

Anchoring and nematic-isotropic transitions in a confined nematic phase

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 A363

(<http://iopscience.iop.org/0953-8984/12/8A/349>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:28

Please note that [terms and conditions apply](#).

Anchoring and nematic–isotropic transitions in a confined nematic phase

I Rodríguez-Ponce†, J M Romero-Enrique†, E Velasco‡, L Mederos§ and L F Rull†

† Departamento de Física Atómica, Molecular y Nuclear, Area de Física Teórica, Universidad de Sevilla, Apartado 1065, Sevilla 41080, Spain

‡ Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, Madrid E-28049, Spain

§ Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, Madrid E-28049, Spain

Received 29 September 1999

Abstract. We present a study of a simple model of a nematic liquid crystal confined between two walls in slab geometry (slit pore). A rich phenomenology, associated with capillary effects as well as orientational transitions, arises. In a previous paper (1999 *Phys. Rev. Lett.* **82** 2697) on the semi-infinite problem (a single wall) we found *anchoring transitions* whose existence depends on the values of the surface parameters and temperature. We discuss the persistence of this transition in the confined problem and the effects of the confinement on the nematic–isotropic transition.

There has been a great interest recently in the effects exhibited by a liquid crystal in contact with a solid surface. A considerable number of experimental results as well as simulation studies have shown a rich phenomenology in these systems: abrupt orientational changes [1, 2], wetting transitions [3], confinement effects [4] etc. Theoretical studies have treated these problems using different approaches: Landau-like theories [5, 6], lattice models [7], density functional theory [8, 9] etc. We consider that the surface-induced effects in liquid crystals can be treated more accurately by a molecular approach.

In a previous paper [9] we presented a theoretical study of a nematic in contact with a solid surface using a density-functional theory. Parameters of the model were chosen such that the nematic director at the isotropic–nematic interface had a preferred orientation parallel to the interface (*planar orientation*). We studied the behaviour of this fluid in the presence of a solid surface which forced the molecules to adopt a perpendicular arrangement with respect to the interface (*homeotropic orientation*). The surface parameters were found to play an important role in the interplay between the anchoring and wetting transitions in the nematic fluid, and we succeeded in giving a qualitative explanation for some experimental studies [11] which have shown the existence of *reentrant anchoring*.

In this paper we use the knowledge gained from our previous work, and consider the same model system of the liquid crystal, but confined between two parallel walls. Our aim is to achieve a more fundamental understanding of the influence of confinement on the anchoring mechanism and wetting properties. We report calculations of the average density and average order parameter and their dependence on the chemical potential for different temperatures.

Jumps in these isotherms reflect *anchoring transitions*, nematic–isotropic transitions as well as capillary condensation.

These are preliminary results obtained with a density-functional theory for the surface free energy in a local density approximation (LDA). This approximation limits the scope of our study though, as a starting point, it provides qualitative results in agreement with experimental observations. 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 [10]. 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 density 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 $f(z, \hat{\Omega})$, which vary locally with the perpendicular distance from the walls, z , from $z = 0$ to $z = L$, where L is the pore width. The expression for $\Omega[\rho]/A$ is given in [9]. The walls, located at $z = 0$ and $z = L$, interact with the fluid molecules via a simple Yukawa potential which contains an anisotropic part (see [9] for details). The orientation of the molecules is described by three order parameters, η , σ and ν . These parameters define the *tilt angle* ψ of the molecule, i.e. the angle that the director forms with the axis perpendicular to the interface:

$$\tan 2\psi = \frac{2\nu}{2\eta - \sigma}. \quad (1)$$

When $\eta \neq 0$, $\sigma = 0$ and $\nu = 0$ we have a homeotropic configuration, whereas $\eta \neq 0$, $\sigma \neq 0$ and $\nu = 0$ correspond to a planar configuration. The strengths of the wall interaction ϵ_W^1 and ϵ_W^2 are taken to be equal in magnitude and sign. Numerical values for the parameters are given in [9]. The model predicts a bulk phase diagram with vapour, isotropic liquid and nematic liquid coexisting at a triple point temperature T_{NIV} . The inhomogeneities arising from the surface interaction makes it convenient to define the average density and order parameter within the pore:

$$\bar{\rho} = \frac{1}{L} \int_0^L dz \rho(z) \quad \bar{\eta} = \frac{1}{L} \int_0^L dz \eta_I(z) \quad (2)$$

where $\eta_I(z)$ is the nematic order parameter η referred to the director reference system.

In our previous paper [9] we studied the competition between the surface parameter ϵ_W and the fluid parameter ϵ_C in establishing an equilibrium interfacial state. We considered the semi-infinite problem, i.e. a nematic fluid in contact with a solid substrate. A positive ϵ_C favours parallel director orientation at the free isotropic–nematic interface, whereas a positive ϵ_W favours (strong) homeotropic anchoring at the substrate. These competing effects result in the existence of an *anchoring line* which divides the bulk phase diagram into a region with homeotropic director orientation and a region with planar orientation [9]. The study of the adsorption profiles shows that there is a relation between the existence of total wetting at coexistence and the appearance of *reentrant anchoring* (at fixed density), in qualitative agreement with experimental results [11]. Orientational transitions close to coexistence have been observed by tilt-angle measurements on SiO substrate, which tend to exhibit complete or nearly complete wetting by the isotropic phase [14].

In our previous study we could relate the *anchoring line* to a *prewetting*-type line; along this line, a thick planar layer coexists with a thin homeotropic layer and, as nematic–isotropic coexistence is approached, the system eventually enters a regime of complete wetting. Our motivation in the present work was to obtain a deeper physical insight into this transition

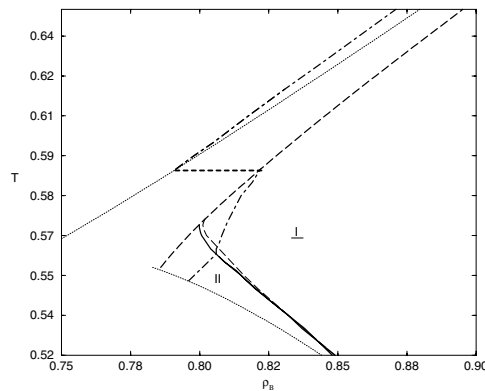


Figure 1. Nematic–isotropic and anchoring transitions for different pore widths as a function of the reservoir parameters. The dotted lines corresponds to the nematic–isotropic and nematic–vapour transitions in the bulk. The dashed line is the nematic–isotropic transition curve for $L = 40\sigma$ and the dot–dashed curve corresponds to the nematic–isotropic transition curve for $L = 20\sigma$. Anchoring lines are also shown. The solid line is the anchoring line for $L = 40\sigma$ and $L = 20\sigma$, where no differences are apparent.

by studying the confined problem since we believe that this geometry can provide a clearer description of the transition.

For the confined problem we have again chosen values for the parameters such that there is an anchoring transition in the semi-infinite problem. We have considered different values for the pore width. For the case $L = 40\sigma$ and symmetric walls ($\epsilon_w^1 = \epsilon_w^2 = 0.53$) we have studied the effect of confinement on the nematic–isotropic transition as well as on the anchoring line.

A convenient way to visualize phase equilibria is to plot the temperature against the density of the bulk fluid in equilibrium with the fluid-pore system, figure 1. This figure also shows the transitions corresponding to $L = 20\sigma$. The nematic–isotropic transition for $L = 40\sigma$ appears unaffected by the confinement. However, for the case $L = 20\sigma$, the corresponding transition presents a different shape in the diagram. The anchoring lines do not change in the confined system, at least for the pore widths considered. However, a genuine effect of confinement is that these lines do not approach the nematic–isotropic transition tangentially, as is the case in the single-wall problem. This is because, in a confined system, the regime of complete wetting is never approached and, as consequence, *reentrant anchoring* no longer occurs.

We now present the former analysis for the case of $L = 20\sigma$ in more detail. As shown in figure 1, a large deformation is observed in the nematic–isotropic curve. Although the pore is wide enough for the density and order-parameter profiles to level off to a constant value, the effects of confinement are more important than in the case of the wider pore. We have found it convenient to use the average density and order parameter to identify the transitions.

Several isotherms have been calculated. In figure 2 we plot the average density versus chemical potential for $T = 0.59$ (the triple point temperature in bulk is $T_{NIV} = 0.5522$; see [9] for a definition of temperature units). On increasing the chemical potential there appears a first jump between two branches. The branches correspond to the vapour and the isotropic liquid respectively. Each branch has metastable and stable regions separated by the transition at $\mu = -4.26$. A second transition appears at $\mu = -3.40$ which proceeds between two liquid-like states. The average order parameter shows that the branches correspond to an isotropic-like fluid and to a nematic-like fluid in a homeotropic configuration respectively. The jump for this transition is significantly smaller than that for the vapour–liquid-like transition.

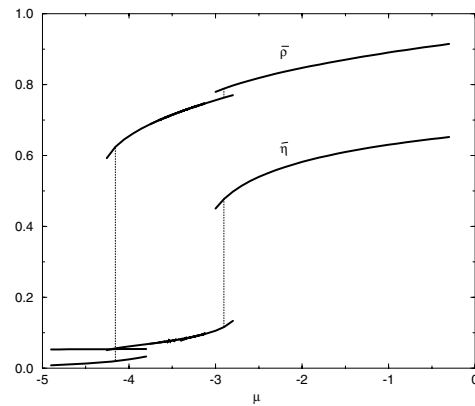


Figure 2. Average density and order parameter. They are calculated at $T = 0.59$ for a pore with $L = 20\sigma$. The dotted lines correspond to the transition points. Only some metastable points are shown.

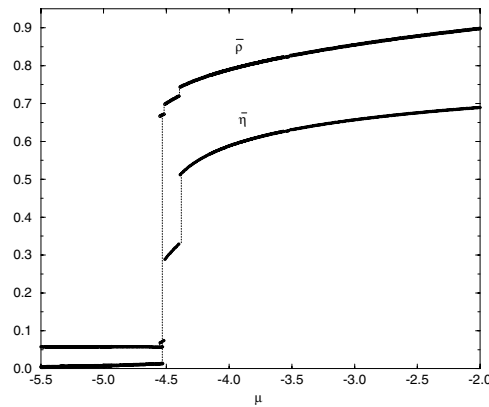


Figure 3. Average density and order parameter for a pore with $L = 20\sigma$ at $T = 0.553$. The dotted lines correspond to the transition points. The isotherm corresponds to a temperature just above the triple point in the bulk ($T_{NIV} = 0.5522$). Only some metastable points are shown.

Also, metastable regions are considerably shorter, indicating that this is a weak first-order transition. We note that $\mu - \mu_b = -0.01$, μ_b being the chemical potential of the bulk nematic–isotropic transition.

In figure 3 we plot the same quantities for the isotherm with $T = 0.553$. $\bar{\rho}$ exhibits three jumps at different values of the chemical potential. As chemical potential is increased, the first jump proceeds between vapour-like and liquid-like branches. At $\mu = -4.51$ both average density and order parameter exhibit another discontinuity, associated with isotropic-like and planar nematic-like phases. The difference in chemical potential with respect to the bulk transition is $\mu - \mu_b = 0.213$. This means that the sign of $\mu - \mu_b$ depends on temperature and not only on surface parameters, as is the case in Landau-like theories. For this pore width the discontinuity in the nematic–isotropic curve plotted in figure 1 also shows this effect in terms of bulk densities.

On further increasing the chemical potential a new transition between ordered states appears. While the jump in $\bar{\rho}$ is not very significant ($\Delta\bar{\rho} = 0.03$), that in $\bar{\eta}$ is considerable

($\Delta\bar{\eta} = 0.19$). The highly ordered state corresponds to a homeotropic configuration along the pore. This indicates that the system has undergone a first-order anchoring transition. Note that in the semi-infinite problem this transition in order parameter does not imply a discontinuity in density; by contrast, capillary effects associated with confinement involve also a jump in density.

In conclusion, using a theoretical model based on a density-functional approximation, we have presented adsorption isotherms corresponding to a slit pore for different values of the pore widths. These results reveal a capillary separation due to confinement but also the anchoring transition observed in the semi-infinite problem. The anchoring line is not affected by confinement, which suggests that, rather than having a direct relation to wetting, anchoring is a surface phenomenon. We conclude by saying that our model, which is probably the simplest realistic model for an inhomogeneous liquid crystal, provides useful insight into the orientational transitions and confinement phenomena in nematically ordered phases. Further work on these phenomena is in progress and will be reported elsewhere.

Acknowledgments

The authors would like to thank M M Telo da Gama, P Tarazona, A Robledo and finally J O Indekeu for useful discussions. This research was supported by grants No PB97-0712 and PB97-0004-C03-01/02 from DGESIC of Spain.

References

- [1] Palermo V, Biscarini F and Zanoni C 1998 *Phys. Rev. E* **57** 2519
- [2] Crawford G P, Ondris-Crawford R, Zumer S and Doane J W 1993 *Phys. Rev. Lett.* **70** 1838
- [3] Vandenbrouck F, Bardon S, Valignat M P and Cazabat A M 1998 *Phys. Rev. Lett.* **81** 610
- [4] Wall G D and Cleaver D J 1997 *Phys. Rev. E* **56** 4306
- [5] Quintana J and Robledo A 1998 *Physica A* **248** 28
- [6] Barbero G, Madhusudana N V and Oldano C 1989 *J. Physique* **50** 2263
- [7] Telo da Gama M M, Tarazona P, Allen M P and Evans R 1990 *Mol. Phys.* **71** 801
- [8] Teixeira P I C 1997 *Phys. Rev. E* **55** 2876
- [9] Rodríguez-Ponce I, Romero-Enrique J M, Velasco E, Mederos L and Rull L F 1999 *Phys. Rev. Lett.* **82** 2697
- [10] Telo da Gama M M 1984 *Mol. Phys.* **52** 585
Telo da Gama M M 1984 *Mol. Phys.* **52** 611
- [11] Ryschenkow G and Kleman J S 1976 *J. Chem. Phys.* **64** 404
- [12] Braun F N, Sluckin T J, Velasco E and Mederos L 1996 *Phys. Rev. E* **53** 706
- [13] Martínez Y, Velasco E, Somoza A M, Mederos L and Sluckin T J 1998 *J. Chem. Phys.* **108** 2583
- [14] van Sprang H A and Aartsen R G 1984 *J. Appl. Phys.* **56** 251