Complete Wetting or Near-Critical Adsorption?

In a recent experiment, Hsiung, Rasing, and Shen[1] studied the effects of a wall on the nematic-isotropic transition of 4'-n-pentyl-4-cyanobiphenyl (5CB). Their data reveal the presence of a "coherence length," ξ, which continuously grows as the transition temperature, T_{NI}, is approached from above. Hsiung, Rasing, and Shen remark that this is the behavior expected for the bulk correlation length, ξ_b. In the Letter,[1] they also regarded their data as evidence for *complete* wetting by the nematic phase and took ξ to be a measure for the thickness, $\bar{l}$, of the wetting layer. In contrast, they say in the erratum[1] that their data are consistent with *partial* wetting. However, the latter point of view does not give any insight into the origin of the growing length scale, ξ.

In this Comment, we will argue that the data on ξ can be interpreted in terms of two *distinct* surface phenomena: (i) either as *complete wetting* which implies $\xi = \bar{l}$, or (ii) as *near-critical adsorption* for which $\xi = \xi_b$. It is important to note that the two length scales, ξ_b and $\bar{l}$, are not related to each other.

For complete wetting,[2] the layer thickness $\bar{l}$ becomes large as $T \to T_{NI}$. In fact, its *asymptotic* behavior is given by

$$\bar{l} \approx C t^{-\psi} \quad \text{with } \psi = \tfrac{1}{2} \tag{1}$$

as $t \equiv (T - T_{Ni})/T_{NI} \to 0$ (and $C \approx 8$ Å for 5CB); see below. Even though this is very similar to the observed behavior of ξ, we expect large correction terms which indicate that (1) might not be observable for the temperature range studied in Ref. 1. Furthermore, the order parameter (OP) close to the wall was found to be small compared with the OP of the nematic phase.[1] This seems difficult to explain by complete wetting. However, it can be understood by analogy with critical adsorption[3] which often occurs when a *second*-order transition point is approached from the disordered phase in the presence of a wall.[4] Since the NI transition is weakly *first* order, the analogous process, termed *near*-critical adsorption, will be truncated sufficiently close to T_{NI}.

Now, consider complete wetting and a nematic liquid layer which intervenes between the isotropic liquid and a solid wall. This layer is bounded by a solid-nematic (SN) and a nematic-isotropic (NI) interface. In general, these two interfaces exhibit different orientations of the molecules. In Ref. 1, the wall was coated with surfactant to assure homeotropic alignment with tilt angle $\theta = \theta_{SN} \approx 0$. In contrast, the director within the NI interface of 5CB is obliquely tilted[5] with $\theta = \theta_{NI} \approx 1.1$. In such a situation, the director is distorted across the nematic layer. This implies that the free energy per unit area of the nematic layer has the asymptotic form

$$V(l) \approx Qtl + \tfrac{1}{2} K(\Delta\theta)^2/l \tag{2}$$

for large l with $\Delta\theta \equiv \theta_{NI} - \theta_{SN}$. The parameters Q and K

are the latent heat per unit volume and an appropriate elastic constant of the nematic, respectively. The equilibrium thickness, $\bar{l}$, follows from $\partial V/\partial l = 0$.[2] This leads to (1) and $C = \Delta\theta (K/2Q)^{1/2}$. For the system in Ref. 1, $\Delta\theta \approx 1.1$, $K \approx 2.1 \times 10^{-7}$ erg/cm, and $Q \approx 2 \times 10^7$ ergs/cm^3 which implies $C \approx 8$ Å. There is an important correction term to (2) which arises because the tilt angles within the interfaces are not fixed but have finite anchoring energies, A_{SN} and A_{NI}. If $A_{SN} \approx A_{NI} \approx A$ is the only relevant energy scale apart from K, the asymptotic behavior of $\bar{l}$ is given by (1) for $\bar{l} \gtrsim l_0 \equiv K/A$. Recent experiments[5] indicate that $10^{-4} \lesssim A \lesssim 10^{-2}$ erg/cm^2 for 5CB. This would lead to $10^{-3} \lesssim l_0 \lesssim 10^{-5}$ cm.

For complete wetting, the surface OP, Q_0, is of the order of the bulk OP, $Q = Q_N$, of the nematic phase. Quite generally, the magnitude of Q_0 depends on the effective surface field which the wall exerts on the fluid molecules. Now, assume that this field is sufficiently small such that Q_0 is larger than but close to the OP, $Q = 0$, of the isotropic phase. Then, one has an OP profile, $Q(z) \approx Q_0 \times \exp(-z/\xi_b)$ for $Q_0 \ll Q_N$, as obtained, e.g., from Landau–de Gennes theory, and a total adsorption proportional to ξ_b. This process of near-critical adsorption correlates well with the data on the optical dielectric constant in Ref. 1. This interpretation implies that ξ and ξ_b diverge at the same temperature. In Ref. 1, two distinct temperatures which differed by about 1 K were deduced from two different experiments. This small difference could well be the result of impurities. Thus, we conclude that Hsiung, Rasing, and Shen probably observed near-critical adsorption rather than complete wetting.

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