Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Lelidis, I.(1998) 'Prewetting transition induced by an external bulk field', Liquid Crystals, 25: 4, 531 — 536
To link to this Article: DOI: 10.1080/026782998206056
URL: http://dx.doi.org/10.1080/026782998206056

LIQUID CRYSTALS, 1998, VOL. 25, NO. 4, 531–536

Prewetting transition induced by an external bulk field

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(*Received 8 May 1998; accepted 12 June 1998*)

The Landau–de Gennes model of the boundary layer phase transition in nematic liquid crystals is extended to include electric field effects. Calculations are performed in the case of a semi-infinite nematic sample bounded by a solid wall. The phase diagrams presented show that the prewetting transition can be induced by the electric field. The transition moves to higher temperature with increasing field and disappears above the prewetting critical point. A system exhibiting partial wetting should transit to complete wetting under a high enough electric field. These predictions are confirmed within the actual experimental limits.

1. Introduction

Wetting phenomena appear at order–disorder transitions of a material in contact with a substrate which enhances order. When the bulk transition temperature is approached from above, an ordered thin layer appears at the interface of the material with the substrate while the bulk is still in the disordered phase. At the bulk transition, the thickness of this ordered boundary layer is expected either to remain finite or to diverge. In the former case, the substrate is partially wetted while in the latter case the wetting is complete. The system can change from partial to complete wetting by the prewetting transition [1–7]. The latter is a first order transition terminating at a critical point. The prewetting transition has been only recently observed in a system of ^{4}He on a Cs substrate [8] and for a binary liquid mixture of methanol–cyclohexane [9].

At the isotropic–nematic phase change, nematic liquid crystals also present an order–disorder transition: the nematic phase has orientational quadrupolar ordering S ($0<S\leqslant 1$) around the director $\mathbf{n}$ ($\mathbf{n}^2=1$), while the isotropic phase has none. In nematic liquid crystals, both partial and complete wetting have been observed [10–14]. On the contrary, the prewetting transition has never been seen. To observe this transition, one could use binary mixtures between a liquid crystal which completely wets the substrate and another liquid crystal which only partially wets the substrate. This method has the drawback that the system does not remain strictly the same, and further problems could arise from demixing. Another way to observe the prewetting transition should be the application of an external ordering bulk field like a magnetic or electric field. Moreover, the use of an external bulk field should give access to the entire prewetting phase diagram and should permit the localization of the prewetting critical point.

Wetting phenomena under an external bulk field were first studied for magnetism [15, 16]. The possibility of inducing the prewetting transition by an external magnetic (or electric) field in nematic liquid crystals was first studied by Poniewierski and Sluckin [17] who used the Maier–Saupe mean field model. As is well known, the Maier–Saupe model fails for quantitative predictions [18–20]. In view of recent experimental results [21] on the electric field induced bulk isotropic$\rightarrow$nematic transition, which are in good quantitative agreement with the predictions of the Landau–de Gennes model [21, 22], it seems natural to use this latter model in the description of the prewetting transition under an external bulk field.

In this paper, the Landau–de Gennes phenomenological model of the prewetting transition proposed by Sheng [23, 24] is extended to include the effect of an external electric field. The case of a semi-infinite liquid crystal sample bounded by a solid substrate which enhances order is considered. The applied electric field induces order in the same direction as the surface field.

The organization of the paper is as follows. In §2, the Landau–de Gennes model is described. In §3, the thermodynamic phase diagram of the prewetting transition is calculated numerically as a function of temperature, surface field strength and electric field strength. Furthermore, the boundary layer order behaviour under an electric field is calculated in the case of a substrate inducing partial wetting, and the surface order parameter profile is calculated for different values of the electric field. Finally in §4, the prospect for observing the prewetting transition is discussed, and some conclusions are presented.

2. Model

Consider a nematic liquid crystal confined to the half space $z>0$ by a substrate at $z=0$. The sample is assumed to be uniform in the x and y directions. Since the substrate breaks the bulk symmetry, the order parameter depends on the distance z from the substrate: $S=S(z)$. It is assumed that the direction of the anisotropy axis on the surface and in the bulk coincides with the z axis (homeotropic alignment). Biaxiality is excluded on the liquid crystal–substrate interface for purely symmetry reasons. In contrast, symmetry permits biaxiality at the interface between the ordered boundary layer and the isotropic phase. In the case of homeotropic boundary conditions, the correction of the interfacial energy due to the biaxiality is of the order of 1% [25]. When a bulk electric field is applied parallel to the z axis, the symmetry of the isotropic phase is broken and the correction due to the biaxility should be even lower than the correction in the absence of the field. Therefore, biaxiality is not considered further. The Landau free energy functional (per unit surface area) describing this semi-infinite system in terms of the scalar order parameter S is given by [23, 24]

$$\Phi\{S\} = \int_0^\infty \left[f_V(S) + \frac{1}{2} L\,(\nabla S)^2 + \delta(z) f_i \right] \mathrm{d}z. \quad (1)$$

The bulk free energy density $f_V(S)$ has the well-known form [7, 18]

$$f_V = f_0 + \frac{1}{2}a(T-T^*)S^2 + \frac{1}{3}bS^3 + \frac{1}{4}cS^4 \quad (2)$$

where f_0 is the free energy of the isotropic phase and is defined here equal to zero; $a>0$, $b<0$, $c>0$ are supposed constants; T^* is the supercooling limit for the isotropic phase. The first order isotropic–nematic phase transition takes place at $T_{NI}=T^*+2b^2/9ac$ with a jump of the nematic order by the amount $S_{NI}=-2b/3c$. $L>0$ is an elastic constant. $f_i=-wS_0$ is the surface contribution in the free energy, $S_0=S(z=0)$. w denotes the surface strength and is positive in order that the surface enhances order. For $w=0$ the surface has no effect at all on the phase transition, while w negative means that the surface is inducing disorder.

In order to consider the system under an external stabilizing electric field $\mathbf{E}$, one has to add to the free energy functional the dielectric term

$$F_E = \int_0^\infty f_E(E, S)\,\mathrm{d}z \quad (3)$$

where f_E to the lowest order reads $f_E=\mu E^2 S$. f_E describes the direct coupling between $\mathbf{E}$ and S via the dielectric anisotropy $\mu=-\varepsilon_{a0}/12\pi$; $\varepsilon_{a0}=\varepsilon_a/S$ is the dielectric anisotropy for $S=1$. In this work, the case under consideration is a thermotropic liquid crystal with positive dielectric anisotropy while $\mathbf{E}$ is applied parallel to the nematic director $\mathbf{n}$. In the presence of $\mathbf{E}$, the bulk undergoes a first order paranematic$\rightarrow$nematic phase transition terminating at a critical point whose coordinates are the critical order S_C, the critical temperature T_C, and the critical field E_C, and which may be expressed as [21]

$$S_C = -\frac{b}{3c}, \qquad T_C = T^* + \frac{b^2}{3ac} \qquad \text{and} \qquad E_C^2 = \frac{bS_C^2}{3\mu}.$$

The total free energy per unit surface area of the system now reads $F=\Phi+F_E$.

The order parameter equilibrium profile is determined, after minimization of F with respect to S, by the Euler–Lagrange equation which yields

$$\frac{\mathrm{d}f_V}{\mathrm{d}S} + \frac{\mathrm{d}f_E}{\mathrm{d}S} = L\,\frac{\mathrm{d}^2 S}{\mathrm{d}z^2} \quad (4)$$

with the boundary conditions

$$L\,\frac{\mathrm{d}S}{\mathrm{d}z}\bigg|_{z=0} = -w \qquad \text{and} \qquad \frac{\mathrm{d}S}{\mathrm{d}z}\bigg|_{z=\infty} = 0,\ S(z=\infty) = S_b. \quad (5a, 5b)$$

S_b is the undistorted bulk order in the presence of an external electric field $\mathbf{E}$. $S_b(E)$ is calculated from the equilibrium equation $f'_V + f'_E = 0$ and it is given in analytic form in [26]. On solving equation (4) with the boundary conditions, equations (5), one finds

$$\begin{cases} \left(\dfrac{\mathrm{d}S}{\mathrm{d}z}\right)^2 = \dfrac{2}{L}\,[f_V(S)+f_E(S)-f_V(S_b)-f_E(S_b)] \\[2ex] f_V(S_0)+f_E(S_0) = f_V(S_b)+f_E(S_b)+\dfrac{w^2}{2L}. \end{cases} \quad (6a, 6b)$$

For negative surface energy, S_0 is larger than the bulk order parameter and $\mathrm{d}S/\mathrm{d}z<0$. Substitution of equation (6a) in F gives the boundary layer free energy

$$f_{BL} = (2L)^{1/2} \int_{S_0}^{S_b} [f_V(S)+f_E(S)-f_V(S_b)-f_E(S_b)]^{1/2}\,\mathrm{d}S - wS_0. \quad (7)$$

The equilibrium value of S_0 is determined by the condition $\mathrm{d}f_{BL}/\mathrm{d}S_0=0$. In the case of multiple roots, one chooses the S_0 which gives the lowest value of f_{BL}. The boundary layer transition temperature is calculated by the supplementary condition of equal free energy between the low and high order phases. The limit of thermodynamical stability is given by the spinodal line described by the equation $\mathrm{d}^2 f_{BL}/\mathrm{d}S_0^2=0$. The profile of the order parameter $S(z)$ is obtained from integration of equation (6 *a*) which yields

$$z = \left(\frac{L}{2}\right)^{1/2} \int_{S_b}^{S_0} \frac{dS}{[f_V(S) + f_E(S) - f_V(S_b) - f_E(S_b)]^{1/2}}. \tag{8}$$

3. Results

In the absence of an electric field, as is well known, a strong enough surface field can induce the prewetting transition when cooling from the disordered phase [5, 6]. One estimates qualitatively the electric field influence on the prewetting transition when equation (6 *b*) is written more explicitly in the following form:

$$f_V(S_0) = f_V(S_b) + \frac{1}{2L}[w^2 + 2L\,|\mu| E^2 (S_0 - S_b)].$$

A comparison with the case in the absence of an electric field shows that the presence of the electric field is *equivalent* to enhancing the surface field. The prewetting transition should appear at a higher temperature.

Numerical resolution of equations (6) and (7) gives $S_0(T, E, w)$ and the thermodynamic phase diagram for the prewetting transition under a field. For the numerical calculations, the following values are used for the constants appearing in the free energy: $a = 0{\cdot}11 \times 10^7$ erg cm^{-3} K, $b = 1{\cdot}56 \times 10^7$ erg cm^{-3}, $c = 3{\cdot}47 \times 10^7$ erg cm^{-3} [21], and $L = 10^{-6}$ erg cm^{-1} [27].

Figure 1 gives the phase diagram of the prewetting transition in the plane of the surface-field and at temperature (w, $t = T - T_{NI}$) for different values of the electric field (isofields). The curve (a) is the prewetting transition line calculated in the absence of an electric field ($E = 0$). When the substrate field is positive, it induces a weak nematic order at the interface; the induced phase is called paranematic. The prewetting transition takes place between two phases (paranematic and nematic) of the same symmetry and thus it is of the first kind. The prewetting transition appears only for temperatures higher than T_{NI} and for values of w higher than a threshold value $w_{thr} = 0{\cdot}0638$ erg cm^{-2}. If $w < w_{thr}$, the prewetting transition does not appear because the bulk transition take place before it. For $w > w_{thr}$, when cooling from the isotropic phase, the prewetting transition occurs at a temperature T_{tr} higher than T_{NI}, and it should be visible. T_{tr} increases with w and for $w_{PWC} = 0{\cdot}1215$ erg cm^{-2} at T_{PWC} the first order transition becomes of the second kind, while disappearing at higher temperature. For $w > w_{PWC}$ the transition disappears. The order of the boundary layer changes continuously from the paranematic to the nematic phase, and these are no longer discernible. The other curves in the same figure are isofields with $E \neq 0$. The curve (b) is calculated at

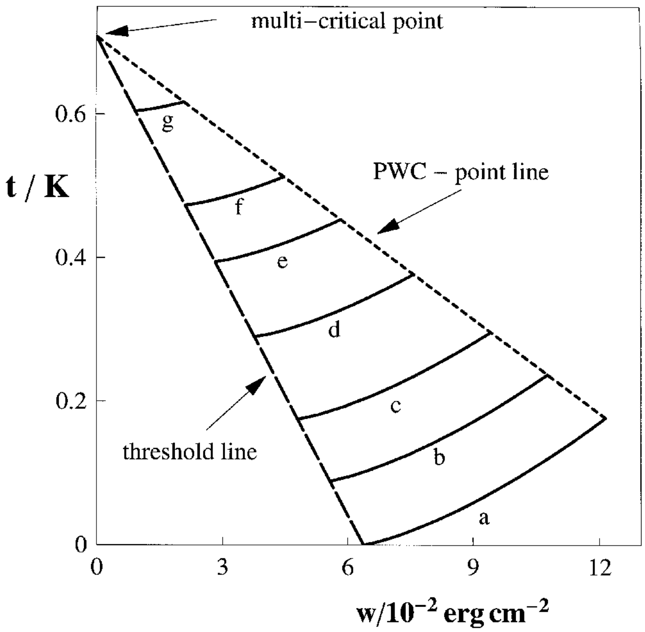

Figure 1. Prewetting transition temperature ($t = T - T_{NI}$) versus surface field strength w for different values of the electric field. (a), (b), (c), (d), (e), (f) and (g) are isofields (see the text). The dotted line is the prewetting critical points line; the dashed line is the prewetting transition threshold line.

$E = 5$ V µm^{-1}, (c) at $E = 9$ V µm, (d) at $E = 10{\cdot}5$ V µm^{-1}. (e) at $E = 11{\cdot}5$ V µm^{-1}, and (f) at $E = 13$ V µm^{-1}.

One remarks that the critical point of the transition under a field appears for weaker surface fields while the corresponding temperature increases with the electric field. Under a field, the transition appears for a weaker surface field $w_{thr}(E)$, but at a higher temperature. Approaching the bulk critical point, the range of the prewetting transition sweeps out. For $w = 0$, one finds $E_{PWC} = E_C$ and $T_{thr} = T_{PWC} = T_C$; the bulk and the prewetting critical points coincide. Both transitions disappear at higher field values. The dotted line gives the variation of the prewetting critical point with the external field; it is a line of prewetting critical points. The dashed line gives the variation of the threshold surface field $w_{thr}(E)$ with the electric field (prewetting transition threshold line). The linear variation of the wetting temperature with the electric field was first pointed out by Poniewierski and Sluckin [17]. The prewetting transition takes place in the region between the prewetting transition threshold line, the prewetting critical points line, and the prewetting line in the absence of an electric field.

Figure 2 presents the influence of the electric field on the boundary layer order parameter in the plane (S_0, $t = T - T_{NI}$). It shows some isofields of S_0 as a function of the temperature at constant surface field

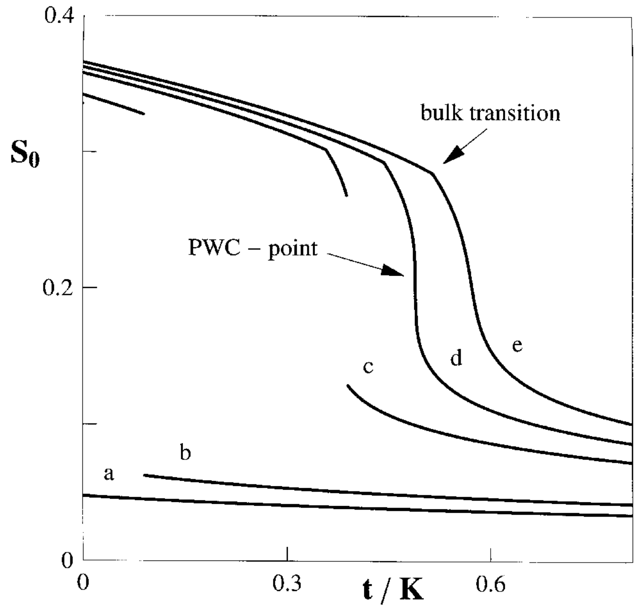

Figure 2. Boundary layer order parameter versus temperature ($t = T - T_{NI}$) for different electric field strengths. (a), (b), (c), (d) and (e) are isofields (see the text). The jump of the order parameter corresponds to the prewetting transition; PWC is the prewetting critical point.

$w = 0{\cdot}05\ \mathrm{erg\,cm^{-2}}$. w is chosen to correspond to partial wetting in the absence of an external field. Isofield (a) is calculated in the absence of an electric field. When cooling, S_0 increases slightly, but it remains lower than the bulk order at T_{NI}, i.e. the wetting is partial. For $E = 5\ \mathrm{V\,\mu m^{-1}}$, isofield (b), the wetting remains partial. Nevertheless, the transition temperature to the nematic phase has been increased because the bulk transition is induced by the electric field at a higher temperature $T_{NI}(E)$ than $T_{NI}(E = 0)$. The isofield (c) is calculated at $E_{thr} < E < E_{PWC}$. When cooling the system, S_0 first increases continuously. With further cooling, S_0 undergoes the prewetting transition and jumps to a higher value, corresponding to the nematic phase. Further fall in the temperature provokes a continuous increase of S_0. At $T_{NI}(E)$, a slope change of $S_0(T)$ appears because the bulk transition arrives. Curve (d) is the prewetting transition critical isofield ($E_{PWC} = 11{\cdot}13\ \mathrm{V\,\mu m^{-1}}$). As the temperature is decreased, S_0 has a vertical inflection point: the critical point of the prewetting transition. There follows a saturation of S_0 with cooling, while at lower temperature the bulk transition appears provoking a slope change of $S_0(T)$. For fields higher than E_{PWC}, isofield (e) the prewetting transition disappears and S_0 changes continuously from the paranematic to the nematic phase. If the electric field is lower than the bulk critical field, S_0 presents a slope discontinuity at a temperature lower than T_C because of the bulk transition.

Figure 3 shows the surface order parameter profile as a function of the distance z away from the substrate. The temperature is fixed at $T = T_{NI} + 0{\cdot}38$ K and the surface field is held at $w = 0{\cdot}05\ \mathrm{erg\,cm^{-2}}$. Curve (a) is calculated from equation (8) in the absence of an electric field. The wetting is partial. For a field of $E = 10\ \mathrm{V\,\mu m^{-1}}$, the prewetting transition has already taken place, curve (b). For $E = 12\ \mathrm{V\,\mu m^{-1}}$, higher than the bulk transition field, curve (c), the bulk changes to the nematic phase.

Figure 4 shows the phase diagram of the prewetting and of the bulk transitions in the plane of the electric field and at temperature (E, $t = T - T_{NI}$). The curve (e) is the bulk binodal. The bulk is nematic on the right of the binodal. The curves (a), (b), (c) and (d) are the prewetting transition lines calculated at w_{PWC}, $w = 0{\cdot}11\ \mathrm{erg\,cm^{-2}}$, $w = 0{\cdot}075\ \mathrm{erg\,cm^{-2}}$, and $w = 0{\cdot}05\ \mathrm{erg\,cm^{-2}}$, respectively. When $w > w_{thr}$, the prewetting line crosses the $E = 0$ axis at a temperature above T_{NI}. For zero field, the curve (d) does not show prewetting but under a strong enough field the prewetting transition appears. The bold points (a), (b), (c), (d) and MCP are prewetting critical points, while the dashed line is the prewetting critical points line. The point MCP is a multicritical point where the bulk critical point and the prewetting critical point line merge.

4. Discussion and conclusion

Recently, it was observed that a sufficiently high electric field induces the bulk isotropic→nematic transition [21] and one expects that the external field should also enhance wetting effects [28, 29]. Experimentally, one should induce the prewetting transition with an electric field lower than the bulk critical field E_C. For a nematic liquid crystal of high dielectric anisotropy $\varepsilon_a \sim 10$ (e.g. nCB), E_C is of the order $14\ \mathrm{V\,\mu m^{-1}}$ [21]. This field is experimentally accessible [21, 28]. The equivalent

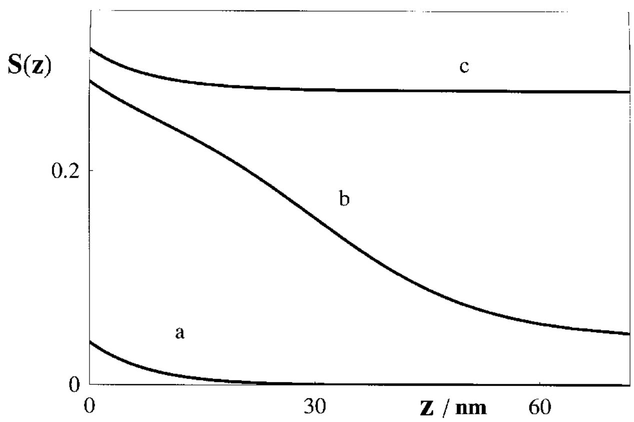

Figure 3. Surface order parameter profile for different values of the electric field: (a) for $E = 0$; (b) for $E = 10\ \mathrm{V\,\mu m^{-1}}$; and (c) for $E = 12\ \mathrm{V\,\mu m^{-1}}$.

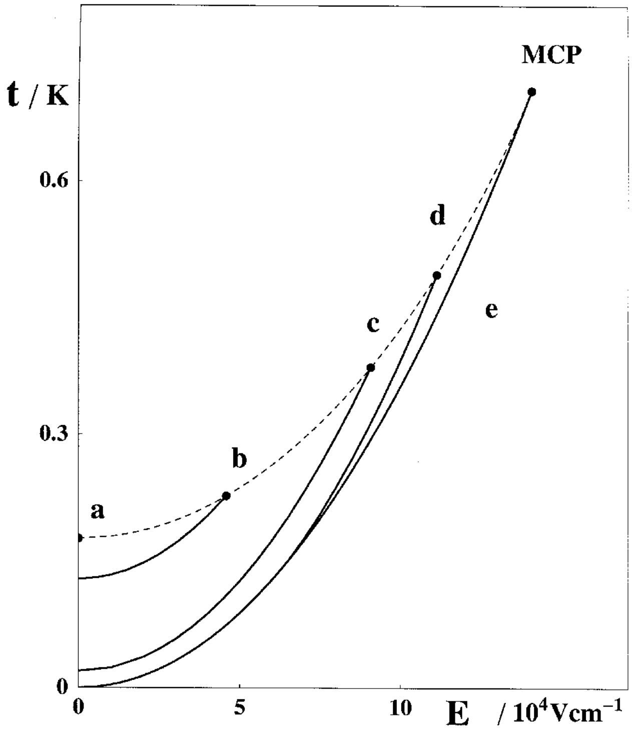

Figure 4. Temperature ($t = T - T_{NI}$) versus electric field phase diagram of the prewetting and bulk phase transitions. Lines (a), (b), (c), and (d) are prewetting lines for different values of the surface field strength (see the text). Line (e) is the bulk binodal, the dashed line is the prewetting critical points line and MCP is a multicritical point.

applied magnetic field may be obtained by replacing μE^2 in the equation $\mu E_C^2 = bS_C^2/3$, by $4\pi\chi_a H^2$ where χ_a is the anisotropic part of the magnetic susceptibility. In thermotropic liquid crystals, χ_a is typically of the order 10^{-7} in cgs unit. The corresponding magnetic critical field $H \sim 1{\cdot}4 \times 10^6$ G is more difficult to achieve.

Another crucial factor which determines the possibility of observing the prewetting transition is its distance from the bulk binodal. As is shown in figure 4, for a temperature higher than the nematic superheating temperature (in order to avoid a spontaneous bulk transition), the prewetting transition should be induced for a field of about 5 V μm^{-1} lower than the corresponding field of the bulk transition. Experimentally, it is easy to obtain a resolution better than 0·1 V μm^{-1} [21, 28, 29], i.e. the prewetting transition should be easily observed using an external bulk electric field. The above estimations are one order of magnitude lower than the predictions of the Maier–Saupe model for the prewetting transition [17]. The predicted threshold value of the surface strength $\sim 0{\cdot}06$ erg cm^{-2}, for a prewetting transition in the absence of any external bulk field, seems to be in good accordance with experimental results for prewetting†.

To conclude, the influence of an external electric field on the prewetting transition and on the wetting behaviour of a nematic liquid crystal has been studied using a phenomenological Landau–de Gennes model. The thermodynamic phase diagram is calculated for a semi-infinite nematic sample bounded by a solid surface. The substrate potential strength is taken to be a linear function of the surface order parameter and its anisotropy direction perpendicular to the substrate. Solving the Euler–Lagrange equations numerically, it is found that the electric field can induce a first order boundary layer transition terminating at the prewetting critical point, even for systems which give partial wetting in the absence of an electric field. With the electric field, the prewetting transition temperature increases, while a line of prewetting critical points appears. When the surface field is zero the prewetting critical point coincides with the bulk phase critical point, giving rise to a multicritical point. The localization of the prewetting critical point and the determination of the phase diagram using a bulk electric field are within the actual experimental limits.

I thank G. Durand and T. J. Sluckin for useful discussions and suggestions.

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†Unpublished data of I. Lelidis and G. Durand. They observed a prewetting transition in a mixture of 8CB and 10CB at 0·1 K above the spontaneous isotropic–nematic transition temperature.

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