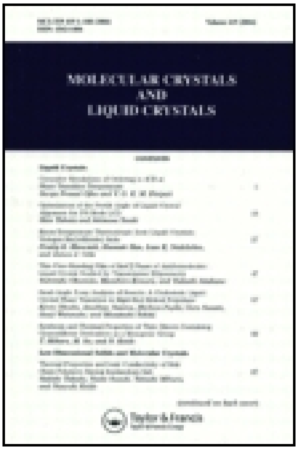

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Structure of the Nematic–Isotropic Interface in Landau Theory

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The structure of the nematic–isotropic interface is probed using Landau theory with a tensor order parameter. Strong biaxiality appears near the isotropic side of the interface when the elastic constants are not equal. However, this effect produces only small changes in the surface tension. The dependence of surface tension on the angle between the bulk director and the interface is explored. Also, when the director in the bulk nematic makes a 38° angle with the interface, the director near the interface "bends" by about 5° to become more parallel with the interface.

I. INTRODUCTION

The structure of the nematic–isotropic interface is of interest for several reasons. Often one would like to interpret the microscopic appearances of nematic or cholesteric drops at the clearing point, and to do this requires a knowledge of the surface anchoring characteristics of the nematic–isotropic interface. Certain theories of the "blue" phase(s)[1] require assumptions about the nature of the defects or nematic–isotropic interfaces thought to be essential parts of the lattice structure. Also, the Landau theory of the N–I transition is one of the few first-order transition theories which can be made to yield results concerning interfaces without atomic-level simulation.

In this paper I report the results of computer calculations done on the Landau theory of the N–I interface. The results include data on the dependence of surface tension on the angle between the director (in the bulk) and the interface, the bending (if any) of the director near the interface, and the appearance of large amounts of biaxiality towards the isotropic side of the boundary. The calculation was done by taking a free energy density of Brazovskii[2] form and looking for the lowest-energy configurations (one-dimensional variations only) with the aid of a computer program.

II. MATHEMATICS

We start with the Brazovskii form for the free energy density of the nematogen as a function of a tensor order parameter Q. This form can be written as

$$F = F_u + F_e \tag{1}$$

with F_u being the part appropriate for a uniform sample (no derivatives of Q) and F_e the part corresponding to the elastic energy. A constant is subtracted from F_u so that the F for an isotropic sample is zero. The two terms of the free energy density can be expressed as:

$$F_u = \frac{L}{\delta}\left(\frac{3(1+t\delta)}{2} Tr\left(\frac{Q}{S_0}\right)^2 - 9Tr\left(\frac{Q}{S_0}\right)^3 + \frac{9}{2}Tr\left(\frac{Q}{S_0}\right)^4\right) \tag{2}$$

and

$$F_e = \frac{1}{2}\left(K_b\left(\frac{Q_{\alpha\beta,\gamma}}{S_0}\right)^2 + K_c\left(\frac{Q_{\alpha\beta,\gamma}Q_{\alpha\gamma,\beta}}{S_0^2}\right)\right), \tag{3}$$

where commas denote differentiation by the appropriate coordinate. Here, Q is a tensor order parameter which for a uniaxial nematic can be written as:

$$Q_{ij} = S(n_i n_j - \delta_{ij}/3) \tag{4}$$

where S is the order parameter, and n_j is the j component of a unit-magnitude director. S_0 is the order parameter at the N–I transition (in bulk), L is the latent heat of the N–I transition, $\delta = -d\ln S/d\ln T$ evaluated at $T = T_c$, T_c being the transition temperature, K_b is $K_{22}/2$, and K_c is $K_{11} - K_{22}$. Also, $t = (T_c - T)/T_c$, with T the temperature. Here, $K_{11} = K_{33}$, and K_{ii} are Frank elastic constants.

The mathematics become much simpler upon expressing various quantities in reduced or dimensionless units. The appropriate units are:

Free energy density	$\frac{L}{\delta}$
Distance	$\sqrt{\frac{K_b\delta}{L}}$
Order parameter	S_0.

Also, for the N–I interface problem, we assume that there is variation only in the z direction (interface in the xy plane). Since an interface is only stable if the free energies of the phases it separates are equal, we put $t = 0$, and restrict the calculation to the N–I transition temperature. The elastic anisotropy is parametrized by the dimensionless ratio r, given by $r \equiv (K_{11} - K_{22})/K_{22}$. The free energy density now takes the form:

$$F = \tfrac{3}{2} TrQ^2 - 9TrQ^3 + \tfrac{9}{2} TrQ^4 + \tfrac{1}{2} Tr\left(Q'\right)^2 + r\left(Q'_{\alpha z}\right)^2, \qquad (5)$$

where primes indicate differentiation with respect to z. In the rest of this paper, the term "surface tension" will be used synonymously with "total free energy", since they are the same for $T = T_c$. The above expression is what we want to minimize with respect to Q. We assume that the director in the bulk nematic phase is in the xz plane, and that the nematic does not "escape" in the y direction, i.e., the system retains symmetry under $y \leftrightarrow -y$, so that $Q_{xy} = Q_{yz} = 0$. We now introduce three variables, y_{1-3}, in terms of which Q will be expressed:

$$Q = \begin{pmatrix} y_1 & 0 & y_3 \\ 0 & -(y_1 + y_2) & 0 \\ y_3 & 0 & y_2 \end{pmatrix}. \qquad (6)$$

The quantities y_{1-3} are what get varied in order to minimize the free energy.

One of the most striking results of the computer calculations discussed below is the occurrence of large amounts of biaxiality in the interface region whenever $r \neq 0$ (anisotropic elasticity). Some simple analytic computations show why this phenomenon occurs. As a test case, we assume that the director is always pointed in the x direction (parallel to the interface). This assumption means that the Q-tensor is diagonal with its largest element being Q_{xx}. We express the order parameter tensor as:

$$Q = \frac{S}{3} \begin{pmatrix} 2 & & \\ & -(1-\epsilon) & \\ & & -(1+\epsilon) \end{pmatrix}. \qquad (7)$$

This form for the eigenvalues of Q will be used to display the results of the computations. S is an overall order parameter, and ϵ is a measure of biaxiality. For a uniaxial nematic, $\epsilon = 0$, and for $\epsilon = \pm 1$ there are two eigenvalues of equal magnitude and opposite sign, which is the signature of "pure" biaxiality. We can write the free energy in terms of S and ϵ, and we find that the terms involving ϵ are positive when $r = 0$. The proof of this theorem is somewhat complicated due to the presence of a term of the form $-(S^2)''\epsilon^2$, which can be negative, but it always turns out that the other positive terms outweigh this lone negative one. Thus, for $r = 0$, no biaxiality appears. However, the r term is of the form $(Q_{zz})'^2$, which expands out to give a term involving ϵ, not ϵ^2. Thus, some biaxiality is guaranteed to appear in this case. Of course, this calculation does not take into account the possibility of tilting of the director, which it might be argued might lead to an "escape" from the need for biaxiality. However, as we shall see, there is considerable biaxiality, even with bending allowed.

III. COMPUTATION

The free energy density takes a special form which is useful for computation:

$$F = F_u + y'My' \tag{8}$$

with

$$\frac{\delta F_u}{\delta y} = N(y)y. \tag{9}$$

Here, y stands for the array y_1, y_2, y_3, considered as a vector, and N and M are 3×3 matrices. We discretize the problem by considering a string of y-vectors, y_i, $i \in [1, n]$. Here, n is the number of points, and we consider the values of y at points number 1 and n to be fixed in order to enforce boundary conditions and keep the interface from drifting. The discrete form of the total free energy is:

$$F_t = h\sum_{i=2}^{n-1} F_u(y_i) + \frac{1}{h}\sum_{i=2}^{n}(y_i - y_{i-1})M(y_i - y_{i-1}), \tag{10}$$

where h is the stepsize (interval in z). As usual, the vector indices are suppressed. We minimize this free energy by taking the functional derivative with respect to a given y_i, $i \in [2, n-1]$, to get an iterative equation for y_i:

$$y_i = \left(M + \frac{1}{4}h^2N\right)^{-1} M\frac{y_{i+1} + y_{i-1}}{2} \tag{11}$$

This is the equation we would like to solve for all the y. Since N depends on y, the equation has y_i on both sides, and thus cannot be solved exactly in one iteration. Instead, we compute the RHS of Eq. 11 and store it in a second array, which we call W. The difference between W and y is called $2Z$. Now, both the vector and positional indices have been suppressed. We now calculate the free energies corresponding to the vectors y, $y + Z$, and $W = y + 2Z$. If the relaxation step (11) were an exact solution to the problem, then the free energy corresponding to W would be the lowest. However, this is not always the case. Let us define quantities f_0, f_1, and f_2:

$$\begin{aligned} f_0 &= F\{y\} \\ f_1 &= F\{y + Z\} \\ f_2 &= F\{y + 2Z\}. \end{aligned} \tag{12}$$

What we want is to find a value of x such that if

$$Y \equiv y + xZ \tag{13}$$

then the free energy for Y is minimized. If the relaxation step were an exact solution, then the x that satisfies this condition would be 2, since this value of x corresponds to the RHS of Eq. 11. Now, if $f_0 < f_1, f_2$, then we look for negative values of x, since positive ones raise the energy. We do this by substituting:

$$\begin{aligned} f_2 &\leftarrow f_1 \\ f_1 &\leftarrow f_0 \\ y &\leftarrow y - Z \\ f_0 &\leftarrow F\{y\} \end{aligned} \tag{14}$$

so that we shift the three points in phase space, y, $y + Z$, W by an amount $-Z$. The free energies are tested again. This test-and-shift process repeats as many times as required to make $f_1 < f_0, f_2$. This condition says that there is an extremum of F vs. x in the interval under test.

Likewise, if $f_2 < f_0, f_1$, then we shift by $+Z$ until a *minimum* is found. Now, we have three points in phase space which bracket a minimum (as a function of x). We consider the free energy to be quadratic in x, with coefficients determined by the points ($x = 0$, $f = f_0$), ($x = 1$, $f = f_1$), ($x = 2$, $f = f_2$). Because we have made sure that

$f_1 < f_0, f_2$, the parabolic curve of f vs. x is guaranteed to have a minimum. Call the value of x at the minimum x_m. Then, we calculate the free energy corresponding to $Y = y + x_m Z$, which we call f_3. Now we have four points to choose from. We pick the y corresponding to the lowest free energy as our new y. This procedure comprises one iteration step. The alternative to this "parabolic relaxation" method is the standard one in which x is taken to be about 1.4 (new y is 2/3 of the way between the old y and what comes out of Eq. (11)). Some calculations have been done both ways, and the parabolic method converges to a given accuracy about three times faster (CPU time) than the standard way, and is less prone to numerical instabilities, since it will not accept an iteration step that increases the free energy.

Any relaxation method needs a starting configuration. In this case, we derive a starting solution by assuming the nematic to be everywhere uniaxial, and with principal axes everywhere the same. Only the magnitude of the order parameter is allowed to vary. This solution is given by:

$$S = \tfrac{1}{2}\left(1 - \tanh\left(x/\sqrt{4/3 + r(10 - 3\sin^2\theta)/9}\right)\right). \tag{15}$$

What comes out of the relaxation part of the program is a set of y-values which are not readily interpretable in terms of physical concepts such as biaxiality, order parameter, etc. Therefore, I define quantities S, ϵ, and ϕ so that Q is expressed as:

$$Q = R_y(\phi)\frac{S}{3}\begin{pmatrix} 2 & & \\ & -(1-\epsilon) & \\ & & -(1+\epsilon) \end{pmatrix} R_y^{-1}(\phi) \tag{16}$$

where $R_y(\phi)$ is a rotation matrix for clockwise rotation about the y-axis by an angle ϕ. Since the starting configuration puts the nematic on the left ($z < 0$), a ϕ between 0 and 90° represents a director which points up (increasing x) and towards the interface. The parameters S and ϵ have the same meanings as in the earlier discussion on the analytical basis for the appearance of biaxiality.

If the absolute value of ϵ exceeds 1, then the eigenvalue of Q with the largest magnitude is no longer positive. Instead, one of the negative eigenvalues has the largest magnitude. This effect can be interpreted as a change in the sign of S, as will be shown for the case in which the director is parallel to the interface.

Finally, it is of interest to be able to suppress the biaxiality in order to see how much of an effect it has on the surface tension. This is done by adding a term

$$F_{biax} = B\left(TrQ^2 - 6\left(TrQ^3\right)^2/\left(TrQ^2\right)^2\right) \tag{17}$$

to the free energy. This term fits into the N, M scheme discussed above, is positive definite, vanishes for any uniaxial Q, is rotationally invariant, and varies as $S^2\epsilon^2$ for small Q, ϵ. A value of B of 100 or more suppresses most of the biaxiality.

IV. RESULTS

Now we can discuss the results. For $r = 0$, the starting solution is the final solution; there is no biaxiality or bending, and the surface tension is .19248 (in our reduced units). The surface tension is independent of the angle between the bulk director and interface. This angle will be referred to below as the interfacial angle θ.

Calculations were done for $r = 1$ with the biaxiality suppression on and off. The results for surface tension as a function of interfacial angle are shown in Figure 1.

The order parameter and biaxiality for the case in which the director is parallel to the interface ($\theta = 0$) are shown in Figure 2. Note the change in the sign of S when ϵ reaches a value of -1.

The biaxiality is largest for the parallel case, and gets smaller as θ increases, finally vanishing for $\theta = 90°$. The biaxiality and order parameter when $\theta = 62.5°$ are shown in Figure 3. Curiously, the largest biaxiality occurs for the parallel orientation, while the largest surface tension decrement due to biaxiality happens when the director-interface angle is about 40°.

When the bulk director is neither parallel nor perpendicular to the interface, the principal axis of the Q-tensor (director when uniaxial) bends away from the bulk direction because of the angular dependence of surface tension. Since the surface tension is smallest when the director is parallel to the interface (for $r = 1$), the director tends to bend in this direction near the interface. The angle between the interface and the principal axis is shown in Figure 4 for $r = 1$, with $\theta = 38°$.

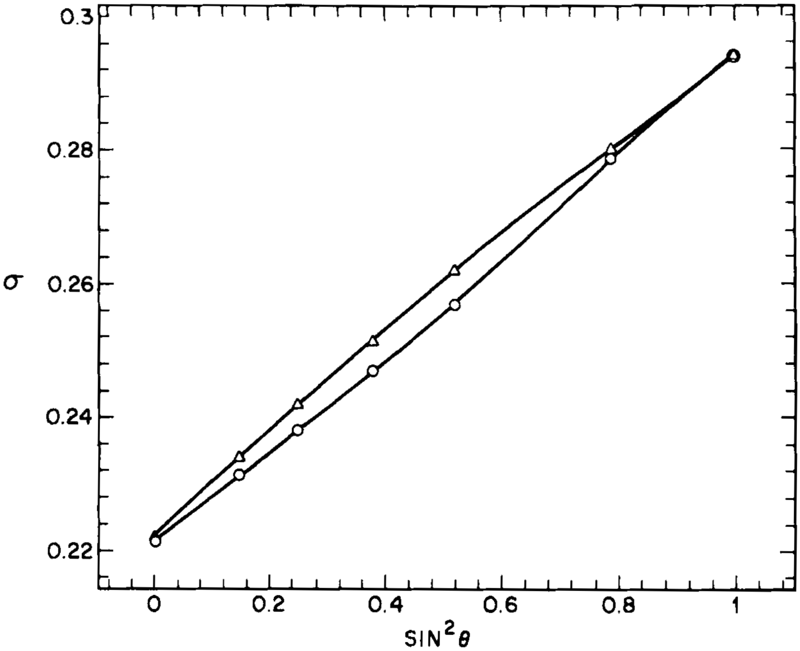

FIGURE 1 Surface tension as a function of $\sin^2\theta$. The lower points were calculated allowing biaxiality to appear, and the upper ones with a biaxiality suppression factor of 100. The curves are spline-fit "eye-guiding" interpolations.

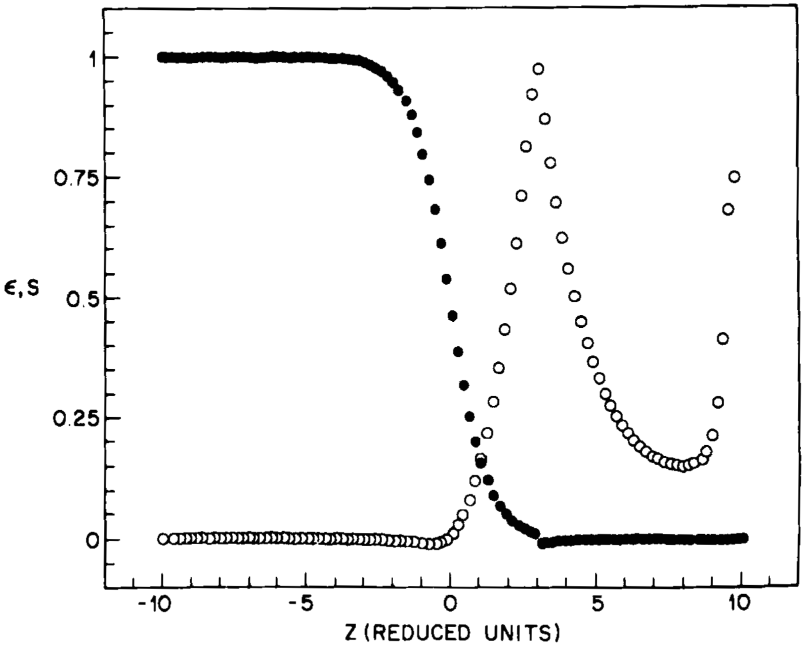

FIGURE 2 Order parameter S and biaxiality $(-\epsilon)$ as a function of distance for $\theta = 0$. Sign of ϵ is reversed to make it fit on the same scale with S. Distance in reduced units.

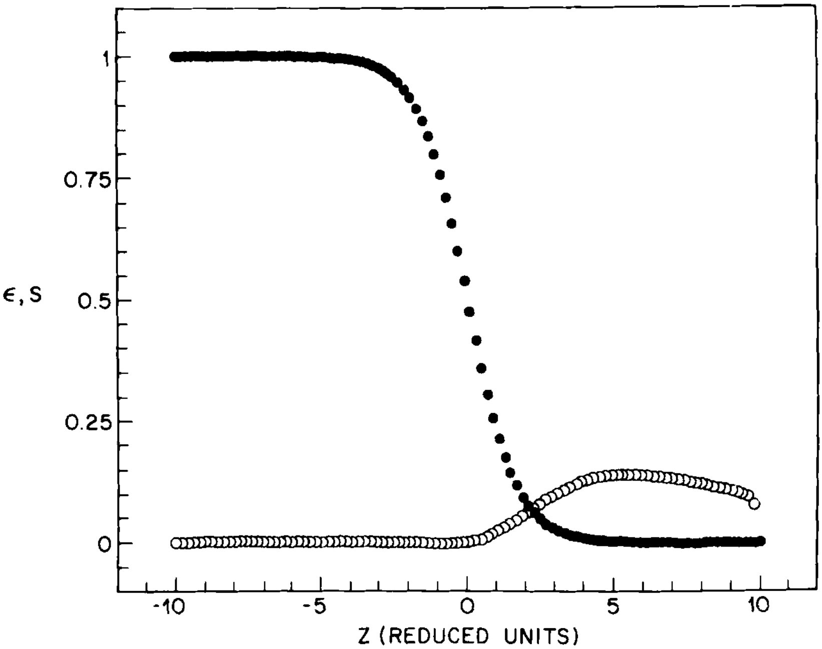

FIGURE 3 Same as Figure 1 except with director making 62.5° angle with interface.

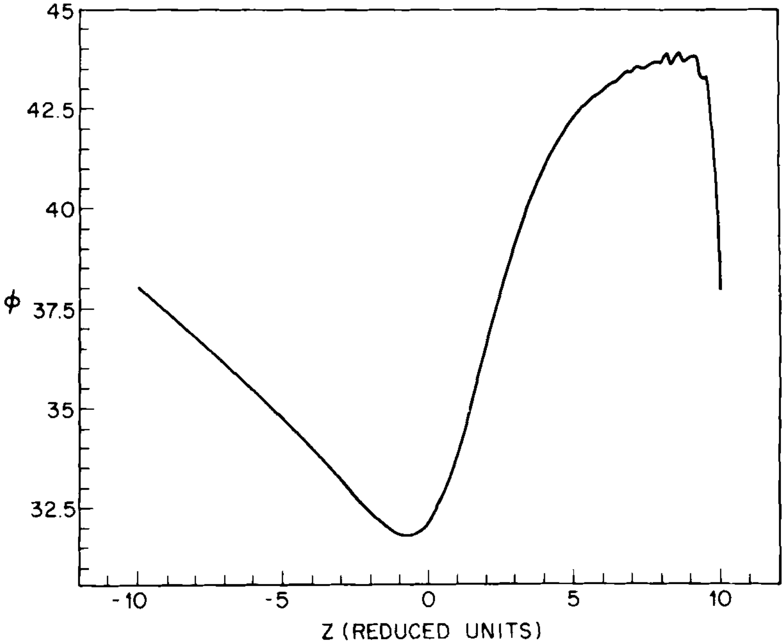

FIGURE 4 Angle between principal axis of Q-tensor and interface as a function of position for $\theta = 38°$. Wiggles at end are sign of incipient numerical instability which tends to disappear after more iterations.

V. CONCLUSIONS

The above results make clear that biaxiality plays an important role in the structure, but not the energetics of the N–I interface. The director does "bend" a little at the interface, but not very much, and this effect may possibly be neglected. The order parameter (S) has nearly the ($1 + \tanh(z)$) form expected for a uniaxial interface. All these effects are due to anisotropic elasticity, and they vanish if all the elastic constants are equal. As expected from a simple theory in which the order parameter is uniaxial and points in a constant direction throughout the interface, the surface tension is greatest when the director is perpendicular to the interface. Thus, in the absence of electrostatic or external forces, the director "prefers" to be parallel to the interface.

How may this biaxiality be detected? Clearly, a very sensitive probe of local ordering is needed, especially as most of the biaxiality occurs where the order parameter is very small ($< .1$). Also, how does one make an interface and keep it where it is needed? A possible answer is to do a frustrated total internal reflection experiment in which the glass surface on which the nematogen sits is treated so as to produce parallel alignment. The surface treatment is known to produce a "proximity effect" in which a thin nematic layer near the surface is stable somewhat above the bulk N–I transition. Thus, by keeping the temperature within a narrow range and using very pure nematogen, an interface may be stabilized for study by some optical probe.

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