

CHAPTER II

THEORIES OF SURFACE TENSION OF LIQUID CRYSTALS

There have been several discussions of the theory of surface tension of liquid crystals. Some are statistical in their approach and some phenomenological. A brief summary of these approaches will be presented in this chapter.

Statistical theory

In 1973, Croxton and Chandrasekhar¹ discussed the consequences of the possible development of excess **orientational** order at the surface of a nematic liquid crystal. This has important consequences on the temperature dependence of the surface tension γ . The slope of the **y-T** curve is determined as a competition between **orientational**

order and spatial disorder which develops at the surface of the liquid crystal. As mentioned earlier $d\gamma/dT$ is related to the excess entropy per unit area at the surface as

$$d\gamma/dT = - (s_\sigma - s_\beta) \quad (1)$$

where σ and β represent the surface and the bulk states respectively. If a relatively higher order develops at the surface compared to the bulk, $d\gamma/dT$ takes a positive sign.

They have discussed the orientational contribution to the γ - T characteristic by considering an intermolecular pair interaction of the form proposed by McMillan²

$$u_{12}(r_{12}, \cos \theta_{12}) = -u_0 \exp[(-r_{12}/r_0)^2] \left(\frac{3}{2} \cos^2 \theta_{12} - \frac{1}{2} \right) \quad (2)$$

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 $\mathbf{r}_0$ is a constant which is of the order of the molecular length.

In the bulk liquid they assume a single particle potential in the mean field approximation

$$u_1 \cos \theta_1 = -u_0 \eta \left(\frac{3}{2} \cos^2 \theta_1 - \frac{1}{2} \right) \quad (3)$$

where η is the usual orientational order parameter.

To allow for spatial **delocalization** of the interaction between the molecules and its environment in the vicinity of the surface, they modify (3) to

$$u_1(z_1, \cos \theta_1) = -u_0 \eta(z_1) \left(\frac{3}{2} \cos^2 \theta_1 - \frac{1}{2} \right) \quad (4)$$

They rule out the possibility of an oscillatory density profile at the surface of a nematic and assume a simple profile of the form shown in **fig.2.1** for the single particle distribution function $g_1(z)$ which describes the spatial distribution of the centres of gravity of the molecules. **The** function $g_1(z)$ is related to

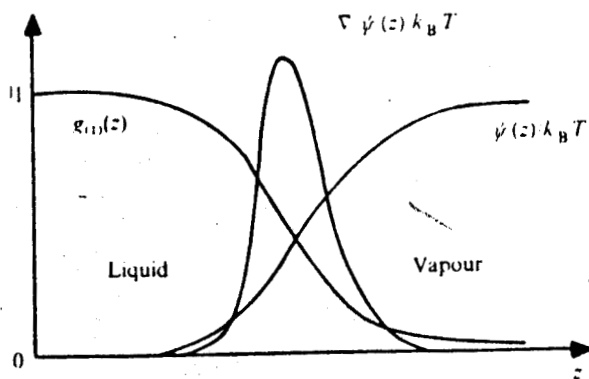


Figure 2.1

Schematic variation of the single particle distribution of molecular centres $g_1(z)$, the potential of mean force $\psi(z)$ and its gradient $\nabla\psi(z)/k_B T$ in the vicinity of the nematic liquid crystal surface. (After ref. 1).

the single particle potential (of mean force)

$\psi(z)$ as

$$g_1(z) = \exp[-\psi(z)/k_B T] \quad (5)$$

The spatial modification of the single particle potential **as** the molecule passes through the collective field in the transition zone is described by a function $\exp(-\psi(z)/k_B T) - 1$.

The surface field then turns out to be $-\nabla\psi(z)$ (fig. 2.1) which enhances the surface **orientational** order. By considering a local orientational potential

$$1 - \exp[-c \nabla \psi(z)/k_B T]$$

where c is a constant governing the strength **and** range of **the** orienting torque, they finally arrive at the following single particle potential

$$u_1(z_1 \cos \theta_1) = -u_0 \left(\frac{3}{2} \cos^2 \theta_1 - \frac{1}{2} \right) [\eta - \xi_0 \{ \exp(-\psi(z)/k_B T) - 1 \}] \\ + \xi_1 \{ 1 - \exp(-c \nabla \psi(z)/k_B T) \}] \quad \dots (6)$$

where ξ_0 and ξ_1 are coefficients to be determined and the quantity in the square brackets represents an effective order parameter. Thus the structural delocalisation across the transition zone diminishes the local order while the surface field enhances it.

Using the standard statistical thermodynamic relations they obtain an expression for the surface excess entropy per unit area ($-\mathrm{d}\gamma/\mathrm{d}T$) which involves $g_1(z)$. In the absence of an accurate and explicit knowledge of $g_1(s)$, nothing much can be said about the behaviour of $\mathrm{d}\gamma/\mathrm{d}T$. They have discussed only the formal aspects of the expression obtained for $\mathrm{d}\gamma/\mathrm{d}T$ in a qualitative way, which will be given at the end of this chapter.

Later Croxton³ elaborated the theory of the statistical thermodynamics of liquid crystal surface and obtained an expression for γ .

In the bulk fluid, the orientation of the director is arbitrary. But at the surface the direction of the director' $\hat{n}$ modifies because of structural discontinuity. The local density and the orientational distribution both depend on the location of the molecular centres relative to the Gibb's dividing surface, located such that

$$\int_{-\infty}^0 [\rho_L - \rho_1(z)] dz = \int_0^{\infty} [\rho_1(z) - \rho_v] dz \quad (7)$$

Here z axis is taken along the surface normal and the origin is located at the Gibb's dividing surface. ρ_L represents the density of the bulk liquid, ρ_v represents the density of the vapour and $\rho_1(z)$ represents that of the interface. The direction of the director $\hat{n}$ is modified in the vicinity of the surface for purely geometrical reasons.

Inside the bulk, far from the surface, the

order parameter is defined by

$$\eta_o = \frac{1}{2} \langle 3\cos^2 \theta - 1 \rangle = \frac{1}{2} \int_0^{\pi/2} (3\cos^2 \theta - 1) f(\theta) \sin \theta \, d\theta \quad \dots (8)$$

where θ is the molecular orientation relative to the director and $f(\theta)$ is the orientational distribution function. Here a thermal average is taken over the set of internal states characteristic of the bulk. However at the surface, we have to take into consideration the effect of torque fields and hence a more general order parameter $\eta(z)\hat{n}$ has to be considered. It can be defined as

$$\eta(z)\hat{n} = 3 \int_0^{\pi/2} (3\cos^2 \theta - 1) f(\theta, z)\hat{n} \sin \theta \, d\theta \quad (9)$$

where $f(\theta, z)\hat{n}$ is the distribution function for the molecules in the surface region.

The surface tension may be expressed in terms of the local excess Helmholtz free energy per particle $a_s(z)\hat{n}$, as

$$\gamma_{\hat{n}} = \int_{-\infty}^{\infty} a_s(z)_{\hat{n}} \rho_1(z) dz \quad (10)$$

Assuming a Van der Waal's interaction for the pair potential and applying the mean field approximation, the integrand in (10) is evaluated for parallel and perpendicular orientations of the molecules at the free surface, to get

$$\begin{aligned} \rho_1(z) a_s(z)_{\parallel, \perp} = & A_{\parallel, \perp} [\rho_1^2(z) - \rho_L^2] + D_{\parallel, \perp} \rho_1(z) \left[\frac{\partial \rho_1(z)}{\partial z} \right]^2 \\ & + B_{\parallel, \perp} [\rho_1^2(z) \eta(z)_{\parallel, \perp} - \rho_L^2 \eta_0] \\ & + E_{\parallel, \perp} \rho_1(z) \left[\frac{\partial \rho_1(z)}{\partial z} \right]^2 \eta(z)_{\parallel, \perp} \end{aligned} \quad (11)$$

The first two terms on the right hand side represent the surface excess free energy of a disordered liquid [$\eta_0 = \eta(z)_{\hat{n}} = 0$], whilst the subsequent terms represent the modification of the free energy due to surface orientational order $\eta(z)_{\hat{n}}$. The coefficients A, D, B and E are related to the positional and

orientational distribution functions of the molecules in the surface. In the absence of any knowledge of these functions, it is difficult to be more specific about these coefficients. The relative magnitudes of these coefficients decide as to ~~which~~ of the two molecular orientations (parallel or perpendicular or indeed some intermediate orientation) leads to a lower free energy. Unfortunately it cannot be ascertained by the formal results of this theory. The expression (11) is very similar to the qualitative proposals for the surface variation of the order parameter proposed by Croxton and Chandrasekhar,¹ on the basis of which they have predicted the possible features of the y - T characteristic curves of ^{nematic} liquid crystal systems.

Parsons⁴ has also discussed the statistical mechanical theory of surface tension of nematic liquid crystals on similar lines. He has simplified

the problem by using Fowler, Kirkwood and Buff approximation (FKB) for the interface. FKB approximation implies -

- a the vapour density is negligible, and
- b the density of the liquid phase has the bulk value up to the Gibbs's dividing surface.

In addition to these, the orientations θ_1 and θ_2 of the interacting molecules are assumed to be uncorrelated and the bulk two particle distribution function is assumed to be isotropic. Further the bulk order parameter η_0 is assumed to remain constant up to the dividing surface, Using a Van der Waals's interaction for the pair potential, final expressions for γ are obtained for parallel and perpendicular orientations of the molecules at the surface, In general it appears to indicate that $\gamma_{||}$ is less than $\gamma_{\perp}$. As a consequence one is led to the conclusion that the molecules prefer a parallel

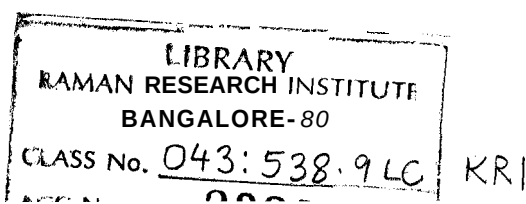
orientation at the free surface. **Further** conclusions from this theory are:

- 1 the surface tension for such a system will show a discontinuous increase across the nematic–isotropic phase transition, **and**
- 2 the surface molecules are strongly anchored in the parallel configuration, and are unlikely to modify their orientation with temperature to any significant extent.

The above conclusions seem to be in agreement with what is found in the case of PAA. Optical reflection **measurements**⁵ have shown that the **mole-**cules of PAA in the nematic phase lie in the plane of the surface **and** their orientation is not affected by the change of temperature. Our own measurements have indicated a discontinuous increase of surface tension across the **N-I** transition in the case of PAA and **5CB** as we shall see in chapter IV. However

in the case of MBBA, it has been found⁵ that the long axes of the molecules are inclined at about 75° to the surface, which is in contradiction to the prediction of this model. In a more recent phenomenological approach,⁶ based on the Landau form⁷ of the free energy, Parsons concludes that polar surface order favours a perpendicular alignment of the molecules at the surface and this may result in the tilt of the molecular axis at the surface. This phenomenological approach has been discussed briefly in the next section.

Another statistical approach to the theory of surface tension of liquid crystals is that of Murakami⁸ who employs the FKB approximations. Applying the standard statistical procedures for the surface tension and assuming a special form for the interaction potential (whose validity is not clearly established), he has calculated the jump



in the value of the surface tension at the transition temperature, in terms of an adjustable parameter. According to his calculations a very high jump in γ is expected at T_{NI} in the case of MBBA, which does not agree with our experimental result.⁹

Phenomenological theory

As mentioned earlier Parsons' phenomenological approach is based on the Landau form of the free energy according to which the free energy in the bulk is

$$F(\eta) = F_0 + a\eta^2 - b\eta^3 + c\eta^4 + d(\nabla\eta)^2 \quad (12)$$

where η is the bulk order parameter, $a = a_0(T - T_c)$ with $a_0 > 0$ and T_c is the 'second order transition temperature', $d > 0$ describes the extra free energy due to a distortion in η . The surface free energy $\gamma(\eta)$ is similarly expanded as

$$\gamma(\eta) = \gamma_0 - \gamma_1\eta + \gamma_2\eta^2 \quad (13)$$

where γ_0 is the surface tension in the absence of ordering. γ_2 is taken to be positive for stability reasons. Assuming η to be small and applying the minimization condition for the total energy Parsons shows that there is a surface excess order which decays into the bulk, over a distance $(d/a)^{1/2}$. He also shows that the surface free energy is lowered by the orientational order at the surface. Hence, the surface tension may increase discontinuously at the transition with a higher value in the isotropic phase. This conclusion agrees with the earlier one that was arrived at by his statistical approach. However the statistical model favours a parallel alignment of molecules at the free surface for the energy to be minimum. For small deviations from this orientation, the surface energy can be written as

$$\gamma = \gamma_0 + \frac{1}{2} \gamma_Q (\hat{n} \cdot \hat{k})^2 \quad (14)$$

where $\gamma_Q > 0$, $\hat{n}$ is the orientation of the molecule and $\hat{k}$ is the normal to the surface.

If one end of a molecule has a highly polar end group, that end will tend to point in the direction of the more polar medium, i.e., into the bulk. This brings about the polar order at the surface, which favours a perpendicular orientation of the molecules at the surface. Phenomenologically the situation is described by a polar order parameter $\vec{P} = p \hat{n}$, with $p \leq 1$. When $p \neq 0$, $\hat{n}$ and $-\hat{n}$ are not equivalent states near the surface. Now the expression for γ can be written as

$$\gamma = \gamma_0 + \frac{1}{2} \gamma_Q (\hat{n} \cdot \hat{k})^2 - \gamma_p \hat{n} \cdot \hat{k} \quad (15)$$

γ_p is the contribution from the polar order. Minimisation of (15) with respect to $\hat{n} \cdot \hat{k} = \cos \theta$ gives

$$\cos \theta = \begin{cases} \gamma_p / \gamma_Q & \text{for } \gamma_p < \gamma_Q \\ 1 & \text{for } \gamma_p > \gamma_Q \end{cases} \quad (16)$$

For $\gamma_p > \gamma_Q$, $\theta = 0$. Hence $\hat{n}$ will be along the surface normal $\hat{k}$. The surface symmetry is uniaxial

in this case. For $\gamma_p < \gamma_Q$, θ will have an intermediate value between 0 and 1 and hence the molecular orientation may be at an angle to the surface, as in the case of MBBA. If $\gamma_p \ll \gamma_Q$ the tilt may not be observable and $\hat{n}$ may appear to be in the plane of the surface, as in the case of PAA.

It may also be mentioned in this context that Gannon and Faber¹⁰ have discussed a simple phenomenological theory of surface tension of nematic liquid crystals which is very similar to that of Parsons', involving only one adjustable parameter. Their experimental results on 5CB and 8CB appear to be in partial agreement with the theory. The discrepancies between the theory and the experimental results have been attributed to the possible smectic like order at the surface.

y-T characteristics of nematic and smectic liquid crystals

In this section we present the qualitative forms of the y-T curves of nematic and smectic liquid crystals, first proposed by Croxton and Chandrasekhar for nematics and later extended to smectics by Croxton.

Smectic A liquid crystal has both translational and **orientational** orders. McMillan² has proposed the following mean field single particle potential by **generalising** the Maier-Saue model of the nematic -

$$u_1(z_1, \cos \theta_1) = \bar{u} \left\{ \eta + \sigma \alpha \cos \left(\frac{2\pi z_1}{d} \right) \right\} \left(\frac{3}{2} \cos^2 \theta_1 - \frac{1}{2} \right) \quad (17)$$

where η and σ are the orientational and translational order **parameters** respectively, a is a constant characterising a particular molecular species and $\bar{u}$

is a constant which depends on the molar volume.

Here,

$a = \eta = 0$ represents the isotropic phase,

$\sigma = 0, \eta \neq 0$ represents the nematic phase, and

$\sigma \neq 0, \eta \neq 0$ represents the smectic phase.

Assuming both a and η to be different at the surface as compared to their bulk values, Croxton gets

$$\hat{\gamma} \approx \frac{\bar{u}^2}{10k_B T} \int_{-\infty}^{+\infty} \left[\left\{ \rho_1(z) \eta_{\hat{n}}^2(z) - \rho_L \eta^2 \right\} + \frac{\alpha^2}{2} \left\{ \rho_1(z) \sigma_{\hat{n}}^2(z) - \rho_L \sigma^2 \right\} \right] dz \quad (18)$$

where $\hat{\gamma}$ is the contribution to the surface tension arising from surface excess orientational order.

The total surface tension is however the sum of the orientational and configurational parts.

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

approximation

$$\begin{aligned}
 -\frac{d\hat{\gamma}}{dT} &= \frac{\bar{u}}{T} \left(\frac{\bar{u}}{10k_B T} - 1 \right) \int_{-\infty}^{+\infty} \left[\left\{ \rho_1(z) \eta_{\hat{n}}^2(z) - \rho_L \eta^2 \right\} \right. \\
 &\quad \left. + \frac{\alpha^2}{2} \left\{ \rho_1(z) \sigma_{\hat{n}}^2(z) - \rho_L \sigma^2 \right\} \right] dz \quad (19)
 \end{aligned}$$

At the temperatures of interest $\bar{u} < 10 k_B T$. Hence $\left(\frac{\bar{u}}{10k_B T} - 1 \right)$ is always **negative** at these temperatures. The qualitative forms of the γ - T curves for nematic and smectic liquid crystals are discussed on the basis of the equations 18 and 19.

Nematic liquid crystals

The nematic phase is **characterised** by $\sigma = 0$ and $\eta \neq 0$. So the equation (18) takes the form

$$\hat{\gamma} = \frac{\bar{u}^2}{10k_B T} \int_{-\infty}^{+\infty} \left[\rho_1(z) \eta_{\hat{n}}^2(z) - \rho_L \eta^2 \right] dz \quad (20)$$

and (19) becomes

$$-\frac{d\hat{\gamma}}{dT} = \frac{\bar{u}}{T} \left(\frac{\bar{u}}{10k_B T} - 1 \right) \int_{-\infty}^{+\infty} [\rho_1(z) \eta_{\hat{n}}^2(z) - \rho_L \eta^2] dz \quad (21)$$

The nematic order parameter in the vicinity of the surface is determined solely by 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. For a sufficiently large enhancement of the surface **orientational** order ($\eta_{\hat{n}}(z)$) over the bulk order (η), the slope ($d\hat{\gamma}/dT$) becomes positive. In some systems, the surface orientational order **may** undergo a large enhancement **just** after the crystal nematic transition and just before the nematic-isotropic transition. At higher temperatures, **the** spatial **delocalisation** of the surface **may** result in the usual monotonic decrease of surface tension with temperature. The schematic γ - T curve for such a system is as shown in figure 2.2.

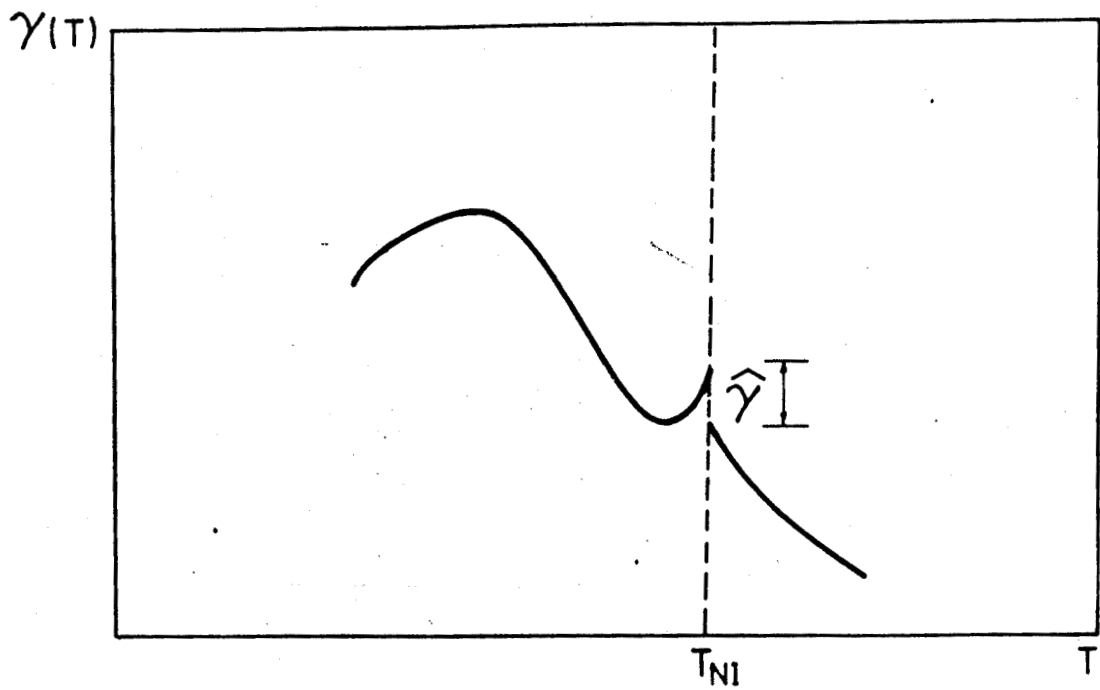


Fig.2.2: Qualitative form of the γ - T characteristic of a nematic liquid crystal system showing **pretransition** phenomena (surface **enhancement** of local order parameter) and a negative discontinuity γ at T_{NI} (After ref. 3).

In some systems, the enhancement in the surface orientational order which develops before T_{NI} may remain for a certain thermal range in the isotropic phase also. As a consequence the γ - T characteristic may develop a positive slope just before T_{NI} and may extend into the isotropic phase for a certain range of temperature. The schematic γ - T characteristic for such a system is as shown in fig. 2.3. On the basis of equations (20) and (21), it can be concluded that the systems showing positive slopes just above T_{NI} must also have positive discontinuities in the value of $\hat{\gamma}$ and vice versa. However in both the cases, the monotonic decreasing trend will be regained at higher temperatures. Our experimental γ - T curves for different systems appear to be in qualitative agreement with the predictions of this model as can be seen in chapter IV.

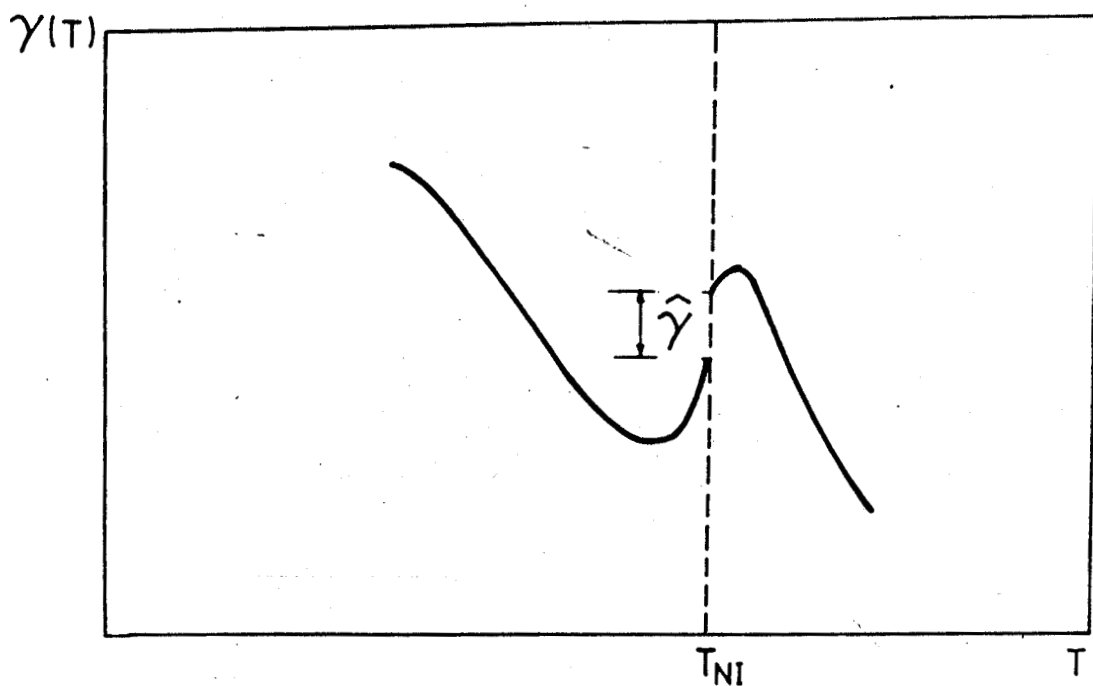


Fig.2.3: Qualitative form of the γ - T characteristic of a nematic **liquid** crystal system showing post transition phenomena (**residuum** of surface enhancement of local order parameter in the isotropic phase) and a positive discontinuity γ at T_{NI} (After ref.3).

Smectic A liquid crystals

The smectic phase is characterised by a $\neq 0$, $\eta \neq 0$. Corresponding to a pronounced layering in the vicinity of the surface, the situation may be such that $\sigma_{\hat{n}}(z) > \sigma$ and $\eta_{\hat{n}}(z) > \eta$. Again a positive slope is anticipated. At the relatively low range of temperatures at which the smectic phase is stable, the sharp density discontinuity at the surface implies strong surface fields. As a result positive slope may be expected throughout the smectic phase. Again, discontinuities in the magnitude and the slope of the surface tension may occur as in nematics, at the transition temperatures. As we shall see in chapter V, our experimental results are again in qualitative agreement with these predictions.

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