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Casimir force in liquid crystals close to the nematic–isotropic phase transition

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Abstract

We show that in nematic liquid crystals, the Casimir effect induced by thermal fluctuations of the orientational order is characterized by a short-range force due to fluctuations of the degree of order and biaxial excitations on top of the long-range interaction caused by director modes, the short-range corrections being important in the vicinity of the phase transition. In the isotropic phase the attraction is entirely short-range. In the case of finite surface coupling, both short- and long-range fluctuation-induced forces are weaker than in the strong anchoring limit. © 1998 Elsevier Science B.V. All rights reserved.

In 1948 Casimir showed that the fluctuations of an electromagnetic field within a conducting vessel give rise to an attraction between its walls [1]. An analogous effect occurs in various systems, the fluctuations being either quantum or thermal [2,3]. In liquid crystals, which consist of orientationally ordered rod- or disklike molecules, the force induced by thermal fluctuations of the average molecular orientation (director fluctuations) is long-range [4–7].

However, the liquid-crystalline ordering cannot be described completely just by the director field. Even in the simplest mesophase – nematic – the order parameter is a traceless second rank tensor, rather than a headless unit vector and, therefore, characterized by five fluctuating degrees of freedom instead of two director modes [8]. Deep in the nematic phase fluctuations of the other three degrees of freedom (i.e. the degrees of order and biaxiality and the orientation of the secondary director) are negligible and the dynamical properties of the material are almost completely controlled by the Goldstone director modes. However, in the vicinity of the nematic-isotropic phase transition, the three non-director modes become more pronounced (see, e.g., Ref. [9]) – especially in the presence of substrates that promote nucleation of the nematic/isotropic phase above/below the transition temperature [10] – and their contribution to the total fluctuation-induced interaction is no longer insignificant. To generalize the existing theory based on Frank elasticity and the director description of the ordering [4,5] and to assess the relevance of the non-director modes' interaction for the structural forces in liquid crystals [11,12], in this Letter, the behavior of the Casimir force in the vicinity of the nematic-isotropic phase transition is studied using the tensorial Landau-de Gennes formalism.

Within this framework [8], close to the phase transition the difference between the free energy densities of the nematic and isotropic phase is ex-

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panded in terms of scalar invariants of the order parameter $Q=Q(\boldsymbol{r})$. In a compact form, which is based on a Q scaled form with the degree of order in the bulk nematic at the phase transition, its one-elastic-constant approximation reads

$$f=\frac{L}{2}\left\{\xi_0^{-2}\left[\theta\ \mathrm{tr}\,Q^2-2\sqrt{6}\ \mathrm{tr}\,Q^3+\left(\mathrm{tr}\,Q^2\right)^2\right]+\nabla Q\vdots\nabla Q\right\}, \quad (1)$$

where L is the elastic constant, $\xi_0=\sqrt{27LC/B^2}$ is the bare correlation length and $\theta=(27AC/B^2)(T-T^*)$ is the reduced temperature; A,T^*,B and C are the usual parameters of the expansion [10]. The interaction between the nematic and the wall is often modeled by

$$f_S=\frac{L}{2\lambda}\,\mathrm{tr}\left(Q-Q_S\right)^2, \quad (2)$$

where λ is the extrapolation length [8] and Q_S is the preferred value of the order parameter at the substrate. Both f and f_S are measured in units of $2B^2/27C^2$.

The order parameter can be divided into a mean-field and a fluctuating part, $Q(\boldsymbol{r})=A(\boldsymbol{r})+B(\boldsymbol{r})$, and can be represented in an appropriate five-fold tensorial base. In uniaxial nematics, a natural choice of the base tensors is $T_0=(3\boldsymbol{n}\otimes\boldsymbol{n}-I)/\sqrt{6}$, $T_1=(\boldsymbol{e}_1\otimes\boldsymbol{e}_1-\boldsymbol{e}_2\otimes\boldsymbol{e}_2)/\sqrt{2}$, $T_{-1}=(\boldsymbol{e}_1\otimes\boldsymbol{e}_2+\boldsymbol{e}_2\otimes\boldsymbol{e}_1)/\sqrt{2}$, $T_2=(\boldsymbol{e}_1\otimes\boldsymbol{n}+\boldsymbol{n}\otimes\boldsymbol{e}_1)/\sqrt{2}$ and $T_{-2}=(\boldsymbol{e}_2\otimes\boldsymbol{n}+\boldsymbol{n}\otimes\boldsymbol{e}_2)/\sqrt{2}$, where $\boldsymbol{n}$ (the director), $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ constitute an orthonormal triad and I is the unit tensor [13]. The component of Q along T_0 is equal to the sum of the mean-field and fluctuating part of the degree of order, whereas its projections onto $T_{\pm1}$ and $T_{\pm2}$ determine the fluctuations of the degree of biaxiality, the orientation of the biaxial director and the orientation of the director (see, e.g., Ref. [9]).

Within the mean-field approximation, the equilibrium configuration in bulk samples corresponds to the global minimum of the free energy density. The uniaxial nematic phase described by $A(\theta)=\frac{3}{4}\left(1+\sqrt{1-8\theta/9}\right)T_0$ is stable up to $\theta_{\mathrm{NI}}=1$ (nematic-isotropic phase transition temperature) and metastable between θ_{NI} and $\theta^{**}=9/8$ (superheating limit), whereas the isotropic phase with $A=0$ is stable for $\theta>\theta_{\mathrm{NI}}$ and metastable between $\theta^*=0$ (supercooling limit) and θ_{NI}. In a confined system, the mean-field equilibrium is determined by the total free energy $\int f\,\mathrm{d}V+\int f_S\,\mathrm{d}S$, which generally leads to inhomogeneous order parameter profiles and makes the analysis of the Casimir effect more involved. To keep the discussion as transparent as possible for the moment, Q_S is assumed to be equal to A (so that the equilibrium structure is bulklike) and λ is set to 0, implying that fluctuations must vanish at the walls of the cavity.

The fluctuating part of the ordering is governed by its Hamiltonian, given by a Gaussian expansion of the free energy around the ground state [13]. Since both in the uniaxial, homogeneous nematic and in the isotropic phase, the five types of fluctuations are uncoupled, the tensorial formalism reduces to an analysis of five independent scalar fields (see, e.g., Ref. [9]). In addition, the two biaxial modes in the nematic phase are degenerate and so are the two director modes; in the isotropic phase all five types of excitations are degenerate. In both phases the Hamiltonian of any of the five fluctuating fields $b\equiv b(\boldsymbol{r})$

$$H[b]=\int h(b)\,\mathrm{d}V=\int\frac{L}{2}\left[\xi^{-2}b^2+(\nabla b)^2\right]\mathrm{d}V \quad (3)$$

consists of a ''mass'' term and an one-constant approximation of the elastic Hamiltonian. The nematic director modes are characterized by the infinite correlation length ξ [4–7], whereas correlation lengths of fluctuations of the degree of order and biaxial excitations in the nematic phase are given by $(\xi_{No}/\xi_0)^{-2}=\frac{9}{4}\sqrt{1-8\theta/9}\left(1+\sqrt{1-8\theta/9}\right)$ (so that ξ_{No} diverges at the superheating limit) and $(\xi_{Nb}/\xi_0)^{-2}=\frac{27}{4}\left(1+\sqrt{1-8\theta/9}\right)$, respectively. – In the isotropic phase, the correlation length of the collective excitations is determined by $(\xi_I/\xi_0)^{-2}=\theta$, which means that ξ_I diverges at the supercooling limit.

To evaluate the free energy of the fluctuating field, it is instructive to introduce its Fourier components. Since the excitations are assumed to be suppressed by two infinite plates, normal to $\boldsymbol{e}_z$ and located at $z=0$ and $z=d$, the normal modes are of the form $b_{\boldsymbol{q}}(\boldsymbol{r}) = \exp\big(i(q_x x + q_y y)\big)\sin(n\pi z/d)$ with $\boldsymbol{q} \equiv (\boldsymbol{q}_\perp = q_x \boldsymbol{e}_x + q_y \boldsymbol{e}_y, n)$ and $n = 0, \pm 1, \pm 2, \ldots$. The partition function can be calculated by expanding $b(\boldsymbol{r})$ in terms of $b_{\boldsymbol{q}}$ to yield

$$F = \frac{kT}{2}\sum_{\boldsymbol{q}} \ln \frac{H_{\boldsymbol{q}}}{kT}, \tag{4}$$

where $H_{\boldsymbol{q}} = \frac{LSd}{2}\left[\xi^{-2} + \boldsymbol{q}_\perp^2 + (n\pi/d)^2\right]$ is the energy of the normal mode $b_{\boldsymbol{q}}$ and S is the area of the plates. The sum over $\boldsymbol{q}_\perp$ can be replaced by the integral.

The finite fluctuation-induced interaction between the plates can be extracted from the infinite total free energy [Eq. (4)] by dimensional regularization, by cutoff methods, etc. [2] – and also by recognizing that the diverging part results from unconstrained fluctuations in a region of volume V and cross-section S [4,5]. Therefore, the Casimir force can be defined by

$$\mathscr{F} = -\frac{\partial}{\partial d}(F - F_{\text{bulk}}), \tag{5}$$

where F_{bulk} is characterized by a continuous spectrum of n. After some rearrangements one obtains

$$\mathscr{F} = -\frac{kTS}{2\pi d^3}\int_{d/\xi}^{\infty}\left(\sum_{n=0}^{\infty}{}' - \int_0^\infty \mathrm{d}n\right) \times \frac{u^2}{u^2 + (n\pi)^2}\, u\,\mathrm{d}u, \tag{6}$$

where the prime indicates that the $n = 0$ term in the sum should be multiplied by $1/2$ and $u^2 = d^2(\xi^{-2} + \boldsymbol{q}_\perp^2)$. Using the Poisson summation formula, this sum can be converted to $\sum_{m=0}^{\infty}{}'$ $u\exp(-2mu)$ and the $m = 0$ term of the new sum cancels exactly with the bulk free energy. The final result – the Casimir force induced by a fluctuating scalar field with a Hamiltonian described by Eq. (3) –

$$\mathscr{F} = -\frac{kTS}{4\pi d^3}\sum_{m=1}^{\infty}\left[\frac{1}{2} + \frac{md}{\xi} + \left(\frac{md}{\xi}\right)^2\right] \times \frac{\exp(-2md/\xi)}{m^3} \tag{7}$$

is consistent with the analysis of the phenomenon in critical magnetic and fluid films [14].

$\mathscr{F}$, which is attractive, strongly depends on the ratio d/ξ. As mentioned above, the nematic phase is characterized by two director modes with infinite correlation length and three other types of excitations whose correlation lengths are finite; in the isotropic phase all five modes are massive. Therefore, one should consider the limiting forms of Eq. (7) for $d \ll \xi$ and $d \gg \xi$, which cover the director modes' attraction and the asymptotic behavior of the Casimir force induced by massive excitations, respectively. In the first case, Eq. (7) reproduces the one-elastic-constant approximation of the Casimir interaction obtained within the Frank elastic theory [4,5]

$$-\frac{kTS}{8\pi d^3}\zeta(3). \tag{8}$$

This long-range force mediated by director modes is generally the most important manifestation of the Casimir effect in nematic liquid crystals. On the other hand, the force induced by nondirector modes in the nematic phase and all types of fluctuations in the isotropic phase

$$-\frac{kTS}{4\pi\xi^2 d}\exp(-2d/\xi) \tag{9}$$

are short-range (unless, of course, d is smaller than ξ).

In the nematic phase, the Casimir attraction is obviously dominated by the long-range force caused by the director modes so that the contribution of the order parameter and biaxial fluctuations may be regarded as a correction, unless d is very small or the temperature is close to the superheating limit. At room temperature and for d equal to, say, 20 nm, the magnitude of the director modes' attraction is about 50 pN/μm^2. Deep in the nematic phase, the correction is negligible and in typical nematics (such as 5CB, where the phase transition occurs close to room temperature and about 1 K above the supercooling limit) it augments the above estimate only by 3.5% (at $d = 20$ nm) even at the phase transition. However, if the sample is superheated above the transition temperature, the correction increases further to become long-range at the superheating limit, where it amounts to 50% of the director modes' force.

The Casimir attraction mediated by fluctuations in the isotropic phase is entirely short-range and therefore much weaker. For example, at the nematic-isotropic phase transition, ξ_I in 5CB is about 8 nm and for $d = 20$ nm, the force is approximately equal to 9 pN/μm^2. However, as the isotropic phase is cooled below the bulk transition temperature, the correlation length increases and eventually diverges at the supercooling limit, where the Casimir force reaches some 125 pN/μm^2 (at $d = 20$ nm).

As suggested, the crossover from a short- to long-range force could be detected by approaching (and surpassing) the phase transition temperature by (super)heating or (super)cooling, where the energy levels of the massive modes decrease considerably. Such an experiment can probably be carried out using a modified AFM [15] or a surface force apparatus [12]. An opposite effect can be induced by an external field [16,17]: in materials with a positive anisotropy of electric/magnetic susceptibility, the aligning action of the field applied along the equilibrium director gives rise to a mass term in the Hamiltonian of the director modes, the role of the correlation length being played by the electric/magnetic coherence length.

The above analysis, based on strong anchoring, outlines the main features of the Casimir force in the nematic and in the isotropic phase and gives an idea of its magnitude. The effect of a finite anchoring strength should be studied within a more elaborate model, which requires a comprehensive regularization procedure. The problem can be solved by the Green function method often used in the theory of Casimir and van der Waals forces [3] and applicable if the modulation of the correlation length caused by subsurface variation of the degree of order is neglected. Within this approximation, the interaction free energy between like substrates characterized by finite λ and uniaxial homeotropic Q_S is given by

$$F' = \frac{kTS}{2}\int\frac{d^2q_\perp}{(2\pi)^2}\ln\left(1-\left(\frac{\sqrt{\xi^{-2}+q_\perp^2}-\lambda^{-1}}{\sqrt{\xi^{-2}+q_\perp^2}+\lambda^{-1}}\right)^2 \times\exp\left(-2\sqrt{\xi^{-2}+q_\perp^2}\,d\right)\right) \quad (10)$$

with the typical form analogous to the theory of a screened van der Waals interaction between two semi-infinite dielectric media separated by a slab of electrolyte [18]: actually the correspondence is exact if ξ is interpreted as the Debye length of the electrolyte and λ as the ratio of the dielectric constants of the electrolyte and the two bounding dielectrics. For $\lambda = 0$ (infinitely strong anchoring), the force resulting from the above free energy reduces to Eq. (7). In addition, $\lambda \to \infty$ (no anchoring) leads to the same result, which is not surprising: the two limiting cases differ in the type of boundary conditions (Dirichlet/Neumann) and, therefore, in the symmetry of the eigenmodes (sines/cosines), but their spectra are identical.

The effect of anchoring can be quantified by a reduction factor defined as the ratio of the Casimir forces corresponding to finite λ and its strong anchoring counterpart, i.e. $R(d/\xi,\lambda/\xi) \equiv \mathscr{F}(d,\xi,\lambda)/\mathscr{F}(d,\xi,\lambda=0)$. Its dependence on d/ξ for finite λ/ξ (as noted above, $R(d/\xi,0) = R(d/\xi,\infty) = 1$) is illustrated in Fig. 1. If $0 < \lambda/\xi < 1$, R descends from 1 to a minimum and then saturates, whereas for $\lambda/\xi > 1$, the reduction factor decreases monotonically to the saturated value. The saturation indicates that for $d/\xi \gg 1$, the functional form of the leading term of the interaction remains unaltered, i.e. $\exp(-2d/\xi)/d$: it can be shown that for small and large λ/ξ, the reduction factor is given by $1 - 4\lambda/\xi$ and $1 - 4\xi/\lambda$, respectively. These two limiting cases comply with the obvious fact that the saturated value of R does not change if λ/ξ is replaced by its

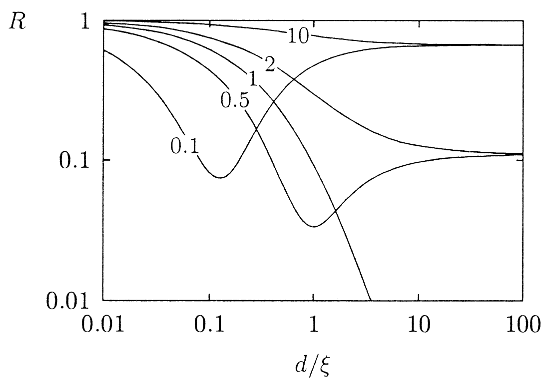

Fig. 1. Reduction factor vs. d/ξ for $\lambda/\xi = 0.1, 0.5, 1, 2$ and 10. If $\lambda/\xi < 1$, R reaches a minimum before saturation; for $\lambda/\xi = 1$, $R(d/\xi \gg 1) \approx \xi^2/2d^2$ (which can be demonstrated analytically) and for $\lambda/\xi > 1$ it decreases monotonically towards the limiting value. The saturated value of the reduction factor for $\lambda/\xi = Z$ matches with the one corresponding to $\lambda/\xi = Z^{-1}$.

inverse. On the other hand, if $d/\xi \ll 1$ and $\lambda/\xi \ll d/\xi$, R can be approximated by the asymptotic expansion $1 - 6\lambda/d$, which means that for large yet finite anchoring strength the correction to the long-range d^{-3}-interaction is proportional to d^{-4}.

In order to find out whether the Casimir forces in nematic liquid crystals are important or not, they should be compared to the mean-field interaction. In hybrid cells the mean-field force is caused mainly by the deformed equilibrium director field, described by the tilt angle profile $\phi(z)$, and can be estimated within the one elastic constant approximation [8] with the surface free energy of the type $f_S = \frac{K}{2\lambda}[\phi(z_i) - \phi_i]^2$, where ϕ_1 (ϕ_2) is the preferred value of the tilt angle at $z_1 = 0$ ($z_2 = d$) and K is the Frank elastic constant. In this case, the mean-field interaction is repulsive and equal to $\frac{1}{2}KS(\phi_2 - \phi_1)^2(2\lambda + d)^{-2}$, which remains finite for $d \ll \lambda$ and decays as d^{-2} for $d \gg \lambda$. The distorted equilibrium director field also modifies the spectrum of one of the two director modes and the analysis of the corresponding Casimir interaction is beyond the scope of this study. The other mode remains unchanged, so that at least a part of the director modes' attraction is proportional to d^{-3} and dominates at small ds, whereas the mean-field repulsion is more important at large ds [1]. Moreover, if the anchoring strengths at the two walls are not equal, the equilibrium director field in small cavities is dictated by the strongest anchoring and is spatially uniform, which implies that in this case the fluctuation-induced force is the only interaction mediated by the liquid crystal.

There is another source of the structural mean-field interaction between plates immersed into either the nematic or isotropic phase: if the degree of order at the substrates is different from the bulk one [19], the inhomogeneity of the mean-field ordering results in an attractive force asymptotically given by $-(LS\Delta^2/4\xi^2)\exp(-d/\xi)$, where Δ is the discrepancy between the surface-induced and the bulk degree of order and ξ is equal to ξ_{No} (ξ_I) in the nematic (isotropic) phase. At this point it must be stressed that the present analysis of the Casimir effect in liquid crystals is consistent only with subsurface variations of the degree of order small enough not to modify the spectrum of the fluctuations qualitatively [10] and we limit the discussion to small Δs. In the nematic phase, the short-range mean-field force is entirely masked by the long-range fluctuation-mediated interaction regardless of the sign of Δ. In the isotropic phase, however, a disordering substrate actually promotes the bulk order and in this geometry the Casimir force is in fact the only interaction induced by the medium itself. On the other hand, an order-inducing substrate gives rise to a short-range mean-field attraction with a range twice as large as the range of the Casimir force. Therefore the mean-field interaction dominates at large distances, whereas at small ds the fluctuation-induced force takes over. The crossover, of course, depends on Δ and on temperature; for example, for $\Delta = 0.01$ and $\theta \approx \theta_{NI}^+$ it occurs at $d \approx 30$ nm in a typical material. This indicates that at separations where the short-range structural forces are strong enough to be measurable, the Casimir interaction does represent a significant part of the total structural force mediated by the isotropic liquid-crystalline phase even between order-inducing substrates.

The Casimir force, therefore, dominates in nematic liquid crystals in cavities without surface-induced frustration and in thin hybrid cells and may well affect the stability of some microconfined liquid-crystalline systems. In this context, the generalization of the basic result [4,5] is important because it provides a complete description of the fluctuation-induced interaction in the nematic phase and its pretransitional behavior. The formalism also covers the field quenching of director fluctuations in the nematic phase and the amplitudon and soft modes near the smectic C-smectic A transition (which is usually continuous, so that the corresponding pretransitional increase of the Casimir force must be quite prominent) as well as the Casimir attraction in the isotropic phase. However, there remains a broad class of liquid-crystalline systems in which the fluctuation-induced forces have not been studied so far: the wetting geometries. The Casimir force in these

[1] Should the crossover from repulsion to attraction be detectable, the critical thickness d_c must be neither too small (so that the effects of the finite molecular size are unimportant) nor too large (otherwise the force would be too weak), say between 10 and 100 nm. These conditions can be met: for $\lambda \sim 100$ nm (i.e. anchoring strength ~ 0.1 mJ/m^2) and $\phi_2 - \phi_1 \sim 30°$, d_c is about 25 nm.

biphase systems stabilized by substrates with large (dis)ordering power and characterized by wetting-specific slow fluctuations [10] will be analyzed in a forthcoming paper.

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