Fig. 1 we plot the fluctuation-induced interaction energy between the film surfaces as a function of film thickness. The reported data were obtained from both discrete and continuous formulations. These give rather coincident results, except by small corrections in the limit of very thin films. The surface tension at one of the surfaces was chosen to be null, representing the weak anchoring condition. The opposite surface was considered strongly anchoring with $\gamma_N=3\gamma_c$. At zero field the interaction energy is repulsive irrespective to the film thickness. However, under the action of a finite field the interaction energy develops a minimum. For thin films the interaction is still repulsive but becomes attractive as the film thickness increases. The thickness ξ_H separating both regimes decreases as the applied field increases. Also the depth of the potential well Δf_{min}, which acts as an effective binding energy, becomes more pronounced for strong fields. In Fig. 2 we analyze the field dependence of these two parameters characterizing the long-range potential. Their absolute values depend on the surface tension at the anchored film surface. However, they exhibit well-defined scaling laws with $\xi_H \propto 1/H^2$ and $\Delta f_{min} \propto H^2$. These data indicate that the potential shall become purely attractive for $H \gtrsim H_c$. The field dependence of the crossover thickness can be used to drive the repulsive fluctuation interaction of a film with a fixed thickness to an attractive one. This feature is shown in Fig. 3, where we plot the Casimir-like force per unit area $F=-d\Delta f/dl$ between the surfaces of a film with 40 layers as a function of the external field. Notice that after crossing to attractive, the force reaches a maximum magnitude before starting to exhibit the asymptotic decay.

The well-defined scaling behavior of the relevant characteristics of the fluctuation-induced interaction suggests that it follows a law of corresponding states after introducing appropriated thickness and energy scales. In Fig. 4 we show the normalized fluctuation-induced energy as function of a scaled film thickness for distinct values of the external field. The collapse of data from different field values indicates that this Casimir-like interaction is a generalized homogeneous function of the film thickness and external field, which can be put in the scaling form

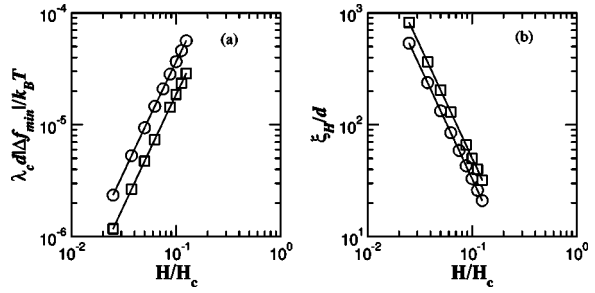

FIG. 2. (a) The effective binding energy and (b) characteristic thickness vs external field. The surface tensions are: $\gamma_1=0$ and $\gamma_N=3\gamma_c$ (circles); $\gamma_1=0$ and $\gamma_N=4\gamma_c$ (squares). Both effective binding energy and characteristic thickness depend on the anchoring at the surfaces. They scale as $\xi_H \propto 1/H^2$ and $\Delta f_{min} \propto H^2$. All quantities are in dimensionless units.

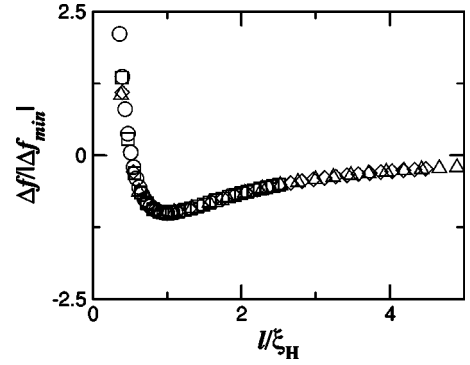

FIG. 4. The normalized fluctuation-induced energy vs normalized film thickness for several values of external fields. The external field are: $H=0.050H_c$ (circles), $H=0.075H_c$ (squares), $H=0.1H_c$ (diamonds), and $H=0.125H_c$ (triangles). Notice that the fluctuation-induced energy has a universal behavior when film thickness is measured in units of characteristic thickness.

$$\Delta f(l,H) = H^2 g(lH^2), \tag{12}$$

where $g(x) \propto 1/x$ for $x \to 0$ and $g(x) \propto (-1/x^2)$ for $x \to \infty$, which are the known asymptotic forms of the fluctuation-induced interaction.

In conclusion, we have shown that the fluctuation-induced surface-surface interaction of asymmetrically anchored smectic liquid-crystal films can be driven from a repulsive character to an attractive one under the action of an external field. This crossover is due to the predominant ordering effect of the external field which acts by reducing the fluctuation profile asymmetry. The resulting long-range potential was shown to follow a law of corresponding states where data from distinct field values fall onto a universal curve. The potential depth, which represents the maximum binding energy of the film associated with the fluctuation-induced interaction, grows quadratically with the applied field. On the other hand, the corresponding film thickness of maximum binding decreases as $1/H^2$. Our results indicate that the wetting of a smectic film bordered on one side by a nematic phase may be driven from complete to incomplete wetting by increasing the external field, with the thickness of the incomplete wetted smectic phase being field controlled. The reversed effect, i.e., the field-induced transit from partial to complete wetting, was previously shown to occur for nematic films [33]. The presently predicted effect can be observed by using either an external magnetic or electric field. According to the diamagnetic anisotropies and elastic constants of typical liquid crystals, the magnetic field required to observe the crossover would be above the present experimental limits [29]. On the other hand, the required electric field in a strongly polar liquid crystal would be of the order of 10^5 V/cm, which is well within experimentally achievable values [32]. However, the external field may influence the anchoring and induce the emergence of additional surface phase transitions. These effects can compete with the fluctuation-induced Casimir force. They should be considered in any experimental set up aiming to probe the predicted transit from complete to partial wetting of a smectic film induced by a strong external field.

This work was partially supported by the Brazilian research agencies CNPq and CAPES, and by the Alagoas State agency FAPEAL.

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