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# Ordering and Distortion at the Nematic–Isotropic Fluid Interface

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A simple phenomenological theory is presented for the dependence of the surface tension $\gamma$ at the nematic–vapor interface in terms of the order parameter $Q_{ij}$. Account is taken of the observations that $\gamma$ is often discontinuous at the nematic–isotropic transition, and that there is usually a preferred orientation at the free surface. The derived $\gamma$ is anisotropic and depends on the angle between the normal to the surface and the orientation at the surface. Two simple examples of possible distortions in the orientation are considered. Since $\gamma$ depends upon the scalar order parameter $S$ it is possible to have an excess order near the surface. The value of the excess order and its decay depth are calculated.

## 1 INTRODUCTION

Consider the interface between a nematic liquid crystal and its vapor. As in an ordinary fluid, the main effect is the change in density across the interface. At the outer part of the surface zone there is an anisotropy in the forces acting on a molecule with the net force toward the bulk of the fluid. This gives rise to the phenomenon of surface tension. In a nematic liquid crystal there is a long range order, the long, rodlike molecules tend to be parallel with, however, no ordering of the centers of mass of the molecules. At a free surface the orientation tends to be fixed, often within the surface or perpendicular to it, depending on the particular material. Orientation at a well defined temperature dependent angle has also been reported.[1] Thus the free surface tends to impose an effective torque on the molecules and hence the surface tension must be anisotropic, depending on the angle between the orientation direction at the surface and the normal to the surface. Anisotropic surface energies have been discussed by several authors.[2–4] The effect of the nematic order (as opposed to the direction of orientation) on the surface tension is not well understood. Experimentally the surface tension vs. temperature curve often shows a gap at the nematic–isotropic fluid transition temperature with the surface tension less in the nematic phase.[5,6] This gap is superimposed on the usual linearlly decreasing temperature behavior observed in most organic liquids.[7] The effect of both the order and the orientation can be treated by including in the surface tension terms involving the tensor order parameter[8]

$$Q_{ij} = S(n_i n_j - (\tfrac{1}{3})\delta_{ij}) \tag{1}$$

$S$ is the scalar order parameter,[9] and roughly measures the fraction of molecules in a small, but macroscopic volume which are aligned parallel to the unit vector $\mathbf{n}$ (the director) at the point in question. Above the transition temperature $T_k, S = 0$ and at $T_k$ there is a discontinuity in $S$ so that $S(T_k) \neq 0$. The transition is first order and a latent heat and volume discontinuity have been measured.[10] The discontinuity of the surface tension at $T_k$ is very likely due to the discontinuity in the density of the fluid across the transition.

In Section 2 we begin by defining the interfacial zone in terms of a Gibbs' surface in the usual way.[11] The surface tension $\gamma$ is then related to the superficial Helmholtz free energy density. To make further progress the local free energy must be specified as a functional of the density $\rho$ and $Q_{ij}$. Anticipating that the order will be a small effect compared to the change in density, we take the form of the free energy conventionally used to discuss the liquid–vapor interface for an ordinary fluid and add to it the simplest possible terms in $Q_{ij}$ that will give the observed torque on the molecules at the surface. The equilibrium density profile is the one that minimizes the surface tension, which is the free energy of inhomogeneity per unit area. The theory gives explicit formulas for the equilibrium surface tension and density profile when the free energy is specified in terms of $\rho$ and the scalar order parameter $S$.

Two simple examples of the distortion in a nematic near the free surface are worked out in Section 3 using the anisotropic surface tension from Section 2. In the first example we have a semi-infinite nematic with a magnetic field applied parallel to the surface. Since the molecules tend to lie parallel to the field, a distortion is possible if the free surface imposes a perpendicular orientation provided the field is less than a critical value $H_c$. For $H < H_c$ the competing torques produce an orientation at an angle $\theta_0$ to the surface. The temperature dependence of this angle, as well as that of $H_c$ can be calculated from the dependence of surface tension upon $S$. The distortion also leads to a dependence of the surface tension on the magnetic field. The results are compared with an experiment on the nematic MBBA.[1] The second example involves the competing influences of a solid boundary and a free surface. A distortion is only possible if the thickness d of the nematic film is greater than a critical value $d_c$. The distortion and temperature dependence of $d_c$ can be found and this leads to a dependence of surface tension on d.

In Section 4 we consider the order parameter $S$ near the free surface in the absence of orientation distortion. The equilibrium configuration is calculated as a function of the distance from the surface by minimizing the total (volume plus surface) free energy. In the nematic phase ($T < T_k$) it is shown that excess order can exist at the surface and this excess order is directly proportional to the derivative ($\mathrm{d}\gamma/\mathrm{d}S$). It decays to zero within a characteristic temperature dependent distance estimated to be about 100 Å. When the liquid is in the isotropic phase ($T > T_k$) it is shown that it is possible to have a nonzero order parameter sufficiently close to the surface provided that the function $\gamma(S)$ has a term linear in $S$. Similar effects occur in some types of polar and associated liquids which do not have a bulk liquid crystal phase.[12]

Finally, we shall make a few remarks on the surface between a nematic and its isotropic melt at equilibrium at temperature $T$. Because of the small difference in density between the nematic and isotropic phase, a stable boundary between them is difficult to establish. Rather what is usually observed is small spherical nematic drops which wander in the isotropic phase near the transition temperature. The surface tension between the two phases has recently been measured by following the growth of the nematic drops.[13] It is about $5 \times 10^{-4}$ dynes/cm. This very small value is about five orders of magnitude smaller than the surface tension between a liquid and its vapor and is due to the fact that the nematic and isotropic phases have about the same density. Although in principle a nonzero surface tension could arise between two fluids of the same density due to the change in order across the interface, we expect that this effect will be extremely small.

## 2 THE SURFACE TENSION

Macroscopically the interface between a fluid and its vapor appears to be sharp but on a molecular scale the change in density and other properties of the medium is continuous. The density profile near the interface looks like that shown in Figure 1. The distance $z$ is measured normal to the surface which is located near $z = 0$. The thickness $\tau$ of the interface is defined so that points $z \gg \tau$ are deep in the interior of the bulk vapor, and points $z \ll \tau$ are deep in the bulk liquid.

It is convenient to specify $z = 0$ as the location of an imaginary Gibbs' surface such that the first moment of the density gradient vanishes:

$$\int_{-\infty}^{+\infty} z\left(\frac{\partial \rho}{\partial z}\right) \mathrm{d}z = 0 \qquad (2)$$

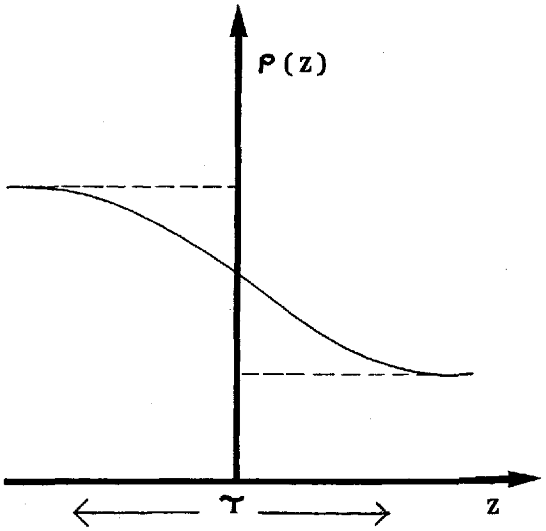

FIGURE 1 The profile of the interface

With this choice for $z = 0$, the surface tension is given by

$$\gamma = \int_{-\infty}^{+\infty} z \frac{\partial F}{\partial z} \mathrm{d}z \tag{3}$$

where $F$ is the local Helmholtz free energy density.

The fundamental postulate of quasi-thermodynamics[14] then asserts that an intensive quantity like $F(z)$ is a unique functional of $\rho(z)$ and $T$ at every point. In order to do the integral in (3) we need an expression for $F\{\rho(z)\}$. In the discussion of liquid-vapor interfaces in ordinary fluids the Van der Waals form is usually assumed:[15]

$$F(z) = \psi\{\rho(z)\} + \tfrac{1}{2}A\left(\frac{\partial \rho}{\partial z}\right)^2 \tag{4}$$

where $A$ is a positive constant except perhaps at the liquid-vapor critical point. The derivative term in (4) must be present since if it were not, $F(z)$ would lead to an interfacial thickness which vanishes at all temperatures, contrary to experiment. However there is really no convincing argument that terms involving higher spatial gradients of $\rho$ may be dropped from (4). This question is discussed in Ref. 15, which also uses (4). We shall be more concerned with the additional terms to (4) which are present in the nematic phase.

As mentioned in the introduction, there are two surface tension effects which are peculiar to the nematic phase. The first is the discontinuity in $\gamma$ at the isotropic–nematic phase transition. This implies terms in (4) involving the order parameter $S$. The second is the fact that a preferred orientation is observed at the free surface. This implies a term like $(\mathbf{n}\cdot\hat{k})^2$ in $F$ where $\hat{k}$ is the outward normal to the surface. This latter effect must have something to do with the density gradient since there is no comparable effect in the bulk. The simplest terms coupling $Q_{ij}$ and $\nabla\rho$ are

$$F' = B_1(Q_{ij}\rho_{,i}\rho_{,j}) + B_2(Q_{ij}\rho_{,j})^2 \tag{5}$$

where $(\nabla\rho)_i \equiv \rho_{,i}$. Terms higher order in $Q_{ij}$ and $\rho_{,i}$ have been neglected. Also terms involving gradients of $Q_{ij}$ are assumed to be small compared to density gradient terms. This is consistent with the very small surface tension between the nematic and isotropic phases. However, additional terms involving the scalar order parameter $S$ may be present in $\psi$. Using (1), we expand (5) and combine with (4) to give:

$$F(z) = \psi(\rho, S) + \tfrac{1}{2}A'\left(\frac{\partial\rho}{\partial z}\right)^2 \tag{6}$$

where

$$A' = A + 2B_1S\{(\mathbf{n}\cdot\hat{k})^2 - (\tfrac{1}{3})\} + (\tfrac{1}{3})B_2S^2\{(\mathbf{n}\cdot\hat{k})^2 + (\tfrac{1}{3})\} \tag{7}$$

We now minimize $\gamma$ with respect to $\rho(z)$ subject to the constraint (2). This gives an Euler–Lagrange equation

$$A'\frac{\mathrm{d}^2\rho}{\mathrm{d}z^2} = \frac{\partial\psi}{\partial\rho} - \lambda \tag{8}$$

with the boundary conditions $\rho(\infty) = \rho_g$, $\rho(-\infty) = \rho_1$. $\lambda$ in (8) is a Lagrange multiplier which can be determined from (2). Once $\rho(z)$ is determined from the solution of (8), the minimized $\gamma$ is then

$$\gamma = A'\int_{-\infty}^{+\infty}\left(\frac{\partial\rho}{\partial z}\right)^2 \mathrm{d}z \tag{9}$$

To evaluate (9) we must postulate a form for $\psi(\rho, S)$. However from (7) and (9) it follows that $\gamma$ will have the form

$$\gamma = \gamma_1(S) + \gamma_2(S)(\mathbf{n}\cdot\hat{k})^2 \tag{10}$$

where $\gamma_1(S)$ is a function determined by $\psi(\rho, S)$ and the two terms in (7) independent of $(\mathbf{n}\cdot\hat{k})^2$. $\gamma_2(S)$ has the form $aS + bS^2$ where $a$ and $b$ are constants. This form for $\gamma$ is general enough to discuss several problems involving free surfaces in nematics. The discontinuity of $\gamma$ at the nematic–isotropic transition depends upon the values of $\gamma_1$ and $a$ and $b$. Their values will depend upon the molecular interactions of the particular nematic being studied, hence a very detailed theory would be needed to predict them in any given case.

The effect of surface orientation is given by the $(\mathbf{n}\cdot\hat{k})^2$ term in (10). If $\gamma_2 > 0$ the surface energy will be minimized when the molecules lie in the surface ($\mathbf{n}\cdot\hat{k} = 0$). If $\gamma_2 < 0$ the surface energy is minimized when the molecules are perpendicular to the surface ($\mathbf{n}\cdot\hat{k} = 1$). However the actual orientation is that which minimizes the *total* free energy:

$$F_T = \int_v (F_0 + F_1 + F_H)\,\mathrm{d}V + \int_\sigma \gamma\,\mathrm{d}\sigma \tag{11}$$

$(F_0 + F_1 + F_H) = F$ is the free energy per unit volume. $F_0$ is that part of $F$ which is a local function of $Q_{ij}(\mathbf{r})$ at point $\mathbf{r}$; it depends only on $S$, not on $\mathbf{n}$. $F_1$ is a function of $Q_{ij}$ at different points in space. It is a function of $n_i$ and its gradient $n_{i,j}$ and has the form proposed by Frank.[16] $F_H$ is the energy associated with an external magnetic field. From (10) we see that $\gamma$ is a function of $n_i$ only. Gradient terms in $\gamma$ could arise if there were a transverse spatial variation in $\mathbf{n}$. If there are no external forces $\delta F = 0$. Let us calculate $\delta F$ allowing for variations in $n_i$ and $n_{i,j}$. We have

$$\int_v \left[\frac{\partial F}{\partial n_{i,j}}\delta n_{i,j} + \frac{\partial F}{\partial n_i}\delta n_i\right]\mathrm{d}V + \int_\sigma \frac{\partial \gamma}{\partial n_i}\delta n_i\,\mathrm{d}\sigma = 0$$

An application of Green's theorem reduces this to

$$-\int_v\left\{\left(\frac{\partial F}{\partial n_{i,j}}\right)_{,j} - \frac{\partial F}{\partial n_i}\right\}\delta n_i\,\mathrm{d}V + \int_\sigma\left\{\left(\frac{\partial F}{\partial n_{i,j}}\right)k_j + \left(\frac{\partial \gamma}{\partial n_i}\right)\right\}\delta n_i\,\mathrm{d}\sigma = 0$$

Thus we get

$$\left(\frac{\partial F}{\partial n_{i,j}}\right)_{,j} - \frac{\partial F}{\partial n_i} = \beta_1 n_i \tag{12}$$

in the volume $V$ and

$$\left(\frac{\partial F}{\partial n_{i,j}}\right)k_j + \frac{\partial \gamma}{\partial n_i} = \beta_2 n_i \tag{13}$$

at the interface. $k_j$ is the outward normal to the interface. The Lagrange multipliers $\beta_1$ and $\beta_2$ arise because $\mathbf{n}^2 = 1$ and they can be determined by multiplying both sides of (12) and (13) by $n_i$. The equilibrium equations (12) and (13) have been derived more rigorously by Barrett and Jenkins.[4]

The same procedure may be used to derive equations which describe a spatial variation of the order parameter $S$ at the surface. We find in the volume $V$

$$\left(\frac{\partial F}{\partial S_{,j}}\right)_{,j} - \frac{\partial F}{\partial S} = 0 \tag{14}$$

and at the interface

$$\left(\frac{\partial F}{\partial S_{,j}}\right)k_j + \frac{\partial \gamma}{\partial S} = 0 \tag{15}$$

These equations may be derived independently from (12) and (13) because the variation $\delta S$ is independent from $\delta n_i$ and $\delta n_{i,j}$.

## 3 DISTORTIONS NEAR THE INTERFACE

Examples of the distortion of orientation near a free surface have been discussed extensively in Ref. 4 without assuming a specific form for $\gamma$ in terms of $(\mathbf{n} \cdot \hat{k})^2$. However temperature effects were not discussed. Here we treat two simple examples using (10).

Consider first a semi-infinite nematic in which a magnetic field $H$ is applied parallel to the surface. Far into the bulk the molecules will tend to lie parallel to $H$. If $\gamma_2 < 0$ in (10), the molecules prefer a perpendicular alignment at the surface. Thus for a small enough field a distortion is possible and we might expect surface alignment at an angle $0 \leq \theta_0 \leq \pi/2$ where $\theta_0$ is measured from the free surface. The bulk free energy is, assuming equal Frank constants, and neglecting order parameter gradients:

$$F = (\tfrac{3}{2})DS^2(n_{k,i})^2 - (\tfrac{1}{3})\chi_a S(\mathbf{n} \cdot \mathbf{H})^2 \tag{16}$$

where $D$ is independent of temperature since the Frank constants all vary like $S^2$ with temperature. $\chi_a$ is the anisotropy of the magnetic suceptibility and is positive for long, rodlike molecules. We look for a solution of the form

$$n_x = \cos\theta,\ n_z = \sin\theta;\ \theta(-\infty) = 0 \tag{17}$$

Then the equation satisfied by $\theta(z)$ is given by (12):

$$-\varepsilon^2 \frac{\mathrm{d}^2\theta}{\mathrm{d}z^2} + \sin\theta\cos\theta = 0 \tag{18}$$

where $\varepsilon^2 = (3DS/\chi_a H^2)$. The solution which satisfies (18) and which vanishes at $z = -\infty$ is

$$\tan\left(\frac{\theta}{2}\right) = \exp\left(\frac{z+\alpha}{\varepsilon}\right) \tag{19}$$

where $\alpha$ is an integration constant. The boundary condition (13) at the interface leads to, with $\gamma(\theta) = \gamma_1 - \gamma_2(S)\sin^2\theta$:

$$3DS^2\left(\frac{d\theta}{dz}\right) - 2\gamma_2(S)\sin\theta\cos\theta = 0 \quad \text{at} \quad z = 0.$$

Using the fact that

$$\left(\frac{d\theta}{dz}\right) = \varepsilon^{-1}\sin\theta$$

this gives

$$\cos\theta_0 = \left(\frac{3DS^2}{2\gamma_2(S)}\right)\left(\frac{\chi_a H^2}{3DS}\right)^{1/2} \tag{20}$$

where $\theta_0$ is the angle at the surface. Thus $\theta_0$ decreases from $\pi/2$ as the field $H$ increases. Above a critical field

$$H_c = \left(\frac{3DS}{\chi_a}\right)^{1/2}\left(\frac{2\gamma_2(S)}{3DS^2}\right) \tag{21}$$

$\theta_0 = 0$ is the only solution. The temperature dependence of $\theta_0$ and $H_c$ is controlled by $S(T)$. If $\gamma_2 \propto S$ the temperature dependence of $\theta_0$ has the same qualitative form as that measured in MBBA by Bouchiat and Langevin-Cruchon[1] and shown in Figure 2. $\theta_0$ increases with $T$, and far below the

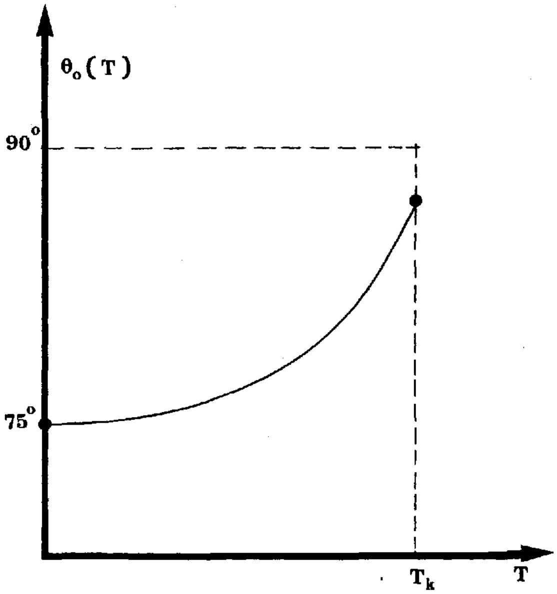

FIGURE 2 Orientation at the free surface as a function of temperature with $\gamma_2(S) \propto S$.

transition temperature it approaches an asymptotic value of about 75°. We can use this value to estimate the magnitude of $\gamma_2$. With $H \simeq 2000$ g we have $\varepsilon \simeq 5 \times 10^{-4}$ cm. Taking $3DS \simeq 10^{-7}$ we find that (20) gives $\gamma_2 \simeq 4 \times 10^{-4}$ dynes/cm, which is about the same as the surface tension observed between the nematic and isotropic phases. However, in the experiment, it was found that $\theta_0$ was independent of $H$ for 1500 g $< H <$ 3000 g whereas (20) predicts a linear dependence of $\cos\theta_0$ on $H$. Further work using a larger range of $H$ would seem desirable. Finally, note that (20) implies a dependence of surface tension on magnetic field:

$$\gamma(H) = \gamma_1 - \gamma_2\left[1 - \left(\frac{\chi_a H^2}{3DS}\right)\left(\frac{3DS^2}{\gamma_2}\right)^2\right] \tag{22}$$

$\gamma(H)$ increases with increasing $H$, but the maximum change is of order $\gamma_2$ which is quite small. Smaller yet would be a possible change in $\gamma$ resulting from the increase in the order parameter $S$ when a magnetic field is applied.

Next, consider a thin film of nematic introduced on top of a solid that maintains a perpendicular alignment of the molecules. If $\gamma_2 > 0$ in (10), the molecules will prefer a parallel alignment at the free surface. For a film thickness d larger than a critical value $\mathrm{d}_c$ (to be determined) a distortion is again possible and the angle of orientation at the surface (measured with respect to the surface normal) will have some intermediate value $0 \leq \theta_0 \leq \pi/2$. We look for a solution

$$n_x = \sin\theta,\, n_z = \cos\theta;\ \theta(-\mathrm{d}) = 0 \tag{23}$$

With the free energy given by the first term in (16), the equilibrium $\theta(z)$ that vanishes at $z = -\mathrm{d}$ is

$$\theta(z) = \frac{\theta_0(z + \mathrm{d})}{\mathrm{d}} \tag{24}$$

An application of the interfacial boundary condition (13) with $\gamma(\theta) = \gamma_1(S) + \gamma_2(S)\cos^2\theta$ gives an implicit relation for $\theta_0$:

$$\chi\theta_0 = \sin 2\theta_0;\ \chi = \left(\frac{3DS^2}{\gamma_2(S)}\right)\mathrm{d} \tag{25}$$

A nonzero solution for $\theta_0$ is possible only when $\chi < 2$. This gives the condition

$$\mathrm{d} > \mathrm{d}_c;\ \mathrm{d}_c = \frac{3DS^2}{2\gamma_2} \tag{26}$$

For $\gamma_2 \simeq 10^{-3}$ dynes/cm we get $\mathrm{d}_c \simeq 100\ \mu$. Its temperature dependence will tell us the form of $\gamma_2(S)$. Equation (25) may be solved graphically or numerically for specific values of $\chi$. We can get an approximate analytical solution

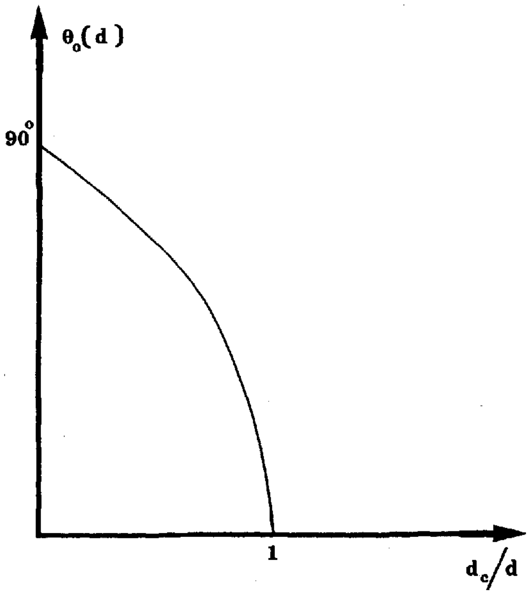

FIGURE 3 Orientation at free surface measured from normal as a function of d in a thin nematic film.

when $\chi \simeq 2(d \gtrsim d_c)$. Then $\theta_0 \simeq 0$ and (25) can be expanded to give

$$\theta_0 \simeq \left(\frac{\sqrt{3}}{2}\right)(2-\chi)^{1/2} \qquad (d \gtrsim d_c) \qquad (27$$

For $\chi \simeq 0(d \gg d_c)$ we have $\theta_0 \simeq \pi/2$ and (25) gives

$$\theta_0 \simeq \left(\frac{\pi}{2}\right)(1-\chi) \qquad (d \gg d_c) \qquad (2$$

Thus $\theta_0(d)$ is a decreasing function of $(d_c/d)$ and is sketched in Figure 3. The surface tension will depend upon d through $\theta$:

$$\gamma(d) = \gamma_1 + \tfrac{1}{2}\gamma_2\{1 + (1 - \chi^2\theta_0^2)^{1/2}\} \qquad (2$$

Again the maximum change is of order $\gamma_2$.

## 4 ORIENTATION NEAR A FREE SURFACE

We consider a semi-infinite sample with the free surface at $z = 0$. Let us suppose that the orientation is uniform everywhere in the sample. A distortion in the scalar order parameter $S$ is still possible, however, because the surface free energy depends upon $S$. In this section we calculate this distortion.

The volume free energy density can be expanded in powers of $S$ (a Landau expansion) near the isotropic–nematic phase transition where $S$ is small.[17]

$$F = F_0 + \tfrac{1}{2}AS^2 - (\tfrac{1}{3})BS^3 + \tfrac{1}{4}CS^4 + \tfrac{1}{2}D(\nabla S)^2 \tag{30}$$

where $A = a(T - T_c^*)$ with $T_c^*$ slightly below the (first order) phase transition temperature $T_k$, and $a, B, C, D$ are positive constants. $D$ is the same value as used in (16) for the case of equal Frank constants. $F_0$ represents the free energy of the isotropic phase and is, of course, independent of $S$. Higher powers of $S$ and $\nabla S$ have been ignored in (30).

The equilibrium $S(z)$ must satisfy the Euler–Lagrange equation (14) which leads to a nonlinear equation:

$$D\frac{\mathrm{d}^2S}{\mathrm{d}z^2} = AS - BS^2 + CS^3 \tag{31}$$

with the boundary conditions $S = S_b$, $(\partial S/\partial z) = 0$ at $z = -\infty$. $S_b$ is the bulk value (the value the order parameter would have if the fluid were unbounded). It satisfies

$$AS_b - BS_b^2 + CS_b^3 = 0 \tag{32}$$

For $T \leq T_k$ the solution of (32) which minimizes (30) is

$$S_b = \left(\frac{B}{2C}\right)\{1 + (1 - \beta)^{1/2}\}; \beta = \frac{4AC}{B^2} \tag{33}$$

with $T_k = T_c^* + (2C/9B^2a)$. For $T > T_k$ the solution which minimizes (30) is $S_b = 0$. Thus at $T = T_k$ there is a discontinuity in $S_b$ and the transition is first order.

An exact solution of (31) is possible in terms of elliptic functions but would be very complex. Here we will obtain an approximate solution for the case where the effect of the free surface can be assumed to be small. Then we can write $S(z) = S_b + S'(z)$ with $S' \ll S_b$ and linearize (31) in $S'$. The result is

$$\frac{\mathrm{d}^2S'}{\mathrm{d}z^2} - \alpha^2S' = 0 \tag{34}$$

where $\alpha^2 = (A - 2BS_b + 3CS_b^2)/D$. From (33) it follows that $\alpha^2 > 0$. $S'$ satisfies homogeneous boundary conditions $S' = 0$, $(\mathrm{d}S'/\mathrm{d}z) = 0$ at $z = -\infty$. The solution is $S'(z) = S_0e^{\alpha z}$, hence

$$S(z) = S_b + S_0e^{\alpha z} \tag{35}$$

where $S_0$ is obtained by applying the interfacial boundary condition (15). This gives

$$D\frac{\mathrm{d}S}{\mathrm{d}z} + \frac{\partial\gamma}{\partial S} = 0 \quad \text{at} \quad z = 0 \tag{36}$$

or

$$S_0 = -\frac{(\partial\gamma/\partial S)}{D\alpha} \tag{37}$$

Typically $D \simeq 10^{-7}$ cgs and $\alpha \simeq 10^6$ cm$^{-1}$. Thus $S(z)$ decays to its bulk value within about a micron of the free surface. The excess order at the surface is proportional to the derivative $(\partial\gamma/\partial S)$ which will be negative when the surface energy is lowered by the order. This will occur when the surface tension near the transition temperature is *less* in the nematic phase. For example suppose that $\gamma(S) = \gamma_0 - \gamma_1 S^n$ where $n \geq 1$. Equation (37) then tells us that the excess order at the surface will be approximately

$$S_0 \simeq \frac{(n\gamma_1 S_b^{n-1})}{D\alpha} \tag{38}$$

For $D$ and $\alpha$ as estimated before and $\gamma_1 \simeq 10^{-3}$ dynes/cm, the excess order at the surface will be roughly 1% of the bulk order.

Finally, suppose the temperature in the sample is slightly above the isotropic–nematic transition so that $S$ vanishes far from the surface. Is it possible to have a nonzero $S$ sufficiently close to the surface? We can linearize (31) directly, assuming $S(z)$ is everywhere small. Since $A > 0$ in the isotropic phase the solution is just

$$S(z) = S_0 e^{mz}; \qquad m^2 = \frac{A}{D} \tag{39}$$

An application of (36) leads to $S_0 = -(\partial\gamma/\partial S)/mD$. Note that we get a nonzero $S_0$ only when $\gamma(S)$ contains a term linear in $S$. Otherwise $S = 0$ right up to the free surface. As the temperature increases both the decay depth $m^{-1}$ and the order parameter at the surface decrease.

## References

1. M. A. Bouchiat and D. Langevin-Cruchon, *Phys. Lett.*, **34A**, 331 (1971).
2. S. Chandrasekhar, *Mol. Cryst., Liquid Cryst.*, **2**, 71 (1966).
3. E. Dubois-Violette and O. Parodi, *J. Phys. (Paris)*, **30**, C. 4–57 (1969).
4. J. T. Jenkins and P. J. Barratt, *Quart. J. Mech. Appl. Math.*, **27**, 111 (1974); *J. Phys. A (G.B.)*, **6**, 756 (1973).
5. W. A. Schwartz and H. W. Moseley, *J. Phys. and Colloid Chem.*, **51**, 826 (1947).
6. C. F. Hayes, *Mol. Cryst., Liquid Cryst.* (to be published).
7. D. Churchill and L. W. Bailey, *Mol. Cryst., Liquid Cryst.*, **7**, 285 (1969).
8. P. G. deGennes, *Phys. Lett.*, **30A**, 454 (1969).
9. W. Maier and A. Saupe, *Z. Naturforch.* A **15**, 287 (1960).
10. A review article on liquid crystals is by I. G. Chistyakov, *Usp. Fiz. Nauk.* (*USSR*), **89**, 563 (1966) [*Soviet Phys. Usp.*, **9**, 551 (1967)].
11. J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, **17**, 338 (1949).

12. H. S. Green in *Handbuch der Physik*, *Vol. X*, p. 80. Ed. by S. Flügge (Berlin: Springer-Verlag, 1960).
13. M. Kahlwett and W. Ostner, *Chem. Phys. Lett.*, **18**, 589 (1973).
14. S. Ono and S. Kondo, *Handbuch der Physik*, Vol. 10, p. 134. Ed. by S. Flügge (Berlin: Springer-Verlag, 1960).
15. See e.g. B. Widom in *Phase Transitions and Critical Phenomena*, Vol. 2, p. 79. Ed. by C. Domb and M. S. Green (London: Academic Press, 1972).
16. F. C. Frank, *Disc. Far. Soc.*, **25**, 19 (1958).
17. C. Fan and M. J. Stephen, *Phys. Rev. Lett.*, **25**, 500 (1970).