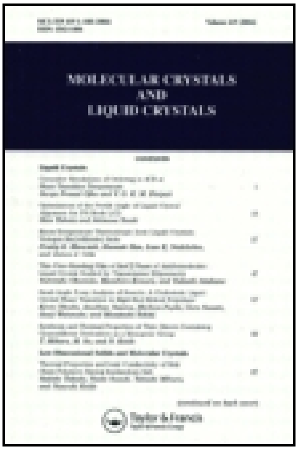

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Statistical Thermodynamics of the Liquid Crystal Surface. Smectic, Nematic and Isotropic Systems

Clive A. Croxton [a]

[a] Department of Mathematics, University of Newcastle, N.S. W., 2308, Australia

To cite this article: Clive A. Croxton (1980): Statistical Thermodynamics of the Liquid Crystal Surface. Smectic, Nematic and Isotropic Systems, Molecular Crystals and Liquid Crystals, 59:3-4, 219-240

To link to this article: http://dx.doi.org/10.1080/00268948008071425

Mol. Cryst. Liq. Cryst., 1980, Vol. 59, pp. 219–240
0026-8941/80/5903-0219$04.50/0

Statistical Thermodynamics of the Liquid Crystal Surface. Smectic, Nematic and Isotropic Systems

CLIVE A. CROXTON
Department of Mathematics, University of Newcastle, N.S.W. 2308, Australia

(*Received December 18, 1978; in final form June 29, 1979*)

The role of surface fields in determining a local order parameter in the vicinity of the liquid crystal-vapour interface is determined, and an expression is obtained for its spatial variation in regions of molecular anisotropy. The consequences of differences between the bulk and surface order parameters are investigated, and are found to be responsible for a wide variety of phenomena related to the surface tension and entropy of liquid crystal systems.

1 INTRODUCTION

Molecular fluids having an anisotropic pair interaction have been shown to develop an orienting torque in regions of structural inhomogeneity, in particular at the free-liquid-vapour interface[1,2,5,6] where the existence of a strong density gradient establishes a surface orienting field. The existence of surface orienting torques may be inferred from the competitive interaction between the entropy term in the surface excess Helmholtz free energy which favours molecular disorientation, and the energy term which favours a specific orientation in the surface field arising from the bulk fluid. Whether oriented molecular states will develop depends upon the details of the density transition profile, the pair interaction and the temperature. For molecular systems whose shape is no more than a perturbative departure from sphericity, there is some evidence for weakly oriented surface states. Liquid nitrogen, for example, appears to show a tendency for alignment of the molecular axis parallel to the liquid surface.[2] These calculations, however, also predict *normally* oriented vapour states just above the free surface which is somewhat difficult to understand physically, although the effect may be almost certainly ascribed to the use of inconsistent one and two-particle distributions and the use of an interpolated pair distribution which is too heavily weighted towards the bulk liquid distributions in the vapour side of the dividing surface.[5]

For strongly anisotropic molecular fluids Parsons[3] has determined the surface tension of a nematic liquid crystal system working in what is essentially the Kirkwood-Buff approximation. Whilst providing some insight into the molecular processes operating at the liquid surface, certain of the assumptions are sufficiently restrictive as to suppress a number of qualitative features which arise from local surface variations in the order parameter. In the second section, this model, which is qualitatively very similar to the ansatz proposed earlier by Croxton and Chandrasekhar, is used to yield the surface tension-temperature characteristics of smectic, nematic and isotropic liquid crystal systems.

2 SURFACE VARIATION OF THE LOCAL ORDER PARAMETER

Whilst the orientation of the director is arbitrary in the bulk fluid, the effect of a bounday—in particular a free surface—is to break the translational symmetry of the system, whereupon both the local density and the orientational distribution will modify and depend upon the location of the molecular centre relative to the Gibbs dividing surface which is located such that

$$\int_{-\infty}^{0}[\rho_L - \rho_{(1)}(z)]\mathrm{d}z = \int_{0}^{\infty}[\rho_{(1)}(z) - \rho_V]\mathrm{d}z.$$

Moreover, the direction of the director $\hat{\mathbf{n}}$ modifies in the vicinity of the surface for purely geometrical reasons and we may therefore expect the surface excess thermodynamic properties to depend upon $\hat{\mathbf{n}}$ at the surface. Far from boundaries, and in the absence of external fields, the bulk liquid order parameter is defined as usual by

$$\eta_L = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle = \frac{1}{2}\int_{0}^{\pi/2}(3\cos^2\theta - 1)f(\theta)\sin\theta\,\mathrm{d}\theta \qquad (1)$$

where θ is the molecular orientation relative to the local director, and where a thermal average has been taken over the set of internal orientational states characteristic of the bulk. At the surface, however, the intervention of interfacial torque fields leads us to expect that a more general order parameter $\eta(z)_{\hat{\mathbf{n}}}$ will be necessary.

We specify two cartesian coordinate frames, the first having its z-axis coincident with the surface normal $\hat{\mathbf{k}}$, and its xy plane defining the Gibbs dividing surface. The second coordinate frame (ξ, η, ζ) is fixed with its ζ-axis along $\hat{\mathbf{n}}$, the local director field axis. In the case of perpendicular orientation of the director $(\hat{\mathbf{n}} \cdot \hat{\mathbf{k}} = 1)$, for example, the two coordinate frames are simply related by spatial translation: both the z and ζ axes are parallel.

The surface tension may be expressed in terms of the local *excess* Helmholtz free energy $a_s(z_1)_{\hat{\mathbf{n}}}$ per particle

$$\gamma_{\hat{\mathbf{n}}} = \int_{-\infty}^{\infty} a_s(z_1)_{\hat{\mathbf{n}}}\, \rho_{(1)}(z_1)\mathrm{d}z_1 \tag{2}$$

where, for rigid molecules with pair interactions u_{12} depending only upon the centre of mass vector $\mathbf{r}_{12}$ and the set of molecular Euler angles (ϕ, θ, ψ)[15]

$$\rho_{(1)}(z_1)a_s(z_1)_{\hat{\mathbf{n}}} = -\frac{1}{2}\iiint\left\{z_{12}\frac{\partial u_{12}}{\partial z_{12}} - x_{12}\frac{\partial u_{12}}{\partial z_{12}}\right\}$$
$$\times\ \rho_{(2)}(z_1, \mathbf{r}_{12}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)_{\hat{\mathbf{n}}}\, \mathrm{d}\hat{\mathbf{e}}_1^3\, \mathrm{d}\hat{\mathbf{e}}_2^3\, \mathrm{d}^3\mathbf{r}_{12} \tag{3}$$

x_{12} and z_{12} represent the components of the vector $\mathbf{r}_{12}$ linking the two centres of mass and $\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2$ denote the sets of Euler angles for the two molecules $\mathrm{d}^3\hat{\mathbf{e}}_i = \sin\theta_i\, \mathrm{d}\theta_i\, \mathrm{d}\Phi_i\, \mathrm{d}\psi_i$. Obviously the distribution amongst the states of the two interacting molecules will, in the vicinity of the surface, depend upon the location of their centres and the direction of the local director: $f(\hat{\mathbf{e}}_1, z_1)_{\hat{\mathbf{n}}}$, $f(\hat{\mathbf{e}}_2, z_2)_{\hat{\mathbf{n}}}$. We assume the orientation of the director varies slowly throughout the interfacial region, which would appear to be a reasonable assumption since the bulk correlation range of the director is typically $> 10^3$ Å.

To make further progress we must decouple the two-particle distribution $\rho_{(2)}(z_1, \mathbf{r}_{12}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)_{\hat{\mathbf{n}}}$ which, in a region whose local director field is $\hat{\mathbf{n}}$, represents the probability of finding molecules 1 and 2 in the configuration $(z_1, \mathbf{r}_{12}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)$. If, in the spirit of the mean field approximation, we assume that there is no angular correlation between neighbouring molecules, then we may write

$$\rho_{(2)}(z_1, \mathbf{r}_{12}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)_{\hat{\mathbf{n}}} = \rho_{(1)}(z_1)\rho_{(1)}(z_2)f(\hat{\mathbf{e}}_2, z_1)_{\hat{\mathbf{n}}}\, f(\hat{\mathbf{e}}_2, z_2)_{\hat{\mathbf{n}}}\, g_{(2)}(z_1, \mathbf{r}_{12}). \tag{4}$$

where $\rho_{(1)}(z_i)$ is the single particle density distribution of molecular centres relative to the Gibbs surface, and $g_{(2)}(z_1, \mathbf{r}_{12})$ is the anisotropic radial distribution function. We point out that even in the bulk $g_{(2)}(-\infty, \mathbf{r}_{12})$ is a strongly anisotropic function. The induced dipole pair interaction may generally be written in dyadic notation which we adopt as our total molecular interaction function:

$$u_{12} = -\frac{v}{r_6}(\hat{\mathbf{e}}_1 \cdot \overleftrightarrow{\boldsymbol{T}} \cdot \hat{\mathbf{e}}_2)^2; \qquad v > 0, r = |\mathbf{r}_{12}| \tag{5}$$

where $\overleftrightarrow{\boldsymbol{T}}$ is the symmetric tensor $\overleftrightarrow{\boldsymbol{T}} = (\overleftrightarrow{I} - (3\mathbf{rr}/r^2))$ and $\overleftrightarrow{I}$ a unit tensor:

$$\overleftrightarrow{\boldsymbol{T}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} - 3 \frac{\begin{bmatrix} R_x R_x & R_x R_y & R_x R_z \\ R_y R_x & R_y R_y & R_y R_z \\ R_z R_x & R_z R_y & R_z R_z \end{bmatrix}}{R^2}$$

Now that the two particle distribution has been decoupled (4), the angular averages over $f(\hat{\mathbf{e}}_1, z_1)_{\hat{\mathbf{n}}}$ and $f(\hat{\mathbf{e}}_2, z_2)_{\hat{\mathbf{n}}}$ may be performed. Assuming the pair distribution $g_{(2)}$ scales as σ/r, where σ is the collision diameter for a particular orientational configuration, the field particle will sample more widely varying regions of $\eta(z)$ in the case $\hat{\mathbf{n}} \cdot \hat{\mathbf{k}} = 1$, compared with $\hat{\mathbf{n}} \cdot \hat{\mathbf{k}} = 0$, for a given density profile. So clearly $f(\hat{\mathbf{e}}_2, z_1)$ will depend upon $\hat{\mathbf{n}}$.

In a mean field approximation we set

$$f(\hat{\mathbf{e}}_2, z_2)_{\hat{\mathbf{n}}} = f(\hat{\mathbf{e}}_1, z_1)_{\hat{\mathbf{n}}} \tag{6}$$

which is likely to be reasonable provided $\eta(z)$ varies relatively slowly.

$$\begin{aligned} \langle u \rangle_{\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2} = -\frac{v}{9r^6}(T_{\xi\xi}^2 + T_{\eta\eta}^2 + T_{\zeta\zeta}^2 + \eta(z_1)_{\hat{\mathbf{n}}}[4T_{\zeta\zeta}^2 + 2T_{\xi\xi}^2 + 2T_{\eta\zeta}^2 \\ - 2T_{\xi\zeta}^2 - 2T_{\eta\eta}^2 - 4T_{\xi\eta}^2] \\ + \eta^2(z_1)_{\hat{\mathbf{n}}}[T_{\xi\xi}^2 + T_{\eta\eta}^2 + 2T_{\xi\eta}^2 + 4T_{\zeta\zeta}^2 - 4T_{\xi\zeta}^2 - 4T_{\eta\zeta}^2]) \end{aligned} \tag{7}$$

where $T_{\kappa\lambda}$ are the cartesian components of $\overleftrightarrow{\boldsymbol{T}}$. The *local* order parameter is now defined as

$$\eta(z_1)_{\hat{\mathbf{n}}} = \frac{1}{2}\int_0^{\pi/2} (3\cos^2\theta - 1) f(\theta, z_1)_{\hat{\mathbf{n}}} \sin\theta \, d\theta \tag{8}$$

where, as before, θ is the angle which the long molecular axis makes with respect to the local director (c.f. (1)). Note that now $\langle u\rangle_{\hat{\mathbf{e}}_1,\hat{\mathbf{e}}_2}$ if a function of z_1 and $\hat{\mathbf{n}}$. We also point out that for mechanical stability the term $z_{12}(\partial u_{12}/\partial z_{12})\rho_{(2)}(z_1, \mathbf{r}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)_{\hat{\mathbf{n}}}$ in (3) is independent of z_1 and, moreover, in either bulk isotropic phase we have

$$z_{12}\frac{\partial u_{12}}{\partial z_{12}}\rho_{(2)}(\pm\infty, \mathbf{r}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) = x_{12}\frac{\partial u_{12}}{\partial x_{12}}\rho_{(2)}(\pm\infty, \mathbf{r}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \tag{9}$$

We take the Φ-distribution to be $f(z, \Phi_{\hat{\mathbf{n}}})$, and we define the integrals

$$\begin{aligned} c_j(z) &= \int_0^{2\pi} f(z, \Phi)_{\hat{\mathbf{n}}} \cos^j \Phi \, \mathrm{d}\Phi \\ s_j(z) &= \int_0^{2\pi} f(z, \Phi)_{\hat{\mathbf{n}}} \sin^j \Phi \, \mathrm{d}\Phi \\ cs_{ij}(z) &= \int_0^{2\pi} f(z, \Phi)_{\hat{\mathbf{n}}} \sin^i \Phi \cos^j \Phi \, \mathrm{d}\Phi \end{aligned} \tag{10}$$

The general case of arbitrary orientation of the surface director $\hat{\mathbf{n}}$ is difficult to analyse. However, two specific cases $\hat{\mathbf{n}}\cdot\hat{\mathbf{k}} = 1$ and $\hat{\mathbf{n}}\cdot\hat{\mathbf{k}} = 0$, corresponding to parallel and perpendicular orientation of the director relative to the surface may be more readily discussed.

(a) $\hat{\mathbf{n}}\cdot\hat{\mathbf{k}} = 1$ (*perpendicular orientation of the surface director*) In this case we make the transformation of axes $\xi \to x$, $\eta \to y$, $\zeta \to z$, and also transform to a cylindrical polar coordinate frame with $\hat{\mathbf{n}}$ along the polar axis. For the case $\hat{\mathbf{n}}\cdot\hat{\mathbf{k}} = 1$ then since the molecules are cylindrically symmetrical, $f(z, \Phi)_\perp = f(-\infty, \Phi)_\perp = 1.00$, and we have from (10)

$$\begin{aligned} c_2 = s_2 &= \pi & cs_{22} &= \frac{\pi}{4} \\ c_4 = s_4 &= \frac{3\pi}{4} & cs_{24} &= \frac{\pi}{8} \\ c_6 = s_6 &= \frac{5\pi}{8} & cs_{42} &= \frac{\pi}{8} \end{aligned} \tag{11}$$

We may now average over the Φ distribution, whereupon (3) becomes, after some tedious analysis,

$$\begin{aligned}
\rho_{(1)}(z_1)a_s(z_1) = {} & -\int_{-\infty}^{\infty} \mathrm{d}z \int_0^{\pi/2} \sin\theta \, \mathrm{d}\theta \int_{|z|}^{\infty} r \, \mathrm{d}r \left(\frac{-v}{9r^6}\right) \\
& \times \Bigg\{ [\rho_{(2)}(-\infty \,|\, \rho_L) - \rho_{(2)}(z_1, \mathbf{r})] \Bigg[-\frac{15\pi}{2} \cos^2\theta \sin^4\theta + \frac{15\pi}{4} \sin^6\theta \\
& + \cos^2\theta(1 + 2\cos^2\theta - 5\cos^4\theta) - \pi \sin^2\theta\left(1 + \frac{3}{2}\sin^2\theta\right) - 5\pi\cos^4\theta \Bigg] \\
& + 2[\rho_{(2)}(-\infty \,|\, \rho_L)\eta_L - \rho_{(2)}(z_1, \mathbf{r})\eta(z)] \Bigg[15\pi \cos^2\theta \sin^4\theta + \frac{15\pi}{4}\sin^6\theta \\
& - \sin^2\theta(5\cos^4\theta - 4\pi + 11\cos^2\theta) - \cos^2\theta(3 - 11\cos^2\theta + 10\cos^6\theta) \Bigg] \\
& + [\rho_{(2)}(-\infty)\eta_L^2 - \rho_{(2)}(z_1)\eta^2(z_1)] \Bigg[-2\pi \sin^2\theta \cos^2\theta(1 + 10(\sin^2\theta - \cos^2\theta)) \\
& + \frac{5\pi}{2}\sin^6\theta - \frac{15\pi}{2}\cos^2\theta\sin^4\theta - 2\sin^2\theta\left(\frac{5\pi}{8}\sin^2\theta + \pi\right) \\
& - 6\cos^2\theta + 20\cos^4\theta(1 + \cos^4\theta(\sin^2\theta - \cos^2\theta)) \Bigg] \Bigg\}. \qquad (12)
\end{aligned}$$

where we have used (9) and the decoupled form (4) for the two-particle density distribution.

Formally

$$\rho_{(2)}(z_1, \mathbf{r}) = \rho_{(1)}(z_1)\rho_{(1)}(z_2)g_{(2)}(z_1, \mathbf{r}) \qquad (13)$$

and it remains to specify $\rho_{(1)}(z_2)$ and $g_{(2)}(z_1, \mathbf{r})$. For near linear density profiles we may expand the single particle density about $\rho_{(1)}(z_1)$, where to first order:

$$\rho_{(1)}(z_2) = \left(\rho_{(1)}(z_1) + z_{12}\left(\frac{\partial\rho_{(1)}(z_1)}{\partial z_1}\right)_{z_1}\right), \qquad (14)$$

such an approximation has been shown elsewhere[7] to be reasonable even for sharp density transitions, and for $g_{(2)}(z_1, \mathbf{r}_{12})$ we adopt the closure

$$g_{(2)}(z_1, \mathbf{r}) = 0.5g_{(2)}[\mathbf{r} \,|\, \rho_{(1)}(z_1)] + 0.5g_{(2)}[\mathbf{r} \,|\, \rho_{(1)}(z_2)] \qquad (15)$$

which is invariant to particle exchange (symmetrical) and is asymptotically correct for slowly varying profiles. The two functions $g_{(2)}[r|\rho_{(1)}(z_1)]$ and $g_{(2)}[r|\rho_{(1)}(z_2)]$ in (15) may be related by the Ornstein-Zernike equation, using (14):

$$\begin{aligned} g_{(2)}(z_1, \mathbf{r}) &= 1 + c(\mathbf{r}) + \left[\rho_{(1)}(z_1) + \tfrac{1}{2}z_{12}\left(\frac{\partial \rho_{(1)}(z_1)}{\partial z_1}\right)_{z_1}\right]F(\mathbf{r}) \\ &= g_{(2)}[\mathbf{r}|\rho_{(1)}(z_1)] + \tfrac{1}{2}z_{12}\left(\frac{\partial \rho_{(1)}(z_1)}{\partial z_1}\right)_{z_1} F(\mathbf{r}) \end{aligned} \tag{16}$$

where $F(\mathbf{r}) = \int c(\mathbf{r}_{13})h(\mathbf{r}_{23})d3$; $F(\mathbf{r})$, $c(\mathbf{r})$ and $h(\mathbf{r})$ being the indirect and total correlation functions, respectively. Implicit in the approximation (16) is the assumption that $c(\mathbf{r})$ varies more slowly with density than does $\rho F(\mathbf{r})$. It is known that the direct correlation function is, in fact, a very strongly density-dependent function at small $\mathbf{r}$ but almost exactly opposed by $\rho F(\mathbf{r})$ in the strongly density-dependent core region. The two functions always occur in product with r^2 whereupon the core behavior is virtually suppressed. Thus, the principal contribution in (13) arises at intermediate to large r, where the approximation is likely to be reasonable. We may formally integrate (13) to yield the local excess Helmholtz free energy density:

$$\begin{aligned} \rho_{(1)}(z_1)a_s(z_1)_\perp = {} & -\rho_L^2[A_\perp + \eta_L B_\perp + \eta_L^2 C_\perp] \\ & + \rho_{(1)}^2(z_1)[A_\perp(z_1) + \eta(z_1)B_\perp(z_1) + \eta^2(z_1)C_\perp(z_1)] \\ & + \rho_{(1)}(z_1)\left(\frac{\partial \rho(z_1)}{\partial z_1}\right)_{z_1}^2 [D_\perp(z_1) + \eta(z_1)E_\perp(z_1) + \eta^2(z_1)G_\perp(z_1)] \end{aligned} \tag{17}$$

where the coefficients $A_\perp(z_1), \ldots, G_\perp(z_1)$ represent the results of integrating (12), following the insertion of (15) and (16). In the absence of explicit expressions for the one and two-particle correlations it is difficult to obtain a more specific description of the interfacial structure and the associated properties. However, we are able nevertheless to gain considerable insight into the statistical thermodynamics on the basis of these formal expressions, as we shall demonstrate below.

b) $\hat{\mathbf{n}} \cdot \hat{\mathbf{k}} = 0$ (*parallel orientation of the director*) Making the transformation $\zeta \to x$, $\eta \to y$, $\xi \to z$, we obtain the analogous expression to (12) for the surface excess Helmholtz free energy. The formal expression is inordinately complicated, the more so since the simplifications (11) cannot be incorporated;

it serves no useful purpose to write the expression out explicitly here, except to say that it shows a similar dependence upon η, $\eta(z)$, $\rho_{(2)}(-\infty, \mathbf{r})$ and $\rho_{(2)}(z_1, \mathbf{r})$ as in Eq. (12). Similar reasoning as for the perpendicular case yields the formal result

$$\begin{aligned}\rho_{(1)}(z_1)a_s(z_1)_{\parallel} = {} & -\rho_L^2[A_{\parallel} + \eta_L B_{\parallel} + \eta_L^2 C_{\parallel}] \\ & + \rho_{(1)}^2(z_1)[A_{\parallel}(z_1) + \eta(z_1)B_{\parallel}(z_1) + \eta^2(z_1)C_{\parallel}(z_1)] \\ & + \rho_{(1)}(z_1)\left(\frac{\partial\rho(z_1)}{\partial z_1}\right)^2_{z_1}[D_{\parallel}(z_1) + \eta(z_1)E_{\parallel}(z_1) + \eta^2(z_1)G_{\parallel}(z_1)]\end{aligned} \tag{18}$$

where the coefficients $A_{\parallel}(z_1), \ldots, G_{\parallel}(z_1)$, represent the result of the integrations following the insertion of (15) and (16).

Although Eqs. (17) and (18) are purely formal results, they do nevertheless show that the local free energy density has limiting Cahn–Hilliard "square-gradient" form in the high temperature isotropic phase[7] ($\eta = \eta(z_1) = 0$) when $\rho_{(1)}(z_1)$ is a slowly varying function of position, whilst in the nematic phase the Cahn–Hilliard form is modified by terms proportional to $\eta(z_1)$ and $\eta^2(z_1)$. Unfortunately, in the absence of any knowledge of the distributions $f(z, \Phi)$ and $g_{(2)}[\mathbf{r}|\rho(z_1)]$, it is difficult to be more specific regarding the coefficients $A, \ldots, G$ appearing in Eqs. (17) and (18). However, physical considerations lead us to require

$$\begin{aligned}A_{\parallel} &= A_{\perp} > 0 \\ A_{\parallel}(z_1) &= A_{\perp}(z_1) > 0 \\ D_{\parallel}(z_1) &= D_{\perp}(z_1) > 0\end{aligned} \tag{19}$$

since in the high-temperature isotropic phase ($\eta = 0$) the Cahn–Hilliard result must be recovered regardless of the director $\hat{\mathbf{n}}$ in the nematic phase. Which of the two molecular orientations, parallel or perpendicular, (or indeed some intermediate orientation) yields a lower free energy depends in a subtle way upon the relative magnitudes of the coefficients $A, \ldots, G$ and unfortunately cannot be ascertained from these purely formal results.

Two further simplifications may be made by setting

$$g_{(2)}[\mathbf{r}|\rho_{(1)}(z_1)] = g_{(2)}^L(\mathbf{r}) \tag{20}$$

in (16), where $g_{(2)}^L$ is the bulk liquid crystal pair distribution. Such an approximation is likely to be reasonable for low temperature nematic systems possessing a relatively sharp surface density transition. Secondly, if we neglect the z dependence of the Φ distribution (which is strictly valid for $\hat{\mathbf{k}} \cdot \hat{\mathbf{n}} = 1.0$ and a reasonable approximation for $\hat{\mathbf{k}} \cdot \hat{\mathbf{n}} = 0$), then we find

$$\begin{aligned}\rho_{(1)}(z_1)a_s(z_1)_{\|,\perp} &= A_{\|,\perp}[\rho^2_{(1)}(z_1) - \rho_L^2] + D_{\|,\perp}\rho_{(1)}(z_1)\left(\frac{\partial\rho_{(1)}(z_1)}{\partial z_1}\right)^2_{z_1} \\ &+ B_{\|,\perp}[\rho^2_{(1)}(z_1)\eta(z_1) - \rho_L^2\eta_L] + E_{\|,\perp}\rho_{(1)}(z_1)\left(\frac{\partial\rho_{(1)}(z_1)}{\partial z_1}\right)^2_{z_1}\eta(z_1) \\ &+ \eta^2(z_1)\rho_{(1)}(z_1)[c_{\|,\perp} + G_{\|,\perp}(\rho'(z_1))^2_{z_1}] \qquad (21)\end{aligned}$$

where the $\|(\perp)$ subscripts are adopted consistently throughout. The first two terms on the right-hand side of (21) represent the surface excess Cahn–Hilliard Helmholtz free energy of a disordered liquid ($\eta = 0$), whilst the subsequent terms represent the modification of the Cahn–Hilliard free energy due to surface orientational order. For a given bulk order parameter η_L, and a given density transition profile $\rho_{(1)}(z_1)$, we should determine the local order parameter $\eta(z_1)$ which minimizes the left-hand side of (21). Thus if we assume that only $a_s(z_1)_{\|,\perp}$ is a function of $\eta(z_1)$, then for given η_L minimization of the free energy density yields

$$\eta(z_1) = \frac{-(B_{\|,\perp}\rho_{(1)}(z_1) + E_{\|,\perp}[\rho'(z_1)]^2)}{2(C_{\|,\perp} + G_{\|,\perp}[\rho'(z_1)]^2)}$$

If however, we assume that $\eta(z_1)$ varies slowly across the interface, we may attribute the spatial variations of the orientational contributions to the surface excess Helmholtz free energy directly to the terms $\rho^2_{(1)}(z_1)$ and $\rho_{(1)}(z_1)(\partial\rho_{(1)}(z_1)/\partial z_1)^2_{z_1}$ neglecting terms of second order in η:

$$\begin{aligned}\rho_{(1)}(z_1)a_s(z_1)_{\|,\perp} &\sim A_{\|,\perp}[\rho^2_{(1)}(z_1) - \rho_L^2] + D_{\|,\perp}\rho_{(1)}(z_1)\left(\frac{\partial\rho_{(1)}(z_1)}{\partial z_1}\right)^2_{z_1} \\ &+ B_{\|,\perp}[\rho^2_{(1)}(z_1)\eta(z_1) - \rho_L^2\eta] + E_{\|,\perp}\rho_{(1)}(z_1)\left(\frac{\partial\rho_{(1)}(z_1)}{\partial z_1}\right)^2_{z_1}\eta(z_1) \qquad (22)\end{aligned}$$

It is on the basis of this expression that the analysis of §4 will proceed. The expression (22) is very similar to the qualitative proposals for the surface variation of the order parameter suggested by Croxton and Chandrasekhar,[4] on the basis of which they predict possible features of the surface tension-temperature characteristics which may, in principle, arise in nematic-isotropic liquid crystal systems. We shall consider their discussion in more detail in §4.

Minimization of the free energy for a disordered fluid ($\eta = 0$) would require that the signs of the first two terms be opposed (i.e. $A_{\|,\perp}, D_{\|,\perp} > 0$). For an ordered fluid ($\eta > 0$) the situation is not so readily assessed. However, we understand that the excess surface free energy to be determined on the basis of the conventional competition between interfacial sharpness and interfacial delocalisation (as in the Cahn–Hilliard analysis) except that here the two components additionally have implications for the surface order: localisation tending to impose an orienting torque, delocalisation tending to disorient (see Eq. 45).

3 THE KIRKWOOD-BUFF MODEL OF THE NEMATIC LIQUID CRYSTAL SURFACE

Few conclusive results may be drawn on the basis of the purely formal analysis of the preceding section: further progress requires more drastic approximation before the expressions (17) and (18) become amenable to discussion. Parsons[13] has considered what amounts to the equivalent of a Kirkwood–Buff analysis, but appropriate to nematic liquid crystal systems. In his treatment, Parsons assumes that the nematic liquid crystal retains its bulk density ρ_L right up to a planar surface of density discontinuity beyond which the fluid density is assumed to be zero.

Thus, as in the case of a simple fluid in the KBF approximation,

$$\begin{aligned} \rho_{(1)}(z) &= \rho_L \qquad z < 0 \\ \rho_{(1)}(z) &= 0 \qquad z > 0 \\ \rho(z_1, \mathbf{r}_{12}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2)_{\hat{\mathbf{n}}} &= \rho_{(1)}(z_1)\rho_{(1)}(z_2)g_{(2)}(\mathbf{r}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) \end{aligned} \tag{23}$$

where $g_{(2)}(\mathbf{r}; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2) = g^L_{(2)}(r)f(\theta_1)f(\theta_2)$, it being assumed that the orientations θ_1 and θ_2 are uncorrelated and that the bulk two-particle distribution is isotropic. The mean field distribution of orientations is, of course, related to the bulk order parameter η_L as follows

$$\eta_L = \frac{1}{2}\int_0^{\pi/2} (3\cos^2\theta - 1)f(\theta)\sin\theta\, \mathrm{d}\theta \tag{24}$$

The above assumptions are identical to the original KBF step model of the liquid surface, with the additional assumption that the uncorrelated orientational distributions $f(\theta_1), f(\theta_2)$ are not modified in the vicinity of the transition zone which, of course, they should be.

Further, and more seriously, the bulk order parameter η_L is assumed to remain constant up to the dividing surface, and the radial distribution function retains a simplified bulk form $g_{(2)}(r)$ up to the interfacial plane. Clearly such an approximation which assumes that neighbouring molecules are spherically symmetrically distributed about the origin molecule is inappropriate to a liquid crystal system. Nevertheless, its adoption enables the integrals (17) and (18) to be evaluated with the final result

$$\left.\begin{aligned} \gamma_\perp &= \gamma_0\left[1 + \frac{2}{3}\eta + \frac{1}{6}\eta^2\right] \\ \gamma_\perp &= \gamma_0\left[1 - \frac{4}{9}\eta + \frac{8}{27}\eta^2\right] \end{aligned}\right\} \gamma_0 = \frac{3}{4}\pi\rho_L^2 v \int_0^\infty g_{(2)}(r)\frac{1}{r^2}\,\mathrm{d}r \tag{25}$$

corresponding to perpendicular and parallel orientation of the surface director. It is immediately apparent that $\gamma_\perp > \gamma_\parallel$, whereupon Parsons concludes that the molecules align parallel to the liquid surface, and that the surface tension for such a system will show a discontinuous increase across the nematic-isotropic phase transition, when $\eta \to 0$:

$$\frac{\Delta\gamma}{\gamma} = -\frac{4}{9}\Delta\eta + \frac{8}{27}(\Delta\eta)^2 \tag{26}$$

where $\Delta\eta = \eta(T \lesssim T_{\mathrm{NI}}) - \eta(T \gtrsim T_{\mathrm{NI}})$.

Since $\eta = 0$ in the isotropic phase and $\sim\frac{1}{3}(T \lesssim T_{\mathrm{NI}})$ in the bulk nematic we have

$$\frac{\Delta\gamma}{\gamma} \sim -10\%$$

The small decrease in density which accompanies the transition is expected to be substantially less than that due to the discontinuous variation in the order parameter.

The difference in free energy between the parallel and perpendicular orientations

$$\frac{\gamma_\perp - \gamma_\parallel}{\gamma_0} = \frac{\eta}{9}\left(10 - \frac{7\eta}{6}\right) \tag{27}$$

is, on the basis of this model, quite substantial; this suggests that the surface molecules are strongly anchored in the parallel configuration, and are unlikely to modify their orientation with temperature to any significant extent. Such a conclusion has been verified for *p*-azoxyanisole and *n*-*p*-methoxybenzylidene *p*′-*n*-butylanilene although in the latter case the long molecular axis is inclined at about 75° to the surface plane, which does not concur with Parson's prediction. There are a number of possible explanations however, the simplest being that the dipole axis of the molecule does not coincide with the geometrical axis. In a more recent analysis, based on the Landau form of the free energy, Parsons[16] concludes that *polar* surface order favours a perpendicular alignment of the molecules at the surface and this may underlie the development of tilted interfacial directors.

4 SURFACE TENSION NEMATIC AND SMECTIC-A LIQUID CRYSTAL SYSTEMS

The Maier–Saupe nematic mean field analysis may be extended to smectic-A liquid crystal systems by assuming that in addition to being preferentially oriented along the z-axis (say), is also layering in the z-direction. McMillan[12] has proposed that in this case the single particle potential in the mean field of its neighbour is

$$u_i(z_i, \cos\theta_i) = \bar{u}\left\{1 + \alpha\cos\left(\frac{2\pi z_i}{d}\right)\right\}\left(\frac{3}{2}\cos^2\theta_i - 1\right)\eta; \tag{28}$$

where both translational and orientational effects are now included, the smectic layering being represented as the density wave $\alpha\cos(2\pi z/d)$. For $\alpha = 0$, (28) reduces to the Maier–Saupe nematic mean field potential. d is the length of the molecule. Now, although the minimum energy configuration corresponds to the molecular centre of mass lying on one of the planes with its long axis in the z-direction, there will be thermal fluctuations in the orientation and location of the molecule. Consequently, a second order parameter σ is introduced into the single particle mean field potential:

$$u_i(z_i, \cos\theta_i) = \bar{u}\left\{1 + \sigma\alpha\cos\left(\frac{2\pi z_i}{d}\right)\right\}\left(\tfrac{3}{2}\cos^2\theta_i - \tfrac{1}{2}\right)\eta \tag{29}$$

$\bar{u} = \text{constant} > 0$.

The magnitude of α characterises a particular molecular species, whilst σ is a measure of the amplitude of the density wave.

Now, the single particle Boltzmann distribution will be of the form

$$f(z_i, \cos\theta_i) = \exp\left(\frac{-u_i}{kT}\right), \tag{30}$$

and we may use this to self consistently determine the single particle mean field potential. If we assume a pair interaction

$$V_{ij}(r_{ij}, \cos\theta_{ij}) = -\left(\frac{\bar{u}}{N r_0 \pi^{3/2}}\right)\left\{\exp - \left(\frac{r_{ij}}{r_0}\right)^2\right\}\left(\tfrac{3}{2}\cos^2\theta_{ij} - \tfrac{1}{2}\right) \tag{31}$$

where the exponential term reflects the short range character of the interaction, and r_0 is of the order of the length of the rigid part of the molecular length, then we have

$$u_i(z_i, \cos\theta_i) = \frac{\iint V_{ij} f(z_j, \cos\theta_j)\mathrm{d}\mathbf{j}\,\mathrm{d}\hat{\mathbf{j}}}{\iint f(z_j, \cos\theta_j)\mathrm{d}\mathbf{j}\,\mathrm{d}\hat{\mathbf{j}}} \tag{32}$$

$$= \bar{u}\left\{(\tfrac{3}{2}\cos^2\theta_i - \tfrac{1}{2})\langle\tfrac{3}{2}\cos^2\theta_j - \tfrac{1}{2}\rangle + \alpha\cos\left(\frac{2\pi z_i}{d}\right)(\tfrac{3}{2}\cos^2\theta_i - \tfrac{1}{2})\left\langle\cos\left(\frac{2\pi z_j}{d}\right)(\tfrac{3}{2}\cos^2\theta_j - \tfrac{1}{2})\right\rangle\right\} \tag{33}$$

Self-consistency between (29) and (33) requires that

$$\eta = \langle\tfrac{3}{2}\cos^2\theta_j - \tfrac{1}{2}\rangle \tag{34}$$

$$\sigma = \left\langle\cos\left(\frac{2\pi z_j}{d}\right)(\tfrac{3}{2}\cos^2\theta_j - \tfrac{1}{2})\right\rangle \tag{35}$$

where the z-average implied in σ is taken over one density wavelength, i.e., $\int_0^d \mathrm{d}z$.

The single particle distribution function is

$$z_1 = \ln\left\{\mathrm{d}^{-1}\int_0^{\mathrm{d}}\int_0^1 \exp\left\{-\frac{\bar{u}}{kT}\left[\eta + \sigma\alpha\cos\left(\frac{2\pi z}{\mathrm{d}}\right)\right] \times (\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\right\}\mathrm{d}(\cos\theta)\mathrm{d}z\right\} \tag{36}$$

and the N body partition function is $Z_N = N \ln z_1$.

The excess thermodynamic functions of the ordered system relative to those of the disordered one can now be readily derived on the basis of Eqs. (31), (32) and (33). For example, the internal energy per mole is

$$U = -N\frac{\int_0^d\int_0^1 u_i \exp(-u_i/kT)\mathrm{d}(\cos\theta_i)\mathrm{d}z_i}{\int_0^d\int_0^1 \exp(-u_i/kT)\mathrm{d}(\cos\theta_i)\mathrm{d}z_i} \tag{37}$$

$$= -N\bar{u}(\eta^2 + (\alpha\sigma)^2). \tag{38}$$

The (orientational) excess entropy with respect to a disordered fluid is

$$S = kT\ln Z + U/T$$

$$= -Nk\left[\frac{\bar{u}(\eta^2 + (\alpha\sigma)^2)}{kT} - \ln\left\{d^{-1}\int_0^d\int_0^1 \exp\left(\frac{-\bar{u}}{kT}\left[\eta + \sigma\alpha\cos\left(\frac{2\pi z}{d}\right)\right]\right.\right.\right.$$

$$\left.\left.\left.(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\mathrm{d}(\cos\theta)\mathrm{d}z\right\}\right], \tag{39}$$

and the (orientational) excess Helmholtz free energy

$$-kT\ln Z_N = -NkT\ln\left\{\mathrm{d}^{-1}\int_0^{\mathrm{d}}\int_0^1 \exp\left\{\frac{-\bar{u}}{kT}\left[\eta + \sigma\alpha\cos\left(\frac{2\pi z}{d}\right)\right]\right.\right.$$

$$\left.\left.(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\right\}\mathrm{d}(\cos\theta)\mathrm{d}z\right\}. \qquad (40)$$

The above analysis may now be extended to yield the *surface* excess functions arising from ordering relative to a disordered fluid by specifying *local* order parameters $\eta(z)_{\hat{\mathbf{n}}}$ and $\sigma(z)_{\hat{\mathbf{n}}}$, where we have explicitly indicated that these will depend upon the surface director field $\hat{\mathbf{n}}$ as outlined in §2. It follows directly from (40) that the contribution to the surface tension arising from surface excess orientational order is, per unit area,

$$\hat{\gamma} = \frac{-kT}{A}\int_{-\infty}^{\infty}\rho_{(1)}(z)\ln\{\mathrm{d}^{-1}\int_0^{\mathrm{d}}\int_0^1$$

$$\times\exp\left(\frac{-\bar{u}}{kT}\left[\eta_{\hat{\mathbf{n}}}(z) + \sigma_{\hat{\mathbf{n}}}(z)\alpha\cos\left(\frac{2\pi z'}{d}\right)\right](\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\right)\ \mathrm{d}(\cos\theta)\mathrm{d}z'\}\mathrm{d}z$$

$$+\frac{kT}{A}\int_{-\infty}^{\infty}\rho^*\ln\left\{\mathrm{d}^{-1}\int_0^{\mathrm{d}}\int_0^1\exp\left(\frac{-\bar{u}}{kT}\left[\eta^* + \sigma^*\alpha\cos\left(\frac{2\pi z'}{d}\right)\right]\right.\right.$$

$$\left.\left.(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})\right)\mathrm{d}(\cos\theta)\mathrm{d}z'\right\}\mathrm{d}z \qquad (41)$$

where $\rho^* = \rho_L(z < 0)$; $\rho^* = \rho_L(z > 0)$, similarly η^*, σ^*.

This somewhat cumbersome expression may be made physically more transparent for illustrative purposes by linearising the functions, whereupon we obtain to second order

$$\hat{\gamma} \sim \frac{-\bar{u}^2}{10kTA}\int_{-\infty}^{+\infty}\left[(\rho_{(1)}(z)\eta^2(z) - \rho\eta^2) + \frac{\alpha^2}{2}(\rho_{(1)}(z)\sigma^2(z) - \rho_L\sigma^2)\right]\mathrm{d}z \qquad (42)$$

In obtaining the above expression we have assumed that the Gibbs dividing surface is located at $z = 0$, where the superficial excess density of matter vanishes, and that $\eta = \sigma = 0$ in the uniform vapour phase.

The temperature derivative, or the orientational surface excess entropy is, to the same degree of approximation,

$$
\begin{aligned}
\frac{-\mathrm{d}\hat{\gamma}}{\mathrm{d}T} = \hat{S}_s = &-\frac{k}{A}\int_{-\infty}^{\infty}\frac{\bar{u}}{kT}(\rho_{(1)}(z)\eta_{\hat{\mathbf{n}}}^2(z) - \rho_L\eta^2 + \alpha^2(\rho_{(1)}(z)\sigma_{\hat{\mathbf{n}}}^2 - \rho_L\sigma^2))\mathrm{d}z \\
&+ \frac{\bar{u}^2}{10kT^2A}\int_{-\infty}^{\infty}(\rho_{(1)}(z)\eta^2(z) - \rho_L\eta^2) \\
&+ \frac{\alpha^2}{2}(\rho(z)\sigma^2(z) - \rho_L\sigma^2)\mathrm{d}z \\
= &\frac{\bar{u}}{AT}\left(\frac{\bar{u}}{10kT} - 1\right)\int_{-\infty}^{\infty}[\rho_{(1)}(z)\eta^2(z) - \rho_L\eta^2] \\
&+ \frac{\alpha^2}{2}(\rho(z)\sigma^2(z) - \rho_L\sigma^2)]\mathrm{d}z \\
= &-\frac{1}{A}\int_{-\infty}^{\infty}\frac{\bar{u}}{T}(\rho_{(1)}(z)\eta_{\hat{\mathbf{n}}}^2(z) - \rho_L\eta^2 + \alpha^2 \\
&+ \alpha^2(\rho_{(1)}(z)\sigma_{\hat{\mathbf{n}}}^2(z) - \rho_L\sigma^2))\mathrm{d}z - \frac{\hat{\gamma}}{T}
\end{aligned}
\tag{43}
$$

It does, of course, remain to specify the spatial variation of the local order parameters $\eta_{\hat{\mathbf{n}}}(z)$ and $\sigma_{\hat{\mathbf{n}}}(z)$. The z dependence of these functions has already been discussed, and is a generalisation based upon an analysis by Croxton and Chandrasekhar[4] for nematic liquid crystals. We shall continue their approach here.

(a) The nematic liquid crystal surface ($\sigma = 0$, $\eta > 0$)

It is proposed that the nematic order parameter in the vicinity of the liquid surface is determined solely on the basis of a competition between the disordering effect of the decreasing density across the liquid-vapour interface, and an ordering effect due to the development of a surface torque field. The analysis in §2 suggests the former is proportional to $\rho_{(1)}(z)$ and the latter to $(\mathrm{d}\rho_{(1)}(z)/\mathrm{d}z)^2$ (Eq. (22)) (Figure 2). On the basis of such a model a number of qualitative forms for the $\gamma(T)$ characteristic have been predicted.[4,5] At low temperatures, for example, just beyond the crystal-nematic transition temperature, the spatial delocalization of the surface may be sufficiently small and consequently the surface orientational field sufficiently high that there is a net *enhancement* of the local order parameter over its bulk value; that is $\eta_{\hat{\mathbf{n}}}(z) > \eta$ in the vicinity of the surface. Setting $\sigma = 0$ in (43), corresponding to the nematic

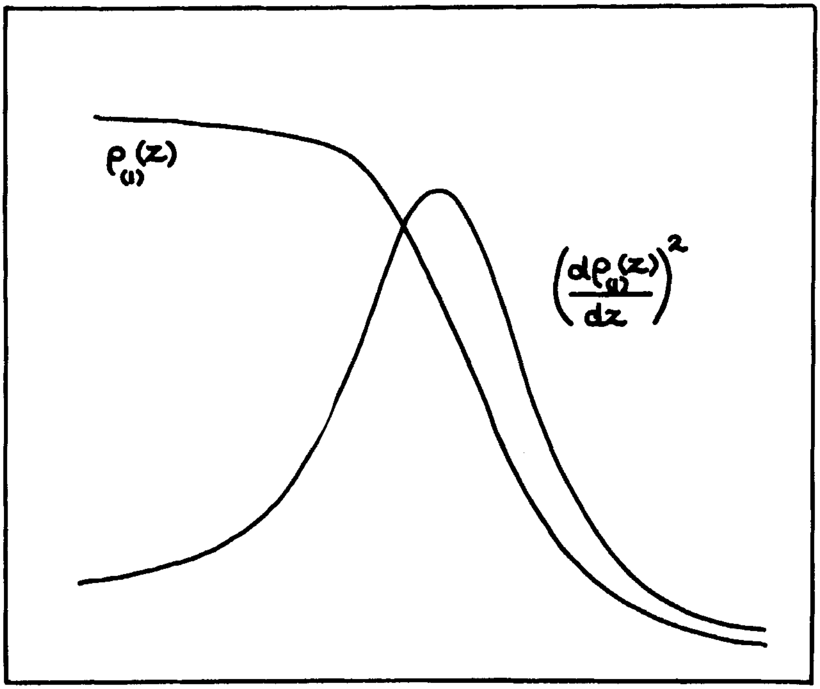

FIGURE 1 The single particle density gradient $\rho_{(1)}(z)$ and $(d\rho_{(1)}(z)/(dz)^2$.

phase, we have

$$\begin{aligned}\hat{S}_s = \frac{d\hat{\gamma}}{dT} &= -\int_{-\infty}^{\infty} \frac{\bar{u}}{T}(\rho_{(1)}(z)\eta^2_{\hat{\mathbf{n}}}(z) - \rho_L\eta^2)dz \\ &+ \frac{\bar{u}^2}{10kT^2A}\int_{-\infty}^{\infty}[\rho_{(1)}(z)\eta^2_{\hat{\mathbf{n}}}(z) - \rho_L\eta^2]dz \\ &= \frac{\bar{u}}{AT}\left(\frac{\bar{u}}{10kT} - 1\right)\int_{-\infty}^{\infty}[\rho(z)\eta^2(z) - \rho_L\eta^2]dz \qquad (44)\end{aligned}$$

We see immediately that for a sufficiently large surface enhancement of orientational order the usual negative monotonic slope of the $\gamma(T)$ characteristic may actually reverse and *increase* with temperature, at least just above the melting point and just below the nematic-isotropic transition temperature T_{NI}, when the rapidly decreasing bulk order parameter is enhanced by the surface torque field (Figure 2). At higher temperatures, of course, spatial delocalization of the surface with a corresponding relaxation in the surface field will ensure the usual monotonic decrease of surface tension with temperature.

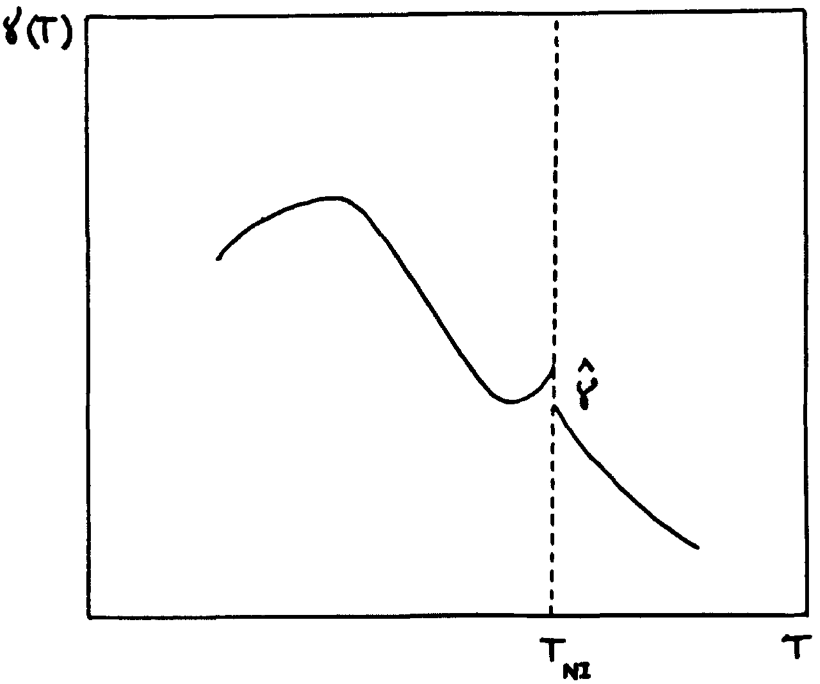

FIGURE 2 Qualitative form of the surface tension-temperature characteristic of a nematic liquid crystal system showing pretransition phenomena (surface enhancement of local order parameter) and a negative discontinuity $\hat{\gamma}$ at T_{NI}.

We have already observed that for spherically symmetrical interactions, minimization of the surface excess Helmholtz free energy is achieved as a competition between the surface excess energy term, which favours a sharp liquid-vapour density transition, and the surface excess entropy, which favours a spatially delocalized surface. In the case of strongly anisotropic molecular systems such as we are considering here, *orientational* contributions to the excess Helmholtz free energy may be similarly regarded as a competitive interplay between the orientational energy term $\hat{U}_s$ which favours molecular orientation aligned with the surface director field, and the excess orientational entropy term $\hat{S}_s$ which favours angular dispersion:

$$\hat{A}_s = \hat{U}_s - T\hat{S}_s \tag{45}$$

(unless the spatial and orientational contributions to the free energy develop independently it is not legitimate to minimize them separately: the two components will generally be inextricably coupled. In the spirit of the preceding analysis, however, we assume here that such a decoupling is in order).

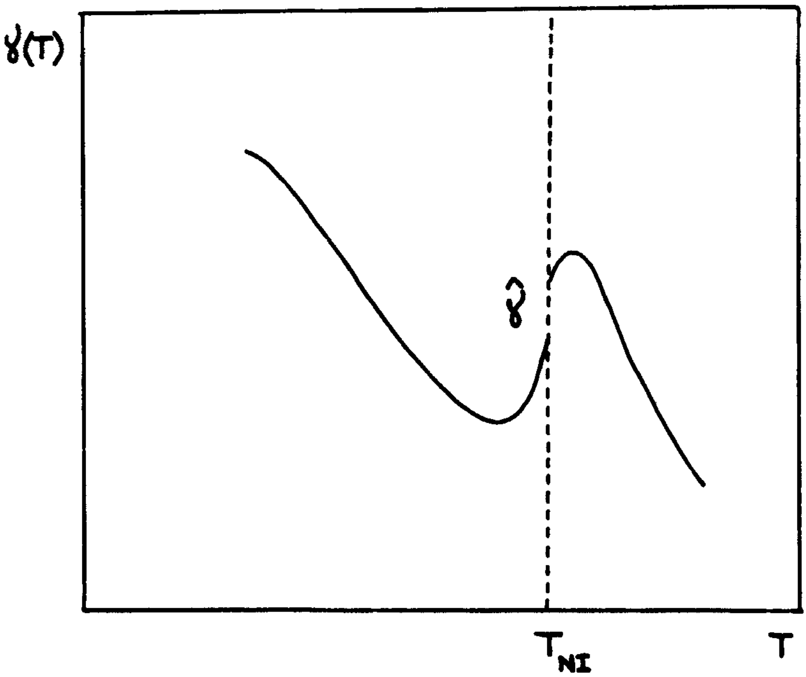

FIGURE 3 Qualitative form of the surface tension-temperature characteristic of a nematic liquid crystal system showing post-transition phenomena (residuum of surface enhancement of local order parameter in the isotropic phase) and a positive discontinuity $\hat{\gamma}$ at T_{NI}.

In terms of molecular quantities Eq. (42) becomes, for a nematic liquid crystal surface

$$\hat{\gamma} = \frac{1}{10A}\int_{-\infty}^{\infty} \frac{\bar{u}^2}{kT}\left[\rho_{(1)}(z)\eta_{\hat{n}}^2(z) - \rho_L \eta^2\right]\mathrm{d}z \tag{46}$$

whose contribution to the total (configurational + orientational) surface tension is positive or negative according as $\int_{-\infty}^{\infty} \rho_{(1)}(z)\eta_{\hat{n}}(z)\mathrm{d}z \gtrless \int_{-\infty}^{\infty} \rho_L \eta_L \,\mathrm{d}z$, the magnitude and sign of the contribution becoming apparent at the nematic-isotropic transition T_{NI}. (Figure 2).

There is a complex interplay of the relative magnitudes of $\rho_{(1)}(z)\eta_{\hat{n}}(z)$ and $\rho_L \eta$ at T_{NI} resulting in a wide variety of pre- and post-transition phenomena. For example, it is possible that a very weak surface orientation (torque) field remains for a short thermal range beyond T_{NI} into the isotropic phase, resulting in a positive discountinuity $\hat{\gamma}$ in the surface tension, and reducing (and even inverting) the negative slope $\mathrm{d}\hat{\gamma}/\mathrm{d}T$. Indeed, we might go so far as to say that on the basis of Eqs. (44), (46) systems showing positive

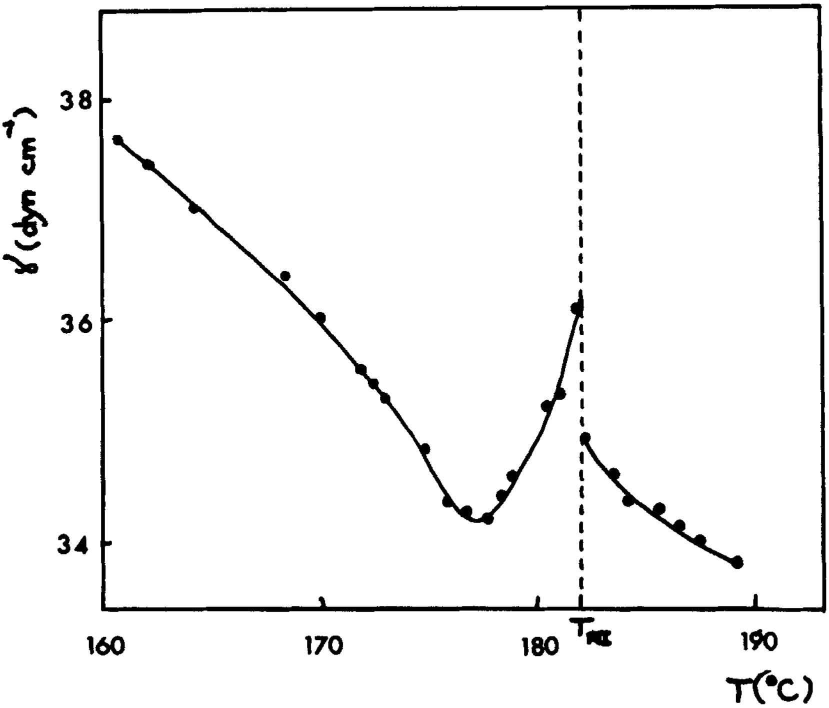

FIGURE 4 Surface tension of p-anisaldazine.[8] (c.f. Figure 2).

slopes just above T_{NI} must also show positive discontinuities $\hat{\gamma}$, and vice versa (Figures 4, 5). Ultimately, of course, all characteristics become monotonic negatively-sloped functions of temperature.

Recent experimental observations on nematic liquid crystal systems[8–10] have confirmed the qualitative features predicted on the basis of the above analysis. For example, the surface tension of *p*-anisaldazine in the nematic and isotropic phases is shown in Figure 4. The development of a surface excess orientational order just before T_{NI} (corresponding to $\int_{-\infty}^{\infty} \rho_{(1)}(z)\eta(z)\mathrm{d}z > \int_{-\infty}^{\infty} \rho_L \eta_L \,\mathrm{d}z$) with a discontinuous change in slope and magnitude of the $\gamma(T)$ characteristic is in qualitative agreement with Figure 3. On the other hand, a residum of surface orientation just beyond T_{NI} in *p*-oxyanisole (Figure 5) agrees qualitatively with the curve in Figure 3. We observe that in this case $\hat{\gamma}$ will be positive since in the isotropic phase $\eta_{\hat{n}}(z) > 0$ for $T \gtrsim T_{NI}$. The question arises as to whether the "anomaly" in the $\gamma(T)$ characteristic is due to a rather sudden reorientation of the molecules in the vicinity of T_{NI}.[13] The alignment of the molecules at the surface of *p*-azoxyanisole (PAA) and *n*-*p*-methoxybenzylidene *p*′-*n*-butylaniline (MBBA) has been

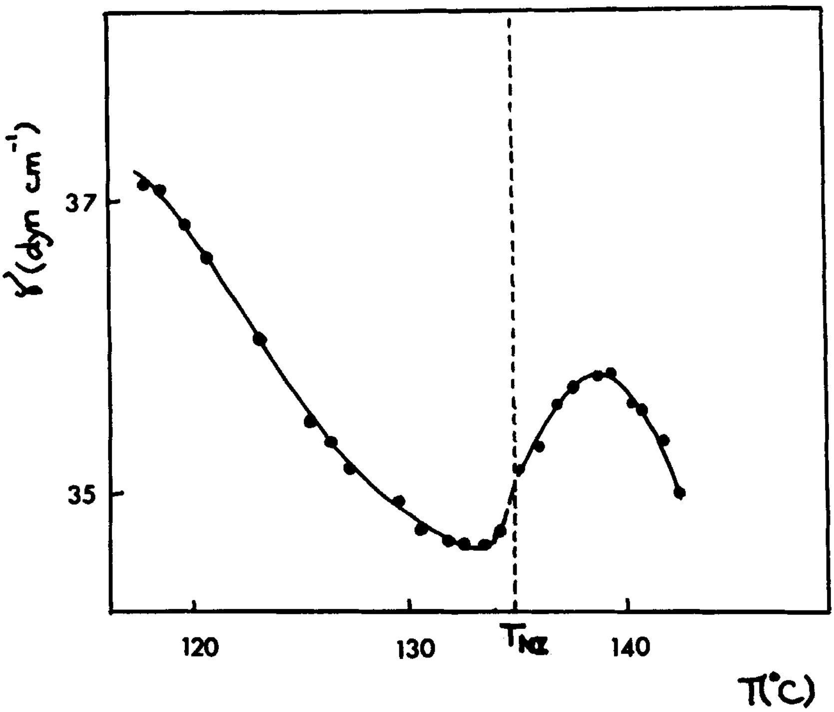

FIGURE 5 Surface tension of p-azoxyanisole.[9] (c.f. Figure 3).

studied by light scattering techniques.[11] In the case of PAA the molecules are found to be aligned parallel to the liquid surface, and the orientation appears to be independent of temperature, whilst for MBBA the molecules are tilted at 75° to the surface, the orientation being only slightly dependent upon temperature. It would therefore seem safe to say that the features of the $\gamma(T)$ curve are not attributable to any molecular reorientation at the surface, although of course, the specific surface orientation of the molecules does affect the magnitude of the surface tension.

The Kirkwood-Buff model of the nematic liquid surface in assuming the bulk order extends up to the discontinuous liquid surface forfeits those features of the preceding analysis which depend on a local order parameter. Indeed, the model specifically neglects spatial and orientational contributions to the entropy component of the surface free energy. It may well be therefore, that $\gamma_{\|}$ is *not* the lowest free energy as obtained by Parsons—a lower value being achieved by inclusion of entropy contributions resulting in some intermediate orientation of the surface director field.

(b) The smectic-A liquid crystal surface ($\sigma > 0$, $\eta = 0$)

A similar line of reasoning is proposed for the smectic-*A* liquid surface where, for values of the local order parameter $\int_{-\infty}^{\infty} \rho_{(1)}(z)\sigma_{\hat{n}}(z)\mathrm{d}z > \int_{-\infty}^{\infty} \rho_L \sigma \, \mathrm{d}z$, corresponding to pronounced layering in the vicinity of the surface, we again anticipate positive slopes in the $\gamma(T)$ characteristic. Indeed, at the relatively low range of temperatures over which the smectic phase is stable, the sharp density discontinuity at the surface implies strong surface fields, with the result that a number of smectic systems appear to show positive $\gamma(T)$ slopes throughout the entire phase.[9] Again, discontinuities in both the magnitude and the slope of the surface tension may occur as for nematic fluids, and beyond the smectic-nematic transition temperature T_{SN} we anticipate the usual nematic $\gamma(T)$ curves: these qualitative features have been reproduced experimentally[9] for *p*-cyanobezylidene *p*′-*n*-octyloxyaniline (CBOOA)

CONCLUSIONS

The bulk order parameters are expected to modify in the vicinity of the free liquid-vapour interface, the local value being determined as a competition between the decreasing density across the transition zone serving to lower the order parameter, and the development of surface torque fields acting to increase it. The former term appears to vary as $\rho_{(1)}(z)$ whilst the latter depends on the square of the density gradient, $(\mathrm{d}\rho_{(1)}(z)/\mathrm{d}z)^2$. There may be a net surface enhancement of the local order parameter which, it is shown, may have the consequence of decreasing the negative $\gamma(T)$ slope, and even inverting it so as to assume positive values. On this basis a number of qualitative predictions have been made regarding the form of the $\gamma(T)$ curve, which appear to be supported experimentally. Both pre- and post-transition phenomena are included in the above description, one consequence of which seems to be that positive discontinuities in the surface tension at T_{NI} are followed by positive slopes, and vice versa.

The inability of a Kirkwood–Buff type of analysis to describe the complex variety of phenomena is understood in terms of its retention of a bulk order parameter right up to a surface of density discontinuity.

Acknowledgement

I am very much indebted to Professor S. Chandrasekhar and the members of his highly stimulating liquid crystals laboratory at the Raman Resëarch Institute, Bangalore, South India for numerous discussions and generous hospitality.

References

1. C. A. Croxton and T. R. Osborn, *Phys. Lett.*, **55A**, 415 (1976).
2. J. M. Haile, K. E. Gubbins, and C. G. Gray, *J. Chem. Phys.*, **64**, 1852 (1976).
3. J. D. Parsons, *J. de Phys.*, **37**, 1187 (1976).
4. C. A. Croxton and S. Chandrasekhar, *Proc. 1st. Intl. Conf. Liquid Crystals*, (Bangalore, 1973). Pramana Suppl. No. 1, p. 237.
5. C. A. Croxton, in *Progress in Liquid Physics*, (C. A. Croxton, ed., John Wiley & Sons Ltd., Chichester, 1978), Ch. 2.
6. C. A. Croxton, *Statistical Mechanics of the Liquid Surface*, (John Wiley & Sons Ltd., in press), Ch. 3.
7. C. A. Croxton, *J. Phys. C.* **12**, 2239 (1979). A theory of the departure from Cahn–Hilliard behaviour for non-uniform fluids: the liquid-vapor interface and stability with respect to spinodal decomposition.
8. S. Krishnaswamy and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **35**, 253 (1976).
9. S. Krishnaswamy and R. Shashidhar, *Mol. Cryst. Liq. Cryst.*, **38**, 711 (1977).
10. T. E. Faber and N. Gannon, *Phil. Mag.*, **A37**, 117 (1978).
11. M. A. Bouchiat and D. Langevin, *Phys.Lett.*, **34A**, 331 (1971).
12. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
13. F. Jahnig, *Proc. 1st. Intl. Conf. Liquid crystals*, (Bangalore, 1973). Pramana Suppl. No. 1, p. 246.
14. F. M. Leslie, *Proc. 1st. Intl. Conf. Liquid Crystals.* (Bangalore, 1973). Pramana Suppl. No. 1, p. 252.
15. H. T. Davis, *J. Chem. Phys.*, **62**, 3412 (1975).
16. J. D. Parsons, *Phys. Lett.*, **41**, 877 (1978).