On the parallel-perpendicular transition for a nematic phase at a wall

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On the parallel–perpendicular transition
for a nematic phase at a wall

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We use an Onsager-level density functional theory to investigate the behaviour of the nematic phase in contact with a solid wall. The nematic consists of hard rigid rods having perfect uniform alignment and uniform spatial density. In the absence of any particle–wall interactions besides excluded-volume forces, we predict a director orientation parallel to the wall. We show that this preference for parallel alignment is due to the entropy associated with the larger volume available to the particles in their parallel orientation. An adsorption energy favouring normal alignment gives rise to a transition from a high temperature parallel orientation to a low temperature normal orientation. We derive expressions for the temperature of this transition, relating it explicitly to the wall adsorption energy, particle axial ratio, and nematic density. Effects such as layering near the wall and imperfect nematic order are argued not to be necessary for the existence of this transition.

1. Introduction

The behaviour of a nematic liquid crystal in contact with a solid wall is of interest from many points of view [1]. It is of technological importance because the nematics used in optical display devices are confined as thin films between glass plates. The folklore of liquid crystal physics includes specific techniques for imposing the alignment of a nematic by putting it in contact with a treated wall, and many experimental studies have been devoted to investigating associated phenomena. In particular, Känel et al. [2] have studied the transition between parallel and perpendicular orientations of the director which occurs as the temperature is lowered.

Theorists have also attempted to describe the behaviour of nematics at walls. Berreman [3] and Wolff et al. [4] have formulated continuum level theories of the smectic at a wavy (for example, grooved) wall. Känel et al. [2] have discussed the contribution of local smectic layering to the free energy of the nematic at a wall, also from a macroscopic, phenomenological point of view. They have used this layering to explain the parallel to perpendicular transition which occurs as the temperature is lowered. A microscopic, density functional, theory of a nematic in contact with a hard planar wall has been proposed by Poniewierski and Hołyst [5]. Their goal, however, was to determine the director alignment with respect to an inert wall rather than to describe the possibility of a parallel to perpendicular transition.

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In this paper we describe a simple theoretical analysis of the nematic phase in contact with a solid wall. We use an Onsager-level density functional theory whose free energy contains a particle–wall interaction as well as the usual positional entropy and second virial hard-core interparticle terms. The orientation of the particles is fixed (i.e. the alignment is saturated) throughout the sample. The wall is planar and impenetrable, and the adsorption energy of a particle near the wall is assumed to depend on the nematic alignment in a manner which favours a normal orientation of the director relative to the wall. It is this latter feature which allows for the possibility of a parallel–perpendicular transition upon lowering the temperature.

We show that the parallel–perpendicular transition can occur even in the absence of layering, and of orientational disorder. The transition is driven by a difference in positional entropy between the parallel and perpendicular states; the entropy of the parallel configuration is greater than that of the perpendicular one because the centres of mass of the particles are able to occupy a greater volume when the particles align parallel to the wall. This effect is shown to result in the parallel orientation being preferred even in the absence of interparticle interactions; the presence of interactions between rods does, however, further stabilize the parallel state and hence lower the temperature of the transition.

2. Description of the model

The system studied in our theory is a liquid consisting of hard spherocylindrical particles, of cylinder length L and diameter D, which interact via excluded volume forces only. The system is assumed to be sufficiently dilute to justify use of the second virial approximation to the interaction free energy. The wall is planar and impenetrable. It interacts with the particles through a potential which is a step function of z extending a distance λ from the wall. In particular, a particle whose centre of mass is within this range has an adsorption energy $V_0 + V_2 \sin^2 \theta$, where θ is the angle between the particle's long axis and the space-fixed z axis (which is taken to lie along the surface normal).

The Onsager-level Helmholtz free energy for this system is (see [5])

$$\beta F[\rho(\mathbf{r}, \omega)] = \int d\mathbf{r} \int d\omega \rho(\mathbf{r}, \omega) \{\ln[\Lambda^3 \rho(\mathbf{r}, \omega)] - 1\} \tag{1}$$

$$- \frac{1}{2} \int d\mathbf{r}_1 \int d\omega_1 \int d\mathbf{r}_2 \int d\omega_2 \rho(\mathbf{r}_1, \omega_1) \rho(\mathbf{r}_2, \omega_2) f_2(\mathbf{r}_{12}, \omega_1, \omega_2)$$

$$+ \beta \int d\mathbf{r} \int d\omega \rho(\mathbf{r}, \omega) V_w(\mathbf{r}, \omega)$$

where $\beta = 1/kT$, $\rho(\mathbf{r}, \omega)$ is the positional-orientational one body distribution function of the liquid, and $f_2(\mathbf{r}_{12}, \omega_1, \omega_2)$ is the Mayer f-function. In the present work, $V_w(\mathbf{r}, \omega)$ is an orientation-dependent interaction potential due to the wall

$$V_w(\mathbf{r}, \omega) = \begin{cases} +\infty & \text{if } z < z_m(\theta); \\ V_0 + V_2 \sin^2 \theta & \text{if } \lambda \geqslant z \geqslant z_m(\theta); \\ 0 & \text{if } z > \lambda, \end{cases} \tag{2}$$

with

$$z_m(\theta) = \frac{1}{2}(L \cos \theta + D).$$

Note that $z_m(\theta)$ is the distance of closest approach for a rod which makes an angle of θ with respect to the surface normal [5].

To simplify further the free energy we assume saturated nematic order, with all particles aligned in the xz-plane (hence azimuthal angle $\varphi = 0$) and tilted at an angle θ_t from the normal. This allows us to eliminate the integrals over orientation in (1). Then we introduce the following trial function form for $\rho(\mathbf{r})$

$$\rho(\mathbf{r}) = \rho(z) = \begin{cases} 0 & \text{if } z < z_m(\theta_t); \\ \rho_0 & \text{if } z \geqslant z_m(\theta_t). \end{cases} \tag{3}$$

This choice coincides with the uniform-density, step-function distribution used in [5].

We evaluate (1) by substituting (2) and (3) into it and performing the spatial integrations over a box of height L_z and volume V having a wall of area A as the face perpendicular to z. This results in an expression for F as a sum of two terms, one proportional to A, the other proportional to V. The term proportional to V does not depend on θ_t; it is equal to the free energy of a bulk nematic filling the box and having no interactions with the wall. We drop this term, thereby subtracting out the free energy of a bulk nematic of volume V. We divide the remaining term by A and take the thermodynamic limit by letting $L_z \to \infty$. This leads to the following expression for $\hat{F}$, the surface Helmholtz free energy per unit area

$$\beta\hat{F} = \rho_{00}[(1 + 4\eta)z_m(\theta_t) + \beta V_w(\theta_t)(\lambda - z_m(\theta_t))], \tag{4}$$

where $\rho_{00} \equiv N/V$ and $\eta \equiv (1/4)\pi D^2(L + \tfrac{2}{3}D)\rho_{00}$. ρ_{00} is the density of a bulk nematic with N particles filling a volume V, and η is the packing (i.e. volume) fraction of rods at that density. For a system of finite volume, ρ_{00} differs from ρ_0 by a term of order z_m/L_z; in particular, from

$$N = \int_V d\mathbf{r}\,\rho(\mathbf{r}),$$

we obtain

$$\rho_{00} = \rho_0\left[1 - \frac{z_m}{L_z}\right],$$

and to obtain the correct surface free energy it is important to take the thermodynamic limit carefully as outlined above.

3. Analytical results

The minima of the surface energy (4) in the physical range of θ_t (0 to $\pi/2$) occur at $\theta_t = 0$ and $\theta_t = \pi/2$ only. For $V_0 = V_2 = 0$ (i.e. for a hard wall with no adsorption energy), the parallel orientation ($\theta_t = \pi/2$) is stable. For $(L - D)V_0 > -(2\lambda - D)V_2$ a parallel–perpendicular transition is found; the orientation of the particles is parallel for $T > T_{tr}$ and perpendicular for $T < T_{tr}$, where T_{tr} is given by

$$kT_{tr} = \frac{(L - D)V_0 + (2\lambda - D)V_2}{(L - D)(1 + 4\eta)}. \tag{5}$$

In the case $V_0 = -V_2 = -V(<0)$ this expression reduces to

$$kT_{tr} = \frac{(2\lambda - L)}{(L - D)(1 + 4\eta)}V. \tag{6}$$

Note that $kT_{tr} \simeq V$ for $\lambda \simeq L$, $L \gg D$, and $\eta \ll 1$, and that T_{tr} is a decreasing function of density (with $T_{tr} \neq 0$ even at $\eta = 0$).

4. Numerical results

We also have evaluated $\hat{F}$ numerically with two alternative trial functions. The first of these trial functions,

$$\rho(z) = \begin{cases} 0 & \text{if } z < z_m; \\ \rho_0\{1 + \mu \exp\left[-(z-z_m)/\xi\right]\cos\left[k(\theta_t)(z-z_m)\right]\} & \text{if } z \geqslant z_m, \end{cases} \qquad (7)$$

with

$$k(\theta_t) = \frac{2\pi}{\alpha z_m(\theta_t)}, \qquad (7\,a)$$

allows the system to undergo layering near the wall. The ansatz $(7\,a)$ for k was motivated by a calculation of wavenumber for the bulk smectic A without a wall and with $D = 0.05L$; our value of $k(0)$ $(4.348L^{-1}$, i.e. $\alpha = 1.376$, to four figures) agrees closely with a value $(\simeq 4.493L^{-1})$ found by Mulder for a bulk smectic in the same density functional approximation [6]. μ is an order parameter for local (wall-induced) smectic order and ξ is the persistence length of that order. We computed $\hat{F}$ in the presence and in the absence of particle–particle interactions for $\lambda = L$ and $D = 0.05L$. In each calculation we fixed T, ρ_0, V_0, V_2 and λ, and calculated the surface free energy for a range of values of θ_t, μ, and ξ. In all cases we found essentially no layering in the perpendicular state at the transition: although μ was non-zero, the persistence length was short compared to the wavelength, for example, $2\pi/k(\theta_t) \simeq 1.5L$, $\xi \lesssim 0.5L$. Such an effect amounts to a depletion $(\mu < 0)$ or enrichment $(\mu > 0)$ of density near the wall rather than true layering.

The second trial function was the same as (7) except with $k = 0$. Using this function we found a depletion of density with $\xi \gtrsim 4L$. This result held both in the presence and in the absence of interparticle interactions.

With both of these trial functions the parallel orientation is stable in the absence of adsorption energy. For the values of λ and D mentioned above, the parallel–perpendicular transition occurs at kT of the order of the adsorption energy, consistent with our analytical result (6).

5. Conclusions

Our microscopic theory of the nematic at a wall predicts the stability of the parallel orientation in the absence of adsorption energy, and a parallel–perpendicular transition in the presence of an adsorption energy favouring the perpendicular orientation. We find these features in the absence of layering and with saturated orientational order. In our model the driving force for the parallel preference at the wall is a difference in entropy between the perpendicular and parallel states. In the case of no interparticle interactions and a density profile given by (3), this term is proportional to $z_m(0) - z_m(\pi/2)$, the difference between the thicknesses of the depletion layers near the wall in the perpendicular and parallel orientations. Calculating this difference for finite V and A one finds that the entropy difference is

$$\Delta S = Nk \ln\left[\frac{V - Az_m(\pi/2)}{V - Az_m(0)}\right].$$

Thus the surface entropy is a volume entropy; it favours states in which the centres of mass of the particles fill up larger regions of space. The preferred orientation will be the parallel one, in which the particles can approach the wall more closely. Inspection of (4) shows that the interparticle interactions enhance this volume entropy term by a factor increasing with density. This is physically reasonable since the presence of repulsive interactions should increase the tendency of the system to expand. Correspondingly, the parallel to perpendicular transition temperature is lowered.

Känel *et al.* [2] have suggested that layering near the wall gives rise to the preference for parallel alignment. Similar layering has been observed at free surfaces of nematics and isotropics [7]. Our results suggest, however, that the layering is not necessary for the parallel preference, even though it might favour such a preference independently or might modify the properties of the transition. One can conjecture that the observed layering is due to *attractive* interactions which favour crowding among molecules. Since smectic order allows molecules to pack closer together, local layering (i.e., near the wall) would allow the attraction energy to be lowered, even though the bulk nematic state is unaltered.

The results of Poniewierski and Hołyst [5] confirm that the parallel alignment is the preferred one when the wall has no adsorption energy. Their theory allows the orientational order to vary near the wall; it predicts a smoothly varying orientational order profile near the wall. Their spatial density, however, coincides with ours. Our analysis suggests that this spatial distribution is sufficient for the parallel preference, and that variable orientational order is not essential either for the parallel preference or for the transition, although it should modify quantitatively the properties of the transition.

Parsons [8] has considered the case of the *free* surface of a nematic liquid composed of particles which interact only through anisotropic dispersional forces. He too takes the density and orientational order parameters to equal their bulk values all the way up to the wall—here, the Gibbs dividing surface. The surface free energy per unit area is then minimized with respect to the tilt angle of the director, and it is concluded that parallel alignment ($\theta_t = \pi/2$) is favoured at all temperatures and densities. We note that this result follows exclusively from the effect of interactions between particles rather than from the volume entropy term featured in the present work: in Parson's theory all molecules can approach the surface equally closely, independently of alignment, since hard core anisotropy is not considered.

Finally, McMullen [9] has studied the theory of the isotropic–nematic interface in a liquid of purely repulsive rods. He uses a trial function form for the density which posits a symmetrical variation of the density about the interface. Since the particles can lie arbitrarily close to the interface, the volume entropy effect discussed here does not appear to play a role (although the thickness of the interface is coupled to the nematic alignment). The parallel state is again found to be the stable one.

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