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Statistical thermodynamics of the nematic liquid crystal free surface

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Abstract. The possible development of stable density oscillations in the form of a structured liquid-vapour density transition at the surface of simple liquids has been proposed and the thermodynamic consequences for the surface tension discussed. The principal effect on the surface tension–temperature characteristic is that just beyond the triple point certain systems should show a surface tension which *increases* with temperature : moreover, such behaviour has been observed experimentally. We now extend the treatment to include the *orientational* contributions to the surface excess quantities for a nematic liquid crystal. It is found that the possibility exists both for the development of positive slopes and discontinuities in the surface tension-temperature characteristic. We find that the slope $\partial \gamma / \partial T$ is determined as a competition between orientational order and spatial disorder which develops at the liquid surface. Should the situation corresponding to highly ordered orientational states occur, the $\gamma(T)$ characteristic will show a *positive* slope, although with increasing temperature and spatial delocalisation of the liquid surface the usual monotonic decreasing function will be regained. Again, discontinuities in the slope and absolute value of the $\gamma(T)$ characteristic would be expected with the discontinuous variation of the order parameter at the nematic-isotropic transition temperature.

Introduction

The complete specification of the structural features of the liquid–vapour transition zone at the surface of a nematic liquid crystal involves both the spatial and the orientational distributions. In the case of simple liquids, the structural features of the density transition have been calculated, and the one and two particle distributions determined. It has been shown[1] that under certain circumstances stable density oscillations in the transition profile may develop in the vicinity of the liquid surface, and these relatively ordered states have a profound effect on the principal excess thermodynamic functions of the free surface, in particular the surface tension $\gamma(T)$.

It may be quite easily shown that the gradient of the $\gamma(T)$ characteristic is related to the excess entropy per unit area developed at the liquid surface as follows :

$$d\gamma/dT = -s = -(S_\sigma - S_\beta)$$

where the subscripts σ and β refer to surface and bulk states respectively. Thus we see that should the situation $S_\sigma < S_\beta$ arise, corresponding to relatively ordered surface states, then the $\nu(T)$ characteristic may actually show a *positive* slope. Of course, such a situation if it is to occur is only likely to be observed at temperatures just above the triple point: thermal delocalisation of the liquid surface with increasing temperature will inevitably result in a progressive disordering and the usual monotonic decreasing form of $\gamma(T)$ will be regained corresponding to $S_\beta < S_\sigma$. Systems exhibiting the stable oscillatory density profile are most likely to be found amongst the liquid metals, and indeed White[2] has shown that provided care is taken to ensure that a truly *equilibrium* measurement of $\gamma(T)$ is made, then such positive slopes are observed and are particularly pronounced in the case of Zn, Cu and Cd. By equilibrium measurement is meant that there should be no net efflux of particles from the liquid surface, or that the chemical potential should be constant across the surface. This is achieved in practice by ensuring that the liquid is in equilibrium with its own vapour. This point is crucial with regard to the observation of positive slopes and as we shall see, the indications are that the $\gamma(T)$ characteristics for liquid crystals are likely to show such positive regions over limited temperature ranges. It is clear then that from an experimental standpoint such precautions are essential.

Theory

It would be fair to say that for simple systems the current theoretical position regarding the one and two particle distribution functions is controversial. It is not appropriate to sustain the controversy here, except to say that the controversy centres primarily on the form of the single particle distribution function $g_{(1)}(z)$ which describes the spatial distribution of the centres of gravity of the particles. In consequence the positive slope to the $\gamma(T)$ function, depending as it does on the development of low entropy (*i.e.*, oscillatory) surface states, is equally controversial. The current theoretical situation is reviewed elsewhere[3] and for present purposes we shall assume an uncontroversial profile of the form shown in figure 1. Stable density oscillations are unlikely to develop in the case of nematic liquid crystal systems although such a situation may arise in the surface states of *smectic* compounds.

We enquire as to what contribution the *orientational* features at the surface of the assembly are likely to make to the $\gamma(T)$ characteristic.

We assume a short range anisotropic intermolecualr pair interaction of the form[4]

$$\phi_{12}(r_{12}, \cos\theta_{12}) = -\phi_o \exp(-r_{12}/r_o)^2 \left(\tfrac{3}{2}\cos^2\theta_{12} - \tfrac{1}{2}\right) \qquad (1)$$

where r_{12} is the separation of the centres of mass of the molecules, θ_{12} is the relative orientation of their long axes, and r_o is a constant $\sim$ molecular length. In the bulk liquid we may assume a single particle potential in the mean field approximation

$$\phi_1 (\cos \theta_1) = -\phi_o (\tfrac{3}{2} \cos^2 \theta_1 - \tfrac{1}{2})\eta \qquad (2a)$$

where ϕ_o is a constant, and θ_1 is the orientation of the respresentative molecule relative to the mean local orientational order whose measure is

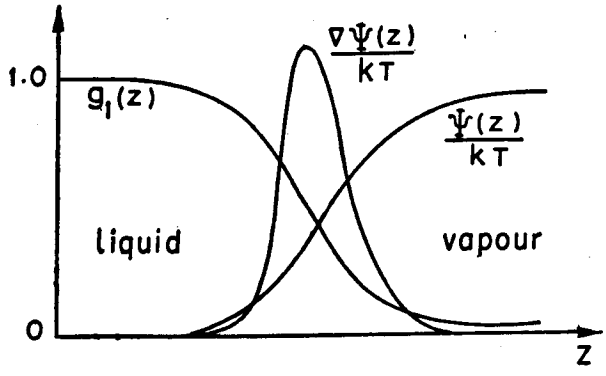

Figure 1 Schematic variation of the single particle distribution of molecular centres $g_1(z)$, the potential of mean force $\Psi(z)$, and its gradient $\nabla\Psi(z)/kT$ in the vicinity of the liquid surface.

given by η. Clearly, the single particle potential at the liquid surface will be modified both by the structural delocalisation across the transition zone, and by the development of a surface field whose effect we assume will be to impress an orienting torque on the surface molecules. The former effect serves to *diminish* the local order, whilst the latter will *enhance* it. Notice that no specification of the orientation of molecules relative to the surface is yet made : we do not, however, generally anticipate that surface tension is likely to be isotropic[5]. In the case of simple spherical molecules, the first effect is discussed in terms of a spatial decoupling of the interaction[1] between a representative molecule and its neighbours. The single particle potential (2 *a*) is now modified in the vicinity of the surface to read

$$\phi_1 (z_1, \cos \theta_1) = -\phi_o (\tfrac{3}{2} \cos^2 \theta_1 - \tfrac{1}{2}) \eta (z) \qquad (2b)$$

The single particle potential of mean force $\Psi(z)$ is related by the Boltzmann relation to the single particle distribution $g_{(1)}(z)$ as

$$g_{(1)}(z) = \exp [-\Psi(z)/kT]$$

so that $\Psi(z)$ serves to 'switch off' or decouple the interaction across the transition zone. A convenient model decoupling potential is then quite simply $[\exp(-\Psi(z)/kT) - 1]$ which we take to describe the spatial modification of the single particle potential as the centre of gravity passes through the collective field in the transition zone. The surface *field* may then be taken as $-\nabla\Psi(z)$ (figure 1) and we propose a local associated *orientational* model potential $[1 - \exp\{-c\nabla\Psi(z)\}/kT]$, where c is a constant governing the strength and range of the orienting torque. We therefore finally arrive at the following single particle potential (see eq. 2*b*):

$$\phi_1(z_1, \cos\theta_1) = -\phi_0(\tfrac{3}{2}\cos^2\theta_1 - \tfrac{1}{2})\left\{\eta - \varepsilon_0\left[\exp\left(-\frac{\Psi(z)}{kT}\right) - 1\right] + \varepsilon_1\left[1 - \exp\left(-\frac{c\nabla\Psi(z)}{kT}\right)\right]\right\} \tag{3}$$

where ε_0 and ε_1 are coefficients which are to be determined. In particular we observe that the factor in the brackets $\{\}$ represents an *effective order parameter,* spatially dependent upon z and appropriate to the liquid surface. Now we may write

$$\phi_1(z_1, \cos\theta_1) = \frac{\iint \phi_{12}(r_{12}, \cos\theta_{12})\, g_{(1)}(z_2, \cos\theta_2)\, dz\, d\hat{z}}{\iint g_{(1)}(z_2, \cos\theta_2)\, dz\, d\hat{z}} \tag{4}$$

where the integrals range over all positions z and orientations $\hat{z}$ of molecule 2, and where $g_{(1)}(z_2, \cos\theta_2) = \exp[-\phi_2(z_2, \cos\theta_2)/kT]$. From (4) and (1) it follows that

$$\eta = \langle \tfrac{3}{2}\cos^2\theta_2 - \tfrac{1}{2}\rangle_{g(1)(2)}; \tag{5}$$

$$\varepsilon_0 = \langle [\exp(-\frac{\Psi(z_2)}{kT}) - 1](\tfrac{3}{2}\cos^2\theta_2 - \tfrac{1}{2})\rangle_{g(1)(2)} \tag{6}$$

$$\varepsilon_1 = \langle [1 - \exp(-\frac{c\nabla\Psi(z_2)}{kT})](\tfrac{3}{2}\cos^2\theta_2 - \tfrac{1}{2})\rangle_{g(1)(2)} \tag{7}$$

and these may be determined self-consistently. It may be shown quite easily that $\eta(z) \to \eta$ as $z \to -\infty$, *i.e.*, $\eta(z)$ attains its asymptotic bulk value. It is now straightforward, using the standard statistical thermodynamic relations to write down expressions for the surface excess entropy per unit area $(= -d\gamma/dT)$ developed at the liquid surface:

$$-\frac{d\gamma}{dT} = -\frac{\phi_0\rho}{T}\int_{-\infty}^{\infty} g_{(1)}(z)\,(\eta^2 - \varepsilon_0^2\,[\exp(-\frac{\Psi(z)}{kT}) - 1]^2$$

$$+\,\varepsilon_1^2\,[1 - \exp(-\frac{c\nabla\Psi(z)}{kT})]\,dz + \frac{\phi_0\rho}{T}\int_{-\infty}^{0}\eta^2 dz$$

$$+\,\rho k\int_{-\infty}^{\infty} g_{(1)}(z)\,ln\,\Xi(z,\eta,\varepsilon_0,\varepsilon_1)\,dz - \rho k\int_{-\infty}^{0} l\eta\,\Xi(z,\eta)\,dz$$

where $\Xi(z,\eta) = \int_0^1 \exp[\frac{\phi_0\eta}{kT}(\frac{3}{2}\cos^2\theta - \frac{1}{2})]\,d(\cos\theta)$

$$\Xi(z,\eta,\varepsilon_0,\varepsilon_1) = \int_0^1 \exp[(\frac{\phi_0}{kT})\left\{\eta - \varepsilon_0(\exp(-\frac{\Psi(z)}{kT}) - 1)\right.$$

$$\left. + \varepsilon_1[1 - \exp(-\frac{c\nabla\Psi(z)}{kT})]\right\}(\frac{3}{2}\cos^2\theta - \frac{1}{2})]\,d(\cos\theta) \qquad (8)$$

In the absence of an accurate and explicit knowledge of the single particle distribution $g_{(1)}(z)$ we can only examine the formal aspects of equation (8). Analogous expressions for the surface excess free energy per unit area $[=\gamma(T)]$ may be written down quite easily: for present purposes, however, we need only consider the temperature derivative given above.

Discussion

As we observed earlier, the surface tension would not, in general, be expected to be isotropic. That is, we would generally expect the surface tension to depend upon the orientation of the molecules at the surface[5], and this in itself may show a weak temperature dependence. We assume, however, that in specifying the *effective* order parameter $\eta(z)$ we specify only the *degree* of local order: details of the precise surface orientation will be implicitly contained in the spatial distribution of molecular centres $g_{(1)}(z)$.

In figure 2 we give a schematic indication of how the effective order parameter may vary with temperature. At low temperatures, just beyond the crystal-nematic point, the spatial delocalisation may be sufficiently low and the surface orientational field correspondingly high such that there is a net *enhancement* of the order parameter over its bulk value. Under these circumstances careful consideration of (1) or (7) shows that initially

at least, the $\nu(T)$ characteristic should actually show a positive slope. Of course, with increasing spatial delocalisation of the surface and the corresponding relaxation of the surface field the usual monotonic decreasing function of temperature is regained. With the discontinuous variation of the bulk order parameter η with temperature we see from (7) that we would expect a discontinuity of slope at the transition temperature. Consideration of the expression for the absolute value of $\gamma(T)$, not given here, would lead us to anticipate a discontinuity in γ also. These features are shown in figure 2. It is also possible that with the catastrophic variation

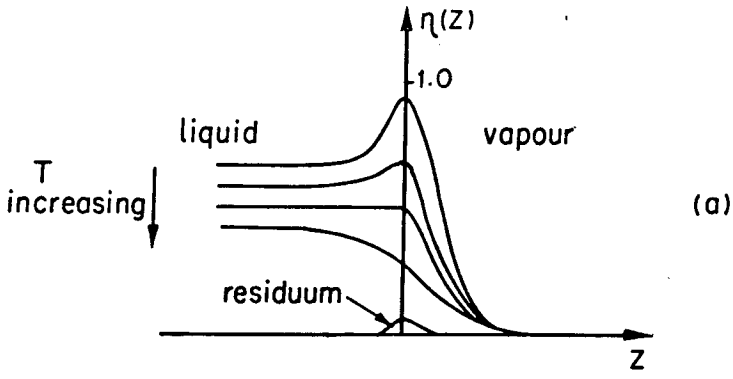

Figure 2*(a)* Schematic variation of the effective order parameter $\eta(z)$ in the vicinity of the nematic liquid crystal surface. At low temperatures there is a net surface enhancement of the local orientational order attributed to surface field effects overcoming spatial delocalizational disorder. With increasing temperature the balance is reversed, and progressive spatial and surface field relaxation results on a surface depression of the local order parameter. With the catastrophic bulk variation of η at the transition temperature, a weak surface residuum may persist for a short thermal range beyond the transition.

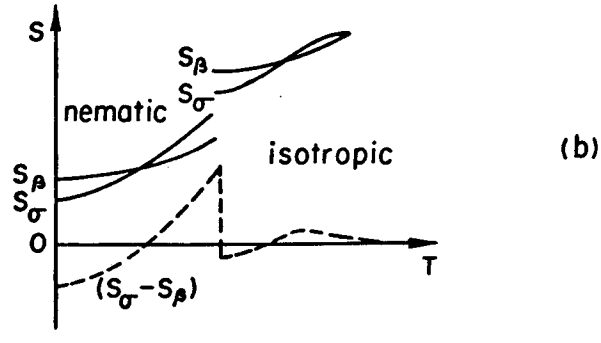

Figure 2*(b)* Schematic variation of the bulk and surface entropy curves with temperature on the basis of the behaviour of $\eta(z, T)$.

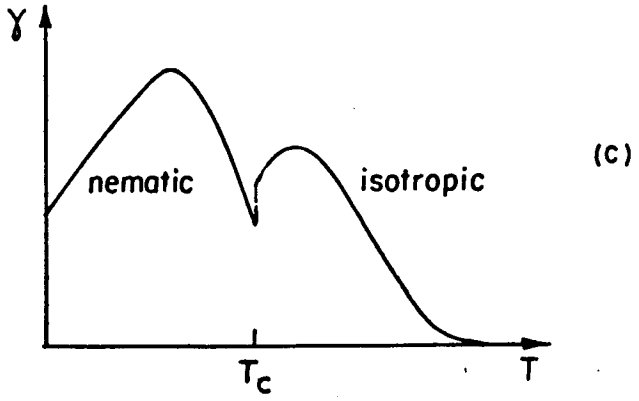

Figure 2(c) Schematic variation of the $\gamma(T)$ characteristic on the basis of equations (1) and (8).

of $\eta \to 0$ at the transition temperature, the weak surface field may establish a small residuum of orientational order at the *isotropic* liquid surface over a short thermal range. In this case, a second positive region to the $\gamma(T)$ characteristic may be observed. This feature is also indicated in figure 2.

One further possibility is the *thermally retarded* surface enhancement of the order parameter (figure 3). In this case the surface orientational order is sufficient to offset the spatial disorder of the molecular distribution of centers, and $\eta(z)$ is depressed at the surface with respect to the bulk value. A monotonic decreasing $\gamma(T)$ characteristic is of course obtained. In the vicinity of the transition temperature, however, the bulk value of η may have decreased sufficiently just prior to the transition that a surface

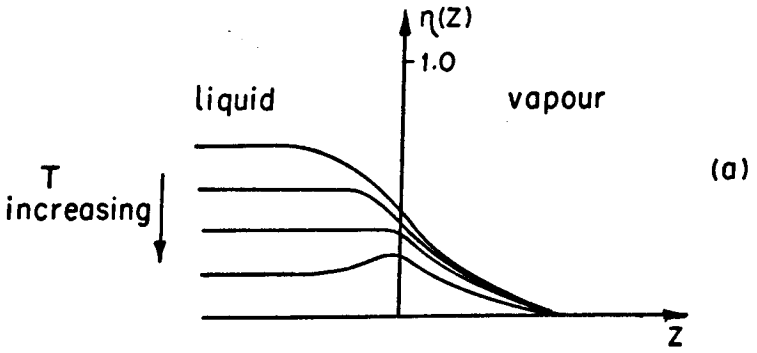

Figure 3(a) Schematic variation of the effective order parameter $\eta(z)$ in the vicinity of the nematic liquid crystal surface. Whilst at low temperatures there is a net depression of the surface value of $\eta(z)$, the bulk value of the order parameter becomes sufficiently low just prior to the transition that an effective surface enhancement develops. Since positive slopes in the $\gamma(T)$ characteristic depend only upon the *relative* values of the bulk and surface entropies per unit area, it is clear that an increase in γ may be anticipated immediately before the nematic–isotropic transition.

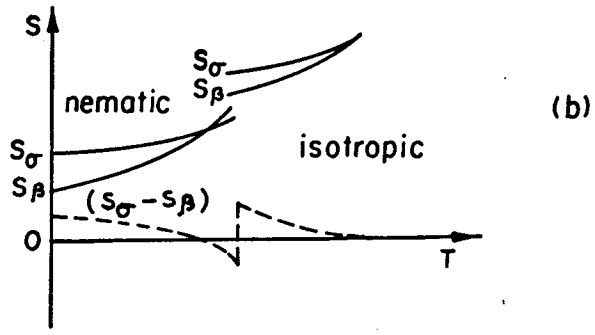

Figure 3(b) Schematic variation of the bulk and surface entropy curves with temperature on the basis of the behaviour of $\eta(z, T)$.

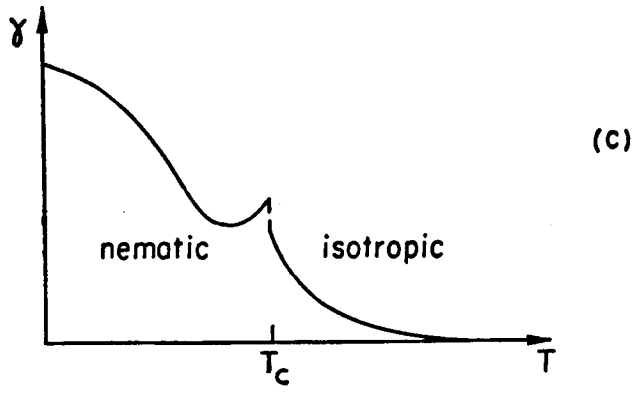

Figure 3(c) Schematic variation of the $\gamma(T)$ characteristic on the basis of equations (1) and (7).

enhancement of $\eta(z)$ is eventually achieved. This requires the rate of surface entropy production to be slower than that of the bulk, where surface entropy production develops with temperature subject to the surface field constraint. Under these circumstances then, we should expect a positive slope to immediately precede the transition to an isotropic system (figure 3). Of course, the discontinuity of slope and absolute value of the $\gamma(T)$ characteristic would occur as before.

It is not being suggested that any one system is likely to develop all these features, but attention is drawn to features of the $\gamma(T)$ characteristics which may develop in principle, and which careful equilibrium experimentation may reveal. Most of the features described above, except for the positive slope immediately after the melting transition, have been observed[6]. The possibility exists of enhancing or suppressing certain features of the $\gamma(T)$ characteristic by means of electric or magnetic fields whose effect would be to enhance or depress the value of the effective order parameter

at the liquid crystal surface. We emphasize once again that the post-melting positive slope in liquid metal systems was not observed experimentally until stringent precautions were taken to ensure liquid-vapour equilibrium across the transition zone, and that similar precautions in the case of liquid crystal measurements are essential bearing in mind the complicated form of the $\gamma(T)$ characteristic.

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DISCUSSION

Nityananda: You emphasized that a net efflux of molecules could destroy surface order. This efflux is of the same order as the unidirectional influx and efflux which occur even for an equilibrium surface. Why is it that they do not destroy surface order?

Croxton: Quite clearly, for the measurement of an equilibrium thermodynamic parameter the physical conditions appropriate to thermodynamic and mechanical stability must apply. For a free liquid surface continuity of normal (perpendicular) pressure and of chemical potential across the liquid vapour density transition specifies the equilibrium and stability of the surface. Unless the liquid surface is in equilibrium with its vapour, the condition on the chemical potential is not satisfied. The equilibrium structure of the transition zone is then established in a statistical sense, and perhaps the analogy with two travelling waves moving in opposite directions yet specifying a standing wave might give some indication of the mechanism. This effect has, in fact, been observed directly in the course of molecular dynamic machine simulation of a free liquid argon surface*. White† has dramatically demonstrated the effect of non-equilibrium on the form of the $\gamma(T)$ characteristic, and it is quite clear that a net transport of particles from the liquid surface has a disruptive effect on whatever structural features there are in the transition zone.

* Croxton C A and Ferrier R P *J. Phys. C* 4 1909 (1971); 4 1921 (1971); 4 2433 (1971); 4 2447 (1971).

† White D W G *Trans. Metall. Soc. AIME* 236 796 (1966); Croxton C A *Liquid state physics – A statistical mechanical introduction*, Cambridge University Press (1974) Ch. 4.

Jahnig: If I understood you correctly, you did not take into account the boundary condition for the orientation of the molecules at the surface of the nematic. But this boundary condition should be important and may give an additional temperature dependence.

Croxton: Certainly the surface tension will be sensitively dependent upon the orientation of the molecular axes with respect to the free surface * : we do not propose that γ is isotropic or independent of the molecular orientation. In specifying an effective order parameter $\eta(z)$ we merely specify the net degree of local order, irrespective of the particular orientation. It may be that the orientation does vary with temperature, but this temperature dependence is not incorporated in $\eta(z, T)$ in this development : indeed it is difficult to see how it could be. We assume that the single particle distribution of molecular centres $g_{(1)}(z)$ in fact contains the information relating to the particular molecular orientation. Certainly we would anticipate different forms of transition profile for a system whose molecules are in one case aligned parallel, and in the other aligned perpendicular to the surface. If there is any thermal variation of the orientation of the molecular axes with temperature, and what evidence there is suggests that such temperature dependence is very weak, then this would be incorporated in $g_{(1)}(z, T)$ which, of course, already exhibits a pronounced spatial relaxation with increasing temperature.

de Gennes: The data recorded by White are on the metal zinc. In what sense are we sure that the statistical effects you describe cannot be related to electronic effects which are quite specific with metals ?

Croxton: I think the statistical structure of the surface is not specific to metals but more to geometric exclusion effects, simply because these effects can be reproduced with nothing more sophisticated than hard spheres. For example, if we consider ball bearings packed in a gravitational field and shake them down, then along the free surface nothing but the geometry will generate 2 or 3 atomic layers. Again if we consider ball bearings in a rectangular tray filled up to a reasonably high density so that geometric effects can assert themselves then all round the boundary we will get two or three layers. This is obviously because of the constraint of the bound ary.

This, in principle, is no different from what we have in liquids. Here the surface molecules are compacted and this is responsible for the structural effects. One need not invoke any electronic effects.

* Chandrasekhar S *Mol. Cryst.* 2 71 (1966).