Fluctuation-Induced Long-Range Forces in Liquid Crystals

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We show that director fluctuations in nematics induce long-range interactions between walls, analogous to van der Waals forces, which are attractive with symmetric boundary conditions, but may become repulsive with mixed ones. They affect the swelling of lamellar phases in a nematic solvent. The same phenomenon takes place in other mesophases, in particular in smectics, where it gives rise to forces with longer range than van der Waals.

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Long-range molecular forces (van der Waals forces) arise from the interplay of electromagnetic-field fluctuations with boundary conditions on ponderable bodies.[1] These fluctuations may be of quantum as well as thermal origin. In the particular case of the interaction between grounded conducting walls, these forces are known as the Casimir effect.[2] A simple-minded interpretation of the phenomenon lies in the remark that voltage fluctuations induce an attraction between the conductors because of image interactions.

We show here that an analogous effects arises from orientational fluctuations in anisotropic mesophases. Consider, e.g., the case of a nematic slab of thickness h, contained between two rigid, flat, parallel walls imposing normal boundary conditions on the director ("strong homeotropic anchoring"). This boundary condition suppresses a number of fluctuating modes of the director in the bulk, yielding a contribution to the nematic-wall interface tension τ, independent of h, and an effective wall interaction. This is represented by an excess free-energy density $\delta\mathcal{F}_n$ given by

$$\delta\mathcal{F}_n = -\frac{kT}{h^2}\frac{\zeta(3)}{16\pi}\left(\frac{\kappa_3}{\kappa_1}+\frac{\kappa_3}{\kappa_2}\right). \tag{1}$$

Here κ_1, κ_2, and κ_3 are the Frank constants[3] and ζ is Riemann's zeta function. The interaction exhibited in (1) is attractive and similar in form to the van der Waals attraction between conducting walls.[4] It is remarkable that the same result is obtained with free boundary conditions ("weak anchoring"). On the other hand, a repulsion is obtained if one has free boundary conditions on one wall and normal ones on the other. One obtains in this case

$$\delta\mathcal{F}_n^* = \frac{kT}{h^2}\frac{3\zeta(3)}{64\pi}\left(\frac{\kappa_3}{\kappa_1}+\frac{\kappa_3}{\kappa_2}\right). \tag{2}$$

Let us remark that this interaction diverges as one approaches the nematic–smectic-A transition, since κ_2 and κ_3 diverge while κ_1 remains finite. This suggests that the effect will have different behavior in smectics. We obtain indeed, for the case of symmetric boundary conditions,

$$\delta\mathcal{F}_s = -\frac{kT}{h}\frac{\zeta(2)}{16\pi}\left(\frac{B}{\kappa_1}\right)^{1/2}, \tag{3}$$

where B is the bulk modulus. The penetration length $\lambda=(\kappa_1/B)^{1/2}$ is usually of the order of the interlayer spacing. For mixed boundary conditions one obtains $-\frac{1}{2}$ times the above result. This interaction decreases much more slowly than the van der Waals one, and should become dominant when the slab thickness is larger than a few times λ.

This effect has a number of interesting physical consequences. Let us consider, e.g., the possibility of swelling a lamellar phase with a nematic solvent. It was shown in Ref. 5 that the bending energy of an undulation mode of wave number $\vec{q}$ for a membrane immersed in a nematic fluid is proportional to q^3. Simple arguments show[6] that the fluctuation-induced steric repulsion decreases as d^{-4}, where d is the lamellar separation. One would thus *a priori* expect the attractive lamellar interactions, Eq. (1), to dominate. This is not quite so obvious, since membrane fluctuations distort the nematic, leading to an energy increment scaling like kT/d^2, and thus comparable to (1). A more detailed analysis shows that the resulting interaction is in fact attractive at large lamellar separations, preventing the formation of highly swollen lamellar phases with a nematic solvent, unless they are stabilized by other repulsive interactions, such as electrostatic ones.

We report here the main steps in the derivation of Eq. (1). Details will be published elsewhere,[7] while the generalization to smectics and columnar phases is fairly straightforward. We consider for definiteness a nematic slab of thickness h, with finite anchoring energies. One of the walls lies on the $z=0$ plane, and the other on the plane $z=h$. Its orientational free energy[3] is the sum of

the Frank-Oseen elastic energy $\mathcal{H}_E$,

$$\mathcal{H}_E = \int dx\,dy \int_0^h dz\, \tfrac{1}{2}\,[\kappa_1(\mathrm{div}\mathbf{n})^2 + \kappa_2(\mathbf{n}\cdot\mathrm{rot}\mathbf{n})^2 + \kappa_3(\mathbf{n}\times\mathrm{rot}\mathbf{n})^2]\,, \tag{4}$$

and the anchoring energy $\mathcal{H}_S$,

$$\mathcal{H}_S = \int dx\,dy(-\tfrac{1}{2})[A^+ n_z^2(x,y,0) + A^- n_z^2(x,y,h)]\,. \tag{5}$$

Here $\mathbf{n}$ is the nematic director, and A^+ and A^- are the anchoring stiffness on the $z=0$ and $z=h$ planes, respectively. The ratios $(\kappa_i\kappa_3)^{1/2}/A^\pm = l_i^\pm$, $i=1,2,3$, define extrapolation lengths.[8] *Strong anchoring* corresponds to the case in which these lengths are of the order of molecular size. *Weak-anchoring* conditions, where these lengths are of mesoscopic size, can also be experimentally realized.

We consider, in the harmonic approximation, the effect of small fluctuations of $\mathbf{n}$ around its ground state, where $\mathbf{n}$ is constant and parallel to the z axis.[9] We define

$$\mathbf{n} \simeq (n_x, n_y, n_z) = (\vec{n}, 1)\,. \tag{6}$$

The two-dimensional field $\vec{n}$ can be split into its longitudinal component $\vec{n}_l$ ($\nabla\times\vec{n}_l = 0$), and its transverse one, $\vec{n}_t$ ($\nabla\cdot\vec{n}_t = 0$), where ∇ is the two-dimensional nabla operator. The orientational free energy in the harmonic approximation then splits into two independent contributions, one involving only $\vec{n}_l$, and the other involving only $\vec{n}_t$. By Fourier transformation along the (x,y) plane, the partition function factorizes into independent contributions, one for each wave vector $\vec{q} = (q_x, q_y)$. These contributions may be evaluated by a number of methods,[7] some of them developed for the Casimir effect, and in particular by exploiting the analogy with the one-dimensional quantum oscillator. One therefore obtains the following expression for the free-energy density $\mathcal{F}$ per unit area:

$$\mathcal{F} = \mathcal{F}_1 + \mathcal{F}_2\,, \tag{7}$$

where $\mathcal{F}_1$ involves only the longitudinal modes, and $\mathcal{F}_2$ the transverse ones. One has

$$\frac{\mathcal{F}_i}{kT} = \frac{h}{2}\int \frac{d^2q}{(2\pi)^2}\omega_i - \int \frac{d^2q}{(2\pi)^2}\frac{1}{2}\ln\left[\left(\frac{\beta_i}{\pi}\right)\left(\frac{2\pi}{\tilde{A}^+ + \beta_i}\right)\left(\frac{2\pi}{\tilde{A}^- + \beta_i}\right)\right] + \frac{1}{2}\int \frac{d^2q}{(2\pi)^2}\ln\left[1 - \left(\frac{\beta_i - \tilde{A}^+}{\beta_i + \tilde{A}^+}\right)\left(\frac{\beta_i - \tilde{A}^-}{\beta_i + \tilde{A}^-}\right)e^{-2\omega_i h}\right],\quad i=1,2\,, \tag{8}$$

where $\tilde{A}^\pm = A^\pm/kT$, and

$$\omega_i = \left(\frac{\kappa_i}{\kappa_3}\right)^{1/2} q,\quad \beta_i = \frac{1}{kT}(\kappa_i\kappa_3)^{1/2} q,\quad i=1,2\,. \tag{9}$$

The first term is extensive and represents a contribution to the nematic free energy. The second term, independent of h, represents a contribution to the nematic-wall interfacial tension. Both these terms are formally divergent and should be regularized by the introduction of a suitable cutoff[7] in the integration over $\vec{q}$. The third term represents the fluctuation-induced interaction. Its expression simplifies in both the strong- ($l_3^\pm \ll h$) and weak- ($l_3^\pm \gg h$) anchoring limits, leading directly to Eq. (1). The result is the same in both cases, since the reduction in the number of degrees of freedom is the same whether the boundary conditions are imposed on the variable itself or on its derivative. The attractive character of the force may be inferred by considering image interactions, since in both cases the nearest images are parallel to each other. With mixed boundary conditions one has on the contrary, e.g., $l_3^+ \gg h$, $l_3^- \ll h$, and one obtains Eq. (2). The repulsive character of the force may again be inferred from image interactions.

Some care is needed to discuss the case of a nematic lamellar phase. The anchoring energy $\mathcal{H}_S$ now has the expression

$$\mathcal{H}_S = \sum_{\alpha=1}^{N}\int dx\,dz\,\tfrac{1}{2}\{A^+[\vec{n}(x,y,\alpha h+0)+\nabla u_\alpha]^2 + A^-[\vec{n}(x,y,\alpha h-0)+\nabla u_\alpha]^2 + K(\nabla^2 u_\alpha)^2\}\,. \tag{10}$$

Here $\vec{n}$ is the two-dimensional director distortion defined in Eq. (6), u_α is the displacement of the αth lamella from its reference plane $z=\alpha h$, K is the bending rigidity of the lamella, and A^+ (A^-) is the anchoring energy on the positive (negative) z side. One usually has $A^+ = A^-$, but more general situations may be envisaged. The calculation leads to the same expressions as in (8) and (9), except that, while $\mathcal{F}_2$ remains unchanged, one has to replace, in $\mathcal{F}_1$, $A^\pm$ by

$$A_{\mathrm{eff}}^\pm = A^\pm (l^\pm)^2 q^2/[1+(l^\pm)^2 q^2]\,,$$

where the lengths $l^\pm = (K/A^\pm)^{1/2}$ define the crossover between the regime ($q^2 l^2 \gg 1$) in which the lamella appears rigid with finite anchoring energy, and a regime with flexible membranes ($q^2 l^2 \ll 1$). Under usual cir-

cumstances, l is of molecular size (i.e., the second regime prevails) and the condition $h \gg K/\kappa_1$ is satisfied, so that $\beta \gg A_{\text{eff}}^{\pm}$ holds in the range of interest and weak anchoring is recovered. Therefore, in most cases, the longitudinal part of the director fluctuations, described by $\mathcal{F}_1$, gives rise to attractive forces. Conversely, transverse fluctuations described by $\mathcal{F}_2$ can contribute to either repulsion or attraction, exactly as in the case of rigid walls.

Nematic solvents will be able to promote the swelling of lamellar phases provided that

$$l_3^+ \gg h \gg l_3^- \text{ and } \kappa_1 > \tfrac{4}{3}\kappa_2 . \tag{11}$$

Indeed, the free energy per unit volume is then given by

$$\mathcal{F} = \frac{kT}{h^3}\left(-\frac{\kappa_3}{\kappa_1}+\frac{3}{4}\frac{\kappa_3}{\kappa_2}\right)\frac{\zeta(3)}{16\pi}-\frac{\sigma}{h}, \tag{12}$$

where $-\sigma$ is the chemical potential of the lamellae. This expression reaches a minimum for

$$h_m^2 = \frac{kT}{\sigma}\left(\frac{\kappa_3}{\kappa_1}-\frac{3}{4}\frac{\kappa_3}{\kappa_2}\right)\frac{3\zeta(3)}{16\pi} . \tag{13}$$

A swollen lamellar phase can be produced if h_m satisfies the inequalities (11). If σ is too small, h_m becomes larger than l_3^+, and the periodicity levels off at values of the order of l_3^+. Note that the inequalities (11) are not difficult to satisfy, since κ_1 is larger than $\frac{4}{3}\kappa_2$ in most nematics and very different $l_3^{\pm}$ values could be realized with highly polarized Langmuir-Blodgett lamellae.

While the methods sketched above can be applied to smectics with little difficulty, some care must be taken in handling the boundary conditions. The elastic energy $\mathcal{H}_E$ has the conventional expression[8]

$$\mathcal{H}_E = \int dx\,dy \int_0^h dz \frac{1}{2}\left[B\left(\frac{\partial u}{\partial z}\right)^2+\kappa_1(\nabla^2 u)^2\right], \tag{14}$$

where u is the layer displacement, B the compression modulus, and κ_1 the Frank constant. The anchoring energy density $\mathcal{H}_S$ is written most easily in Fourier space:

$$\mathcal{H}_S = \int \frac{d^2q}{(2\pi)^2}\frac{1}{2}[c^+ q^{\Delta}|\tilde{u}(\vec{q},z=0)|^2 + c^- q^{\Delta}|\tilde{u}(\vec{q},z=h)|^2] . \tag{15}$$

For a smectic-fluid interface, $\Delta=2$, and the $c^{\pm}$ are interfacial tensions. For a smectic-solid interface, $\Delta=1$ because of the $1/|\vec{q}|$ penetration of the distortion in a solid, and $c^{\pm}$ are suitable averages of the elastic moduli. By going through the calculations one obtains an expression analogous to (8), where, however, only the longitudinal mode is allowed, and

$$\omega = \left(\frac{\kappa_1}{B}\right)q^2 = \lambda q^2, \quad \beta = \frac{(\kappa_1 B)^{1/2}}{kT}, \quad \tilde{A}^{\pm} = \frac{c^{\pm}}{kT}q^{\Delta-2} . \tag{16}$$

The notion of strong or weak anchoring depends on the nature of the interface. For a solid-smectic one, the typical smectic deformation energy should be compared with that of the neighboring solid, given by $c^{\pm}q$, at the cutoff wave vector $(\lambda h)^{-1/2}$. Strong boundary conditions correspond therefore to $h \gg (B/c)^2\lambda$, which is usually satisfied for h of the order of a single-layer thickness. For fluid-smectic interfaces, one compares the interface tension c with its smectic counterpart[8] $(\kappa_1 B)^{1/2}$. Close enough to the nematic-smectic transition, one always reaches strong-anchoring conditions, but in general any situation could be produced.

Using the example of liquid crystals, we have illustrated the following points: Long-range forces take place in systems whose energy is a quadratic form of the space derivatives of a fluctuating variable. Those arising in a nematic are akin to van der Waals forces: The case of a crystal would be similar. In this latter case they would obviously give rise to negligible effects: They are important, on the contrary, in the stabilization of lamellar phases by nematic solvents. They may be even more interesting in smectics where they are of longer range, decaying like h^{-2} instead of h^{-3}. They could therefore play a role in the spreading of smectic droplets.[10] Columnar phases are intermediate between crystals and smectics: For columns parallel to the walls, simple scaling predicts a $h^{-5/2}$ decay. All these forces are comparable to or larger than van der Waals interactions and should thus be measurable with the current force apparatuses.[11]

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