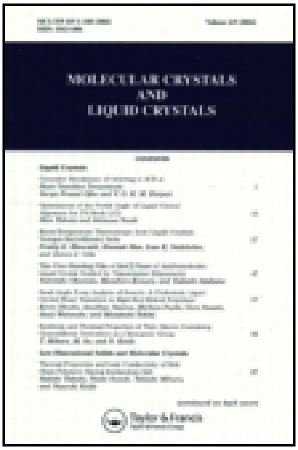

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Ordering and Dynamics in Paranematic Surface Layers

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ORDERING AND DYNAMICS IN PARANEMATIC SURFACE LAYERS

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Abstract Our recent advances in understanding of static and dynamic behavior of partially ordered nematic systems are illustrated by a systematic DNMR study of anchoring and wetting on surfaces, treated by aliphatic acids, and by a theoretical analysis of collective excitations in a simple one dimensional planar geometry with order-inducing surface interaction.

INTRODUCTION

A decade ago, the discovery of polymer dispersed liquid crystals (PDLC's) has boosted scientific interest in confined liquid crystals.[1] Since then, these materials have been used for a number of electro-optical applications.[2] This progress has stimulated research in liquid crystalline systems restricted to cylindrical channels and various random porous materials. Nowadays, microconfined liquid crystals represent one of the most vivid topics in the physics of mesomorphic systems.

Among experimental methods used for investigation of these systems, NMR techniques have a special place.[3,4] They have proved to be very successful in probing nematic structures well below the resolution of the optical microscope in restricted geometries such as PDLC droplets,[5] polymer networks,[6] cylindrical cavities,[7] silica aerogel matrices,[8] and Vycor glass.[9] In addition, NMR methods also reveal information about molecular dynamics in confined systems.[10,11] As far as studies of nematic director fields are concerned, deuterium nuclear magnetic resonance (DNMR) is the most extensively used NMR technique because the deuterium nucleus has the advantage of carrying the quadrupole moment and its spectra are dominated by the quadrupole interaction with electric field gradients probing the local liquid crystal ordering.

In the following, we present some of our recent advances in the understanding of surface-induced paranematic ordering. A systematic DNMR line shape study of such ordering is briefly described in the next section. The second part of the paper is devoted to a theoretical analysis of order fluctuations in a surface induced paranematic phase, which may account for pretransitional increase of low frequency nuclear magnetic relaxation rate observed in some microconfined systems[11].

DNMR STUDY OF WETTING IN MICROCONFINED LIQUID CRYSTALS

DNMR line splitting

Deuterium NMR is an ideal experimental tool for studies of ordering in nematic liquid crystals since it is sensitive to both nematic director distribution and orientational order parameter. The quadrupole splitting frequency is given by

$$\delta\nu(\mathbf{r}) = Q(\mathbf{r})\frac{3\cos^2\Theta(\mathbf{r}) - 1 + \eta(\mathbf{r})\sin^2\Theta(\mathbf{r})\cos 2\Psi(\mathbf{r})}{2}\delta\nu_0, \tag{1}$$

where $Q(\mathbf{r})$ is the local degree of the orientational order and $\delta\nu_0$ is the bulk quadrupole splitting in a perfectly ordered phase.[3] The angles $\Theta(\mathbf{r})$ and $\Psi(\mathbf{r})$ describe the orientation of the magnetic field in the frame of the local director, which corresponds to the direction of the principal axis of the electric field gradient tensor averaged over fast orientational fluctuations. The biaxiality parameter $\eta(\mathbf{r})$ is zero for bulk nematic liquid crystals, but it can become important if the averaging motion (orientational fluctuations) loses its symmetry because of confinement.

If the characteristic size of the confining geometry is of the order ~ 0.1 μm (as, for instance, in cylindrical channels in Anopore membranes), the motional averaging in nematic phase is negligible since the characteristic distance a molecule traverses during the characteristic NMR time is at least an order of magnitude smaller than the size of the cavity. Therefore, the deuterium NMR spectrum directly reflects the static director field. In the isotropic phase, the situation is quite different. The characteristic diffusion length is comparable to the size of the pore and the NMR spectra are motionally averaged. In this case and for $\eta(\mathbf{r}) = 0$, Equation (1) can be approximated by

$$\langle\delta\nu\rangle = \langle Q(r)\rangle\left\langle\frac{3\cos^2\Theta(\mathbf{r}) - 1}{2}\right\rangle\delta\nu_0, \tag{2}$$

where $\langle\ldots\rangle$ denote the motional average. In the isotropic phase, the averaged splitting $\langle\delta\nu\rangle$ is proportional to the adsorption parameter Γ, which characterizes the effective thickness of the partially ordered paranematic layer and is given by the integral of the order parameter over the sample, i.e.,

$$\Gamma = \int_0^\infty Q(z)\,\mathrm{d}z. \tag{3}$$

By monitoring $\langle\delta\nu\rangle$ as a function of temperature, the wetting regime can be classified: if Γ (or $\langle\delta\nu\rangle$) remains finite for $T \to T_{NP}$, the wetting is partial; if it diverges on approaching the transition temperature, the wetting is complete. In order to explain the experimentally observed temperature dependence of $\langle\delta\nu\rangle$, a phenomenological approach already employed in a study of the wetting behavior[12] is used.

Landau-de Gennes free energy

The basic assumption of Landau-de Gennes theory states that close to the nematic-isotropic phase transition, the difference between the free energy densities of nematic and isotropic phase can be expressed in powers of invariants of the tensor order parameter $\underline{Q} = \underline{Q}(\mathbf{r}, t)$

$$f = \frac{1}{2}A(T - T^{*})\,\mathrm{tr}\,\underline{Q}^{2} - \frac{\sqrt{6}}{3}B\,\mathrm{tr}\,\underline{Q}^{3} + \frac{1}{4}C\left(\mathrm{tr}\,\underline{Q}^{2}\right)^{2} + \ldots + \frac{1}{2}L\,\nabla\underline{Q} \vdots \nabla\underline{Q}, \tag{4}$$

where $A, B, C, \ldots,$ and L are temperature-independent constants and T^{*} is the supercooling temperature. The anchoring energy is frequently described by

$$F_S = -\frac{1}{2}G\,\mathrm{tr}\,(\underline{Q} - \underline{Q}_S)^2, \tag{5}$$

where G is the anchoring strength and $\underline{Q}_S$ is the preferred value of the order parameter at the nematic-substrate interface. It is convenient to express the order parameter (a symmetric, traceless second rank tensor) in an appropriate base. If the equilibrium structure is expected to be uniaxial and homeotropic, the five base tensors read[13]

$$\begin{aligned} \underline{T}_0 &= \frac{1}{\sqrt{6}}\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}, \underline{T}_1 = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \underline{T}_{-1} = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \\ \underline{T}_2 &= \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \underline{T}_{-2} = \frac{1}{\sqrt{2}}\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}. \end{aligned} \tag{6}$$

The component of the ordering along $\underline{T}_0$, Q_0, and the usual scalar order parameter, Q, are related by $Q_0 = \sqrt{\frac{3}{2}}Q$, its $\underline{T}_{\pm 1}$ counterparts describe the degree of biaxiality of the ordering and the orientation of the secondary direction of alignment, and the projections of $\underline{Q}$ onto $\underline{T}_{\pm 2}$ are related to the orientation of the director. For homeotropic, uniaxial equilibrium structure in planar geometry, $Q_{\pm 1}(\mathbf{r}) = Q_{\pm 2}(\mathbf{r}) = 0$ and $Q_0(\mathbf{r}) \neq 0$.

In case of order-inducing interaction between the liquid crystal and the confining cavity, the high temperature phase is characterized by the partially ordered boundary layer. As an illustration, the nematic structures between two parallel planes favoring homeotropic ordering are shown in Figure 1. The transition from the low temperature nematic phase to the high temperature weak paranematic phase with approximately exponential profile of the scalar order parameter takes place via an intermediate strong paranematic phase, characterized by nematic-like degree of order in boundary layer. In principle, both phase transitions (i.e., nematic/strong paranematic phase and strong paranematic/weak paranematic phase) are first order.

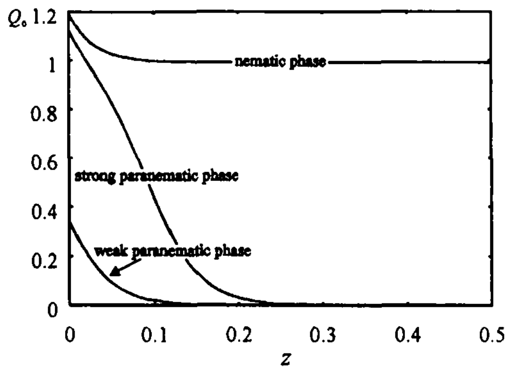

FIGURE 1 Nematic and the two paranematic phases in planar homeotropic geometry for $F_S = -\sqrt{6}\,G\,\mathbf{e}_z\cdot \underline{Q}\cdot \mathbf{e}_z/2$ with $G = 0.0018B^3d/C^2$, where d is the thickness of the sample. The (rescaled) scalar order parameter, Q_0, is given in units of $3C/2B$. The correlation length $\sqrt{9LC/2B^2} = 0.032d$ and the dimensionless distance from the left substrate, x, are expressed in units of d.

Interpretation of experimental data

The cylindrical cavities of Anopore membranes with almost 40% porosity are very suitable host material for nematic liquid crystals[12] mostly because of controllability of the anchoring characteristics of their walls. In a recent DNMR study of orientational wetting by Crawford et al.,[14] the 0.2 μm pores in these membranes were treated with aliphatic acids C_nH_{2n+1}-COOH and permeated with the α-deuterated 5CB. In a cylindrical cavity with radius R much larger than nematic correlation length, the line splitting frequency is given by

$$\langle \delta\nu \rangle = \frac{\kappa\Gamma}{R}\,\delta\nu_0. \tag{7}$$

The geometrical factor κ is related to the relative orientation of nematic director and magnetic field.

In Figure 2, the quadrupole splitting in the isotropic phase is shown as a function of carbon number n, the length of the surfactant tail. As n decreases from 15 to 7, $\langle \delta\nu \rangle$ decreases as well, dropping practically to 0 at $n = 7$. For even smaller n, the reverse trend occurs. Since $\langle \delta\nu \rangle$ is directly proportional to the surface order parameter $Q(0)$, it is evident that for chain length $n = 7$ the molecular coupling and anchoring are very weak.

More information is obtained by monitoring $\langle \delta\nu \rangle$ as a function of temperature for a wide variety of n's. These data are presented in Figure 3. The temperature dependencies of splittings for $n = 5, 6$ and 20 are weak, whereas for $n = 9$ to $n = 18$ there is a pronounced critical increase of $\langle \delta\nu \rangle$ with a peak at $n = 17$. By plotting the value of $\langle \delta\nu \rangle$ on a logarithmic scale, one can determine whether the wetting is characterized as complete or partial: within Landau-de Gennes theory, Γ exhibits a logarithmic singularity on approaching the nematic-isotropic transition. This test proves that even the most critical case, $n = 17$, does not

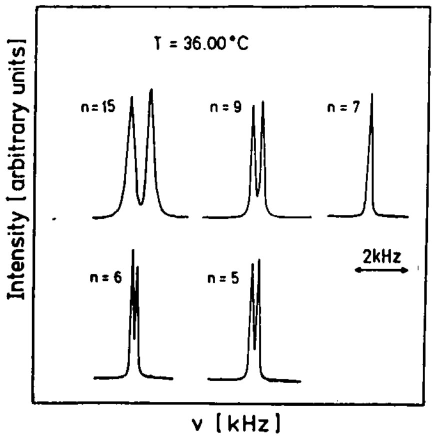

FIGURE 2 DNMR line shapes of isotropic 5CB in Anopore membranes treated C_nH_{2n+1}-COOH for $n = 5, 6, 7, 9$, and 15. Note that the line splitting vanishes for $n = 7$.

exhibit a truly divergent behavior. To stress the difference between the cases $n = 5, 6$ and 20 (which we declare as partial wetting), the behavior of the adsorption parameter Γ for $n = 9 - 18$ is referred to as *quasicomplete wetting*.

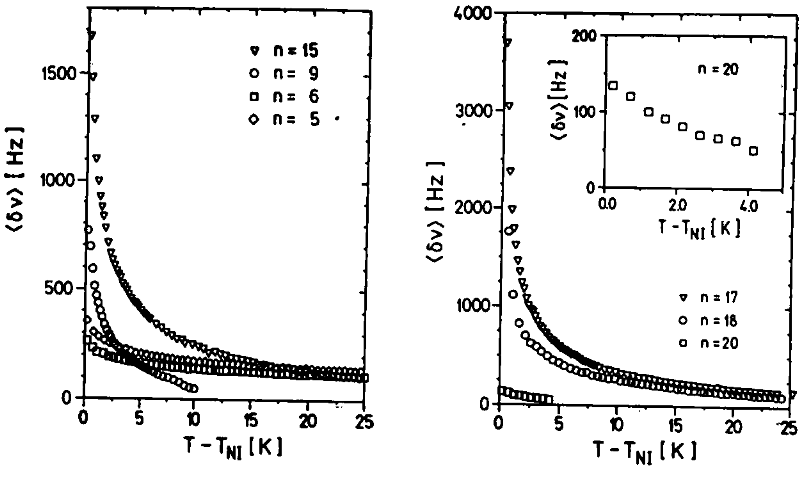

FIGURE 3 The line splitting frequency as a function of temperature for $n \leq 15$ (left) and $n \geq 17$ (right). $n = 5, 6$ and 20: partial wetting regime; $n = 9 - 18$: quasicomplete wetting.

By a quantitative analysis of these data, based on Landau-de Gennes theory, the values of the parameters of the nematic-substrate coupling can be obtained. The temperature dependence of the nematic order parameter at the surface, $Q(0)$, is presented in Figure 4. The data and the theoretical fit of $Q(0, T)$ show a strong critical increase on approaching the nematic-isotropic transition temperature. However, even for $n = 17$ the surface order parameter only approaches 0.13 and therefore it does not reach the nematic value (~ 0.3),

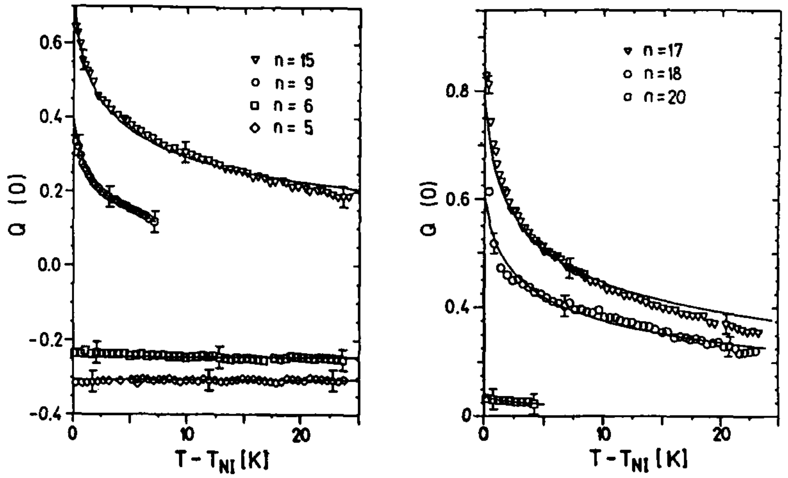

FIGURE 4 The temperature dependence of the nematic order parameter at the surface, $Q(0)$, for $n \leq 15$ (left) and $n \geq 17$ (right). Solid line: theoretical fit.

which could assure complete wetting regime.

Using these fits, the preferred degree of order and the surface coupling strength G can be determined. The values of the parameter Q_S are plotted in Figure 5, which clearly shows that the maximal ordering effect of the surfactant occurs for $n = 17$. The ordering power of the surfactant quickly falls off at $n = 18$ and reenter the partial wetting regime. The value of the coupling constant G is — within the experimental error — the same $\sim 7 \times 10^{-4}$ J/m^2 for all $n > 7$, whereas for short carbon tails ($n = 5$ and 6) it is nearly one order of magnitude larger, i.e., $\sim 6 \times 10^{-3}$ J/m^2. These large values of G ensure a non-critical behavior of $Q(0)$.

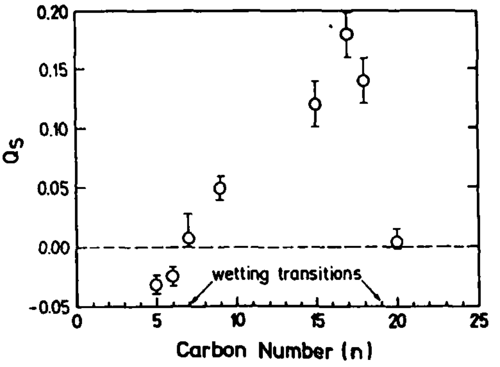

FIGURE 5 The preferred degree of order at the surface, Q_S, as a function of surfactant chain length.

The first wetting transition (at $n = 7 - 9$) is a consequence of the change in the preferred anchoring direction caused by an increase in the steric interactions with increasing chain length. At the same time, the direct ordering power of the surfactant layer, which stimulates homeotropic achoring, is increasing. This trend does not go beyond $n = 18$, where the second transition to weakly ordered paranematic occurs. This could be interpreted as an ordering transition in the surfactant layer, when the chain length surpasses a critical value.

FLUCTUATIONS IN PARANEMATIC LAYER

The collective excitations in the liquid crystalline phase represent an important aspect of its dynamics. In particular, they could be responsible for experimentally observed slow processes in partially ordered microconfined systems. In order to broaden the understanding of these phenomena, the tensor order parameter fluctuations in a nematic liquid crystal between two order-inducing plates, parallel to the plane xy and located at $z = 0$ and $z = 1$ (the coordinates being given in units of d, the distance between the plates), are analyzed within the framework of Landau-de Gennes theory. If the hydrodynamic degrees of freedom are adiabatically eliminated, the equation of motion of the tensor order parameter can be expressed in dimensionless form[15,16]

$$\tau_a \frac{\partial \underline{Q}}{\partial t} = -\theta\, \underline{Q} + 3\sqrt{6}\, \underline{Q}^2 - 2\underline{Q}\, \mathrm{tr}\, \underline{Q}^2 + \xi^2 \nabla^2 \underline{Q}, \tag{8}$$

where τ_a is phenomenological relaxation time, typically $\sim 10^{-7}$ s, $\theta = (T - T^*)/(T_{NI} - T^*)$ is the reduced temperature, and ξ is the dimensionless correlation length $\sqrt{9LC/2B^2d^2}$. (The rescaled order parameter $\underline{Q}$ is introduced in caption to Figure 1.)

The tensor order parameter is decomposed into static and fluctuating part $\underline{Q}(\mathbf{r}, t) \to \underline{Q}(\mathbf{r}) + \underline{A}(\mathbf{r}, t)$, which are represented in the tensorial base [Equation (6)]. The magnitude of the fluctuating ordering $\underline{A}(\mathbf{r}, t) = \sum_{i=-2}^{2} a_i(\mathbf{r}, t)\underline{T}_i$ is assumed to be small and the equation of motion is linearized with respect to $\underline{A}$. The ansatz for the normal modes $a_i(\mathbf{r}, t) = \exp[i(k_x x + k_y y)]\alpha_i(z)\exp(-\mu_i t)$ leads to the set of uncoupled equations of motion

$$\begin{aligned} &\xi^2 \alpha_0'' - \left[\theta - \tau_a \lambda_0 - 6Q_0 + 6Q_0^2\right]\alpha_0 = 0, \\ &\xi^2 \alpha_{\pm 1}'' - \left[\theta - \tau_a \lambda_{\pm 1} + 6Q_0 + 2Q_0^2\right]\alpha_{\pm 1} = 0, \\ &\xi^2 \alpha_{\pm 2}'' - \left[\theta - \tau_a \lambda_{\pm 2} - 3Q_0 + 2Q_0^2\right]\alpha_{\pm 2} = 0, \end{aligned} \tag{9}$$

[$Q_0 = Q_0(z)$ is the equilibrium (rescaled) scalar order parameter profile], which determine the reduced relaxation rates $\lambda_i = \mu_i - \xi^2(k_x^2 + k_y^2)$ of the fluctuations of order parameter, biaxiality, and director. The boundary conditions, corresponding to the surface interaction of the form $\propto \mathbf{e}_z \cdot \underline{Q} \cdot \mathbf{e}_z$, read $\alpha_i'(0) = \alpha_i'(1) = 0$. In Figure 6, the lowest three modes of each kind in the strong paranematic phase are presented.

The two slow modes are localized at the partially ordered boundary layer. The elementary order parameter mode obviously corresponds to fluctuations of the thickness of the boundary layer and the slowest director eigenmode represents fluctuations of alignment within

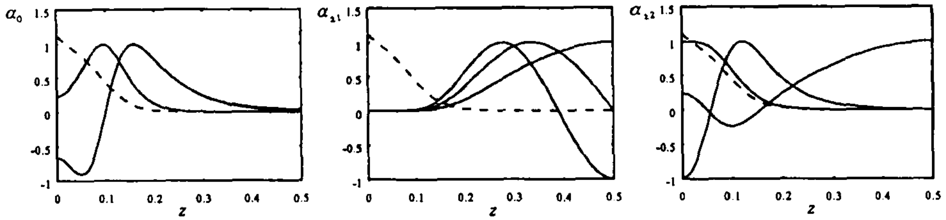

FIGURE 6 The lowest fluctuations' modes in the strong paranematic phase: order parameter modes (left), biaxiality modes (center), and director modes (right). The elementary order parameter mode corresponds to fluctuations of thickness of the boundary layer and the slowest director modes represent nematic director fluctuations in the boundary layer. The biaxiality modes are localized in the central, isotropic part of the sample. Dashed line: equilibrium (rescaled) scalar order parameter profile.

the partially ordered boundary layer.

The lower limits of the reduced relaxation rates of order parameter, biaxiality and director modes in vicinity of the critical temperature ($\theta = 1$) are shown in Figure 7. In nematic phase, the director modes are significantly slower than the other two types of excitations, but in both paranematic phases the slowest normal modes correspond to order parameter mode, i.e., fluctuations of thickness of partially ordered boundary layer.

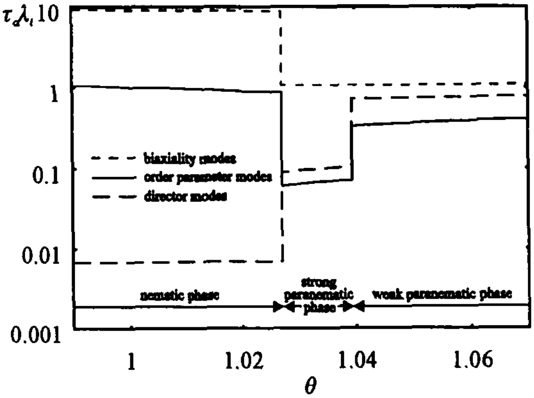

FIGURE 7 The lower limit of the spectra of the three types of fluctuations in planar geometry. In nematic phase, the lowest modes correspond to fluctuations of director, whereas in both paranematic phases the elementary order parameter mode is slowest than its director counterpart.

Thus, an order-inducing substrate can give rise to slow excitations in confined liquid crystals above the nematic-isotropic phase transition temperature. These modes correspond to fluctuations of thickness of the partially ordered boundary layer and to nematic director fluctuations within this region, respectively. Immediately above the transition temperature, the former can be significantly slower than the latter.

CONCLUSIONS

The usefulness of the deuterium NMR for investigations of microconfined liquid crystals is illustrated by a recent study the details of orientational wetting transitions at liquid crystal-surfactant interface. Above the nematic-isotropic transition, the quadrupolar splitting strongly depends on temperature and on the length of the surfactant tail. Its pretransitional behavior is well explained by wetting as predicted by Landau-de Gennes theory.
This theoretical approach is also used for an analysis of the fluctuations of the tensorial order parameter in partially ordered nematic system. In the high-temperature paranematic phase, the slowest modes correspond to fluctuations of thickness of the partially ordered boundary layer.

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