Structural Critical Point at the Free Surface of a Nematic Liquid Crystal

J. D. Parsons

Department of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio 44106

I discuss simple Landau theory of the free surface of a nematic, including possible polar ordering effects near the surface. It is found that polar surface order favors a perpendicular alignment of molecules at the surface and this may compete with the usual quadrupolar order which favors parallel alignment. At a critical point, the surface symmetry changes from uniaxial to biaxial and there are large pretransitional fluctuations of the tilt angle of the molecules. The possibility of a soft mode associated with the transition is pointed out.

In the bulk region of a nematic liquid crystal, long organic molecules tend to align parallel to one another along a direction specified by a unit vector $\tilde{n}$. The degree of ordering is given by a rotational order parameter[1] Q such that $0 \leqslant Q \leqslant 1$. $Q = 1$ refers to perfect order and $Q = 0$ is for an isotropic liquid with no long-range rotational order. If there are no applied fields, the system has complete rotational symmetry and all directions of $\tilde{n}$ are equivalent.

At the free surface the translational symmetry is broken; this implies that the rotational symmetry is broken as well if the surface properties depend on orientation. The free surface will then single out a direction of $\tilde{n}$ that leads to a minimum in the total (bulk plus surface) free energy.

Quadrupolar order.—The Landau form for the free energy in the bulk is[2]

$$F(Q) = F_0 + aQ^2 - bQ^3 + cQ^4 + d(\nabla Q)^2 , \tag{1}$$

where $a = a_0(T - T_c)$ with $a_0 > 0$ and T_c the "second-order transition temperature"; $d > 0$ describes the extra free energy due to a distortion in Q. The surface free energy $\gamma(Q)$ is similarly expanded as

$$\gamma(Q) = \gamma_0 - \gamma_1 Q + \gamma_2 Q^2 , \tag{2}$$

where $\gamma_0 > 0$ is the surface tension in the absence of ordering and we take $\gamma_2 > 0$ for stability. Let $z = 0$ be the plane of the free surface and consider a distortion $Q = Q(z)$ such that $Q(z) \to 0$ in the bulk liquid. If Q is small near the surface, the equilibrium condition from (1) is

$$d^2Q/dz^2 - \xi^2 Q = 0; \quad Q(z) = Q_0 e^{\xi z} , \tag{3}$$

with $\xi = (a/d)^{1/2}$ and $z < 0$ in the bulk of the fluid. Q_0 is the value of the surface order and is determined by the surface boundary condition[3]

$$[\partial F/\partial(\nabla Q)] \cdot \hat{k} + \partial \gamma/\partial Q = 0 , \tag{4}$$

where $\hat{k}$ is the normal to the surface. One finds

that

$$Q_0 = \gamma_1/(\xi d + 2\gamma_2) . \tag{5}$$

Since $Q_0 > 0$ for prolate uniaxial order, we must have $\gamma_1 > 0$ in (2). Then (5) implies there is an excess order at the surface which decays into the bulk over a distance $1/\xi$. Typically $\xi d \approx 0.1$ dyn/cm or less, so that Q_0 is expected to be observable for moderate values of $\gamma_1/2\gamma_2$. Finally from (2) it follows that $\gamma(Q)$ is lowered by the orientational order at the surface. That is, as a sample is cooled down past the nematic transition temperature, the surface tension may drop discontinuously across the transition. This effect has actually been observed experimentally.[4] A recent molecular calculation[5] shows that when molecules interact with an anisotropic van der Waals force of quadrupolar symmetry the term $\gamma_1 \neq 0$ in (2) and furthermore the equilibrium state occurs when $(\tilde{n} \cdot \hat{k}) = 0$ so that the molecules tend to lie in the plane of the free surface. For small deviations away from this alignment, one can write

$$\gamma = \gamma_0 + \tfrac{1}{2}\gamma_Q(\hat{n} \cdot \hat{k})^2 , \tag{6}$$

with $\gamma_Q > 0$. γ must be even in $(\hat{n} \cdot \hat{k})^2$ in quadrupolar-order–type systems by symmetry.

Polar order.—This type of ordering can occur if the two ends of the molecule are not equivalent and the surface orders the preferential end so that the density gradient across the surface exerts a directional torque on the molecules. For example, if one end of the molecule has a highly polar end group, that end will tend to point in the direction of the more polar medium (i.e., into the bulk and away from the surface). Deep into the bulk all directions should be equivalent so that polar order can exist only close to the free surface.[6] Phenomenologically the situation is described by a polar order parameter $\tilde{p} = p\hat{n}$ with $p \leqslant 1$. When $p \neq 0$, $\hat{n}$ and $-\hat{n}$ are not equivalent

states near the surface so that

$$\gamma = \gamma_0 + \tfrac{1}{2}\gamma_Q(\hat{n} \cdot \hat{k})^2 - \gamma_p \hat{n} \cdot \hat{k}, \tag{7}$$

where we take $\gamma_p > 0$ with no loss of generality. Polar order always has the effect of lining up the molecules perpendicular to the free surface so that there is now a direct competition with the quadrupolar order. Minimization of (7) with respect to $\hat{n} \cdot \hat{k} = \cos\theta$ gives

$$\cos\theta = \begin{cases} \gamma_p/\gamma_Q & (\gamma_p < \gamma_Q), \\ 1 & (\gamma_p > \gamma_Q). \end{cases} \tag{8}$$

This implies that $\gamma_p = \gamma_Q$ is a *critical point*. For $\gamma_p > \gamma_Q$, I have $\theta = 0$ and the surface symmetry is uniaxial with $\hat{n}$ along the surface normal $\hat{k}$. But when $\gamma_p < \gamma_Q$, $\hat{n}$ tilts and the surface symmetry is biaxial. The transition is the two-dimensional analog of a structural transition in a crystal. Near the transition point, θ is small and $\gamma(\theta)$ can be expanded in a Landau form with the tilt angle θ playing the role of an order parameter:

$$\gamma(\theta) = \gamma_0 + \tfrac{1}{2}(\gamma_p - \gamma_Q)\theta^2 + \tfrac{5}{48}\gamma_Q\theta^4. \tag{9}$$

Since in general γ_p and γ_Q will be different functions of temperature, the tilt angle may also vary with temperature. This may be the origin of the anomolous effect in N-[p-methoxybenzylidine]-p-butylaniline.[7] If $\gamma_p \ll \gamma_Q$, a tilt might not be observable and $\hat{n}$ may appear to be in the plane of the surface. This appears to be the case in p-azoxyanisole.[8] Finally, if it so happens that $\gamma_p = \gamma_Q$ at a temperature in the nemtic range, one may see this transition thermally.

I can show that $\gamma_p = \gamma_Q$ has another aspect of a critical point: Fluctuations in the tilt angle θ tend to diverge at this point. Let $\vec{r}$ be a two-dimensional vector lying in the plane of the surface and expand $\theta(\vec{r})$ in a set of normal modes:

$$\theta(\vec{r}) = A^{-1/2}\sum_q \theta_q e^{i\vec{q}\cdot\vec{r}}, \tag{10}$$

where A is the area of the interface. Insertion of (10) into (9) gives, to lowest order,

$$\gamma = \gamma_0 + (1/2A)\sum_q |\theta_q|^2(\gamma_p - \gamma_Q), \tag{11}$$

and an application of the equipartition theorem leads to

$$|\theta_q|^2 = k_B T/(\gamma_p - \gamma_Q), \tag{12}$$

so that strong fluctuations in the tilt angle occur near the critical point $\gamma_p = \gamma_Q$. In practice these modes are coupled to the hydrodynamical motion of the liquid; a more complete surface-wave analysis will be published elsewhere. One expects that the ordinary capillary ripplon spectrum will be modified near the critical point, but also a second propogating mode should exist which physically involves oscillations of $\hat{n}$ with respect to the surface normal $\hat{k}$. At $\gamma_p = \gamma_Q$, the oscillation frequency of this second mode should vanish so that this mode can be interpreted as a *soft mode* associated with the structural transition.

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[1]A. Saupe and W. Maier, Z. Naturforsch. 15a, 287 (1960).

[2]P. G. de Gennes, Phys. Lett. 30A, 454 (1969).

[3]J. D. Parsons, Mol. Cryst. Liq. Cryst. 31, 79 (1975); J. T. Jenkins and P. J. Barratt, Q. J. Mech. Appl. Math. 27, 111 (1974).

[4]S. Krishnaswamy and R. Shahidhar, Paramana, Suppl. No. 1, 247 (1975); A. Ferguson and S. Kennedy, Philos. Mag. 26, 41 (1938); W. M. Schwartz and H. W. Moseby, J. Phys. Colloid Chem. 51, 826 (1947).

[5]J. D. Parsons, J. Phys. (Paris) 37, 1187 (1976).

[6]This type of order is different from that which can result from pair interactions between dipole moments.

[7]M. A. Bouchiat and D. Langevin-Cruchon, Phys. Lett. 34A, 331 (1971).

[8]V. Naggier, C. R. Acad. Sci. 208, 1916 (1939); D. Meyerhofer, A. Saussman, and R. J. Williams, Appl. Phys. 43, 3685 (1972).