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Statistical Mechanics of a Simple Model of the Nematic Liquid Crystal - Wall Interface II

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A simple model of the nematic liquid crystal-wall interface introduced in our previous paper¹ has been extended. The effect of an impenetrable wall has been taken into account by making a gradient expansion with respect to the orientational order parameter profile, resulting in an additional term in the effective surface potential as a function of the order parameter at the wall. Either a first-order or a second-order surface phase transition is possible with the modified surface potential. In addition to the wetting transition found in our previous paper, another wetting transition, in which a layer of the paranematic intrudes between the nematic and the wall, is also possible.

1. INTRODUCTION

In our previous paper,¹ hereafter denoted as I, we investigated the surface behaviour of a nematic liquid crystal in the presence of an impenetrable wall and a bulk magnetic field perpendicular to the wall, both exerting an ordering potential on the fluid. We showed that the nematic undergoes a first order orientational surface phase transition, which we called a “wetting transition” by analogy to simple fluid-solid systems. The transition occurs at conditions determined by the nematic-paranematic coexistence when a macroscopic film of the nematic phase is adsorbed at the wall. Our bulk/surface phase diagram with the orientational order parameter Q appearing in the place of density was very similar to such diagrams for simple fluid-

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solid systems. We followed rather closely Sheng's model,² assuming the orientational order parameter perpendicular to the wall to be the only order parameter of our problem. We used a Maier-Saupe free energy density instead of a Landau-de Gennes form used by Sheng, but the external potential due to the substrate was as prescribed by Sheng: a short ranged contact interaction at the wall proportional to Q .

In this paper we present a calculation for a rather more realistic, but only slightly modified model, in which the effective surface potential contains the square of the orientational order parameter at the wall $Q(z = 0)$ in addition to the linear term in the original Sheng model. To obtain the square term we have used arguments closely analogous to those used by Teletzke *et al.*³ in their gradient theory of surface behaviour in simple fluid-solid systems. These authors predicted that the wetting transition could be either first or second order. In our case inclusion of the square term has the same effect. Moreover, it leads to the possibility of a wetting transition to a state in which a macroscopic film of the paranematic phase is adsorbed between the wall and the bulk nematic phase, rather than the reverse. This result, in the absence of the magnetic field, was also recently obtained by Telo da Gama⁴ who used a molecular model of the nematic free energy with two order parameters: the density and the orientational order parameter.

The paper is arranged as follows: in Section 2 we present the continuum model for the nematic-wall interface, and explain how the surface parameters in the theory may be obtained from the inter-particle potential. In Section 3 we present the results of the calculations discussing in detail the phase diagram in our parameter space. In Section 4 we make some final remarks.

2. MODEL

We consider a system containing an impenetrable wall of area A in the xy plane at $z = 0$, and a nematogen with density ρ in the region $z > 0$, the statistical mechanics of which is described by Maier-Saupe model, the details of which are described in I. Mainly for theoretical reasons we also allow an external uniform magnetic field H to be applied to the system. This gives rise to a potential energy per unit volume

$$-VQ(r) = -\frac{1}{3}\rho\Delta\kappa H^2Q(r) \quad (2.1)$$

where $Q(r) = \langle P_2(\cos \theta) \rangle$ is the orientational order parameter at position r , θ is the angle between molecular direction and the z -axis, and $\Delta\kappa$ is the anisotropy of the molecular diamagnetic susceptibility. We assume constant density of the fluid and concentrate our attention on variations of the orientational order parameter Q only.

We treat the statistical mechanisms of the non-uniform semi-infinite system by minimising an approximate free energy functional:

$$F[Q(z)] = F_b[Q(z)] + F_s[Q_0] \quad (2.2)$$

This free energy functional has contributions from the bulk and from the surface. The bulk contribution,

$$F_b[Q(z)]/A = \rho \int \{ \omega(Q(z)) + L(dQ(z)/dz)^2 \} dz, \quad (2.3)$$

where $\omega(Q(z))$ is the Maier-Saupe free energy per particle with interaction energy U in the presence of magnetic field H , has been discussed in I; L is an effective elastic constant. The surface contribution

$$F_s[Q_0]/A = -GQ_0 - \frac{1}{2} U_1 Q_0^2 \quad (2.4)$$

where $Q_0 = Q(z=0)$, differs only from the functional employed in I by the addition of the term proportional to Q_0^2 . Nevertheless this difference leads to some profound physical consequences.

It is of some interest to understand why the terms in (2.4) follow naturally from the forms of the wall-molecule and intermolecular potential energies. The bulk free energy density is expressed as the sum of a local free energy density plus a contribution due to changes in $Q(z)$; if these changes are small this contribution can be expanded in gradients of $Q(z)$. The leading such term is $L(dQ/dz)^2$. Clearly this approximation breaks down very close to an interface, where $Q(z)$ changes very rapidly at $z=0$. The price for being allowed to retain the bulk free energy (2.3) right up to $z=0$ is the introduction of the surface terms (2.4). These terms express, in an integrated way, the effect of an external ordering field due to the surface and the reduction in the mean field near the interface because a molecule in this region has fewer nearest neighbours.

Indeed, in the simplest Maier-Saupe case we may suppose that the anisotropic part of the interparticle potential is $-U(r_{12})P_2(\cos \theta_{12})$, where θ_{12} , r_{12} are the angle between the orientations of molecules 1

and 2, and the distance between them, respectively. We also suppose that there is a wall-molecule potential $-W(z)P_2(\cos \theta)$, and that $W(z)$ and $U(r)$ fall off rather quickly with distance. The Maier-Saupe parameter U is given, of course by

$$U = 4\pi\rho \int_0^\infty U(r)r^2dr. \quad (2.5)$$

The integrated effect of the external ordering field $W(z)$ is given by

$$G = \rho \int_0^\infty W(z)dz. \quad (2.6)$$

It is because the free energy contribution from the interparticle interaction is quadratic in Q that the surface contribution to the reduction in mean field is also quadratic in Q_0 . In fact we obtain

$$U_1 = -\pi\rho^2 \int_0^\infty U(r)r^3dr. \quad (2.7)$$

Teletzke, Scriven and Davis² have discussed in detail the question of surface boundary conditions for a simple atomic fluid. We shall give details of our derivation elsewhere,⁵ which follows the spirit of Teletzke *et al.*,² but has complications due to the liquid crystal nature of the problem. We note, however, that the derivation does not in any way depend on the simple form of the interparticle potential used for pedagogical purposes in our discussion.

The theory is parametrisable in terms of a number of crucial quantities. One such is the correlation length $\xi = (L/U)^{1/2}$; this is roughly speaking the range of the interparticle potential and sets length scales in the problem. The surface free energy is defined in terms of two dimensionless parameters $\delta = G/\rho\xi U$ and $\alpha = U_1/\rho\xi U$. In previous works,^{1,2} α has been taken as zero. The qualitative considerations above suggest that under normal circumstances the phenomenological parameter $\alpha \sim -1$; abnormal circumstances could include a rather strange form of $U(r, \Omega, \Omega')$, and significant density changes near the wall. Indeed a strong density enhancement near the wall could increase α and even make it positive.

We now carry out the minimisation of Eq. (2.2) using identical

procedures to those we have used in I. Minimisation of Eq. (2.3) for fixed Q_0 leads to the expression for the surface tension [1, 2]

$$\sigma_w/\rho\xi U = \pm 2 \int_{Q_0}^{Q_b} \sqrt{f(Q) - f(Q_b)} dQ - \frac{1}{2} \alpha Q_0^2 - \delta Q_0 \quad (2.8)$$

where $f(Q) = \omega(Q)/U$ is a non-dimensional free energy and $Q_b = Q(z=\infty)$. The signs “+” or “-” in (2.8) corresponds to two possible signs of the gradient dQ/dz . For given parameters α and δ , the surface tension σ_w is a function of Q_0 , temperature T and the magnetic field H . To obtain the equilibrium values of σ_w and Q_0 , the surface tension is to be minimized with respect to Q_0 which gives

$$\alpha Q_0 + \delta = \pm 2\sqrt{\Delta f(Q_0)} \quad (2.9)$$

with $\Delta f(Q) = f(Q) - f(Q_b)$.

In I we considered only the case of $\alpha = 0$ and $dQ/dz < 0$. For that case a positive sign of the gradient corresponds to a negative value of δ in the surface potential. When this happens, sufficiently close to the wall, it is energetically favourable for the liquid crystal molecules to lie parallel to it, rather than perpendicular to it. It is then necessary to take into account the variation of the full orientational order parameter tensor $Q_{ij}(z)$, and not merely $Q(z) = Q_{zz}(z)$; we expect surface-induced biaxiality, and the scalar order parameter approximation fails. Thus in our case, with a scalar order parameter, we treat $\delta < 0$ as unphysical.

However the modification of F_s by the extra $-1/2 \alpha Q_0^2$ term does lead to physical solutions of Eq. (2.10) for both signs of the gradient dQ/dz . It is now possible for Q_0 to be either smaller or larger than Q_b (whereas in I $Q_0 > Q_b$ always), and thus it is possible to have either the nematic or the paranematic phase wetting the wall (whereas in I only the nematic phase wets the wall). For a given sign in (2.9) there can be one, two or three solutions of the equations depending on values of α and δ . The relation between α , δ and the behaviour of surface phase transitions is presented in the next section.

We are also interested in the extra surface order near the wall. This is described using the surface adsorption Γ defined by

$$\Gamma = \rho \int_0^\infty \{Q(z) - Q_b\} dz = \pm \rho \xi \int_{Q_0}^{Q_b} \frac{Q - Q_b}{\sqrt{\Delta f(Q)}} dQ = - \left(\frac{\partial \sigma_w}{\partial V} \right)_T \quad (2.10)$$

3. RESULTS

We now consider the wetting properties of the model. The question of wetting is of interest at or approaching thermodynamic conditions allowing the coexistence of two phases. In our case these two phases are the nematic (n) and paranematic (p) phases. We recall from *I* that in a thermodynamic phase space defined by temperature T and magnetic field H (it is more convenient in theoretical work to deal with the bulk ordering field V , which is related to H by Eq. (2.1)) there is a line of first order transitions between a slightly ordered p phase and a highly ordered n phase. This line terminates at one end at the familiar nematic-isotropic transition; the i phase is the $V = 0$ limit of the p phase. At the other end, the line terminates at a critical point with T slightly greater than T_{NI} , at rather large magnetic field. For the Maier-Saupe model, $k_B T_{NI}/U = 0.2202$, $k_B T_C/U = 0.231$ and $V_C/U = 0.0105$.

Along the coexistence line, the surface properties of the system are described by the contact angle θ between the paranematic phase and the wall:

$$\sigma_{PW} = \sigma_{NW} + \sigma_{NP} \cos \theta, \quad (3.1)$$

where σ_{PW} , σ_{NW} and σ_{NP} are the paranematic-wall, nematic-wall and nematic-paranematic surface tensions respectively. Where there is no ambiguity (everywhere other than actually *on* the coexistence line), we merely refer to the liquid-wall surface free energy σ_w .

An orientational surface phase transition occurs when $\cos \theta$ reaches ± 1 . It turns out that, for very general reasons which transcend this particular problem, close to the critical point $\cos \theta = \pm 1$, but that at lower temperatures intermediate values of $\cos \theta$ are allowed. When $\cos \theta = +1$, a nematic layer intrudes between the bulk paranematic phase and the wall. The nematic phase is said to wet the wall. The surface free energy discussed in *I* imposes this wetting behaviour near the n-p critical point. Conversely when $\cos \theta = -1$ there is a paranematic layer between the bulk nematic phase and the wall, and the surface is said to be wet by the paranematic phase. The behaviour of the adsorption Γ is closely linked with the wetting behaviour. As the bulk boundary conditions change so that the n-p coexistence line is approached, Γ may have a number of different behaviours. If $\cos \theta \neq \pm 1$, Γ remains finite always. If $\cos \theta = 1$, $\Gamma \rightarrow \infty$ if the coexistence line is approached from the paranematic side, but has no anomalous behaviour when it is approached from the nematic side.

If $\cos \theta = -1$, $\Gamma \rightarrow -\infty$ if the coexistence line is approached from the nematic side, but has no anomalous behaviour when it is approached from the paranematic side. The last two sentences merely rephrase the earlier statements about the intrusion of nematic or paranematic layers, respectively

Wetting transitions divide the regions where $\cos \theta = \pm 1$ (complete wetting) from those regions in which $\cos \theta \neq \pm 1$ (partial wetting). These transitions may be first order, in which case $d\sigma_w/dT$ is discontinuous through the transition, as also is Γ . They may on the other hand be second order, in which case only $d^2\sigma_w/dT^2$ is discontinuous, and Γ diverges as the transition is approached from the partial wetting regime along the coexistence curve. The wetting transition takes place at a wetting temperature T_w . If the transition is first order, there is an associated set of first-order surface transitions, known as the pre-wetting line. These transitions take place away from coexistence; as bulk boundary conditions are continuously changed, Γ undergoes a discontinuity, as does $d\sigma_w/dT$. The transitions from a line in the phase diagram, terminating at one end at T_w on the coexistence line, and at the other end there is a surface critical point (at T_{scp}), at which Γ for the first time becomes discontinuous, and $d\Gamma/dT$ diverges. As discussed extensively in I, any special surface boundary phase transition is associated with the existence of such a line. We return to this point below.

As α and δ change, so does the nature of the wetting transition. For completeness, we discuss the phase diagram over the whole range of α and δ , although as discussed in the last section the physical region certainly has $\delta > 0$, and probably has $\alpha < 0$. The way in which the wetting transition changes with α and δ is shown in Figure 1. The (α, δ) plane is divided into two regions divided by the line (d); above this line sufficiently close to T_c the nematic phase wets the surface (W), whereas below it, sufficiently close to T_c the paranematic phase wets the surface (D). The line (d) is $\delta = -\alpha Q_c$, where Q_c is the order parameter at the n-p critical point. As (d) is approached in (α, δ) space T_w approaches T_c . Along (d), exceptionally, there is partial wetting everywhere along the coexistence curve. In both W and D regions, as T is reduced, there is wetting transition, which is second order for (α, δ) close to (d), in the regions marked 2nd W and 2nd D respectively, and first order further away from (d).

There has been interest recently in the question of the existence of boundary phase transitions, and we have tried to answer some questions about this from Figure 1 as well. In some cases the surface field is sufficiently strong that even in the absence of a magnetic field,

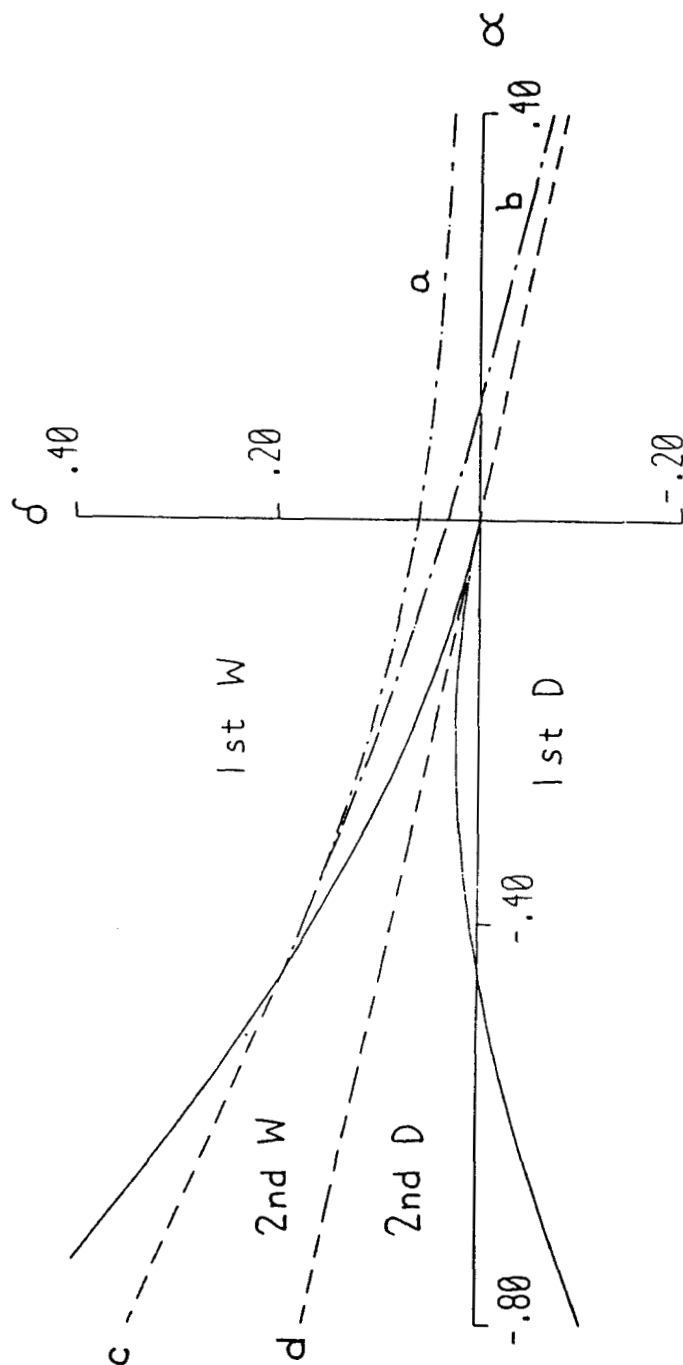


FIGURE 1. Regions of the first and the second order wetting transitions in the parameter space (α, δ) . The solid lines are boundaries between the first and second order transition regions. W- and D- wetting occur above (below) the straight line (d) defined by $\delta = -\alpha Q_c$. The curves (b) and (c) correspond to $V_w = 0$, while the curve (a) corresponds to $V_{SCP} = 0$. The boundary layer phase transition at zero magnetic field, as defined by Sheng,² occurs for α, δ lying between (a) and (b).

the nematic phase wets at T_{NI} . Equivalently, we say that $T_w < T_{NI}$; the wetting transition only takes place at unphysical bulk values of the coexistence curve. The point at which this begins to occur is shown by line (b). On the other hand, if $T_w < T_{NI}$ there will be a prewetting line, terminating in a surface phase transition at T_{SCP} . This will be physical unless this too occurs for $T_{SCP} < T_{NI}$, and the line at which this begins to occur is shown in Figure 1 as line (a). The region between lines (a) and (b) is the only region for which a boundary phase transition, corresponding to the prewetting line crossing the $H = 0$ axis, is possible. As lines (a) and (b) approach the transition between 1st and 2nd order regions, the prewetting line becomes shorter, and finally T_{SCP} reaches T_w . Thus in the second order region lines (a) and (b) merge to form line (c).

We can make contact with I by considering $\alpha = 0$. The boundary phase transition occurs for $\delta_1 < \delta < \delta_2$, where δ_1 and δ_2 can be identified respectively with points on $\delta = 0$ lying on (b) and (a). However it disappears entirely at $\alpha \approx -0.42$, whereas we have guessed in §2 that $\alpha \sim -1$. It seems that the boundary phase transition is an exotic phenomenon, depending crucially on small or positive values of α , which might be induced by a greatly enhanced density near the interface. In any event, if this transition occurs at T_b , then $T_b > T_{NI}$.

There is also the possibility of a prewetting transition associated with the first order wetting transition in the D region. These prewetting curves (d) and (e) are shown in Figure 2, superimposed on the example used in I to demonstrate the boundary phase transition. The following special points are associated with them. First, they occur at non-zero magnetic field. If the D-wetting transition takes place at or below T_{NI} it is always second order. So there *can* be a boundary phase transition, but only if temperature is reduced at constant, *non-zero* magnetic field. Second, the prewetting lines are very short—so short, in fact, that we have had to exaggerate them on Figure 2 in order to show them at all. This is a result of the fact that the physical region of 1st order D transitions is very close to the line (d) and in any case rather small, and has the consequence that these boundary phase transitions are likely to be very hard to observe—there will be a very small window of magnetic field in which the transition occurs. Third, if the transition does occur, for fixed field it occurs at a temperature below T_{NP} .

In the calculations we have considered some attention on the second order D-wetting transition, which is essentially a new phenomenon in the case of the nematic liquid crystal-wall interface. We have chosen $\alpha = -0.5$, $\delta = 0.05$ for which the transition occurs at

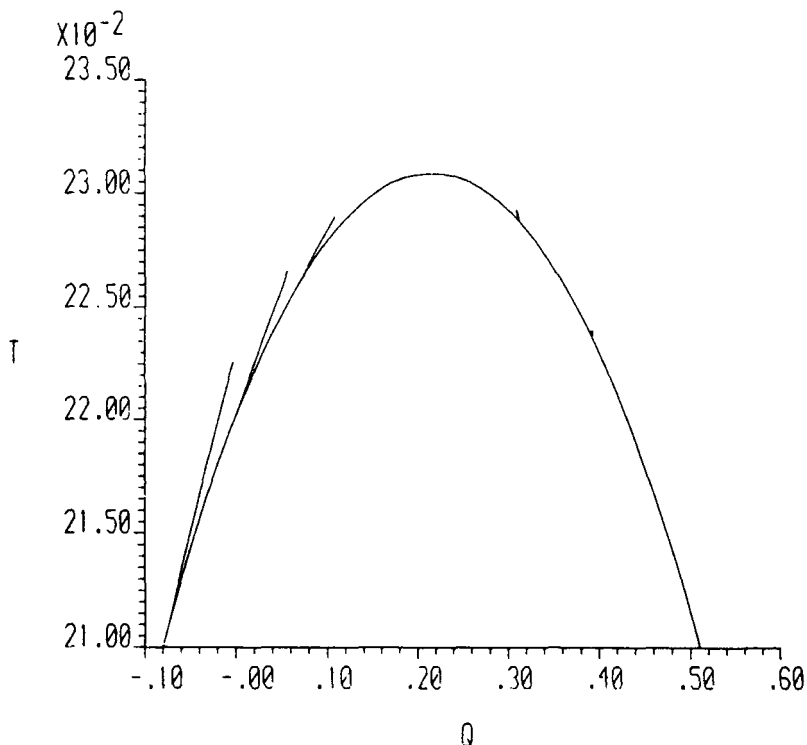


FIGURE 2 Parane-matic-nematic phase diagram as a function of temperature with surface diagrams superimposed. Prewetting lines (a), (b), (c) are associated with W-wetting with $\alpha = 0$, and were exhibited in Figure 2 of I. For comparison we show prewetting lines (d) $\alpha = -0.1$, $\delta = 0.01$ with $T_w/U = 0.2288$, $T_{scp}/U = 0.2291$ and (e) $\alpha = -0.3$, $\delta = 0.01$ with $T_w/U = 0.2236$, $T_{scp}/U = 0.2237$. As emphasized in the text, these lines are very short, and in the figure they have been exaggerated slightly.

$T_w/U = 0.2279$ and $V_w/U = 0.00749$. The cosine of the contact angle at the n-p-w contact line as a function of temperature is plotted in Figure 3. It tends smoothly to -1 at $T = T_w$ so $d\cos \theta/dT$ is continuous and only the second derivative changes discontinuously at T_w .

The equilibrium values of the surface tension σ_w and the adsorption Γ (see Eqs. (2.9–10)) depend on T and V . In Figures 4–7 we have plotted σ_w and Γ as functions of $\tau = (T - T_{NP})/T_{NP}$ at constant V and V/V_{NP} at constant T where T_{NP} , V_{NP} refer to n-p coexistence. In all cases the coexistence line is approached from the side of the nematic phase. The curves denoted by (a) correspond to the situation when $T(V)$ tends to T_{NP} (V_{NP}) above T_w (V_w) (high adsorption

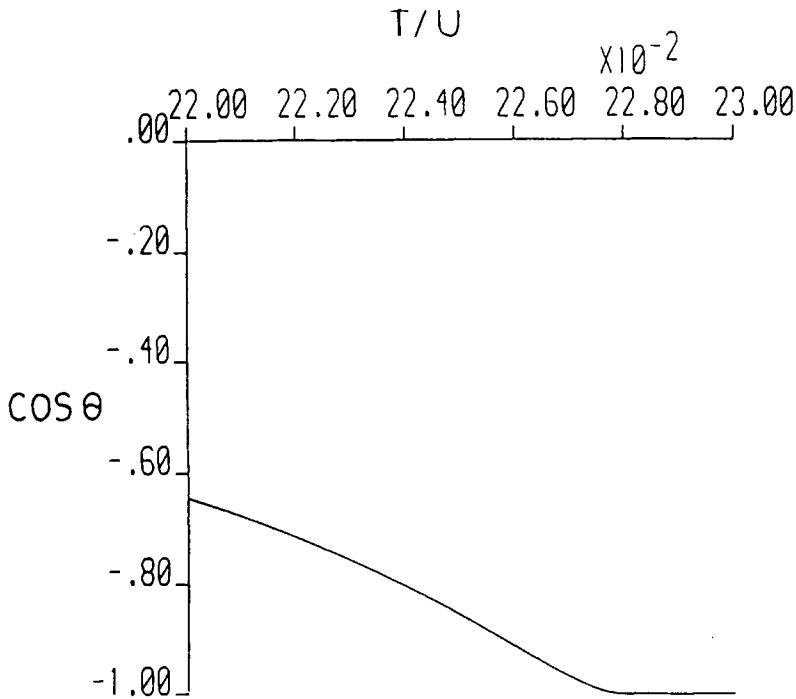


FIGURE 3 Contact angle θ at the nematic-paranematic-wall line of contact, along the nematic-paranematic phase boundary, as a function of temperature for $\alpha = -0.5$, $\delta = 0.05$. The second order D-wetting transition occurs at $T_w/U = 0.2279$ and $V_w/U = 0.00749$.

region). The surface tension exhibits a jump at coexistence (Figures 4 and 6) while the adsorption, which is negative in the case of D-wetting, tends continuously to $-\infty$ (Figures 5 and 7). For curves denoted by (b) the coexistence line is approached below T_w (V_w) (low adsorption region). In that case Γ has a finite value at coexistence. Metastable and unstable solutions have been shown either for σ_w or Γ . In our model the unstable branch of Γ (curves(b)) terminates at a finite value while in the case of simple fluid-solid systems it tends to infinity.³

Finally in Figures 8–9 we show order parameter profiles for five different values of $T(V)$ at constant $V(T)$. The closer the bulk nematic is to the coexistence with the paranematic phase, the thicker the film of adsorbed paranematic is. The two lowest profiles in both figures correspond to T, V just above and just below the n-p phase transition. Profiles are almost horizontal when the paranematic is the bulk phase.

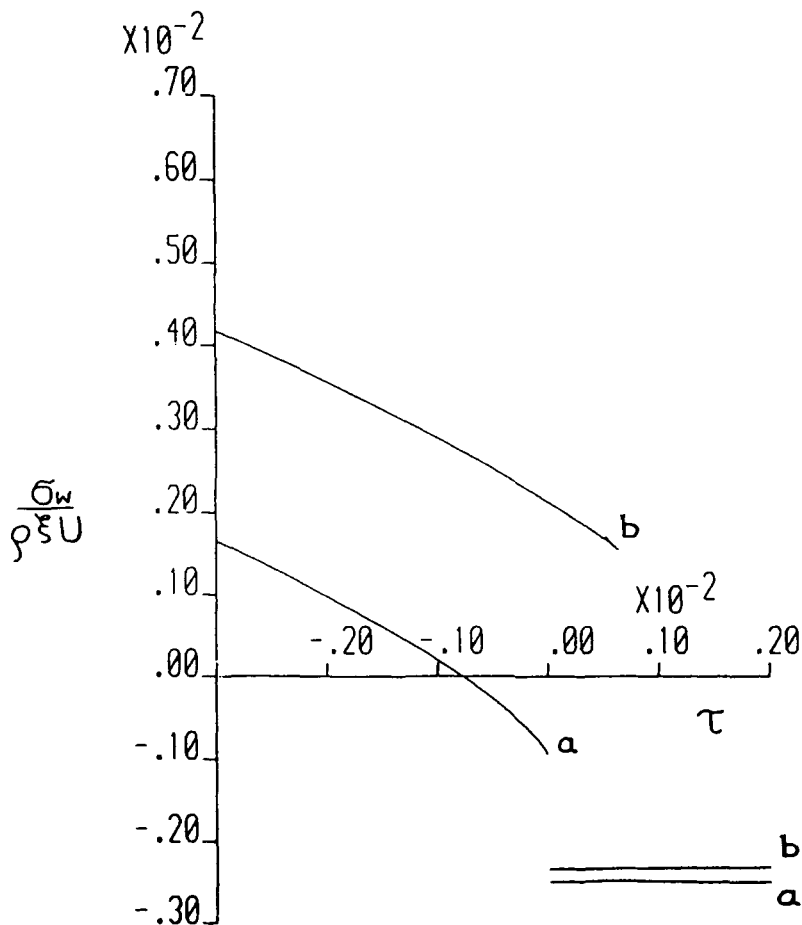


FIGURE 4 Surface free energy as a function of $\tau = (T - T_{NP})/T_{NP}$ at $V/U = 0.008$ (a) and $V/U = 0.005$ (b). The unstable branch of the curve (b) is hardly seen. The coexistence temperatures are: $T_{NP}/U = 0.2284$ for (a) and $T_{NP}/U = 0.2253$ for (b).

4. DISCUSSION AND CONCLUSIONS

We have studied a simple model of a liquid crystal-wall interface, defined in our previous paper,¹ with a modified form of the surface potential. The modification is the result of considering the reduced mean field on the liquid crystal molecules close to the wall, as well as the effect of the wall-molecule interactions. Thus we obtain the effective surface potential as a sum of two terms. The first, linear in

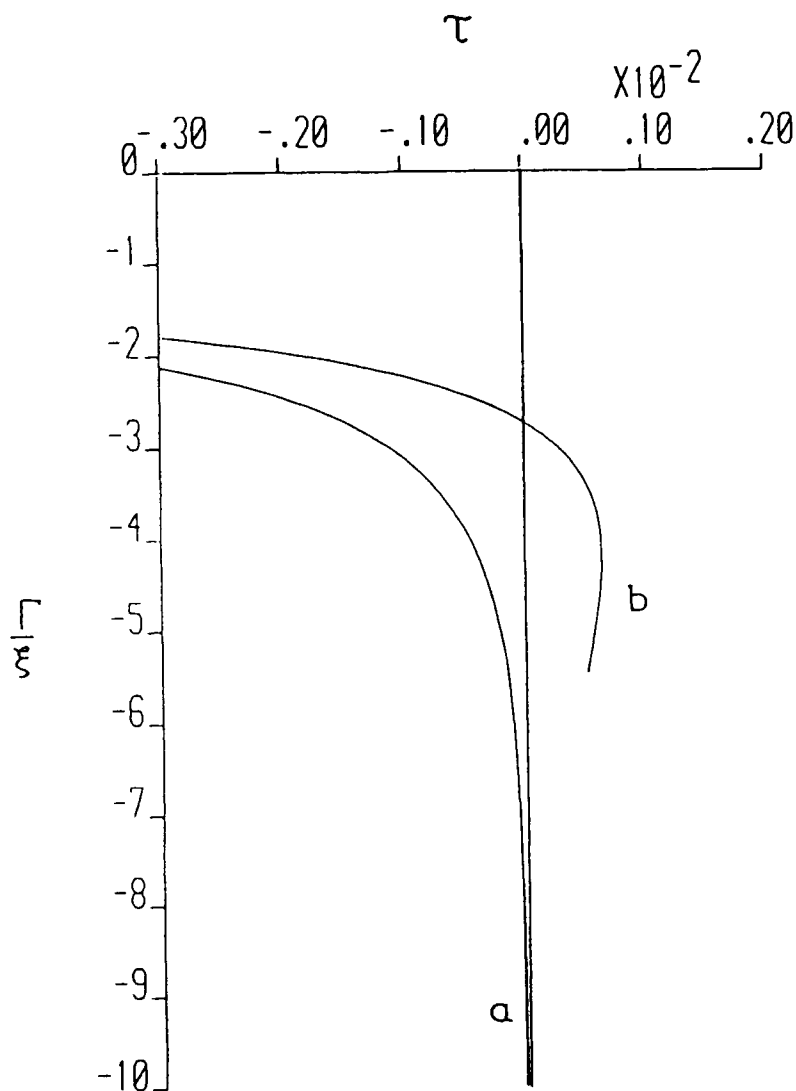


FIGURE 5 Adsorption Γ as a function of τ at $V = 0.008$ (a) and $V = 0.005$ (b). The metastable and unstable branches of (b) are shown.

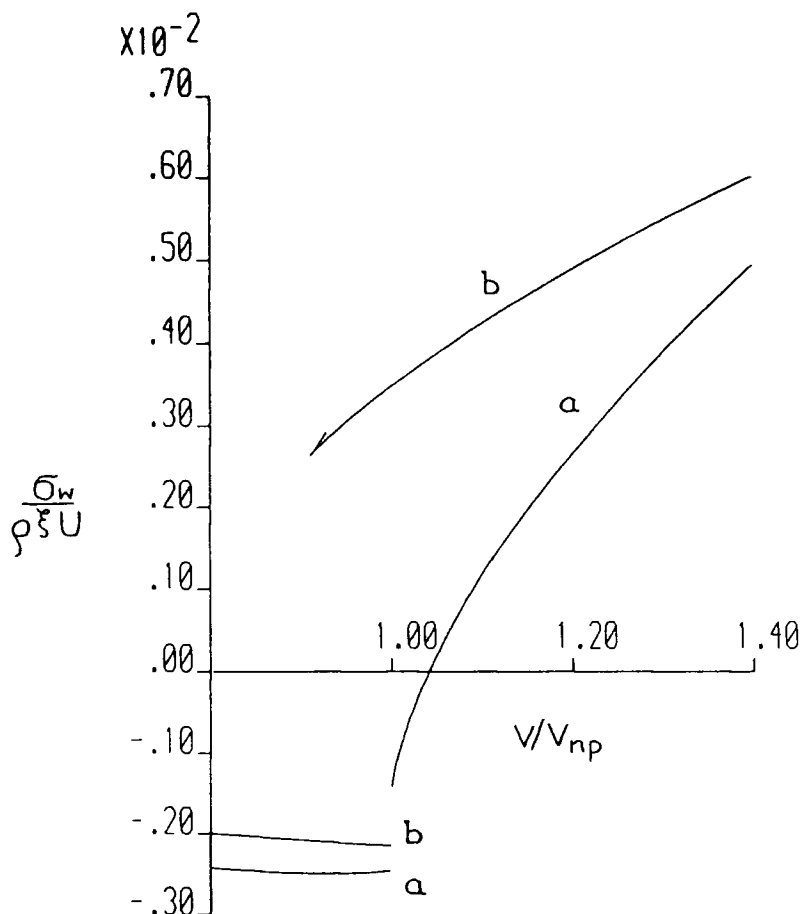


FIGURE 6 Surface free energy as a function of V/V_{np} at $T/U = 0.229$ (a) and $T/U = 0.224$ (b). The corresponding n-p coexistence fields are $V_{np}/U \approx 0.00857$ for (a) and $V_{np}/U \approx 0.00371$ for (b).

Q_0 , is the true surface attractive potential of the substrate while the second, squared term, is due to the impenetrable wall.

Having derived such a simple form of the effective surface potential we have investigated a pure orientational surface phase transition at nematic- or paranematic-wall interfaces. We find that near the paranematic-nematic critical point the wall is always completely wet by one of the paranematic or nematic phases. There also exist surface phase transitions, which by analogy with the ordinary fluid-solid interface problem, we identify as wetting transitions: W-wetting and

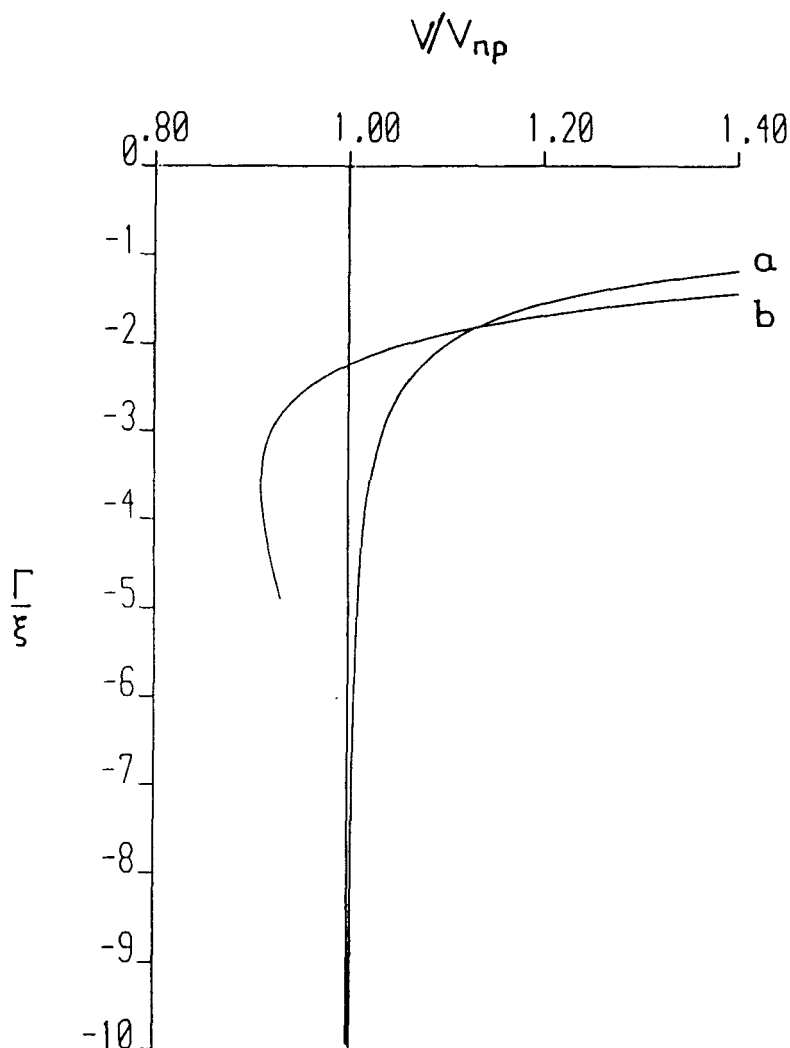


FIGURE 7 Adsorption Γ as a function of V/V_{NP} for the case described in Figure 6.

D-wetting depending on whether the nematic or paranematic phases are preferred near the wall. The wetting transitions may be first or second order; in general if they occur close to the nematic-paranematic critical point they are likely to be second order. If first order there are associated prewetting lines, and associated with these lines are separate boundary phase transitions, in which the surface orders

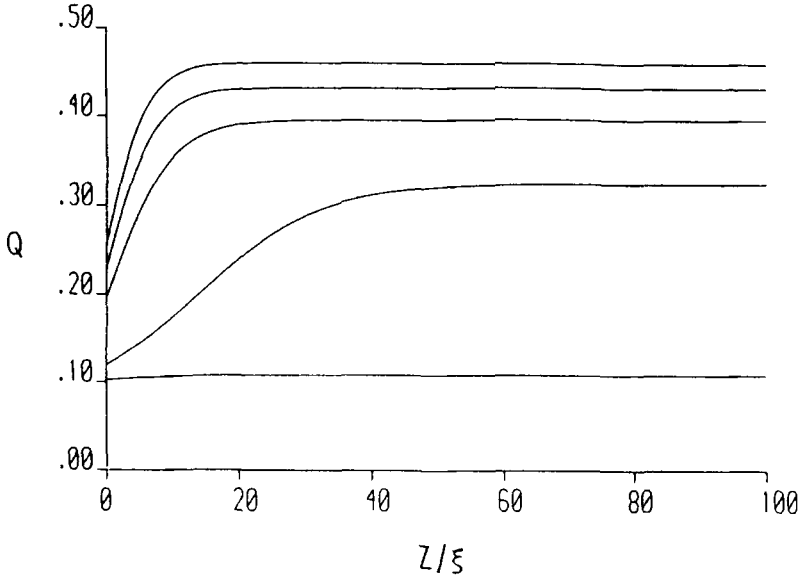


FIGURE 8 Order parameter profiles, in decreasing order of Q_b , for $T/U = 0.2220, 0.2240, 0.2260, 0.2283, (T_{NP}/U) -$ for $V/U = 0.008$ ($T_{NP}/U = 0.2284$).

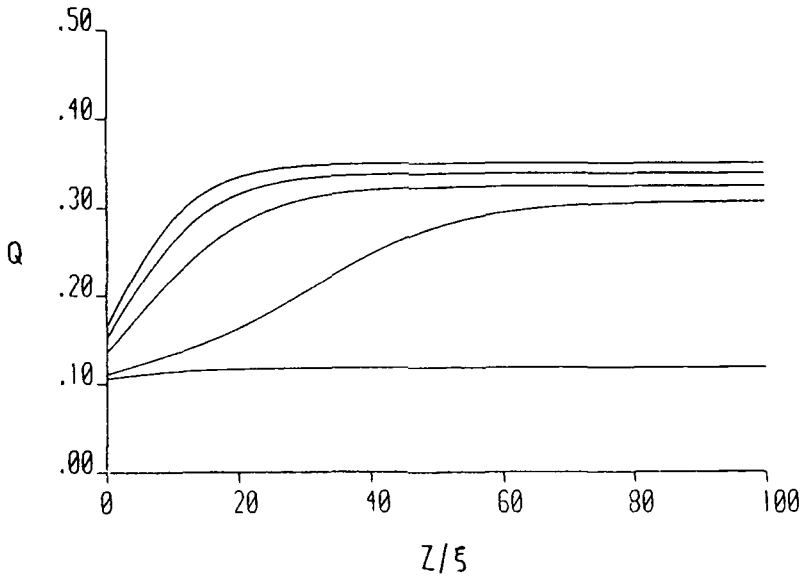


FIGURE 9 Order parameter profiles, in decreasing order of Q_b , for $V/U = 0.010, 0.0095, 0.0090, 0.0086, (V_{NP}/U) -$ for $T/U = 0.229$ ($V_{NP}/U = 0.00857$).

at a temperature higher than the bulk (W-prewetting) or lower than the bulk (D-prewetting). The D-prewetting phenomenon is only observable at non-zero magnetic field, however.

We have restricted our interest to the case where both the bulk and surface ordering fields are perpendicular to the interface, and some values of the parameters we choose give formal results, but it is reasonably easy to see that these formal results do not have physical significance because there will be a complicated orientational structure near the interface. Studies of such systems are in progress.

Two effects which have been ignored are the density-orientation coupling in the liquid crystal, and the interaction of the wall with the mass centres of the molecules. It seems unlikely that these effects will cause qualitative changes in the results, however. The former effect will give rise to a further term linear in Q , and change δ , and the latter effect will change the free energy density (and thus the propensity for liquid crystal formation) in the neighbourhood of the surface. This in the end may be regarded as giving rise to a change in α .

Finally, we may ask about the experimental realisation of the surface phase diagrams we have investigated. Mean field theories of liquid crystals are notoriously unreliable, and it seems likely that there is little *quantitative* significance in our results. We have also pointed out¹ that different but similar mean field theories give rise to widely differing quantitative predictions of the surface thermodynamics. On the other hand it seems likely that the qualitative picture is as we have discussed. The surface free energy (or spreading pressure) at a fluid-solid interface is not readily investigated, unlike that at a liquid-vapor interface. On the other hand the angle of contact θ and the adsorption Γ are experimentally accessible.⁶ Experiments on the contact angle θ are somewhat difficult in pure systems where isotropic-nematic coexistence only occurs at T_{NI} ; for impure systems there is a finite range of temperatures at which coexistence can occur; it seems likely that slightly impure systems in magnetic fields may be a fruitful area for surface investigations of the variations of θ and the onset of wetting. The theory of such systems is currently under investigation. Γ may also be studied by ellipsometry. Beaglehole⁷ has carried out investigations of Γ at the nematic-liquid crystal interface; a set of systematic studies of Γ at a nematic-wall or paranematic-wall interface is clearly desirable. Such studies would immediately show whether or not Γ diverges at T_{NI} , and whether or not a surface boundary phase transition across the prewetting lines occurs. In this context the simple, wetting, behaviour of $\Gamma \propto \ln(T - T_{NI})$ found by Beaglehole⁷

at the nematic-isotropic transition is rather uninteresting; more interesting would be Γ remaining finite at T_{NI} ; our prediction is that increasing magnetic field, and thus ordering field, would eventually lead to a wetting transition at a high field.

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