On the free energy of nematic wetting layers

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This paper is dedicated to Professor J. A. Morrison

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The contributions to the free energy of a nematic wetting layer as a function of its thickness l are analyzed. The longest-range contribution is due to distortion of the nematic director across the film, resulting from different preferred molecular orientations at the two interfaces bounding the film. Van der Waals forces as well as the decaying tails of the interfacial order-parameter profiles yield contributions to the free energy of successively shorter range. These effects lead to crossovers between different scaling régimes for variation of the mean wetting-layer thickness with temperature. Experimental implications of the results are described.

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On a étudié l'influence de l'épaisseur (l) de couches nématiques mouillantes sur l'énergie libre. La contribution qui se fait sentir à la plus grande distance est dûe à une distorsion du directeur nématique à travers le film; cette distorsion résulte elle-même d'orientations moléculaires préférentielles différentes aux deux interfaces qui lient le film. Utilisant les forces de van der Waals ainsi que les profils de l'ordre interfacial/paramètres, on a pu déduire les contributions à l'énergie libre pour des distances de plus en plus courtes. Ces effets conduisent à des croisements entre divers régimes d'échelles pou la variation de l'épaisseur moyenne de la couche mouillante avec la température. On décrit les implications expérimentales de ces résultats.

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Consider a liquid crystalline material at a temperature T slightly above the transition temperature T_{NI} for the onset of nematic (N) ordering. While the bulk of the material then exists as an isotropic (I) liquid phase with no long-range orientational order, some degree of local nematic order may be spontaneously induced at the interface with another phase α such as a solid substrate or the vapour in coexistence with the liquid. If, on lowering the temperature, the mean thickness $\bar{l}$ of that nematic layer diverges over microscopic length scales as $T \rightarrow T_{\mathrm{NI}}$, then we say that the nematic phase *completely wets* the α–I interface. Experimental evidence of this effect has been seen for a number of nematic substances, at both solid–liquid (1–3) and liquid–vapour (3–5) interfaces.[2] Entirely analogous wetting phenomena involving three distinct thermodynamic phases have recently come under extensive study for a variety of physical systems (7).

In this note we draw attention to some novel critical properties characterizing the approach to complete wetting in the case of a nematic layer. In particular, we focus on the asymptotic scaling laws describing the divergence of the mean wetting-layer thickness $\bar{l}$ in the limit that $t \equiv (T - T_{\mathrm{NI}})/T_{\mathrm{NI}}$ goes to zero. Our approach is similar to ones used successfully to describe wetting in other systems (7–10), based on analysis of the free energy $\sigma(l)$ per unit area of the layer as a function of its thickness l, when the latter is viewed as a thermodynamic order parameter. This approach is meaningful if l is large compared with the characteristic widths $\xi_{\alpha\mathrm{N}}$ and ξ_{NI} of the two interfaces bounding the film. We shall discuss later the consequences of a large interfacial width ξ_{NI}, associated with the coherence length for fluctuations in the bulk liquid crystal. In mean-field theory, which neglects *interface* fluctuations, the equilibrium thickness $\bar{l}$ follows from $[\partial\sigma(l)/\partial l]_{l=\bar{l}} = 0$.

The free energy $\sigma(l)$ has the form (7–10)

$$[1] \quad \sigma(l) = Hl + \sigma_{\alpha\mathrm{N}} + \sigma_{\mathrm{NI}} + V(l)$$

where $\sigma_{\alpha\mathrm{N}}$ and σ_{NI} are the equilibrium surface tensions of the α–N and N–I interfaces, respectively, in the limit of infinite separation l and at $T = T_{\mathrm{NI}}$. The term Hl describes the increase in free energy due to the presence of a metastable nematic layer when $T > T_{\mathrm{NI}}$, where H is the difference in (grand canonical) free energies per unit volume between the bulk nematic and either one of the coexisting α or I phases. For small t, we have

$$[2] \quad H \approx \Lambda t, \; \Lambda \equiv T_{\mathrm{NI}}(S_{\mathrm{I}} - S_{\mathrm{N}})$$

where S_{I} and S_{N} are the bulk entropies per unit volume at $T = T_{\mathrm{NI}}$. The remaining term $V(l)$ in [1] represents all other contributions to the film free energy when its thickness l is finite rather than infinite. Here we shall *assume* that $V(l)$ has its absolute minimum at infinite l, consistent with the occurrence of complete wetting at N–I coexistence. Whether this indeed occurs or not ultimately depends on the short-range behaviour of $V(l)$, which in turn is related to the nature of microscopic forces in the system (7–10). In contrast, *if* complete wetting does occur, then it is the long-range behaviour of $V(l)$ which determines the critical properties that we shall examine here.

The leading-order contribution to $V(l)$ at large thickness l is due to distortion of the nematic director across the film. This effect arises whenever the separate α–N and N–I interfaces favour different orientations of the molecules, which we argue should be the rule rather than the exception. For example, the director at isolated N–I interfaces is usually observed to be obliquely aligned, with tilt angle Θ_{NI} (relative to the co-ordinate direction z perpendicular to the interface) falling in the range

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[2] In a recent study (6), near-complete-wetting growth of a *smectic-A* film at a liquid–vapour interface was observed.

0.8–1.3 radians (11, 12). This has been found for several different nematic substances, and thus appears to be a universal phenomenon. On the other hand, the alignment at isolated vapour–nematic interfaces is most often found to be homeotropic (4–6, 13), with $\Theta_{VN} = 0$, although one exception is currently provided by the liquid crystal PAA, for which $\Theta_{VN} = \pi/2$ (14). The alignment at a solid substrate is well-known to be highly variable, depending on the specific nature of both the liquid crystal and the substrate surface.

When $\Theta_{\alpha N}$ and Θ_{NI} differ, the director is distorted across the nematic layer if the latter is sufficiently thick. Using standard arguments of the Frank elastic theory (15, 16), in the approximation where one keeps only one elastic constant K,[3] the distortion is described by the tilt-angle variation

$$[3] \qquad \Theta(z) = \Theta_{\alpha N} + (\Delta\Theta)z/l, \Delta\Theta \equiv \Theta_{NI} - \Theta_{\alpha N},$$

where the α–N and N–I interfaces are located at $z = 0$ and $z = l$, respectively. This yields a contribution (16)

$$[4] \qquad V_d(l) \approx \tfrac{1}{2}K(\Delta\Theta)^2/l$$

to the free energy $V(l)$. The power-law dependence $V_d(l) \sim l^{-1}$ is the same,[4] and arises by the same mechanism, as that characterizing distortions of the magnetization vector through domain walls in a Heisenberg ferromagnet. Strain effects in a *solid* wetting layer also produce an l^{-1} contribution to the film free energy, which leads to a thinning of the layer (19). In contrast, $V_d(l)$ as discussed here is positive and thus gives a *repulsive* interaction between the α–N and N–I interfaces, which stabilizes wetting-layer growth at large l.

The mean-field prescription $[\partial\sigma/\partial l]_{l=\bar{l}} = 0$ is valid here, as it is more generally whenever $V(l)$ is dominated by power-law terms in three dimensions (9, 20). The asymptotic behaviour of $\bar{l}$ then follows from [1], [2], and [4] as

$$[5] \qquad \bar{l} \approx Bt^{-\psi},$$

where $\psi = 1/2$ and $B = |\Delta\Theta|\sqrt{K/2\Lambda}$. Although the relevance of the distortion energy [4] to nematic wetting was first recognized some time ago (16), we believe that [5] is a new theoretical result.[5] This is the exact leading-order result describing spontaneous growth of a nematic wetting layer as $t \rightarrow 0$ in the presence of director distortion. A number of additional asymptotic relations follow from this analysis. For instance, the deviation of the equilibrium α–I surface tension from its value at N–I coexistence, $\Delta\sigma \equiv \sigma(\bar{l}) - (\sigma_{\alpha N} + \sigma_{NI})$, is given by $\Delta\sigma \approx Ct^{2-\alpha_s}$ where $\alpha_s = 3/2$ and $C = (2K\Lambda)^{1/2}|\Delta\Theta|$. This leads to a critical divergence $\sim t^{-\alpha_s}$ in the interfacial specific heat. The parallel correlation length $\xi_{||}$ for interface fluctuations, which is in principle measurable by scattering expeiments with momentum transfer parallel to the interface, follows from standard Ornstein–Zernike arguments (7, 9) to be given by $\xi_{||} = [\sigma_{NI}/V''_d(\bar{l})]^{1/2}$, where the primes denote derivatives with respect to l.[6] Thus one finds $\xi_{||} \approx Dt^{-\nu_{||}}$, with $\nu_{||} = 3/4$ and $D = (|\Delta\Theta|\sigma_{NI})^{1/2}K^{1/4}/(2\Lambda)^{3/4}$.

There is a possible limitation on the above results due to the fact that the tilt angles at the separate α–N and N–I interfaces are not fixed but have finite anchoring energies, $A_{\alpha N}$ and A_{NI}. This leads to l-dependent deviations $\delta\Theta_{\alpha N}(l)$ and $\delta\Theta_{NI}(l)$ of the tilt angles from their equilibrium values at infinite l, and corresponding deviations $\delta\sigma_{\alpha N}(l) \approx A_{\alpha N}(\delta\Theta_{\alpha N})^2$, $\delta\sigma_{NI}(l) \approx A_{NI}(\delta\Theta_{NI})^2$ of the separate surface tensions. Extension of the elastic–theoretic arguments (16) which led to [4] now gives

$$[6] \qquad V_d(l) \approx \frac{K}{2l}(\Delta\Theta)^2 \Big/ \left[1 + \frac{K}{2l}\left(\frac{1}{A_{\alpha N}} + \frac{1}{A_{NI}}\right)\right]$$
$$= \frac{K}{2l}(\Delta\Theta)^2 - \left(\frac{K}{2l}\right)^2\left(\frac{1}{A_{\alpha N}} + \frac{1}{A_{NI}}\right)(\Delta\Theta)^2 + O(l^{-3})$$

The linearization in the second line of [6] is valid, hence the asymptotic formula [4] is realizable only for distances $l \gtrsim l_0 \equiv K/A$, where A is the weaker of the two anchoring energies. This is consistent with arguments given in the context of macroscopic nematic films, namely, that director distortion occurs only when l exceeds the "extrapolation length" l_0 (15, 16). Using a typical value for K of 10^{-7} erg/cm and current estimates (11) that $10^{-4} \leq A_{NI} \leq 10^{-2}$ erg/cm^2, we have $10^{-5} \leq l_0 \leq 10^{-3}$ cm. This rather substantial magnitude for l_0 suggests that it would be difficult to observe the power law [5] within the temperature range of current experiments. However, this does not rule out the fact that [5] is what *should* be observed for sufficiently small t. Furthermore, we conjecture that distortion-induced corrections of $O(l^{-2})$ to the leading-order result in [4] may result from other mechanisms besides that based on the anchoring energies of the separate α – N and N–I interfaces. Model calculations, for example, based on a Landau – de Gennes theory allowing for director tilt (22), are needed to elucidate this point.

In the absence of director distortion, the longest-ranged contribution to $V(l)$ is expected to result from van der Waals forces between the molecules. For l on the order of 10–100 nm, this has the form (7–10)

$$[7] \qquad V_{vdw}(l) \approx W/l^2$$

where the Hamaker constant W depends on the polarizability densities of the different phases present. Due to anisotropy of the polarizability of liquid crystalline molecules, W has a more complex character than in recent treatments of wetting by ordinary liquids (7–10), but a detailed analysis of this is beyond the scope of the present paper. Here we shall simply make the following observations. For complete nematic wetting to occur, it is necessary (though not sufficient) that $W > 0$. In that case, we obtain the well-known result (8) that the mean thickness $\bar{l}$ obeys [5] with exponent $\psi = 1/3$. This is universally observed at the approach to complete wetting by ordinary liquids (7). In the absence of director distortion, a negative value of W would preempt complete wetting by giving an absolute minimum in $V(l)$ at some finite value of l. It is not clear, however, that this outcome is maintained if the expected crossover to director distortion develops at very large l. Note that the sign of W bears no direct relation to the nature of shorter range intermolecular forces, e.g., due to steric interactions, which can also be important in determining wetting behaviour (7–10).

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[3] Generalizations of [3] and [4] to account for anisotropy of the elastic constants are derived in ref. 17. These exhibit a slightly more complex angle-dependence than the present equations.

[4] A repulsion $\sim 1/l$ between two interfaces will also be present for other physical systems, provided the order parameter in the layer breaks a continuous symmetry and the two interfaces bounding the layer prefer different states of the order parameter. This follows quite generally from finite-size scaling (18) when applied to such layers.

[5] The scaling relation [5] with exponent $\psi = 1/2$ also applies to complete wetting in a quite different context, namely for systems containing quenched random impurities (21).

[6] This expression for $\xi_{||}$ holds when only the N–I interface bounding the layer is rough, as in the case where α is a solid. If the α–N interface is also rough, then σ_{NI} is replaced by $\sigma_{NI}\sigma_{\alpha N}/(\sigma_{NI} + \sigma_{\alpha N})$, see ref. 9*b*.

As remarked earlier, it is important to account for the large magnitude (e.g., up to several hundred Å (11)) of the bulk coherence length ξ_{NI}, which in turn results from the *weakly* first-order nature of the nematic–isotropic transition. The effects of this can be analyzed in the framework of Landau – de Gennes type theories (15, 22, 23) for the spatial variation of orientational order parameters. As also found in Landau theories of wetting by ordinary liquids (7–10, 24), the exponentially decaying tails of the order-parameter profiles yield a contribution to $V(l)$ of the form

$$[8] \quad V_{SR}(l) \approx a\sigma_{NI} \exp -l/\xi_{NI}$$

where $a \sim O(1)$ is a numerical coefficient. Even in the presence of long-range (i.e., van der Waals) forces, the order-parameter profiles will still decay exponentially on intermediate length scales as long as ξ_{NI} is sufficiently large (25). In such a situation, a contribution of the form [8] should be added to the film free energy (26). Neglecting other contributions to $V(l)$, minimization of [1] in the case $a > 0$ now leads to

$$[9] \quad \bar{l} \approx b\xi_{NI} \ln (t_0/t)$$

where $t_0 \equiv a\sigma_{NI}/(\Lambda\xi_{NI})$ and b is a non-universal numerical coefficient which is appended to account for effects of interface fluctuations (9*a*, 27). We therefore envision the possibility for a sequence of crossovers between the behaviours indicated by [9] and [5], with successively $\psi = 1/3$ and $1/2$ in the latter, as t approaches zero.

The logarithmic growth of $\bar{l}$ according to [9] agrees with the ellipsometric results of Beaglehole (5) for a nematic wetting layer at the liquid–vapour interface of 5CB, obtained over a reduced temperature range $5 \times 10^{-5} \le t \le 10^{-3}$. These results do not rule out the existence of a crossover to power-law behaviour at smaller t. In a more recent experiment, Hsiung *et al.* (28) observed a divergence in the thickness of a *weakly* ordered nematic layer of 5CB at a liquid–solid interface. Their data in the range $4 \times 10^{-4} \le t \le 4 \times 10^{-3}$ are well fitted by [5] with $\psi = 1/2$ and $B \approx 7$ Å. This value of the critical amplitude B agrees closely with that predicted by the expression after [5], using values for 5CB of $\Delta\Theta = \Theta_{NI} = 1.1$ (11), $K = 2.1 \times 10^{-7}$ erg/cm, and $\Lambda = 2 \times 10^7$ erg/cm^3 (29). The maximum film thickness measured in this experiment corresponds to about 400 Å, considerably less than current estimates for the length l_0 mentioned earlier. On the other hand, the nematic order parameter (OP) near the substrate, $Q(0)$, was found to be much smaller than the order parameter of the bulk nematic phase. As remarked by Hsiung *et al.* (28), this is difficult to reconcile with present theories of wetting (7, 23). An alternative interpretation of the results in ref. 28 is that they do not describe complete wetting but rather a different surface phenomenon which one might call near-critical adsorption.

If the surface OP $Q(0)$ is positive but close to the value, $Q = 0$, in the bulk isotropic phase, then the Landau – de Gennes theory yields an exponentially decaying OP profile,

$$[10] \quad Q(z) \approx Q(0) \exp -z/\xi_{NI}$$

at large distances from the substrate. In terms of the adsorption Γ, i.e., the integrated value of $Q(z)$, then [10] leads to $\Gamma \sim Q(0)\xi_{NI}$. This is similar to [9], but lacks the logarithmic term associated with complete wetting that arises when $Q(0)$ approaches the bulk nematic OP and the profile $Q(z)$ develops a kink. The above scaling for Γ should hold even beyond the Landau – de Gennes theory as long as $Q(0)$ is small compared to the bulk order parameter of the ordered phase at the transition. A similar effect occurs whenever a *continuous* transition point is approached from the disordered phase in the presence of a wall (30). In such a case, Γ diverges at the bulk transition temperature. Due to the weakly first-order nature of the N–I transition, ξ_{NI} does not actually diverge as $t \rightarrow 0$ but presumably obeys $\xi_{NI} \sim (T - T^*)^{-\nu}$, where T^* is slightly less than T_{NI} and ν is an appropriate exponent. At present, there is still some uncertainty (31) about the correct theoretical values for both T^* and ν (in the Landau – de Gennes theory, $\nu = 1/2$), as well as in the analysis of experimental data from different types of measurements in terms of these parameters. Hence the results of ref. 28, i.e., $T^* \approx T_{NI}$ and $\nu = 1/2$, are not inconsistent with an interpretation based on near-critical adsorption. Another factor which could well contribute to the small difference (about 1 K) between the value $T^* \approx T_{NI}$ deduced in ref. 28 and previous estimates (32) of T^* is the presence of impurities.

In conclusion, further experiments on nematic systems which clearly exhibit complete wetting would be useful. In particular, one should try to extend measurements such as those of refs. 5 and 28 to smaller values of t. While on the basis of current theory, the crossover to the distortion régime with $\psi = 1/2$ in [5] may be difficult to observe, it is possible that the correction terms discussed below [6] are sufficiently small to render this régime experimentally accessible. Furthermore, there may exist other possibilities (16) for adsorption of a nematic layer between two phases both of which exhibit large anchoring energies and hence yield a smaller value of l_0, to which the present analysis can be adapted. For example, one could in principle study adsorption of the nematic phase out of the vapour phase in the presence of a solid substrate.

NOTE ADDED IN PROOF

In a subsequent erratum to ref. 28, Hsiung *et al.* (33) report that new measurements on a purer sample of 5CB yield results consistent with partial wetting, with a value of T^* distinctly less than T_{NI}. This finding supports the arguments described here. A short account of these arguments has been given by Lipowsky and Sullivan (34).

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