

Orientational transitions in a nematic confined by competing surfaces

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The effect of confinement on the orientational structure of a nematic liquid crystal model has been investigated by using a version of density-functional theory. We have focused on the case of a nematic confined by opposing flat surfaces, in slab geometry (slit pore), which favor planar molecular alignment (parallel to the surface) and homeotropic alignment (perpendicular to the surface), respectively. The spatial dependence of the tilt angle of the director with respect to the surface normal has been studied, as well as the tensorial order parameter describing the molecular order around the director. For a pore of given width, we find that, for weak surface fields, the alignment of the nematic director is perpendicular to the surface in a region next to the surface favoring homeotropic alignment, and parallel along the rest of the pore, with a sharp interface separating these regions (S phase). For strong surface fields, the director is distorted uniformly, the tilt angle exhibiting a linear dependence with the distance normal to the surface (L phase). Our calculations reveal the existence of a first-order transition between the two director configurations, which is driven by changes in the surface field strength, and also by changes in the pore width. In the latter case the transition occurs, for a given surface field, between the S phase for narrow pores and the L phase for wider pores. A link between the L-S transition and the anchoring transition observed for the semi-infinite case is proposed.

PACS numbers: 61.30.Cz, 61.30.Pq, 61.30.Hn

I. INTRODUCTION

In the last years there has been a vast theoretical effort to understand the properties of liquid crystals in bulk phases. However, it is only recently that the interfacial phenomena presented by these complex fluids have attracted an increasing interest. The ability to manipulate the direction of the preferred molecular alignment, the *director*, by coupling to surfaces, is a property with a great practical interest. For this reason, there is a new effort trying to describe this rich *surface phenomenology* in the liquid crystals. These studies have mainly used phenomenological Landau-de Gennes approaches and aimed to describe, with more or less success, different phenomena such as subsurface deformations [1–3] (ordering close to a surface), changes in the alignment of the director due to the interaction with a solid substrate [4], nematic-isotropic transition [5], wetting [6], etc. On the other hand, microscopic-type theories claim to provide a more precise description of these inhomogeneous problems since they take account of the structure at the molecular scale. In this framework, there is a recent literature describing attempts to answer such questions and it is supposed to provide more satisfactory theories in the interfacial phenomena. For example, by employing an Onsager-type theory R. van Roij *et al.* [7] investigated the problem of biaxiality and wetting for the Zwanzig model. P. I. C Teixeira has discussed, in a recent work [8], the existence of subsurface deformations for the case of a confined nematic phase by using a generalized van der Waals theory. In previous papers, also employing this last approach, we studied surface phenomena in the case of a nematic in contact with a single wall [9] as well as capillary effects in the case of a nematic in slab geometry with symmetric walls [10]. In Ref. [9] our attention was restricted to the study of a nematic in the presence of a solid interface. Model parameters were chosen such that the surface forced the molecules to lie perpendicular to the interface (homeotropic orientation) while in the nematic-isotropic interface the nematic director had a preference to lie parallel to the interface (planar orientation). In the model, surface parameters responsible for the order are the particle-wall interaction (ϵ_W) and the particle-particle interaction (ϵ_C) which played an important role in the interplay between anchoring and wetting transitions. A first-order anchoring transition between planar and homeotropic regimes was found; in a $\mu - T$ (chemical potential-temperature) representation (see Fig. 1) this transition appears as a line called anchoring line. This line approaches the nematic-isotropic transition line tangentially (at constant μ , eventually cuts this line at T_D), due to the existence of total wetting state at the coexistence. Later, the nematic phase was confined by symmetric walls, i.e both walls favored the same orientation (homeotropic) [10]. Then, also the same anchoring line appeared and it was found to be very insensitive to the pore width except with respect to the localization of T_D that is shifted by capillary effects. These findings have a bearing on the new phenomenology which appears when the liquid crystal is confined.

In the present paper, the theory is generalized to the case where the walls compete in molecular alignment. We believe that deeper insight into the surface-induced effects in liquid crystals can be obtained from a molecular approach

and, in this respect, density functional theory appears to be a powerful tool. The confinement of the nematic phase is imposed by the presence of a boundary made up of two opposing flat surfaces, one favoring homeotropic orientation and the other favoring planar orientation. In these conditions, a spatial variation in the tilt angle between the director and the surface normal is found. The textures adopted by the nematic director depend very dramatically on the values of both surface field and pore width. For the case of a strong surface field ϵ_W and a wide pore this dependence is linear with respect to the coordinate normal to the interfaces except close to the surfaces. This configuration satisfies surface boundary conditions but entails an elastic energy which is minimum for a linear tilt configuration. For weaker surface fields and/or narrow pores a different texture occurs where the tilt angle adopts a steplike configuration. Our calculations also reveal the existence of biaxial behavior close to the surface favoring planar orientation as well as in a small region associated to the change of orientation in the steplike configuration. These biaxialities are direct surface effects due to the existence of different interfaces.

In the next section we give a short account of the theoretical model used to describe the structure and thermodynamics of the confined liquid crystal. In section III we show the different tilt configurations that result and argue that the phase transition between the linear-tilt and the steplike-tilt configurations can be related with the anchoring transition found in the semi-infinite problem. We also discuss how biaxiality is affected by the pore width. We end up with a section of conclusions.

II. THE MODEL

The theoretical model is a standard generalized van der Waals theory based on a perturbative expansion, using a hard-sphere (HS) fluid as reference system [11]. Details on the physical basis of the model and how to obtain its solutions numerically can be found elsewhere [12,13]. Our starting point is the grand potential functional per unit system area A , $\Omega[\rho]/A$, whose functional minimum with respect to the one-particle distribution function, $\rho(\mathbf{r}, \hat{\Omega})$, which depends on both molecular positions \mathbf{r} and orientations $\hat{\Omega}$, gives the equilibrium structure of the interface. This function, $\rho(\mathbf{r}, \hat{\Omega}) \equiv \rho(z)f(z, \hat{\Omega})$, contains a mass distribution $\rho(z)$ and an angular distribution $f(z, \hat{\Omega})$. These quantities vary locally with the distance from $z = 0$ to $z = H$, H being the pore width. The expression for $\Omega[\rho]$, in a mean field approximation is,

$$\begin{aligned} \Omega[\rho] = & F_r[\rho] + \frac{1}{2} \int \int \int \int d\mathbf{r} d\mathbf{r}' d\hat{\Omega} d\hat{\Omega}' \rho(\mathbf{r}, \hat{\Omega}) \rho(\mathbf{r}', \hat{\Omega}') \\ & \times v(\mathbf{r} - \mathbf{r}', \hat{\Omega}, \hat{\Omega}') - \int \int d\mathbf{r} d\hat{\Omega} \rho(\mathbf{r}, \hat{\Omega}) [\mu - v_W(\mathbf{r}, \hat{\Omega})], \end{aligned} \quad (1)$$

where μ is the chemical potential and

$$F_r[\rho] = \int d\mathbf{r} f_{hs}(\rho(\mathbf{r})) + k_B T \int d\mathbf{r} \rho(\mathbf{r}) \langle \ln(4\pi f(z, \hat{\Omega})) \rangle$$

is the reference system free energy. In the above expression $f_{hs}(\rho(\mathbf{r}))$ is the hard-sphere free energy density of a uniform fluid with a density equal to the local density at \mathbf{r} and ' $\langle \dots \rangle$ ' is an angular average. The attractive potential v contains anisotropic (dispersion) forces driving the liquid-crystalline behavior of the model material:

$$v(\mathbf{r}, \hat{\Omega}, \hat{\Omega}') = v_A(r) + v_B(r) P_2(\hat{\Omega} \cdot \hat{\Omega}') + v_C(r) \left[P_2(\hat{\Omega} \cdot \hat{\mathbf{r}}) + P_2(\hat{\Omega}' \cdot \hat{\mathbf{r}}) \right], \quad (2)$$

where $\hat{\mathbf{r}} = \mathbf{r}/r$, and $v_A(r)$, $v_B(r)$, $v_C(r)$ are functions of the intermolecular center-of-mass distance r . Note that this potential is adequate to model uniaxial molecules with top-bottom symmetry. In this work we choose them to have a simple Yukawa form, i.e. $v_i(r) = -\epsilon_i \exp(-\lambda_i(r - \sigma))/r$ for $r > \sigma$, and $v_i(r) = 0$ otherwise, where σ is the diameter of a hard sphere.

The walls are modeled via the following potentials:

$$v_W^1(z, \theta) = -\epsilon_W e^{-\lambda_W(z-\sigma)} P_2(\cos \theta) \quad (\text{left wall, } z = 0) \quad (3)$$

which favors homeotropic anchoring, and

$$v_W^2(z, \theta) = \epsilon_W e^{-\lambda_W(-(z-H)-\sigma)} P_2(\cos \theta) \quad (\text{right wall, } z = H) \quad (4)$$

which favors planar alignment. The parameter ϵ_W is the surface strength of the walls and plays an important role in anchoring phenomena.

In order to describe the orientational structure of the fluid a tensorial order parameter is defined as,

$$Q_{\alpha\beta} = \int d\hat{\Omega} f(z, \hat{\Omega}) \left(\frac{3\hat{\Omega}_\alpha\hat{\Omega}_\beta - \delta_{\alpha\beta}}{2} \right) \quad (5)$$

where $\delta_{\alpha\beta}$ is the Kronecker symbol and $\hat{\Omega}_\alpha$ is the α -component of $\hat{\Omega}$. This quantity is a traceless symmetric tensor with eigenvalues $\lambda_1 \geq \lambda_2 \geq \lambda_3$. In this description, the isotropic state is defined by the condition $\lambda_1 = \lambda_2 = \lambda_3 = 0$. Uniaxial states occur when there is a twofold degenerated eigenvalue and then two cases can be distinguished: uniaxial nematic state ($\lambda_1 > \lambda_2 = \lambda_3$) and random planar ($\lambda_1 = \lambda_2 > \lambda_3$). In the first case, the molecules align preferently along the director, defined as the eigenvector corresponding to the largest eigenvalue (the uniaxial order parameter $U \equiv \lambda_1$). In the second case, the molecular orientations are uniformly distributed on a plane perpendicular to the eigenvector corresponding to the lowest eigenvalue.

For the case of non-degenerated eigenvalues, we can define the uniaxial (U) and biaxial (B) order parameters in terms of the eigenvalues of this tensor. The former is defined, as before, as the largest eigenvalue of the order parameter tensor (λ_1) and the corresponding eigenvector is the local director of the fluid. The biaxial parameter is proportional to the difference of the two smallest eigenvalues. This quantity gives information of the amount of the orientational order on the plane perpendicular to the director. In this way, a secondary director can be defined as the eigenvector corresponding to the eigenvalue λ_2 . By the symmetry of the problem, we have focused in the case where the director varies in the xz plane and is invariant with respect to a reflexion $y \rightarrow -y$. In these conditions, the director is characterized by the tilt angle ψ , defined as the angle formed between the director and the z axis. By convention, we define $B = \pm 2(\lambda_2 - \lambda_3)/3$, with $B > 0$ if the secondary director is on the xz plane and $B < 0$ if it is along the y axis.

For numerical reason, it is convenient to obtain the orientation distribution of the molecules referred to a laboratory reference system, described by three order parameters,

$$\eta(z) = \int d\phi \sin \theta d\theta f(z, \hat{\Omega}) P_2(\cos \theta) \quad (6)$$

$$\nu(z) = \int d\phi \sin \theta d\theta f(z, \hat{\Omega}) \sin 2\theta \cos \phi \quad (7)$$

$$\sigma(z) = \int d\phi \sin \theta d\theta f(z, \hat{\Omega}) \sin^2 \theta \cos 2\phi \quad (8)$$

These independent parameters can be related to the set $\{\psi, U, B\}$ by the following expressions,

$$\tan \psi(z) = \frac{\nu(z)}{\eta(z) - \sigma(z)/2 + \sqrt{[\eta(z) - \sigma(z)/2]^2 + \nu(z)^2}} \quad (9)$$

$$U(z) = \frac{1}{4} \left(\eta(z) + \frac{3}{2}\sigma(z) + 3\sqrt{[\eta(z) - (1/2)\sigma(z)]^2 + \nu(z)^2} \right) \quad (10)$$

$$B(z) = \frac{1}{2} \left(\eta(z) + \frac{3}{2}\sigma(z) - \sqrt{[\eta(z) - (1/2)\sigma(z)]^2 + \nu(z)^2} \right). \quad (11)$$

Numerical values for the potential parameters were taken as $\epsilon_A = 1$ (which sets the temperature scale), $\epsilon_B/\epsilon_A = 0.847$ and $\epsilon_C/\epsilon_A = 0.75$. The range parameters λ_i are set, in units of σ (throughout we choose this unit to set the length scale), to $\lambda_i = 2, 4, 1.75$, $i = A, B, C$ respectively, and $\lambda_W = 1$. The model predicts a bulk phase diagram with vapor, isotropic liquid and nematic liquid coexisting at a triple point temperature T_{NIV} [11].

III. RESULTS

Confinement of simple liquids generally brings about capillary effects and associated capillary condensation phenomena whereby condensation occurs below the saturation point in bulk, as measured for example by the chemical potential. Similar phenomena must occur in nematic liquid crystals but with additional complicating factors due to the orientational order induced by the confining surfaces.

In the following we use the chemical potential μ as the external thermodynamic potential, in addition to the temperature T . Capillary condensation of the nematic from the isotropic phase occurs when, at fixed μ , the temperature $T_{NI}(H)$ at which the pore becomes filled with an oriented (nematic) phase is shifted with respect to the corresponding

temperature in bulk $T_{NI}(\infty)$. We are thus seeking a non-zero value of $\Delta T \equiv T_{NI}(H) - T_{NI}(\infty)$. Our calculations reveal that, contrary to the case of symmetric walls [10] and, for large pore widths (H larger than 20σ), no significant capillary effect exists, i.e. we find that the NI transition occurs at the same temperatures as in the bulk state. However, there are indications that for smaller pore widths this situation is not true longer (this aspect is being studied currently). Note though that condensation lines involving confined vapor states are expected to be affected by confinement; since these lines are not central to our argument we do not give any results in the following.

Fig. 1 shows the bulk phase diagram, with vapor (V), isotropic (I) and nematic (N) phases and their corresponding phase transitions. We have superimposed the anchoring line, representing surface phase transitions between states with different director alignment for the semi-infinite problem (i.e. only one surface, inducing homeotropic alignment); these results have been obtained with a surface field $\epsilon_W = 0.53$, for larger values this transition curve tends to approach the coexistence lines reducing then the region of planar states [9].

Now, we have calculated equilibrium states but with the sample confined between two opposing walls separated a distance H . There is a molecular ordering field due to the surfaces through the potential parameter ϵ_W . If the surface field strength is sufficiently high, one expects the director to adopt the configuration which satisfies the orientation favored by each surface, at least approximately. However, this necessarily demands that the director becomes distorted within the pore which entails a free energy cost due to the elastic contribution. In fact, the distribution of this inhomogeneity along the pore is found to depend sensitively on the values of pore width and surface field strength, and is expected to also depend on the thermodynamic parameters μ and T .

Competition between these two energies results in the existence of two tilt configurations: L, where the tilt angle rotates uniformly along the pore and the resulting tilt-angle profile is linear in z ; S, where the tilt angle adopts a step-like configuration, being constant throughout the sample except in a narrow region close to the $z = 0$ surface where a crossover exists from 0° (homeotropic) to 90° (planar).

Fig. 2 shows an L phase for $H = 20\sigma$, $\epsilon_W = 0.7$ and for thermodynamic conditions of temperature and chemical potential where, in the semi-infinite case, the nematic is clearly in the homeotropic state ($\mu = -3.7$, $T = 0.57$). In the middle of the pore the tilt profile is almost a linear function of z , approaching smoothly the walls to their favored values.

In the Fig. 3 the density, the uniaxial and biaxial order parameter profiles are plotted. The profiles present a smooth behavior, reaching a clear plateau in the middle of the pore with values close to the bulk values. The vanishing value of B in regions far from the interfaces is consistent with the uniaxial nature of the fluid particles. Close to walls the profile behaves differently depending on the favored orientation. Around the $z = 0$ surface the U order parameter increases due to the strong surface interaction (despite of a decay in density). However, these deformations do not induce biaxiality (i.e. $B = 0$) due to the smooth character of the tilt profile along the pore. On the other hand, near the $z = H$ surface, where the tilt angle is 90° , the U order parameter gets lower values and $B < 0$, that reflects the orientation of the molecules are mainly distributed on the xy plane, being the x axis the in-plane preferred direction. The decrease of the amount of order is due to surface potential that promotes a random planar distribution.

If the surface field strength is reduced the director tilt configuration changes over to a step, i.e. a S phase. Here the tilt angle is uniform and equal to 90° except in a narrow homeotropic region close to the homeotropic wall (Fig. 4). In general, this homeotropic region increases with the wall-particle potential range and with the strength of the surface field, so for the case of $\epsilon_W = 0$ one recover the configuration which corresponds to a nematic-hard walls interfaces (planar throughout the pore). Note that the S phase is spatially asymmetric, the tilt orientation being different from planar only in a small region close to the homeotropic wall. In fact, a corresponding S phase where the tilt were in a homeotropic configuration except in a very small region close to the planar wall is not observed in our calculations because of the effect due to the ordering field coming through the potential parameter ϵ_C . This field promotes molecular configurations where the director lies along a direction either perpendicular or parallel to the direction of inhomogeneity, depending on the sign of ϵ_C ($\epsilon_C > 0$ or $\epsilon_C < 0$, respectively). In our case $\epsilon_C > 0$, which means that the preferred director orientation is planar except in the region, close to $z = 0$, where the effect of the wall promoting homeotropic alignment is more pronounced.

In the figure 5 we plot the density, uniaxial and biaxial order parameters profiles in the S phase obtained with $\epsilon_W = 0.30$. Again the profiles only deviate from the bulk values close to the surfaces. The deviations around $z = H$ has the same origin that in the L phase. However, close to $z = 0$ this behavior has different nature. An analysis of the order parameteres profiles reveals that the system goes *smoothly* from an homeotropic to a planar configuration via a random planar state in the xz plane. This point (z_1 at fig. 5) corresponds to the jump of the tilt (origin of the step function profile). This mechanism is reponsible of the decay of the order and the biaxial behavior around this region. In fact, the existence of a crossover between homeotropic configuration and a planar configuration is closely linked to the capability of the fluid to have biaxial behavior in a small spatial range between both anchoring states. So, the roles that the z and x axes play as the local director and secondary director, respectively, for $0 < z < z_1$ are exchanged at $z = z_1$. However, in order to make this mechanism feasible a dramatic depletion on the amount of order is needed. Moreover, the secondary director changes its alignment from the z axis to the y axis as z is increased (i.e.

B changes its sign), before that biaxiality virtually disappears in the middle of the pore. Biaxiality directly induced by the breaking of symmetry associated with the presence of the interfaces and, in the case of a free interface with planar director alignment, has been observed in simulations [14].

In order to study in more detail the dependence of the nematic ordering on the pore width, we have calculated uniaxial order and biaxiality profiles for different values of H and for $\epsilon_W = 0.7$ (Fig. 6). For pore widths $H = 20, 30$ and 40 , for which the L phase is the stable phase, the profiles exhibit inhomogeneity regions close to the surface favoring planar alignment, being almost constant in the rest of the pore. Note that biaxiality occurs only where the tilt angle is significantly close to 90° . An interesting feature is that the order parameter profiles converge around to $z = 0$ (resp. $z = H$) to the profiles obtained for the $z = 0$ surface against a nematic in a homeotropic configuration (resp. the $z = H$ surface against a nematic in a planar configuration). Furthermore, such semi-infinite profiles are the equilibrium ones for these values of ϵ_W , μ and T . On the other hand, for $H = 7.5$, the stable phase is the S phase, and additional regions of inhomogeneity (and biaxiality) develop in the neighbourhood of the $z = 0$ surface.

The transition between the L and S phases involves a finite free-energy barrier, implying the existence of a thermodynamic first-order phase transition between the two phases. This is revealed by computing the relevant free energy for confined systems, i.e. the grand potential, as a function of the potential parameters and/or the thermodynamic parameters μ and T . In our case we have chosen to fix the latter and vary ϵ_W . Fig. 7 shows the behavior of the grand potential as a function of ϵ_W . Two branches, corresponding to the L and S phases, are shown. The point where the branches cross, ϵ_W^c , gives the transition point. Note the existence of metastable branches in both phases, which indicates the first-order nature of the phase transition. Tilt angle profiles along the pore corresponding to the coexisting L and S phases at $\epsilon_W = \epsilon_W^c = 0.554$ for $H = 20\sigma$ are shown in Fig. 8. Note that the linear behavior in the L phase has a smaller range and its slope is also less than in the case presented in Fig. 2. On the other hand, the step in the S phase is located further from the $z = 0$ surface than in the case presented in Fig. 4.

As in any analysis of metastable states, some caution has to be exercised in analysing the occurrence of the different phases. In particular, the initial conditions required in our numerical minimisation scheme have to be chosen carefully. For example, the reality of the metastable L branch is shown by performing the following analysis: i) Equilibrium S states at low ϵ_W are obtained by conducting minimisation processes starting from linear and step-like profiles; these processes give the same equilibrium S states. ii) For higher, increasing values of ϵ_W , using step-like profiles or linear profiles as starting conditions give different final states beyond the transition point ϵ_W^c , the final L states having lower grand potential energies than the final S states. This is the region of metastability of the S phase. Proceeding in the same way but from the L branch at high ϵ_W and decreasing ϵ_W provides the metastability region for the L phase.

Fig. 9 shows the global phase diagram with respect to the parameters ϵ_W and H and for thermodynamic conditions $T = 0.57$ and $\mu = -3.7$. The line indicates the phase transition separating L and S phases. As the pore width is increased, the region of stability of the L phase is enlarged since the elastic energy associated with the deformation of the director along the pore (proportional to the integrated squared gradient of the tilt profile) decreases as opposed to the case of the S phase, for which this energy is essentially constant and seems to approach asymptotically to the value of $\epsilon_W = \epsilon_W^a$, at which the anchoring transition occurs for the semi-infinite case of the nematic against the $z = 0$ wall. For narrow pores, we find a quick increase of ϵ_W^c as the pore width is reduced, indicating that, in order for the L phase to become stable, a large surface field is required to compensate for the large elastic energy associated with a high tilt angle gradient. An interesting issue, which we have been unable to address due to technical reasons, is whether this first order phase transition may end up at a critical point as the pore width is reduced or even become second order through the appearance of a tricritical point.

An analysis of the results quoted above shows that there is a relationship between the L-S transition and the anchoring transition observed in the semi-infinite problem. Let us consider the case of $H \gg \sigma$. We have observed that the density and order parameter profiles deviate from the bulk values only in regions around of the surfaces, being the ranges of the inhomogeneities of the order of the molecular interactions. This feature is not surprising for the S phase, since in the middle of the pore the nematic is in a non-distorted tilt configuration (i.e. planar), so its tilt profile can be understood as two uncorrelated semi-infinite profiles linked via the bulk planar state. However, this fact is also true for the L phase even when the tilt distortion is propagated through the pore (see discussion for the Fig. 6 above). This is the scenario that the phenomenological theory implicitly assumes: the excess free energy $\Delta\Omega = \Omega + pV$ (where p is the bulk pressure and $V = AH$ is the volumen of the sample) can be split in two terms, an elastic term $\Delta\Omega^e$ that comes from the distortions of the director field in a macroscopic scale, and surface terms, $\Delta\Omega_{z=0}^{surf}$ and $\Delta\Omega_{z=H}^{surf}$, that include the effect of the density and order parameter inhomogeneities in a microscopic scale close to the boundaries. The elastic term is given in terms of the elastic constants K_1 , K_2 , K_3 and K_{24} by the Oseen-Frank free energy [15,16] as:

$$\Delta\Omega^e = \frac{K_1}{2}(\nabla \cdot \mathbf{n})^2 + \frac{K_2}{2}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{K_3}{2}(\mathbf{n} \times \nabla \times \mathbf{n})^2 - (K_2 + K_{24})\nabla \cdot (\mathbf{n}\nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}) \quad (12)$$

where $\mathbf{n}(\mathbf{r})$ is the director field. Note that the splay-bend term is not included since $K_{13} = 0$ in bulk [17]. If we

restrict our study to the cases in which there is translational symmetry in the xy plane and the director is assumed to be in the xz plane (there is no twist), then $\mathbf{n}(\mathbf{r}) = (\cos(\psi(z)), 0, \sin(\psi(z)))$. In our model of uniaxial molecules with top-bottom symmetry, $K_1 = K_3 = -2\pi\rho_b^2 U_b^2 \int_0^\infty dr r^4 v_B(r)$, where ρ_b and U_b are the bulk density and uniaxial order parameter, respectively [19,17]. So, the total excess free energy is given by:

$$\frac{\Delta\Omega}{A} = \frac{\Delta\Omega_{z=0}^{surf}(\psi(0), \psi'(0))}{A} + \frac{\Delta\Omega_{z=H}^{surf}(\psi(H), \psi'(H))}{A} + \frac{K_3}{2} \int_0^H dz (\psi'(z))^2 \quad (13)$$

where $\psi' \equiv d\psi/dz$. Note that the dependence of the surface terms on the contact values at the boundaries of the tilt angle and its derivative respect to z [18]. Functional minimization of (13) leads to an equilibrium tilt linear profile $\psi' = \text{constant} = O(1/H)$. The exact expression for the profile will depend on the surface terms of the free energy, so it is needed some information about them. The values of $\Delta\Omega_{z=0}^{surf}$ can be obtained microscopically from the excess free energy corresponding to a case of the wall against a distorted nematic whose tilt profile goes asymptotically as $\psi(0) + \psi'(0)z$ for $\sigma \ll z \ll H$ (this discussion is analogous for the $z = H$ case). Since $\psi'(0) \ll 1/\sigma$ the effect of the distortion far from the $z = 0$ surface will be a perturbation respect to the case $\psi' = 0$, that corresponds to the semi-infinite case studied in [9]. In this Reference it was shown that if the wall promotes homeotropic anchoring, depending on the ratio between ϵ_W and ϵ_C two local minima can appear for $\psi = 0^\circ$ and $\psi = 90^\circ$ with a free energy barrier between them. However, if the surface favors a planar anchoring only a global minimum at $\psi = 90^\circ$ can exist. We can expand now the surface free energy in a series of both ψ and ψ' around $(\psi, \psi') = (0^\circ, 0)$ and $(90^\circ, 0)$. The special symmetry of our problem (rotational invariance around the z axis and the top-bottom symmetry of the molecules) implies that the linear term in ψ' vanishes. From this analysis we can conclude that for $H \gg \sigma$ two different states can exist: a linear state that goes from a tilt close to 0° at $z = 0$ to a value close to 90° at $z = H$, and a state with non-distorted planar tilt through the pore, and that correspond to the L and S states we have found, respectively. Furthermore, by using this phenomenologic approach a first-order transition can be predicted close to the anchoring line, inside the homeotropic region. The equation (13), up to terms of the order of $O(1/H)$, is:

$$\frac{\Delta\Omega}{A} = \frac{\Delta\Omega_{z=0}^{surf}(\psi_0, 0)}{A} + \frac{\Delta\Omega_{z=H}^{surf}(\pi/2, 0)}{A} + \frac{K_3}{2H} \left(\frac{\pi}{2} - \psi_0\right)^2 \quad (14)$$

where $\psi_0 = 0$ or $\pi/2$ for the L and S states, respectively. The transition occurs for

$$H_t = \frac{\pi^2 K_3}{8 \left(\Delta\Omega_{z=0}^{surf}(\pi/2, 0) - \Delta\Omega_{z=0}^{surf}(0, 0) \right)} \quad (15)$$

which implies that $\Delta\Omega_{z=0}^{surf}(\pi/2, 0) > \Delta\Omega_{z=0}^{surf}(0, 0)$, i.e. the conditions should correspond to have an homeotropic configuration in the semi-infinite case, and the transition is first-order due to the free-energy barrier that exists between the two minima for the semi-infinite case. So, for $H > H_t$ an stable L configuration exists and for $H < H_t$ the S state is the stable one. From the Eq. (15) it is clear that $H_t \rightarrow \infty$ as the system approaches to the anchoring line (characterized by the condition $\Delta\Omega_{z=0}^{surf}(\pi/2, 0) = \Delta\Omega_{z=0}^{surf}(0, 0)$), i.e. the L-S transition occurs for infinitely wide pores and, consequently, the anchoring line can be understood as the limit of the L-S transition for $H \rightarrow \infty$.

Strictly speaking, the scenario presented above is only true for $H \gg \sigma$. However, our calculations reveal that the L-S transition observed by our Density Functional Theory (DFT) calculations is the continuation of the transition predicted for wide pores. First of all, the free energy of the S phase is expected to converge towards its limiting value given by equation (14) very fast, as it was observed in the symmetric walls case in [10]. For the L phase, we have compared the DFT results for $\epsilon_W = 0.7$ with the limiting expression given by the Eq. (14) (see Fig. 10). The values of μ and T are the same as in all our calculations, i.e. $\mu = -3.7$ and $T = 0.57$. For such conditions, $K_3 = 0.615$. On the other hand, calculations for the semi-infinite case show that the asymptotic value for $H \rightarrow \infty$ is given by $\Delta\Omega/AK_B T = 1.841$. It is clear that the values of $\Delta\Omega$ converge for relatively small values of H to the expression given by the phenomenologic theory, and in any case the behavior is qualitatively correct. From this analysis we conclude that the L-S transition is driven by the anchoring (surface) transition that occurs for the semi-infinite case of the nematic against the $z = 0$ surface.

IV. CONCLUSIONS

In this paper we have employed a well-tested generalised van der Waals theory to investigate the effect of confinement on the thermodynamics and the microscopic structure of a nematic liquid crystal. The presence of two confining

surfaces favoring opposite orientations of the nematic director makes the order parameter, which is a tensorial quantity, exhibit all of its richness, giving rise to capillary effects not present in simple, non-orientable fluids. The competing conditions at the surfaces imply a deformed state of the director inside the pore.

The main result of our study is that the system may adopt two possible states: one where the director changes orientation at an interface located close to the surface that favors homeotropic anchoring (depending on the wall-particle potential range), and one where the deformation takes place uniformly, giving rise to a basically linear tilt profile, with some degree of deformation close to the surfaces. The director may change from one configuration to another via a first-order phase transition. The interplay between these two phases may be understood in terms of the competition between the elastic energy associated with a deformed director state and the energy associated with the orienting surfaces. We have also shown that this transition is closely linked with the planar-homeotropic transition observed in the semi-infinite problem. In order to prove this aspect, a phenomenologic treatment has been employed. On the one hand, the theory shows how for big pores ($H \gg \sigma$) the L-S first order transition can occur at threshold value of the pore width H_t . On the other hand, the phenomenological approach also reveals that for $H \rightarrow \infty$ the L-S transition corresponds to the anchoring transition of the semi-infinite problem. We also conclude that the transition obtained by the DFT is the continuation to shorter scales of the transition predicted by the phenomenological theory, that in principle is only valid for much larger pore widths.

ACKNOWLEDGMENTS

I.R.P. would like to thank Prof. R. Netz for his hospitality at LMU, which helped to develop this work. This research was supported by grants No. PB97-0712 from DGICYT of Spain and No. FQM-205 from PAI of the Junta de Andalucía.

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FIG. 1. Phase diagram containing bulk phase transitions and the anchoring transition for the case $\epsilon_W = 0.53$ (they join at the temperature T_D). NI coexistence is denoted by the thick solid line. The dotted line is the anchoring line for the case of a nematic in the presence of a single surface which favors homeotropic orientation; this line divides the nematic phase into a region with homeotropic (\perp) and planar (\parallel) nematic states. The thin solid line corresponds to the bulk transitions involving the vapor phase.

FIG. 2. Tilt-angle profile for a confined nematic at $T = 0.57$ and $\mu = -3.7$ (L phase). Values for the surface field and pore width are $\epsilon_W = 0.7$ and $H = 20\sigma$, respectively.

FIG. 3. Density (ρ), uniaxial (U) and biaxial (B) order parameter profiles for the L phase. $\epsilon_W = 0.7$ and values of T and μ are given in text.

FIG. 4. Tilt-angle profile for a confined nematic with surface field $\epsilon_W = 0.30$ (S phase). The values of T , μ and H are the same as in Fig. 2.

FIG. 5. Density(ρ), uniaxial (U) and biaxial (B) order parameters profiles for the S phase. $\epsilon_W = 0.3$ and the values of T and μ are the same as in Fig. 2.

FIG. 6. Uniaxial (U) and biaxial (B) order parameter profiles for different pore widths and $\epsilon_W = 0.7$. The pore widths H are, from left to right: 7.5, 20, 30, and 40. The values of T and μ are the same as in Fig. 2.

FIG. 7. Thermodynamic grand potential as a function of the surface field ϵ_W for thermodynamic conditions and pore width as in Fig. 2. Branches corresponding to step-like (S) and linear (L) tilt-angle profiles are shown. The point at which these branches cross gives the transition point at $\epsilon_W^c = 0.554$. The values of T , μ , and H are the same as in Fig. 2.

FIG. 8. Tilt-angle profiles for L and S phases at coexistence corresponding to pore width $H = 20$ and critical value $\epsilon_W^c = 0.554$. The values of T and μ are the same as in Fig. 2.

FIG. 9. Phase diagram in the $\epsilon_W - H$ plane. The values of T and μ are the same as in Fig. 2.

FIG. 10. Comparison between the Density Functional Theory and the phenomenologic theory (expression in the text). The diamonds correspond to the excess free energy per area in units of $K_B T$ of a nematic confined by opposing walls in the L state with $T = 0.57$, $\mu = -3.7$ and $\epsilon_W = 0.7$, calculated by using the Density Functional approach. The solid line is the surface tension given by the phenomenologic theory given by the Eq. (14).



















