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Theory of light scattering by thin nematic liquid crystal films

S. Stallinga,* M. M. Wittebrood, D. H. Luijendijk, and Th. Rasing

Research Institute for Materials, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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Light scattering by thin nematic liquid crystal films is considered. The confinement has two important consequences. First, fluctuations with wave vectors not equal to the difference between the wave vectors of the scattered and the incident light ray can contribute to the scattering. The distribution of fluctuation wave vectors relevant to the scattering is peaked around this difference and has a width inversely proportional to the film thickness. Second, only a discrete set of fluctuation wave vectors is allowed due to restrictions imposed by the boundary conditions. Consequently, the relaxation times of the different fluctuation modes depend on the film thickness. It appears that the relaxation time decreases due to the confinement. In the limit of vanishing thicknesses the relaxation time goes linearly to zero with the film thickness. The main conclusions are expected to hold qualitatively for other confined nematic systems, e.g., for nematics confined in porous media. [S1063-651X(96)00305-4]

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I. INTRODUCTION

The physics of liquid crystals in thin films [1–4] and in porous media [5–12] has received a lot of attention in recent years. Light scattering techniques are very important for this research. Nematic liquid crystals scatter light strongly due to thermal fluctuations of the local orientation. The theory of orientational fluctuations and of light scattering by orientational fluctuations in bulk materials is treated in textbooks on liquid crystals [13,14]. The aim of this paper is to modify this theory in order to account for finite size effects. It appears that these modifications are quite important for the description of light scattering by nematic liquid crystals in a confined geometry, e.g., thin nematic liquid crystal films.

The present theory modifies two important elements of the theory of [13,14]. The first element concerns the relation between the scattering wave vectors q and the wave vectors of the incident and scattered light ray k_i and k_f , respectively. In contrast to the case of bulk nematics, orientational fluctuations with a wave vector q differing from $k_f - k_i$ contribute to the scattering process as well. However, orientational fluctuations with a wave vector q close to $k_f - k_i$ do give the dominant contribution to the scattering cross section. The second element concerns the set of allowed wave vectors q . This set is discrete for confined nematics because of restrictions imposed by the boundary conditions, whereas it is continuous for bulk nematics. This means that the orientational fluctuations can be considered as overdamped standing waves for confined nematics, whereas they can be considered as overdamped traveling waves for bulk nematics.

This paper is organized as follows. The next section deals with the scattering condition between the wave vectors q , k_i , and k_f . The orientational fluctuations of a planarly aligned nematic film are analyzed in Sec. III. Section IV deals with the orientational fluctuations of a hybridly aligned film. Finally, the results are discussed in Sec. VI.

II. SCATTERING CONDITION

A detailed treatment of the theory of light scattering due to fluctuations of the dielectric properties of the scatterer can be found in the classical book of Jackson [15]. The application of this theory to scattering by nematics is treated in [13,14]. In this section only the essentials of that theory and its modifications due to the finite size of the nematic are discussed. It should be mentioned that a detailed calculation of the angular dependence of the scattering cross section of thin nematic films can be found in [16].

Figure 1 shows a schematic picture of the scattering geometry. The incoming plane wave has a dielectric displacement field

$$D^n(\mathbf{r}, t) = D_0 i e^{i(\mathbf{k}_i \cdot \mathbf{r} - \omega t)}, \quad (1)$$

with D_0 the amplitude, \mathbf{k}_i the wave vector of the incoming light, i the polarization vector of the incoming wave, and

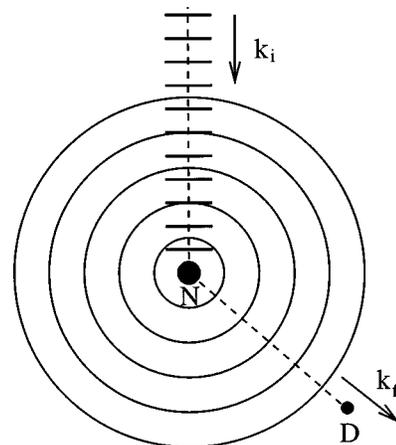


FIG. 1. The parallel lines represent the incoming plane wave, the circles represent the scattered wave. N indicates the nematic scatterer whereas D indicates the detector.

*Present address: Philips Research Laboratories, Professor Holstlaan 4, 5656 AA Eindhoven, The Netherlands.

$\omega = c|\mathbf{k}_f|$ the angular frequency, where c denotes the velocity of light. The scattered wave far away from the scatterer can be expressed as

$$D^{\text{out}}(\mathbf{r}, t) = D^s(\mathbf{k}_f) \frac{e^{i\mathbf{k}_f \cdot \mathbf{r}}}{r} e^{-i\omega t}, \quad (2)$$

with $k = \omega/c$, the outgoing wave vector $\mathbf{k}_f = k\mathbf{r}/r$, and the so-called scattering amplitude $D^s(\mathbf{k}_f)$. The scattering amplitude is related to the differential cross section (the intensity of the scattered light with polarization vector \mathbf{f} , per unit solid angle in the direction along \mathbf{k}_f , relative to the intensity of the incoming light) in the following way:

$$\frac{d\sigma}{d\Omega} = \frac{|\mathbf{f} \cdot D^s(\mathbf{k}_f)|^2}{D_0^2}. \quad (3)$$

The scattering amplitude can be expressed within the Born approximation as

$$D_\alpha^s(\mathbf{k}_f) = \frac{D_0}{4\pi} \sum_{\mathbf{q} \neq 0} \sum_{v, \beta=x, y, z} i_v (q_\beta + k_{i\beta}) [(q_\alpha + k_{i\alpha}) \chi_{\beta v}(\mathbf{q}) - (q_\beta + k_{i\beta}) \chi_{\alpha v}(\mathbf{q})] \int d^3 r \exp[i(\mathbf{q} + \mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}] \quad (4)$$

with $\chi_{\alpha\beta}(\mathbf{q})$ the fluctuating components of the dielectric susceptibility tensor. These quantities can be expressed in terms of the fluctuations of the local orientation of the nematic. The integral over \mathbf{r} depends on the shape and size of the nematic. The shape is approximated by that of a rectangular box with length, width, and height B_x , B_y , and B_z , respectively. Then

$$\int d^3 r e^{i\mathbf{k} \cdot \mathbf{r}} = V \frac{\sin(k_x B_x/2)}{k_x B_x/2} \frac{\sin(k_y B_y/2)}{k_y B_y/2} \frac{\sin(k_z B_z/2)}{k_z B_z/2}, \quad (5)$$

with $V = B_x B_y B_z$ the volume of the liquid crystal and $\mathbf{k} = \mathbf{q} + \mathbf{k}_i - \mathbf{k}_f$. This integral is sharply peaked around the maximum at $\mathbf{k} = 0$. The width of the distribution over component k_α is roughly π/B_α ($\alpha = x, y, z$). It follows that only those fluctuating components of the susceptibility tensor $\chi_{\alpha\beta}(\mathbf{q})$ contribute to the scattering amplitude that have a wave vector \mathbf{q} satisfying

$$|q_\alpha - (k_{f\alpha} - k_{i\alpha})| \leq \pi/B_\alpha, \quad (6)$$

for $\alpha = x, y, z$. Clearly, in the limit of an infinitely large liquid crystal, this condition reduces to

$$q_\alpha = k_{f\alpha} - k_{i\alpha}. \quad (7)$$

Next, a thin film of liquid crystal material is considered. Then the dimensions of the liquid crystal are

$$B_x = B_y = \sqrt{V/d}, \quad (8a)$$

$$B_z = d, \quad (8b)$$

where d is the thickness of the film. For sufficiently large V it follows that condition (6) applies to the z components of

the wave vectors, whereas condition (7) applies to the x and y -components of the wave vectors.

III. ORIENTATIONAL FLUCTUATIONS OF A PLANARLY ALIGNED NEMATIC FILM

In this section a fluctuation theory similar to de Gennes' bulk theory is formulated that takes into account the effect of the boundaries. In this theory the fluctuating components of the dielectric susceptibility tensor are related to small fluctuations $\delta\mathbf{n}(\mathbf{r}, t)$ of the director field around the equilibrium orientation \mathbf{n}_{eq} . The dependence of the fluctuations on the spatial coordinates and on time can be solved from the hydrodynamic equation and the boundary conditions for the director field. The general form of these equations is derived in the Appendix, using the one-constant approach for the elastic free energy and the Rapini-Papoular approximation for the surface free energy.

A nematic film of thickness d is considered, with substrates at $z=0$ and $z=d$ that give rise to planar anchoring. It is assumed that the easy axes of both substrates point in the x direction. Then the director field is uniformly planar in equilibrium:

$$\mathbf{n}_{\text{eq}} = \hat{\mathbf{e}}_x. \quad (9)$$

The fluctuation of the director field is given by

$$\delta\mathbf{n}(\mathbf{r}, t) = \delta\phi(\mathbf{r}, t) \hat{\mathbf{e}}_y + \delta\theta(\mathbf{r}, t) \hat{\mathbf{e}}_z \quad (10)$$

where $\delta\phi(\mathbf{r}, t)$ and $\delta\theta(\mathbf{r}, t)$ are the twist and tilt angle, respectively, which are assumed to be small.

Substituting (9) and (10) in the general equations of the Appendix, the hydrodynamic equations for the small fluctuations $\delta\phi(\mathbf{r}, t)$ and $\delta\theta(\mathbf{r}, t)$ appear to be:

$$\gamma \delta \dot{\theta} = K \nabla^2 \delta \theta, \quad (11a)$$

$$\gamma \delta \dot{\phi} = K \nabla^2 \delta \phi, \quad (11b)$$

whereas the boundary conditions at $z=0$ and $z=d$ can be expressed as

$$-K \frac{\partial \delta \theta}{\partial z} \Big|_{z=0} + C_1 \delta \theta \Big|_{z=0} = 0, \quad (12a)$$

$$K \frac{\partial \delta \theta}{\partial z} \Big|_{z=d} + C_2 \delta \theta \Big|_{z=d} = 0, \quad (12b)$$

$$-K \frac{\partial \delta \phi}{\partial z} \Big|_{z=0} + C_1 \delta \phi \Big|_{z=0} = 0, \quad (12c)$$

$$K \frac{\partial \delta \phi}{\partial z} \Big|_{z=d} + C_2 \delta \phi \Big|_{z=d} = 0. \quad (12d)$$

Here K is the effective elastic constant, γ the effective viscosity coefficient, and C_1 and C_2 the anchoring constants of the substrates at $z=0$ and $z=d$, respectively. The hydrodynamic equation as well as the boundary conditions are the same for both fluctuation modes. Therefore the same results apply to the tilt and the twist mode. For this reason we will

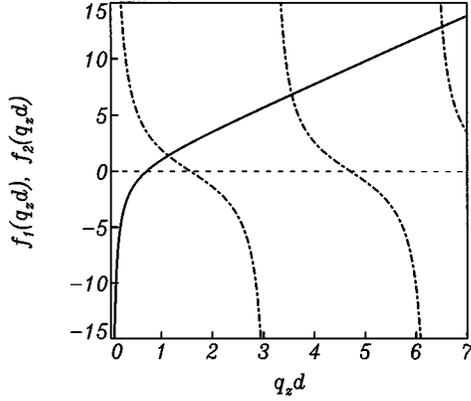


FIG. 2. Plot of the functions $f_1(q_z d) = L_1 L_2 (q_z d) / d^2 - 1 / (q_z d)$ (solid curve) and $f_2(q_z d) = (L_1 + L_2) \cot(q_z d) / d$ (dot-dashed curve) for $L_1 / d = 2$ and $L_2 / d = 1$. The intersections of both curves give the allowed $q_z d$ values of the fluctuation modes of a planarly aligned film.

restrict the discussion in the following to the twist fluctuation mode. The solution of the hydrodynamic equation is

$$\delta\phi(x, t) = [\alpha \cos(q_z z) + \beta \sin(q_z z)] e^{i(q_x x + q_y y)} e^{-t/\tau} \quad (13)$$

with the relaxation time

$$\tau = \gamma / K q^2. \quad (14)$$

The boundary conditions for the twist fluctuation can now be expressed as

$$C_1 \alpha + K q_z \beta = 0, \quad (15a)$$

$$[C_2 \cos(q_z d) - K q_z \sin(q_z d)] \alpha + [C_2 \sin(q_z d) + K q_z \cos(q_z d)] \beta = 0. \quad (15b)$$

This set of linear homogeneous equations for α and β has a nontrivial solution if the determinant of the set of equations equals zero. This condition leads to

$$\frac{L_1 + L_2}{d} \cot(q_z d) = -\frac{1}{q_z d} + \frac{L_1 L_2}{d^2} q_z d \quad (16)$$

with the extrapolation lengths $L_i = K / C_i$ ($i = 1, 2$). The secular equation (16) has an infinite number of solutions, labeled by a discrete index n ($n = 0, 1, 2, \dots$), as can be concluded from graphs as in Fig. 2. Consecutive solutions for q_z in this row are separated by approximately π / d .

In general, the secular equation (16) must be solved numerically. However, an analytical solution can be obtained for values of the thickness d much smaller than L_1 and L_2 . In this limit the second term on the right hand side of the secular equation (16) is the largest term of this equation. Consequently, mode n will have a value of $q_z d$ close to $n\pi$ (as can also be concluded from graphs as in Fig. 2). Expanding the secular equation (16) in terms of this small difference gives an analytical expression for $q_z d$ of mode n . For example, by using

$$\cot(x) = \frac{1}{x} - \frac{1}{3}x + \dots$$

for $x \ll 1$, it is found for the mode $n = 0$ that

$$(q_z d)^2 = \frac{L_1 + L_2}{L_1 L_2} d + \frac{d^2}{L_1 L_2} - \frac{1}{3} \left(\frac{L_1 + L_2}{L_1 L_2} \right)^2 d^2. \quad (17)$$

The corresponding relaxation time is given by

$$\begin{aligned} \gamma / \tau &= K(q_x^2 + q_y^2) + K \frac{L_1 + L_2}{L_1 L_2} \frac{1}{d} + \frac{K}{L_1 L_2} - \frac{K}{3} \left(\frac{L_1 + L_2}{L_1 L_2} \right)^2, \\ &= K(q_x^2 + q_y^2) + \frac{C_1 + C_2}{d} + \frac{C_1 C_2 - (C_1 + C_2)^2 / 3}{K}. \end{aligned} \quad (18)$$

It follows that in the limit of vanishing film thicknesses the relaxation time goes linearly to zero with the film thickness. Analytical expressions for the relaxation time of the fluctuation modes $n \geq 1$ can be derived in a similar way. The dependence of τ on d as given by (18) seems to be in agreement with experiments of Wittebrood *et al.* [17] in the scattering geometry with $k_{iz} - k_{iz} = 0$. The $n = 0$ mode is the dominating scattering mode in this geometry.

Analytical expressions for the allowed wave vectors q_z can also be obtained in the strong anchoring limit, i.e., in the limit of large anchoring constants C_1 and C_2 or in the limit of large d . In this limit the secular equation (16) can be approximated by

$$\sin(q_z d) = 0. \quad (19)$$

Then the solutions are $q_z = (n + 1)\pi / d$ ($n = 0, 1, 2, \dots$). Consequently, the fluctuation mode n has a relaxation time

$$\gamma / \tau = K(q_x^2 + q_y^2) + K(n + 1)^2 \frac{\pi^2}{d^2}. \quad (20)$$

For large d the set of allowed values of q_z is approximately continuous, leading to the classical expression $\tau = \gamma / K q^2$, independent of d .

Figure 3 shows the thickness dependence of the relaxation time for the $n = 0$ mode according to an exact numerical solution of (16), the analytical approximation (18), and the approximation of infinitely thick layers. The parameters used in the calculations are $K = 3$ pN, $\gamma = 15$ mPas, $C_1 = 15 \mu\text{J}/\text{m}^2$ and $C_2 = 5 \mu\text{J}/\text{m}^2$ (leading to extrapolation lengths $L_1 = 0.2 \mu\text{m}$ and $L_2 = 0.6 \mu\text{m}$). The analytical approximation is reasonable for values of d that are of the order of L_1 and L_2 and increasingly better for smaller values of d . On the other hand, d needs to be at least one order of magnitude larger than L_1 and L_2 for the approximation of infinitely thick layers to be reasonable.

IV. ORIENTATIONAL FLUCTUATIONS OF A HYBRIDLY ALIGNED NEMATIC FILM

In a hybridly aligned film, one of the substrates favors homeotropic alignment, whereas the other substrate favours planar alignment. The substrate at $z = d$ is taken to be the

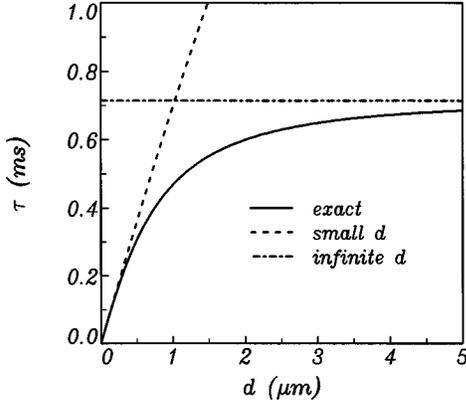


FIG. 3. The relaxation time of the $n=0$ mode as a function of the thickness according to the exact numerical solution of (16) (solid line), the approximate analytical formula (18) for small d (dashed line), and the approximation for infinitely large d (dot-dashed line).

substrate with homeotropic anchoring conditions. The easy direction of the substrate at $z=0$ is assumed to point in the x direction. The equilibrium director field as a function of thickness has been studied in [18]. It appears that the equilibrium director field can be expressed as

$$\mathbf{n}_{\text{eq}}(z) = \cos\theta_{\text{eq}}(z)\hat{\mathbf{e}}_x + \sin\theta_{\text{eq}}(z)\hat{\mathbf{e}}_z, \quad (21)$$

with the equilibrium tilt angle

$$\theta_{\text{eq}}(z) = \theta_1 + \frac{\theta_2 - \theta_1}{d}z. \quad (22)$$

The tilt angles at the substrates θ_1 and θ_2 must be solved from the boundary conditions, which can be written as

$$\theta_2 - \theta_1 - \frac{d}{L_2}\sin\theta_2\cos\theta_2 = 0, \quad (23a)$$

$$\theta_2 - \theta_1 - \frac{d}{L_1}\sin\theta_1\cos\theta_1 = 0, \quad (23b)$$

with the extrapolation lengths $L_i = K/C_i$ ($i = 1, 2$). Figure 4 shows the numerically calculated thickness dependence of θ_1 and θ_2 . The parameters used in the calculation are $K = 3$ pN, $C_1 = 15$ $\mu\text{J}/\text{m}^2$, and $C_2 = 5$ $\mu\text{J}/\text{m}^2$ (leading to extrapolation lengths $L_1 = 0.2$ μm and $L_2 = 0.6$ μm). It appears that a second order transition to a uniformly planar director profile takes place at $d = d_c = L_2 - L_1$, provided that $C_1 > C_2$ [18].

The fluctuation of the director field is given by

$$\begin{aligned} \delta\mathbf{n}(\mathbf{r}, t) = & [-\sin\theta_{\text{eq}}(z)\hat{\mathbf{e}}_x + \cos\theta_{\text{eq}}(z)\hat{\mathbf{e}}_z]\delta\theta(\mathbf{r}, t) \\ & + \cos\theta_{\text{eq}}(z)\delta\phi(\mathbf{r}, t)\hat{\mathbf{e}}_y, \end{aligned} \quad (24)$$

with the tilt and twist fluctuations $\delta\theta(\mathbf{r}, t)$ and $\delta\phi(\mathbf{r}, t)$. Substituting the expressions for the equilibrium director field and the small fluctuation in the general equations of the Appendix, it appears that the linearized hydrodynamic equations are given by

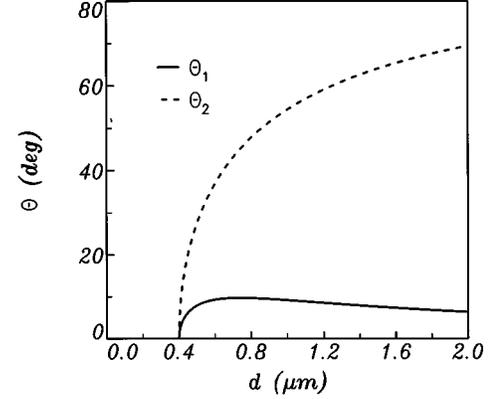


FIG. 4. The equilibrium tilt angle at the planarly anchoring substrate θ_1 (solid line) and the equilibrium tilt angle at the homeotropically anchoring substrate θ_2 (dashed line) as a function of the thickness.

$$\gamma\delta\dot{\theta} = K\nabla^2\delta\theta, \quad (25a)$$

$$\gamma(\cos\theta_{\text{eq}}\delta\dot{\phi}) = K\nabla^2(\cos\theta_{\text{eq}}\delta\phi) + K\frac{(\theta_2 - \theta_1)^2}{d^2}(\cos\theta_{\text{eq}}\delta\phi), \quad (25b)$$

whereas the boundary conditions can be expressed as

$$-K\frac{\partial\delta\theta}{\partial z}\Big|_{z=0} + C_1\cos(2\theta_1)\delta\theta\Big|_{z=0} = 0, \quad (26a)$$

$$K\frac{\partial\delta\theta}{\partial z}\Big|_{z=d} - C_2\cos(2\theta_2)\delta\theta\Big|_{z=d} = 0, \quad (26b)$$

$$-K\frac{\partial(\cos\theta_{\text{eq}}\delta\phi)}{\partial z}\Big|_{z=0} + C_1\cos^2\theta_1(\cos\theta_{\text{eq}}\delta\phi)\Big|_{z=0} = 0, \quad (26c)$$

$$K\frac{\partial(\cos\theta_{\text{eq}}\delta\phi)}{\partial z}\Big|_{z=d} + C_2\cos^2\theta_2(\cos\theta_{\text{eq}}\delta\phi)\Big|_{z=d} = 0. \quad (26d)$$

The solutions of the linearized hydrodynamic equations are

$$\delta\theta(\mathbf{r}, t) = [\alpha_\theta\cos(q_z z) + \beta_\theta\sin(q_z z)]e^{i(q_x x + q_y y)}e^{-t/\tau_{\text{tilt}}}, \quad (27a)$$

$$\begin{aligned} \cos\theta_{\text{eq}}(z)\delta\phi(\mathbf{r}, t) = & [\alpha_\phi\cos(q_z z) \\ & + \beta_\phi\sin(q_z z)]e^{i(q_x x + q_y y)}e^{-t/\tau_{\text{twist}}}, \end{aligned} \quad (27b)$$

with the relaxation times

$$\gamma/\tau_{\text{tilt}} = K\mathbf{q}^2, \quad (28a)$$

$$\gamma/\tau_{\text{twist}} = K\mathbf{q}^2 + K\frac{(\theta_2 - \theta_1)^2}{d^2}. \quad (28b)$$

The boundary conditions for the tilt fluctuations appear to be identical to the corresponding equations in the case of the planarly aligned film, if the following substitutions are made:

$$\begin{aligned} C_1 &\rightarrow C_1 \cos(2\theta_1), \\ C_2 &\rightarrow -C_2 \cos(2\theta_2), \end{aligned}$$

e.g., for $d < d_c$ this boils down to substituting the anchoring constant C_2 by $-C_2$. The boundary conditions for the twist fluctuations are also identical to the boundary conditions in the case of the planarly aligned film, if proper substitutions are made. These substitutions for the twist mode are

$$\begin{aligned} C_1 &\rightarrow C_1 \cos^2 \theta_1, \\ C_2 &\rightarrow C_2 \sin^2 \theta_2, \end{aligned}$$

e.g., for $d < d_c$ this is equivalent to setting C_2 equal to zero. Now it follows that the secular equation for the tilt fluctuation changes to

$$\begin{aligned} &\frac{L_2/\cos(2\theta_2) - L_1/\cos(2\theta_1)}{d} \cot(q_z d) \\ &= \frac{1}{q_z d} + \frac{L_1 L_2}{d^2 \cos(2\theta_1) \cos(2\theta_2)} q_z d, \end{aligned} \quad (29a)$$

whereas the secular equation for the twist fluctuation changes to

$$\begin{aligned} &\frac{L_1/\cos^2 \theta_1 + L_2/\sin^2 \theta_2}{d} \cot(q_z d) \\ &= -\frac{1}{q_z d} + \frac{L_1 L_2}{d^2 \cos^2 \theta_1 \sin^2 \theta_2} q_z d. \end{aligned} \quad (29b)$$

In general, Eqs. (29a) and (29b) must be solved numerically. Analytical solutions are possible for thicknesses d much smaller than L_1 and L_2 . The tilt and twist mode with smallest q_z have relaxation times given by

$$\gamma/\tau_{\text{tilt}} = K(q_x^2 + q_y^2) + \frac{C_1 - C_2}{d} - \frac{C_1 C_2 + (C_1 - C_2)^2/3}{K}, \quad (30a)$$

$$\gamma/\tau_{\text{twist}} = K(q_x^2 + q_y^2) + \frac{C_1}{d} - \frac{C_1^2/3}{K}. \quad (30b)$$

In the limit of vanishing film thicknesses the relaxation times go linearly to zero with the film thickness.

Equations with the thickness dependence of (30a) and (30b) appear to describe the experiments of [17] reasonably. Figures 5 and 6 show the thickness dependence of the relaxation time of the tilt and twist mode with smallest q_z , respectively, according to exact numerical solutions of (29a) and (29b), to the analytical approximations (30a) and (30b), and to the approximation for infinitely thick layers. The parameters used in the calculations are $K=3$ pN, $\gamma=15$ mPa s, $C_1=15$ $\mu\text{J}/\text{m}^2$, and $C_2=5$ $\mu\text{J}/\text{m}^2$, i.e., the same elastic constant and anchoring constants as used in the calculation for Fig. 4. It appears that q_z for the tilt mode goes to zero pro-

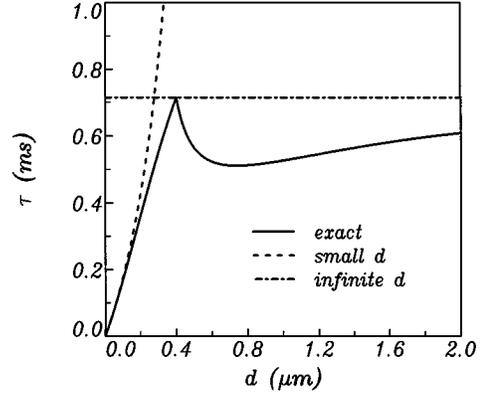


FIG. 5. The relaxation time of the tilt mode with smallest q_z as a function of the thickness according to the exact numerical solution of (29a) (solid line), the approximate analytical formula (30a) for small d (dashed line), and the approximation for infinitely large d (dot-dashed line).

portional to $\sqrt{|d_c/d-1|}$ as d approaches $d_c=0.4$ μm , leading to the cusp at the critical thickness in Fig. 5. This cusp is a direct consequence of the nonanalytical character of $\theta_1(d)$ and $\theta_2(d)$ at $d=d_c$. The nonanalytical behavior of the twist mode is less pronounced, as can be seen from the small kink in the curve of Fig. 6 at $d=d_c$.

V. DISCUSSION

All fluctuation modes give a contribution to the scattering amplitude proportional to

$$\frac{\sin[(q_z - (k_{fz} - k_{iz})d)/2]}{[q_z - (k_{fz} - k_{iz})d]/2}.$$

For small thicknesses q_z of mode n is approximately equal to $n\pi$. Clearly, the mode with minimal $|n\pi - (k_{fz} - k_{iz})d|$ gives the dominant contribution to the scattering process. However, the contributions from other modes with a sufficiently small value for the difference $|n\pi - (k_{fz} - k_{iz})d|$ can be expected to be important as well. This implies that for very thin films the

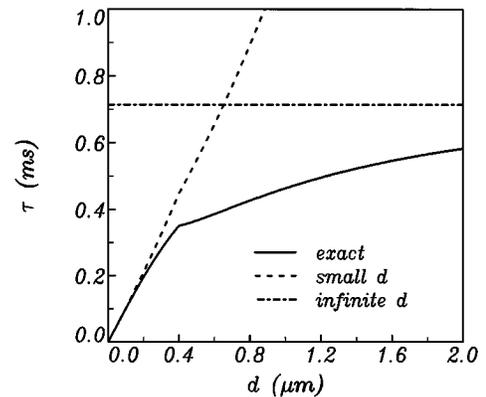


FIG. 6. The relaxation time of the twist mode with smallest q_z as a function of the thickness according to the exact numerical solution of (29b) (solid line), the approximate analytical formula (30b) for small d (dashed line), and the approximation for infinitely large d (dot-dashed line).

decay of the autocorrelation function may be nonexponential. The mode $n=0$ is the dominating scattering mode if the thickness is smaller than approximately $\pi/(k_{fz}-k_{iz})$. As $(k_{fz}-k_{iz})$ is always smaller than $4\pi/\lambda$, with λ the wavelength of the light in the nematic, it follows that the $n=0$ mode is responsible for most scattering events in films thinner than approximately $\lambda/4$, whatever the scattering geometry is.

In case the elastic anisotropy (the difference between K_1 , K_2 , and K_3) is taken into account the problem of determining the fluctuation eigenmodes of the hybrid film becomes a formidable mathematical problem. This is due to the fact that the fluctuation eigenmodes can then no longer be expressed in terms of a single wave vector \mathbf{q} . Instead, the eigenmodes correspond to an infinite Fourier sum of terms with different wave vectors \mathbf{q} .

Recently, fluctuations of confined nematic liquid crystals were treated under the assumption of strong anchoring [19]. The present theory improves some of the results of [19] by incorporating weak anchoring, i.e., by allowing the director field at the boundary to deviate from the preferred direction. This is more appropriate in the limit of small film thicknesses d . When d is much smaller than the extrapolation length K/C the anchoring properties dominate the fluctuations, instead of the elastic properties. Therefore, the expression for the inverse of the relaxation time contains a term proportional to C/d , instead of the term proportional to K/d^2 as appears in the limit of strong anchoring. Consequently, in the limit d going to zero, τ goes to zero linear in d , instead of quadratic in d . It should be noted that deviations from this behavior can be expected in scattering geometries with $(k_{fz}-k_{iz}) \neq 0$ for thicknesses larger than approximately $\pi/(k_{fz}-k_{iz})$.

The present theory can also be applied to light scattering by nematics confined in porous media. If these media are approximated by a set of randomly oriented cylindrical pores, an effective relaxation time for sufficiently small average pore sizes R can be defined as

$$\gamma/\tau_{\text{eff}} = K\langle q_{\parallel}^2 \rangle + \frac{2C}{R}, \quad (31)$$

with C the anchoring constant and q_{\parallel} the magnitude of the component of the scattering vector along the pore direction. The brackets denote averaging over the randomly oriented pores. Deviations from the C/R dependence of τ_{eff}^{-1} can occur for values of R larger than approximately $\lambda/4$. A K/R^2 dependence of τ_{eff}^{-1} [7,11,12] seems appropriate for values of R much larger than K/C . A crossover between the two types of behavior may be expected for the intermediate regime. Due to the distribution over the various pore sizes and pore orientations (and because of the smallness of the pore sizes) many fluctuation modes with different relaxation times contribute to the scattering process. This means that the autocorrelation function may be expected to deviate substantially from exponential decay [5,11].

Concluding, the light scattering by thin nematic liquid crystal films differs in two important respects from the light scattering by nematic layers of infinite thickness. First, the

orientational fluctuations that contribute to the scattering cross section have wave vectors \mathbf{q} with a z component that satisfies

$$|q_z - (k_{fz} - k_{iz})| \leq \pi/d$$

with d the thickness of the film. Second, only orientational fluctuations with wave vectors that belong to a discrete set of wave vectors are allowed by the boundary conditions. This means that the orientational fluctuations are overdamped standing waves rather than overdamped traveling waves. As a consequence, the relaxation time depends on the thickness of the nematic liquid crystal film.

APPENDIX

The hydrodynamic equation for the director field is

$$\gamma \dot{\mathbf{n}} = \mathbf{h} - \lambda \mathbf{n}, \quad (A1)$$

with γ the effective viscosity coefficient, \mathbf{h} the so-called molecular field, and λ a parameter that must be solved from the orthonormality condition for the director field

$$\mathbf{n} \cdot \mathbf{n} = 1. \quad (A2)$$

The components of the molecular field are defined by

$$h_{\alpha} = \sum_{\beta=x,y,z} \frac{\partial}{\partial r_{\beta}} \left[\frac{\partial f_{\text{el}}}{\partial (\partial n_{\alpha} / \partial r_{\beta})} \right] - \frac{\partial f_{\text{el}}}{\partial n_{\alpha}}, \quad (A3)$$

with f_{el} the elastic free energy density. In the one-constant approach, this quantity can be expressed as

$$f_{\text{el}} = \frac{1}{2} K \sum_{\alpha=x,y,z} (\nabla n_{\alpha})^2, \quad (A4)$$

where K is the effective elastic constant. This leads to a molecular field

$$\mathbf{h} = K \nabla^2 \mathbf{n}. \quad (A5)$$

Using the orthonormality condition (33) and the hydrodynamic equation (A1) for the director field an explicit expression for the constant λ can be derived:

$$\lambda = \lambda \mathbf{n} \cdot \mathbf{n} = [\mathbf{h} - \gamma \dot{\mathbf{n}}] \cdot \mathbf{n} = \mathbf{h} \cdot \mathbf{n} = K \mathbf{n} \cdot \nabla^2 \mathbf{n}. \quad (A6)$$

Now the hydrodynamic equation can be written as

$$\gamma \dot{\mathbf{n}} = K \nabla^2 \mathbf{n} - K (\mathbf{n} \cdot \nabla^2 \mathbf{n}) \mathbf{n}. \quad (A7)$$

The equilibrium director field only depends on the coordinate z . Then it follows that

$$\frac{d^2 \mathbf{n}_{\text{eq}}}{dz^2} - \left(\mathbf{n}_{\text{eq}} \cdot \frac{d^2 \mathbf{n}_{\text{eq}}}{dz^2} \right) \mathbf{n}_{\text{eq}} = 0. \quad (A8)$$

The hydrodynamic equation for small fluctuations $\delta \mathbf{n}$ is obtained by substituting

$$\mathbf{n} = \mathbf{n}_{\text{eq}} + \delta \mathbf{n}, \quad (A9)$$

in Eq. (A7) and linearizing this equation in $\delta \mathbf{n}$. It is found that

$$\begin{aligned} \gamma \delta \dot{\mathbf{n}} = & K \nabla^2 \delta \mathbf{n} - K \left(\mathbf{n}_{\text{eq}} \cdot \frac{d^2 \mathbf{n}_{\text{eq}}}{dz^2} \right) \delta \mathbf{n} - K \left(\mathbf{n}_{\text{eq}} \cdot \frac{\partial^2 \delta \mathbf{n}}{\partial z^2} \right) \mathbf{n}_{\text{eq}} \\ & - K \left(\delta \mathbf{n} \cdot \frac{d^2 \mathbf{n}_{\text{eq}}}{dz^2} \right) \mathbf{n}_{\text{eq}}. \end{aligned} \quad (\text{A10})$$

The boundary conditions can be derived using an expression for the surface free energy density W . The Rapini-Papoular approximation leads to the following simplified form:

$$W = -\frac{1}{2} C_1 (\mathbf{\Pi}_1 \cdot \mathbf{n})^2 \Big|_{z=0} - \frac{1}{2} C_2 (\mathbf{\Pi}_2 \cdot \mathbf{n})^2 \Big|_{z=d}. \quad (\text{A11})$$

Here C_1 and C_2 are the anchoring constants and $\mathbf{\Pi}_1$ and $\mathbf{\Pi}_2$ are unit vectors along the easy axes of the substrates at $z=0$ and $z=d$, respectively. In order to avoid unnecessary mathematical complications no surface elasticity is taken into account. The boundary conditions at the substrates are

$$\begin{aligned} \mathbf{0} = & \frac{\partial W}{\partial \mathbf{n}} \Big|_{z=0} - \frac{\partial f_{\text{el}}}{\partial (\partial \mathbf{n} / \partial z)} \Big|_{z=0} + \lambda_{s1} \mathbf{n} \Big|_{z=0} \\ = & -C_1 (\mathbf{\Pi}_1 \cdot \mathbf{n}) \mathbf{\Pi}_1 - K \frac{\partial \mathbf{n}}{\partial z} \Big|_{z=0} + \lambda_{s1} \mathbf{n} \Big|_{z=0}, \end{aligned} \quad (\text{A12a})$$

$$\begin{aligned} \mathbf{0} = & \frac{\partial W}{\partial \mathbf{n}} \Big|_{z=d} - \frac{\partial f_{\text{el}}}{\partial (\partial \mathbf{n} / \partial z)} \Big|_{z=d} + \lambda_{s2} \mathbf{n} \Big|_{z=d} \\ = & -C_2 (\mathbf{\Pi}_2 \cdot \mathbf{n}) \mathbf{\Pi}_2 + K \frac{\partial \mathbf{n}}{\partial z} \Big|_{z=d} + \lambda_{s2} \mathbf{n} \Big|_{z=d}. \end{aligned} \quad (\text{A12b})$$

Here λ_{s1} and λ_{s2} are parameters that must be solved from the orthonormality condition for the director field. Analogous to the hydrodynamic equation for the bulk it follows that

$$\begin{aligned} \lambda_{s1} = & \lambda_{s1} \mathbf{n} \cdot \mathbf{n} \Big|_{z=0} = \left[C_1 (\mathbf{\Pi}_1 \cdot \mathbf{n})_1 + K \frac{\partial \mathbf{n}}{\partial z} \cdot \mathbf{n} \right] \Big|_{z=0} \\ = & C_1 (\mathbf{\Pi}_1 \cdot \mathbf{n})^2 \Big|_{z=0}, \end{aligned} \quad (\text{A13a})$$

and similarly

$$\lambda_{s2} = C_2 (\mathbf{\Pi}_2 \cdot \mathbf{n})^2 \Big|_{z=d}. \quad (\text{A13b})$$

Now the boundary conditions can be written as

$$-C_1 (\mathbf{\Pi}_1 \cdot \mathbf{n}) [\mathbf{\Pi}_1 - (\mathbf{\Pi}_1 \cdot \mathbf{n}) \mathbf{n}] \Big|_{z=0} - K \frac{\partial \mathbf{n}}{\partial z} \Big|_{z=0} = \mathbf{0}, \quad (\text{A14a})$$

$$-C_2 (\mathbf{\Pi}_2 \cdot \mathbf{n}) [\mathbf{\Pi}_2 - (\mathbf{\Pi}_2 \cdot \mathbf{n}) \mathbf{n}] \Big|_{z=d} + K \frac{\partial \mathbf{n}}{\partial z} \Big|_{z=d} = \mathbf{0}. \quad (\text{A14b})$$

The boundary conditions for the equilibrium director field read

$$-C_1 (\mathbf{\Pi}_1 \cdot \mathbf{n}_{\text{eq}}) [\mathbf{\Pi}_1 - (\mathbf{\Pi}_1 \cdot \mathbf{n}_{\text{eq}}) \mathbf{n}_{\text{eq}}] \Big|_{z=0} - K \frac{d \mathbf{n}_{\text{eq}}}{dz} \Big|_{z=0} = \mathbf{0}, \quad (\text{A15a})$$

$$-C_2 (\mathbf{\Pi}_2 \cdot \mathbf{n}_{\text{eq}}) [\mathbf{\Pi}_2 - (\mathbf{\Pi}_2 \cdot \mathbf{n}_{\text{eq}}) \mathbf{n}_{\text{eq}}] \Big|_{z=d} + K \frac{d \mathbf{n}_{\text{eq}}}{dz} \Big|_{z=d} = \mathbf{0}, \quad (\text{A15b})$$

whereas the linearized boundary conditions for the small fluctuations can be expressed as

$$\begin{aligned} -C_1 (\mathbf{\Pi}_1 \cdot \delta \mathbf{n}) [\mathbf{\Pi}_1 - 2(\mathbf{\Pi}_1 \cdot \mathbf{n}_{\text{eq}}) \mathbf{n}_{\text{eq}}] \Big|_{z=0} \\ + C_1 (\mathbf{\Pi}_1 \cdot \mathbf{n}_{\text{eq}})^2 \delta \mathbf{n} \Big|_{z=0} - K \frac{\partial \delta \mathbf{n}}{\partial z} \Big|_{z=0} = \mathbf{0}, \end{aligned} \quad (\text{A16a})$$

$$\begin{aligned} -C_2 (\mathbf{\Pi}_2 \cdot \delta \mathbf{n}) [\mathbf{\Pi}_2 - 2(\mathbf{\Pi}_2 \cdot \mathbf{n}_{\text{eq}}) \mathbf{n}_{\text{eq}}] \Big|_{z=d} \\ + C_2 (\mathbf{\Pi}_2 \cdot \mathbf{n}_{\text{eq}})^2 \delta \mathbf{n} \Big|_{z=d} + K \frac{\partial \delta \mathbf{n}}{\partial z} \Big|_{z=d} = \mathbf{0}. \end{aligned} \quad (\text{A16b})$$

It is often advantageous to use the parametrization of the director field in terms of the so-called tilt and twist angles θ and ϕ :

$$\mathbf{n} = (\cos \theta \cos \phi, \cos \theta \sin \phi, \sin \theta), \quad (\text{A17})$$

e.g., the two independent components of the fluctuation $\delta \mathbf{n}$ can be related to the tilt and twist fluctuations $\delta \theta$ and $\delta \phi$.

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