Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Fluctuations in Confined Liquid Crystals and Pretransitional Evanescent Light Scattering

Andreja Šarlah [a], PrimoŽ Ziherl [a] & Slobodan Žumer [a]

[a] Physics Department, University of Ljubljana, Jadranska 19, 1000, Ljubljana, Slovenia

Version of record first published: 24 Sep 2006

To cite this article: Andreja Šarlah, PrimoŽ Ziherl & Slobodan Žumer (1998): Fluctuations in Confined Liquid Crystals and Pretransitional Evanescent Light Scattering, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 320:1, 231-238

To link to this article: http://dx.doi.org/10.1080/10587259808024397

Mol. Cryst. Liq. Cryst., Vol. 320, pp. 231–238
Reprints available directly from the publisher
Photocopying permitted by license only

FLUCTUATIONS IN CONFINED LIQUID CRYSTALS AND PRETRANSITIONAL EVANESCENT LIGHT SCATTERING

ANDREJA ŠARLAH, PRIMOŽ ZIHERL, and SLOBODAN ŽUMER
Physics Department, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia

The effect of surface-induced (dis)order on collective orientational fluctuations in nematic liquid crystals is studied within Landau-de Gennes theory. Close to the nematic-isotropic phase transition the corresponding spectra are characterized by soft modes, which are associated with fluctuations of the thickness of the (dis)ordered wetting layer. In this range the dynamical part of the evanescent light scattering is dominated by the soft modes.

Keywords: confined liquid crystals; orientational fluctuations; light scattering

INTRODUCTION

Several recent experimental studies of the pretransitional dynamics in confined nematic liquid-crystalline systems[1–5] indicate that the spectra of excitations in microconfined liquid crystals are substantially different from that in macroscopic samples. The theoretical understanding of the experimental results is rather incomplete as opposed to those corresponding to bulk samples.[6] Motivated by the lack of methodical insight into the dynamical mechanisms in confined liquid crystals, we have decided to extend our preliminary study of the effects of surface-induced order on collective excitations in systems close to the nematic-isotropic phase transition.[7] In the following, we focus our attention to the soft mode associated with the thickness of the wetting layer in case of com-

plete wetting of the substrate by either nematic or isotropic phase and examine its detectability by evanescent light scattering.

In the next section the eigenmodes of fluctuations in one-dimensional model geometry are studied theoretically using Landau-de Gennes approach, whereas the effect of the pretransitional excitations on the light scattering is discussed in the second part of the paper.

EQUILIBRIUM ORDERING AND FLUCTUATIONS

The model system consists of a liquid crystal film of thickness d sandwiched between two parallel substrates that induce either local disorder in the field-stabilized homeotropic nematic structure (case 1) or local homeotropic nematic-like order in the isotropic phase (case 2) (Figure 1). In both cases, the interaction between the liquid crystal and the confining surface is assumed to be strong.

According to de Gennes[8,9] close to the nematic-isotropic phase transition temperature the difference between the free energy densities of nematic and isotropic phase (f) can be expanded in terms of scalar invariants of the order parameter $\underline{Q}$ (a symmetric, second rank tensor)

$$f = \frac{1}{2}A(T - T^*)\mathrm{tr}\underline{Q}^2 - \frac{1}{3}B\mathrm{tr}\underline{Q}^3 + \frac{1}{4}C(\mathrm{tr}\underline{Q}^2)^2 + \frac{1}{2}L\nabla\underline{Q}\vdots\nabla\underline{Q}\,, \qquad (1)$$

where A, B, C, and L are temperature-independent material constants, T is the temperature, and T^* is the so-called supercooling limit.

The tensor order parameter can be written as a sum of a static and a fluctuating part: $\underline{Q}(\mathbf{r},t) = \underline{Q}_{static}(\mathbf{r}) + \underline{B}(\mathbf{r},t)$. By definition, the equilibrium ordering is only slightly perturbed by the fluctuations, i.e., $\underline{B} \ll \underline{Q}_{static}$. Both $\underline{Q}_{static}$ and $\underline{B}$ can be represented in a suitable base, which is spanned by five orthogonal base tensors, such as $\underline{T}_0 = (3\mathbf{n}\otimes\mathbf{n} - \underline{I})/\sqrt{6}, \underline{T}_1 = (\mathbf{e}_1\otimes\mathbf{e}_1 - \mathbf{e}_2\otimes\mathbf{e}_2)/\sqrt{2}, \underline{T}_{-1} = (\mathbf{e}_1\otimes\mathbf{e}_2 + \mathbf{e}_2\otimes\mathbf{e}_1)/\sqrt{2}, \underline{T}_2 = (\mathbf{e}_1\otimes\mathbf{n} + \mathbf{n}\otimes\mathbf{e}_1)/\sqrt{2}$, and $\underline{T}_{-2} = (\mathbf{e}_2\otimes\mathbf{n} + \mathbf{n}\otimes\mathbf{e}_2)/\sqrt{2}$, where $\mathbf{n}$ (the director), $\mathbf{e}_1$, and $\mathbf{e}_2$ constitute an orthonormal triad and $\underline{I}$ is the unit second rank tensor.[7,10] In this base the projection of $\underline{Q}$ onto $\underline{T}_0$ is equal to the magnitude of the scalar order parameter, the components of the tensor order parameter along $\underline{T}_{\pm1}$ are related to the biaxiality of the ordering, and its $\underline{T}_{\pm2}$ counterparts to the orientation of the director.[7]

It is convenient to introduce dimensionless variables and parameters: spatial coordinates and the bare nematic correlation length are scaled by the sample

thickness $[(x, y, z) \leftarrow (x/d, y/d, z/d)$ and $\zeta = \sqrt{27CL/B^2d^2}]$, the temperature is controlled by $\vartheta = (T - T^*)/(T_{NI} - T^*)$, where $T_{NI} = T^* + B^2/27AC$ is the nematic-isotropic phase transition temperature in bulk, and the rescaled tensor order parameter is of form $\underline{Q} \leftarrow (3\sqrt{6}C/2B)\underline{Q}$, so that its magnitude is measured in units of the magnitude of scalar order parameter at the phase transition temperature. Our calculations correspond to 800 nm thick liquid crystal 5CB ($A = 0.13 \cdot 10^6$ J/m^{3}K, $B = 3.89 \cdot 10^6$ J/m^3, $C = 3.92 \cdot 10^6$ J/m^3, $L = 9 \cdot 10^{-12}$ N, and $T^* = 307.1$ K[11,12]) film yielding $\zeta = 0.01$.

Equilibrium ordering

Since we limit our discussion to structures characterized by an uniform director field, the only nonzero coefficient in the expansion of the equilibrium order parameter $[\underline{Q}_{static}(\mathbf{r}) = \sum_{i=-2}^{2} a_i(\mathbf{r})\underline{T}_i]$ is a_0, the rescaled degree of order. Configuration is determined by the Euler-Lagrange equation, which is given by

$$\zeta^2 a_0'' - \vartheta a_0 + 3a_0^2 - 2a_0^3 = 0\,, \tag{2}$$

where $a_0' = \mathrm{d}a_0(z)/\mathrm{d}z$. The boundary conditions read

$$a_0(z = 0) = a_0(z = 1) = a_s\,, \tag{3}$$

where $a_s = 0$ in the case of surface-induced disorder in the nematic phase, and $a_s = 1.1$ in the paranematic case characterized by an ordering effect of the substrate. Some of the equilibrium order parameter profiles are given in Figure 1.

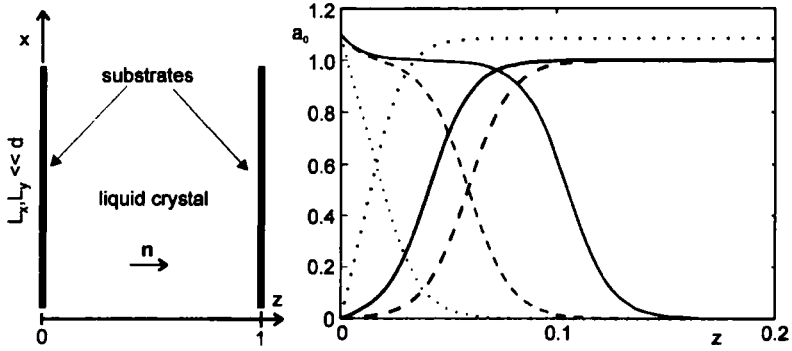

FIGURE 1 Model geometry and scalar order parameter profiles in the nematic (case1–thicker lines) and paranematic (case 2–thiner lines) phase at $|\vartheta - \vartheta_{NI}| = 10^{-5}$ (solid lines), $|\vartheta - \vartheta_{NI}| = 10^{-3}$ (dashed lines) and $|\vartheta - \vartheta_{NI}| = 10^{-1}$ (dotted lines), where $\vartheta_{NI} = 1$.

In both cases the equilibrium profile is uniform far from the substrates, where

the degree of order is equal to its bulk value. However, the surface layer is disordered in nematic (case 1) and ordered in isotropic phase (case 2), and its thickness is increasing on approaching the nematic-isotropic phase transition temperature.[13,14]

Fluctuation modes

If the hydrodynamic degrees of freedom are neglected,[7,10] the orientational dynamics of the nematic liquid-crystalline system is described by Landau-Khalatnikov equation,[15] which in a dimensionless representation reads

$$\frac{\partial \underline{Q}}{\partial t} = -\vartheta \underline{Q} + 3\sqrt{6}\,\widetilde{\underline{Q}^2} - 2\underline{Q}\mathrm{tr}\underline{Q}^2 + \zeta^2 \nabla^2 \underline{Q}\,, \tag{4}$$

where the tilde above the tensor denotes its traceless part. The dimensionless time $t \leftarrow t/\tau_a$ is measured in units of phenomenological relaxation time $\tau_a \sim 10^{-8}$ s, which is proportional to the rotational viscosity of the material.[7,10,15]

The linearized dynamic equations that govern the evolution of fluctuation amplitudes $b_i(\mathbf{r},t) = \exp(i(k_x x + k_y y))\,\beta_i(z)\exp(-\mu_i t)$ in the expansion $\underline{B} = \sum_{i=-2}^{2} b_i(\mathbf{r},t)\underline{T}_i$ are given by

$$\zeta^2 \beta_i'' - (\vartheta - \lambda_0 - s_i)\,\beta_i = 0, \tag{5}$$

where $s_0 = 6a_0 + 6a_0^2$, $s_{\pm 1} = 6a_0 + 2a_0^2$, $s_{\pm 2} = -3a_0 + 2a_0^2$, and $\lambda_i = \mu_i - \zeta^2(k_x^2 + k_y^2)$ are the reduced relaxation rates of the modes. (k_x and k_y, the dimensionless wave vectors of the transverse modulation of the mode, are subject to periodic boundary conditions.) Due to strong anchoring fluctuations must vanish at the substrates, so that the boundary conditions read $\beta_i(0) = \beta_i(1) = 0$.

The elementary order parameter mode is associated with the fluctuations of the thickness of the (dis)ordered part of the film (Figure 2). Its relaxation rate decreases towards 0 with temperature dependence $\lambda_{0,0} \propto \mp(\vartheta - 1)$, where " $-$ " corresponds to the wetting with the isotropic phase in the nematic phase (case 1) and " $+$ " to the wetting with the nematic phase in the isotropic phase (case 2). In the nematic phase the relaxation rate decreases faster than in the paranematic phase (Figure 3), which is in agreement with a slower rate of growth of the wetting layer.[14] Due to this soft mode the phase transition in the confined nematic or paranematic film is only weakly discontinuous. Higher modes are spread over the whole of the sample and similar to bulk modes.

Biaxial collective excitations in uniaxial nematic phase relax fast: close to the

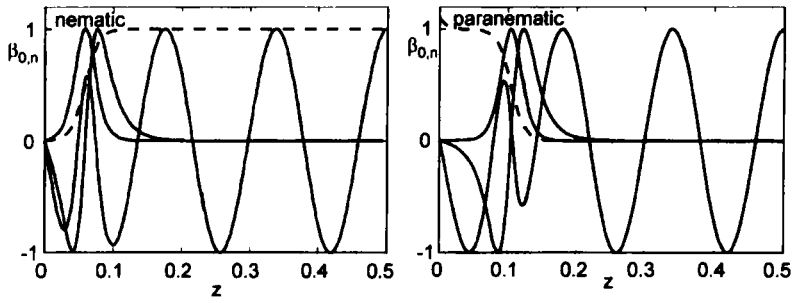

FIGURE 2 Profiles of some of the order parameter modes ($n = 0, 2, 14$) at $\vartheta = \vartheta_{NI} \mp 10^{-5}$, where " $-$ " corresponds to case 1 and " $+$ " to case 2; n-th mode is characterized with n nodes in the interval $z \in (0, 1)$. In both cases, the lowest order parameter mode corresponds to fluctuations of thickness of the (dis)ordered boundary layer. Dashed lines: equilibrium order parameter profile.

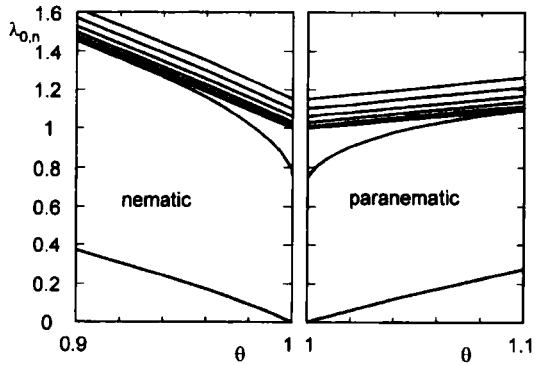

FIGURE 3 Spectrum of reduced relaxation rates of the lowest 8 symmetric order parameter modes in the nematic (case 1) and paranematic phase (case 2) as a function of dimensionless temperature ϑ. The soft modes are well-separated from the bulklike part of the spectrum.

transition, the corresponding reduced relaxation rates in the nematic phase are approximately 10 times larger than the reduced relaxation rates in the paranematic phase (Figure 4), where they disturb only the central isotropic part of the film.

The Goldstone director modes are associated with the spatial modulation of the orientation of the nematic director and constitute the slowest part of the spectrum in the nematic phase (case 1). On approaching ϑ_{NI} from below, the relax-

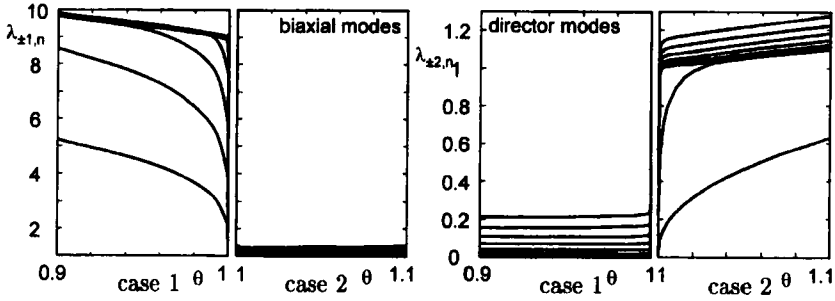

FIGURE 4 Spectra of reduced relaxation rates of the lowest 8 even biaxial and director modes for the substrates providing the wetting with isotropic (case 1) and nematic phase (case 2) as a function of dimensionless temperature ϑ. In the paranematic case the biaxial relaxation rates can be approximated by the relaxation rates characteristic for the isotropic phase.

ation rates increase due to a decrease of thickness of the central ordered part, which determines the maximum wavelength of the deformation. In the paranematic phase (case 2) director modes are characterized by a slow mode associated with director fluctuations in the ordered boundary layer (Figure 4).

DYNAMIC LIGHT SCATTERING

Fluctuations of the nematic tensor order parameter give rise to fluctuations of the dielectric constant tensor responsible for the scattering of light. Here we are particularly interested in the slow order parameter fluctuations, which can be detected by choosing appropriate polarizations of the incoming (**i**) and the scattered light (**f**) (**i** = **f** = **n**).

In the evanescent light scattering experiment the light is totally reflected at the substrate-liquid crystal interface so that the incoming light is of form

$$\mathbf{E}_e(\mathbf{r},t) = \mathbf{E}_0 \exp(i(k_0 x \sin\alpha - \omega_0 t) - \kappa z)\,, \tag{6}$$

where k_0 is the magnitude of the wavevector in the substrate. The penetration depth is characterized by $\kappa = k_0\sqrt{\sin^2\alpha - \sin^2\alpha_c}$ where α_c is the angle of total reflection and $\alpha > \alpha_c$ is the angle between the incident wavevector and substrate normal. The magnitude of the scattered light is therefore[16]

$$E_s \propto \int E_e(\mathbf{r},t)\exp(-i\mathbf{k}_s\cdot\mathbf{r})\mathbf{f}\cdot\underline{\epsilon}(\mathbf{r},t)\cdot\mathbf{i}\,d\mathbf{r}\,. \tag{7}$$

If $\mathbf{i} = \mathbf{f} = \mathbf{n}$, the product $\mathbf{f}\cdot\underline{\epsilon}(\mathbf{r},t)\cdot\mathbf{i}$ is proportional to $\epsilon_a[a_0(z)+b_0(\mathbf{r},t)]$, where ϵ_a is the difference between the two principal values of the dielectric constant tensor in the completely ordered state. The dynamical part of the autocorrelation function of the scattered field is then given by

$$G(t)_{dyn} = \langle E_s(0)E_s^*(t)\rangle_{dyn} \propto \sum_n \frac{R_{0,n}^2}{\mu_{0,n;q}} \exp(-\mu_{0,n;q}t) \,, \tag{8}$$

where $R_n = \int \beta_{0,n}(z)\exp(-\kappa z)dz$ and $q = |\mathbf{k}_i - \mathbf{k}_f|$ the magnitude of the scattering wavevector.

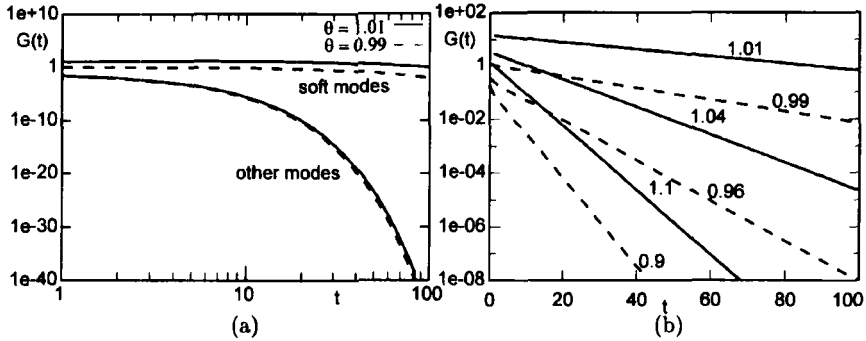

FIGURE 5 (a) Contributions of the soft modes and other modes in the nematic (case 1 – dashed lines) and paranematic phase (case 2 – solid lines) to the correlation function at $\vartheta = \vartheta \mp 0.01$. (b) Total correlation function for both cases at different temperatures. $q = 0.1$ and $\kappa = 1$.

As implied by Figure 5, both below (case 1) and above (case 2) the phase transition temperature the correlation function is well described by a single exponential function corresponding to the relevant soft mode.

If $\mathbf{i}$ and $\mathbf{f}$ are not precisely parallel to the director $\mathbf{n}$ the correlation function also includes contributions of director and biaxial modes. In the paranematic phase (case 2) the results would not change much whereas in the nematic phase (case 1) the director modes would mask the soft mode.

CONCLUSIONS

In restricted geometries, both static and dynamic aspect of liquid-crystalline ordering are modified by the confining substrates. Here we show that in the case of complete wetting by either nematic or isotropic phase the dynamics of collective

fluctuations in the vicinity of the nematic-istropic phase transition temperature is characterized by soft modes. The illustrated soft modes are expected to be one of possible mechanisms contributing to slow dynamics in confined systems. The existence of soft modes could be probed with the evanescent light scattering method.

Acknowledgment

Support from Ministry of Science and Technology of Slovenia (Grant J1-7470), European Comission (INCO–Copernicus project No. IC15CT96–0744) and US-Slovene NSF Joint Found (Grant NSF 95–457) is acknowledged.

References

1. G. P. Crawford and S. Žumer (eds.), Liquid Crystals in Complex Geometries (Taylor & Francis, London, 1996).
2. X.-I. Wu, W. I. Goldburg, M. X. Liu, and J. Z. Xue, Phys. Rev. Lett., 69, 470 (1992).
3. F. M. Aliev, V. V. Nadtotchi, Mat. Res. Soc. Symp. Proc., 407, 125 (1996).
4. T. Bellini, N. A. Clark, and D. W. Schaefer, Phy. Rev. Lett., 74, 2740 (1995).
5. G. Schwalb and F. W. Deeg, Phys. Rev. Lett., 74, 1383 (1995).
6. Z. H. Wang and P. H. Keyes, Phys. Rev. E, 54, 5249 (1996).
7. P. Ziherl and S. Žumer, Phys. Rev. Lett., 78, 682 (1997).
8. P. G. de Gennes, Mol. Cryst. Liq. Cryst., 12, 193 (1971).
9. P. G. de Gennes and J. Prost, The Physics of Liquid Crystals (Oxford University Press, New York, 1995).
10. S. Hess, Z. Naturforsch., 30 a, 728 (1975).
11. P. Sheng, Phys. Rev. A, 26, 1610 (1982).
12. G. P. Crawford, R. J. Ondris-Crawford, J. W. Doane, and S. Žumer, Phys. Rev. E 53, 3647 (1996).
13. K. Miyano, Phys. Rev. Lett., 43, 51 (1979).
14. D.W. Allender, G. L. Henderson, and D. L. Johnson, Phys. Rev. A, 24, 1086 (1981).
15. L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR, 96, 469 (1954).
16. M. Čopič, C. S. Park, and N. A. Clark, Mol. Cryst. Liq. Cryst., 222, 111 (1992).