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

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The orientational profile near a liquid-wall interface has been studied, concentrating, in the spirit of recent theories of wetting, on the existence of surface phase transitions. The Maier–Saupe theory has been used to investigate the behaviour of a nematic near a wall in the presence of both bulk and surface ordering fields. We find that the surface ordering transition predicted by Sheng is extremely sensitive to the form of the bulk nematic free energy. The surface transition is also dependent on the bulk ordering field, and terminates at a wetting temperature; it is symptomatic of prewetting behaviour and occurs near a wide variety of first order phase transitions. The surface adsorption, contact angle at a nematic-isotropic-solid contact line, and surface free energy as a function of bulk field and temperature are also studied.

1. INTRODUCTION

Recently there have been a number of experimental[1,2,5] and theoretical[3,4,6] studies of the possibility of a substrate ordering field inducing enhanced surface order in a nematogen. Sheng[3] has suggested that the enhanced order near an ordering substrate may under suitable circumstances cause there to be a special surface ordering transition above, and separate from, the bulk nematic-isotropic transition.

There has also been a considerable advance in the last few years in the understanding of surface behaviour near bulk first order phase transitions. In the main, studies have concentrated on the liquid-vapour transition, or the zero field first order line between the

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opposite magnetisations in the Ising model at low temperatures[7,8]. Dash[9] introduced a classification of this behaviour. He considered a semi-infinite fluid bounded by a wall exerting a potential on the fluid. For bulk vapour pressures less than but close to liquid-gas coexistence there will be extra fluid Γ adsorbed at the wall. As the pressure approaches liquid-vapour coexistence, Γ may diverge (class I behaviour, or perfect wetting) or it may remain finite (class II behaviour, or partial or non-wetting). Cahn[10] showed that generically class I is expected near the liquid-vapour critical point, and if class II behaviour exists, it will occur at lower temperatures. These regions are separated by a surface phase transition at a wetting temperature T_w; if this transition is first order, there will be a line of first order surface phase transitions away from liquid-vapour coexistence at temperatures above T_w, running from the wetting point to a surface critical point—this line is often called the prewetting line.[11]

This behaviour is generic at first order phase transitions. Several authors[12,13,14] have pointed out that the phase diagram of a nematic in a finite external ordering field V has the same form as the liquid-vapour, binary mixture and Ising phase diagrams—there is a phase transition between a highly ordered nematic phase and a slightly ordered paranematic phase. This line of first order phase transitions crosses the zero field axis at T_{NI}, and terminates at a critical point $T_C > T_{NI}$ at finite V. The complex wetting phase diagrams predicted for first order phase transitions should apply in this case also, and in particular there should be a prewetting line, which may under some circumstances cross the $V = 0$ axis at a temperature above T_{NI}. We identify this phenomenon with the surface phase transition discussed by Sheng.[3]

In this paper, we investigate some more consequences of Sheng's model of the nematic-wall interface within the perspective outlined above. We use a Maier–Saupe model for the bulk nematic free energy, whereas Sheng used a Landau-de Gennes model. We find qualitatively similar results, but an apparently small change in the form of the bulk free energy has drastic quantitative significance. This extreme sensitivity is characteristic of wetting problems.[15] A very recent, very detailed study of the nematic wall interface has also been made by Telo da Gama,[6] who has used a molecular rather than a continuum model of the nematic free energy; her results are in line with ours, though a detailed comparison is at this stage difficult.

The plan of the paper is as follows. In section 2 we present the model that we use to describe the nematic-wall interface. In section 3 we present our results, and in section 4 we make some concluding comments.

2. MODEL

We follow rather closely the model surface free energies used by Sheng[3] and Cahn[10]. Nematic fluid in the region $z > 0$ near a surface, area A, at $z = 0$, uniform in the $x - y$ plane is subject to an orientational potential $-G\delta(z)Q(z)$ where $Q = \langle P_2(\cos\theta)\rangle$ and θ is the angle between the long axis of the molecule and the z-axis. We restrict our interest, for simplicity, to systems which have bulk and surface ordering potentials perpendicular to the wall. We therefore miss any interesting effects due to competing orientational potentials. However it enables us to describe the nematic locally in terms of a scalar order parameter $Q(z)$, rather than use the full tensor order parameter. We shall not be concerned with the effects of anisotropic Frank constants. We assume that the potential is such that the fluid density ρ does not change near the wall. This unrealistic but computationally simple assumption decouples orientational and density fluctuations.

The state of the system at a temperature T is obtained by minimising a surface free energy functional

$$\Phi[\{Q(z)\}] = -GQ_0 + \rho A\int_0^\infty dz\left[\omega[Q(z)] - \omega[Q_b] + L\left(\frac{dQ(z)}{dz}\right)^2\right] \tag{2.1}$$

where $Q_0 = Q(z = 0)$, $Q_b = Q(z = \infty)$, $\omega[Q]$ is the grand thermodynamic potential per particle of a uniform fluid with order parameter Q, and non-uniformities in the nematic order parameter are taken account of using the square gradient approximation,[16,17] and L is an average elastic constant.

The nematic fluid is subject to a bulk ordering field

$$-VQ = -\tfrac{1}{3}\Delta\kappa H^2 Q \tag{2.2}$$

where $\Delta\kappa$ is the anisotropic part of the magnetic susceptibility, and H is an external magnetic field. We suppose $\Delta\kappa > 0$ and hence $V > 0$, and hence that ordering takes place parallel to the z-axis, though for formal reasons we shall also consider $V < 0$.

We obtain $\omega(Q)$ by the following procedure, which is equivalent to Maier–Saupe theory. We consider only the orientational contribution to ω. Further details are given in another publication.[18] We first regard ω as a functional of the orientational distribution function

$h(\Omega) = h(\cos\theta)$. Then

$$\omega[h(\cos\theta)] = k_B T \int h(\Omega) \ln 4\pi h(\Omega)\, d\Omega - \frac{1}{2} UQ^2 - VQ \quad (2.3)$$

where $Q = \int d\Omega\, P_2(\cos\theta) h(\Omega)$ and U is the usual Maier–Saupe interaction energy. In this approximation the nematic and isotropic densities are the same. The equilibrium value of Q is determined by the equation

$$\frac{\delta\omega}{\delta h} = \text{constant} \quad (2.5)$$

(there is a constraint $\int h(\Omega)\, d\Omega = 1$). The values of Q_b and $\omega(Q_b)$ are determined from this condition; one obtains, as usual, that

$$h^{eq}(\cos\theta) = \frac{1}{4\pi Z} \exp\{\beta(UQ + V) P_2(\cos\theta)\} \quad (2.6)$$

$$Z = \int_0^1 \exp\{\beta(UQ + V) P_2(x)\}\, dx \quad (2.7)$$

[$\beta = (k_B T)^{-1}$; k_B is Boltzmann's constant]

$$\omega^{eq}[Q] = \tfrac{1}{2} UQ^2 - k_B T \ln Z \quad (2.8)$$

Results (2.6), (2.7) and (2.8) are well known and lead to the well-described nematic-paranematic phase diagram.[12,13,14]

If on the other hand we wish to find the value of $\omega[Q]$ appropriate for a non-equilibrium value of Q we adopt the usual techniques of density functional theory,[19] and minimise

$$g[h(\cos\theta)] = \omega - \mu Q \quad (2.9)$$

where μ is a Lagrange multiplier, determined self-consistently from eqs. (2.4) and (2.10) below.

The results (2.6), (2.7) and (2.8) can now be utilised to yield

$$h_Q(\cos\theta) = \frac{1}{4\pi Z_Q} \exp\{\beta(UQ + V + \mu) P_2(\cos\theta)\} \quad (2.10)$$

$$Z_Q = \int_0^1 \exp\{\beta(UQ + V + \mu) P_2(x)\}\, dx \quad (2.11)$$

$$g(Q) = \tfrac{1}{2} UQ^2 - k_B T \ln Z_Q \quad (2.12)$$

and

$$\omega(Q) = \tfrac{1}{2}UQ^2 - k_B T \ln Z_Q + \mu Q \tag{2.13}$$

The free energy $\omega(Q)$ now has sensible properties—in particular $\delta\omega/\delta Q = 0$ for stable and metastable solutions, and at coexistence between the paranematic and nematic phases with $Q = Q_p$, $Q = Q_N$ respectively, $\omega(Q_p) = \omega(Q_N)$.

The functional (2.1) gives rise to a bulk Euler–Lagrange equation, which can be solved in the manner of references[3,10] to yield the surface tension σ_w between the fluid and the wall.

$$\frac{\Phi}{A\rho\xi U} = \frac{\sigma_w}{\rho\xi U} = 2\int_{Q_b(T,V)}^{Q_0} \sqrt{f(Q) - f(Q_b)}\, dQ - \delta Q_0 \tag{2.14}$$

where $f(Q) = \omega(Q)/U$, the correlation length $\xi = (L/U)^{1/2}$ and $\delta = G/U\rho A\xi$ is the dimensionless parameter characterising the surface potential.

The equilibrium value of Q_0 is given by

$$\sqrt{f(Q_0) - f(Q_b)} = \delta/2 \tag{2.15}$$

The qualitative features of the solution of this equation can be understood using a well-established graphical construction.[8,10]

We shall also be interested in the extra order near the wall; this is best described using an adsorption parameter Γ where

$$\Gamma = \int_0^\infty [\, Q(z) - Q_b \,]\, dz \tag{2.16}$$

$$= \xi \int_{Q_b}^{Q_0} \frac{[\, Q - Q_b \,]\, dQ}{\sqrt{f(Q) - f(Q_b)}} \tag{2.17}$$

One may straightforwardly obtain, using eqs. (2.16) and (2.14), that

$$\Gamma = -\frac{1}{\rho}\left(\frac{\partial \sigma_w}{\partial V}\right)_T \tag{2.18}$$

This result is merely Gibbs' adsorption isotherm, and is familiar in adsorption theory.

3. RESULTS

We first discuss the paranematic-wall interface at the nematic-paranematic phase boundary. We recall that at finite bulk ordering field V the nematic (high order) and paranematic (low order) phases can exist in equilibrium at a temperature $T_{NP}(V) > T_{NI}$, and that the line of first order phase transitions terminates at T_c, V_c. For the Maier–Saupe model we have adopted, $k_B T_{NI}/U = 0.220$, $k_B T_c/U = 0.231$ and $V_c/U = 0.0105$. The nematic-paranematic surface tension σ_{np} can be derived from the free energy functional (2.1);

$$\sigma_{Np} = \rho \int_{-\infty}^{\infty} dz \left[\omega[\, Q(z)] - \omega_N(\, Q_N) + L\left(\frac{dQ}{dz}\right)^2 \right] \tag{3.1}$$

where $\omega_N(\, Q_N) = \omega_p(\, Q_p)$ is the grand thermodynamic potential at the nematic-paranematic phase boundary, at which $Q = Q_N$ in the nematic phase and $Q = Q_p$ in the paranematic phase. Then[8,10]

$$\frac{\sigma_{NP}}{\rho \xi U} = 2 \int_{Q_p}^{Q_N} \sqrt{f(\, Q) - f(\, Q_p)}\; dQ \tag{3.2}$$

Along the $n - p$ phase boundary, the wetting properties of the fluid-wall interface are determined by whether or not a nematic layer intrudes between the paranematic phase and the wall. If

$$\sigma_{PW} = \sigma_{NP} + \sigma_{NW} \tag{3.3}$$

the surface is wet; in general

$$\sigma_{PW} = \sigma_{NW} + \sigma_{NP} \cos\theta \tag{3.4}$$

where $\cos\theta$ is the contact angle at the nematic-paranematic-wall line of contact.

We obtain σ_{PW} from eqs. (2.14) and (2.15); in general there can be three solutions of eq. (2.15) for Q_0; a solution with $Q_0 \ll Q_N$ corresponding to a thin nematic layer at the wall, an unstable solution with larger $Q_0 < Q_N$, corresponding to a maximum of the functional (2.14), and a solution with $Q_0 > Q_N$ corresponding to a macroscopic nematic layer at the wall. The absolute stability of these solutions is governed by the functional (2.14).

In all cases, sufficiently close to T_c the high Q_0 solution obtains, and the surface is wet; there is a wetting transition at T_w belong

which there is a finite contact angle. T_w decreases with increasing δ and the dependence is linear in δ; the higher the field at the wall, the more likely there is to be a nematic layer. In Fig. 1 we plot the contact angle at the $n - p - w$ contact line as a function of temperature for a number of different values of δ.

As we generically expect, away from coexistence and above T_w there is a prewetting line, terminating at a surface critical point, along which there is coexistence between surface phases with a high and low Q_0 or Γ. In Fig. 2 we plot the wetting-prewetting phase diagram for a number of different values of δ. We note in particular that the prewetting line lies very close to the coexistence curve. This result seems to be a general phenomenon.[6,7,8,11,15]

A particular interesting feature of this phase diagram is only observable by extending it to the non-physical $V < 0$ region. In this region,[12,14] the bulk nematic actually orders perpendicular to the surface; we concentrate on the unphysical $Q_p < 0$ solution. As can be seen from Fig. 2, for $\delta > 0.032$ $T_w < T_{NI}$, but $T_{NI} < T_{scp}$, and the prewetting line crosses the $V = 0$ line. This situation obtains with

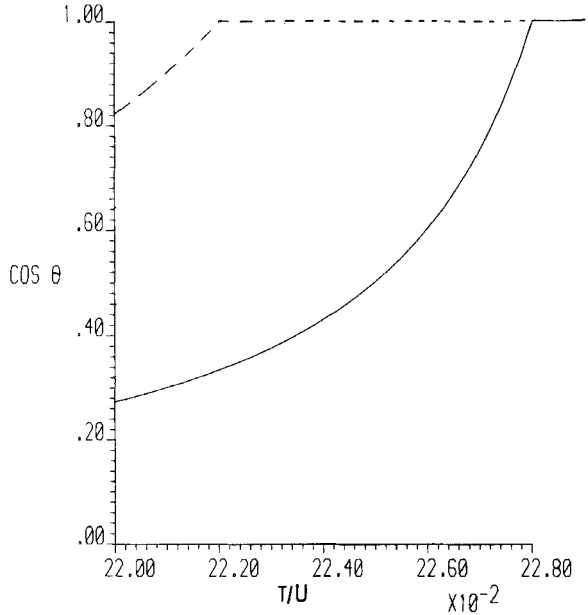

FIGURE 1. Contact angle θ at the wall-nematic-paranematic line of contact, along the nematic-paranematic phase boundary, as a function of temperature. Broken curve $\delta = 0.0267$, $T_w/U = 0.222$, solid curve $\delta = 0.0087$, $T_w/U = 0.228$.

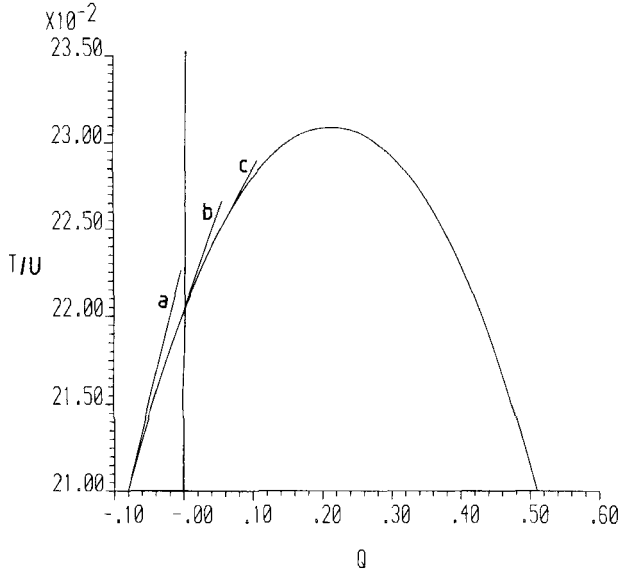

FIGURE 2. Paranematic-nematic phase diagram as a function of temperature with surface phase diagram superimposed. Prewetting line (a) is unphysical and corresponds to $T_w/U = 0.210$, $\delta = 0.061$. Prewetting line (b) with $T_w/U = 0.220$ $\delta = 0.032$, and prewetting line (c) with $T_w/U = 0.226$, $\delta = 0.0147$ are physical.

increasing δ and hence decreasing T_w and hence decreasing T_w and T_{scp} until at $\delta = 0.61$ the surface critical point occurs on the $V = 0$ line. For these values of δ we expect a surface phase transition as the prewetting line is crossed. This situation is exhibited in Fig. 3, where the surface free energy is plotted as a function of temperature at zero external field for a value of δ giving rise to a surface phase transition. The surface free energy has a discontinuity on gradient at the surface phase transition reflecting the jump to a different branch of the surface free energy curve; the metastable and unstable branches of this curve are also shown. At T_{NI}, there is a jump in the surface free energy as the nematic phase no longer intrudes between the isotropic phase and the wall; because there is perfect wetting, Antonow's law holds.

We show another aspect of the same phenomenon in Fig. 4, where we plot the adsorption, as defined in eq (2.16) as a function of temperature. We see an adsorption increasing with decreasing temperatures for high T; a van der Waals loop leading to an unstable region as the surface phase transition is crossed, high adsorption below this,

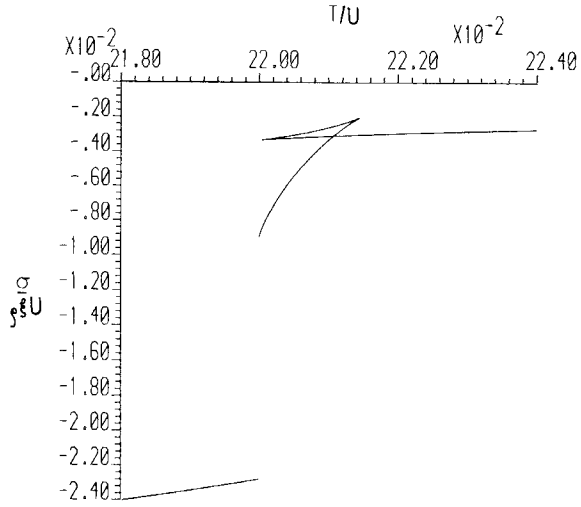

FIGURE 3. Surface free energy as a function of temperature at $V = 0$, $T_w/U = 0.215$, $\delta = 0.048$. The metastable and unstable branches of the curve are in the loop.

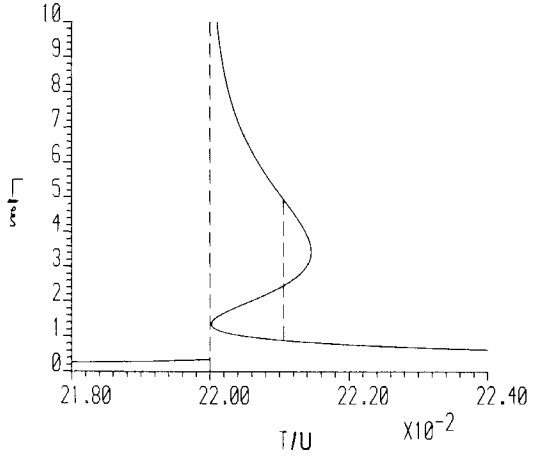

FIGURE 4. Adsorption Γ as a function of temperature for case adumbrated in Fig. 3. The prewetting transition and the nematic-isotropic transition are indicated by dotted lines.

but above T_{NI}, corresponding to a nematic layer between the bulk isotropic fluid and the wall, and finally below T_{NI} low adsorption as the orienting potential of the wall is unable to improve on the bulk values of Q in the bulk nematic phase.

It is important to note, however, that although Γ has a discontinu-

ity at T_{NI}, the value of the order parameter at the wall Q_0 does not do so; in this situation, near the wall the fluid is nematic-like, and the discontinuity in Γ arises because the nematic-isotropic interface finally reaches $z = \infty$ as $T \to T_{NI}$ and the bulk fluid becomes nematic. This is made evident in Fig. 5, in which order parameter profiles are plotted for different temperatures above T_{NI}, for the same value of δ. The enormous difference between the two profiles on the prewetting line is immediately evident; the interpretation of this transition in terms of a thin film-thick film transition is less obvious, although for $T < T_{pw}$, a shoulder in the order parameter profile, corresponding to the incipient emergence of a nematic-isotropic interface, begins to show itself.

The same phenomena can also be observed as a function of V at constant T. In Fig. 6 we show the surface free energy as a function of V; this graph shows the same generic features as Fig. 4, including metastable sections, an unstable section, and the surface free energy jump at the paranematic-nematic bulk phase boundary. Fig. 7 shows the analogous curve for adsorption as a function of external field; the van der Waals loop and corresponding discontinuity in Γ can be seen along with the divergence of Γ as the bulk phase boundary is approached, followed finally on the nematic side of the phase bound-

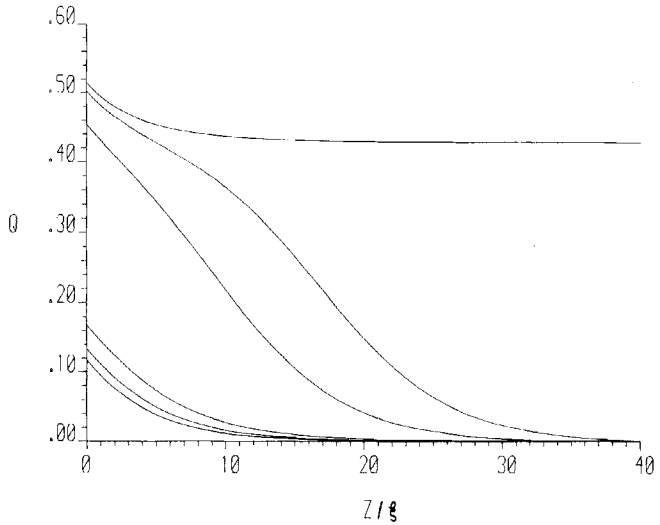

FIGURE 5. Order parameter profiles for different tempeatures for system described in Figs. 3 and 4. In decreasing order of temperature and increasing order of Q_0: $T/U = 0.227, 0.224, 0.2214(= T_{pw}), 0.2214(= T_{pw}), 0.2205, 0.2202(= T_{NI})$.

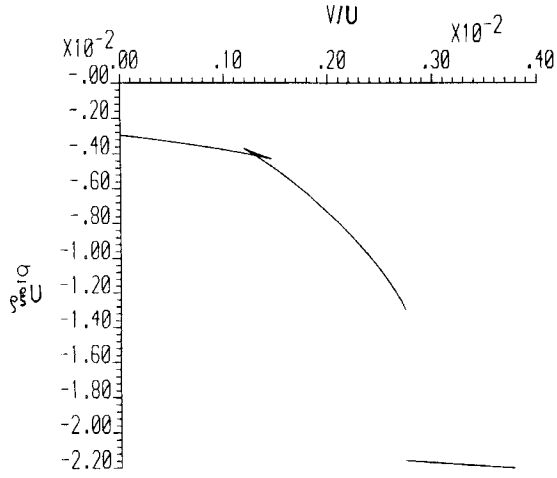

FIGURE 6. Surface free energy as a function of external field in paranematic and nematic region above T_{NI}; $T/U = 0.223$, $T_w/U = 0.215$. Note discontinuities corresponding to prewetting and paranematic and nematic transition.

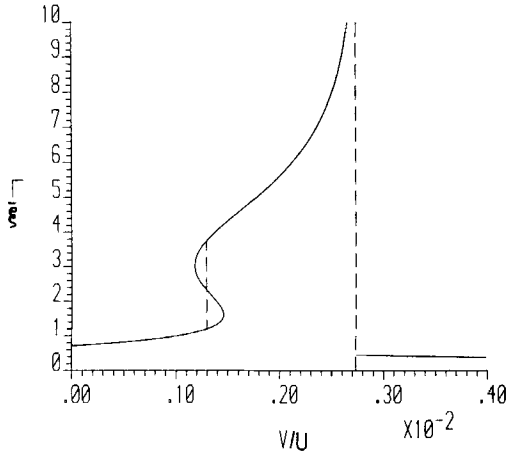

FIGURE 7. Adsorption Γ, as a function of field for case described in Fig. 6.

ary by a low value of Γ. Finally in Fig. 8 we exhibit order parameter profiles for different values of V; the discontinuity in Q_0 at the prewetting line, followed by the emergence of a shoulder in the profile with increasing V, and finally the fact that Q_0 is continuous across the nematic-paranematic phase boundary, can be seen in this figure.

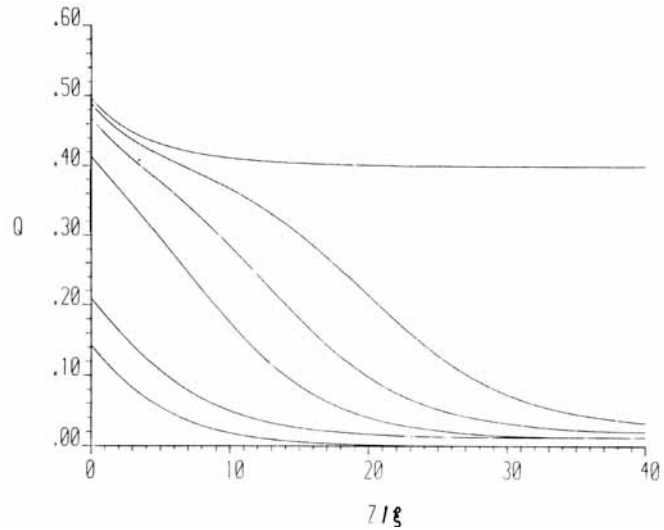

FIGURE 8. Order parameter profiles for different fields for system of Figs. 6 and 7. In increasing order of V and Q_0, $V/U = 0, 0.0013-, 0.0013+, 0.0020, 0.0025, 0.00273$. The last case corresponds to nematic-paranematic coexistence.

4. DISCUSSION AND CONCLUSIONS

We have carried out a study of the behaviour of a particularly simple model of a liquid crystal near a wall. The wall exerts a local orienting potential on the liquid crystal; the liquid crystal admits no density-orientation coupling, and the wall does not exert a potential which interacts with the density. In the bulk, the liquid crystal has a free energy of the Maier–Saupe form. The liquid crystal director is constrained to be perpendicular to the wall. The global surface phase diagram can be better understood by studying the interaction of the wall with nematic and paranematic phases in a bulk external field. In this respect our study is an extension of a study of Sheng,[3] whose model suffers from similar defects to ours, but whose bulk free energy is of a Ginzburg–Landau form. The study enables a connection to be made between the results of Sheng and more general results on layer formation derived over the last few years.[7-11]

Like ourselves, Sheng predicts a boundary layer transition for an intermediate set of values of the dimensionless parameter g, where $g = G/A[LaT_{NI}]^{-1/2}$, and for small Q

$$\omega(Q) = a(T - T^*)Q^2 \tag{4.1}$$

The identification[20] $a = (5k_B\rho/2)$ enables us to make contact with the dimensionless parameter δ we have defined in §2; we find

$$g = 1.35\delta \tag{4.2}$$

Sheng finds a boundary layer transition for

$$\delta_1 = 0.0042 < \delta < 0.0089 = \delta_2 \tag{4.3}$$

whereas we find a transition for

$$\delta_1 = 0.032 < \delta < 0.061 = \delta_2 \tag{4.4}$$

(both at zero field). We remark upon the enormous difference between the quantitative predictions of the two closely related models; the quantitative reliability of each is suspect as a consequence, although similar disparities between the predictions of similar models has occurred before in the theory of wetting.[15]

We have concentrated, in presenting our results, on those regions of δ for which a boundary phase transition is predicted. For $\delta > \delta_2$, T_w and T_{scp} are lower than T_{NI}, and perfect wetting obtains at zero field; as Sheng finds, we find that σ is discontinuous at T_{NI}, the discontinuity is given by Antonow's rule, Γ diverges continuously at $T \to T_{NI}$ from above, and Q_0 is continuous through the transition. Contrariwise, for $\delta < \delta_1$ T_w and T_{scp} are higher than T_{NI}, the discontinuity in is given by eq. (3.4), and Γ remains finite as $T \to T_{NI}$ from above, and Q_0 is discontinuous at the transition.

At this stage we are very hesitant about making detailed comparisons of our theoretical results with experiment.[1,2,5] The restrictions we place on our model are very severe; relaxing some of these restrictions may leave the results quantitatively changed, but qualitatively similar, as we find, for instance, when comparing our results to those of Sheng. In particular, the orientational contribution to the surface free energy may be swamped by a density dependent contribution. Telo da Gama[6] and we, in preliminary calculations, find that changing the form of the surface potential, even within mean field theory, can change the order of the wetting transition from first to second, thus eliminating the prewetting line and the boundary phase transition. In any event it is clear that a correct calculation of the wetting properties of a model depends on a good understanding of the bulk phase diagram; the nematic-isotropic transition is not well understood either microscopically or phenomenologically and mean field theories vastly underestimate the role of fluctuations. These fluctuations may have

an equally profound effect on the nature of the surface transitions. Finally, we observe that an experimental manifestation of a nematic boundary phase transition would be of some significance in surface physics, because it would be an observation of the prewetting line; despite much experimental effort no such observation has yet been made in any adsorption experiment.[21]

Acknowledgements

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