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MEANFIELD THEORY OF THE NEMATIC LIQUID CRYSTAL FREE SURFACE

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ABSTRACT. The nematic liquid crystal free surface is treated within Landau - de Gennes formalism. Numerical solutions for order parameter gradient, temperature dependence of isotropic layer thickness and surface tension are obtained for two nematogens which are reported to show pre-transitional anomaly for the surface tension. We find normal behaviour for both nematogens, that is $d\gamma/dT < 0$ and the surface tension on the nematic side is greater than that on the isotropic side.

INTRODUCTION

Over the last few years there has been much progress in understanding the surface tension at the liquid-vapour interface of simple and molecular fluids [1]. In contrast the liquid-vapour interface of a liquid which undergoes a transition to a nematic liquid crystal phase is more complicated, and presents additional features of interest [2,3]. These include the anomaly, if any, associated with the phase transition from an isotropic liquid phase to a nematic, the possibility that the nematic order parameter near the interface may differ from its value in the bulk, and the connection between these two phenomena.

Experimental studies of the surface properties of nematogens have revealed an intriguing richness of behaviour. In general, it appears that there is a small discontinuity, $\Delta\gamma$ ($\approx \gamma_N - \gamma_I$), in the liquid-vapour surface tension, of the order of a few percent, on going from the isotropic to the nematic phase. For certain materials, for example 4-4-'-dimethoxyazoxybenzene (4), and 4-n-pentyl-4'-cyanobiphenyl [5] $\Delta\gamma$ is negative. For other nematogens $\Delta\gamma$ is found to be positive (e.g. 1,4-di(4'-methoxyphenyl)-2,3-diaza-1,3-butadine [6]) and even zero for 4-cyanobenzylidene-4'-n-octyloxyaniline [7].

In simple fluids γ is monotonically decreasing function of temperature. This may be thought of as a reflection of the decreasing difference between the liquid and the vapour phase as temperature is increased. If this rule is not obeyed there is generally some peculiarity in the surface structure, such as for instance, some temperature dependent adsorption effects. Over most of the temperature range liquid crystals have $d\gamma/dT < 0$ - so called normal behaviour. Abnormal behaviour of $\gamma(T)$, i.e. $d\gamma/dT > 0$ is exhibited in various ways for different nematogenic materials This anomalous pre-transitional behaviour has been reported to occur on both sides of the transition (e.g. 4,4'-dimethoxyazoxybenzene [8]), just above T_{NI} in the isotropic phase (e.g. 4-cyanobenzylidene-4'-n-octyloxyaniline [5,7]) and just below T_{NI} in the nematic phase (e.g. 4-Methoxybenzylidine-4'-n-butylaniline [9] and 4-n-pentyl-4' - cyanobiphyenyl [5]).

It has been realized for some time that there is a connection between the discontinuity $\Delta\gamma$ at T_{NI} and the nature of the surface order. In general, if $\Delta\gamma < 0$ there is enhanced surface order, that is the orientational order in the bulk is less than that in the surface, whereas if $\Delta\gamma > 0$ the nematic order in the surface is reduced.

In view of the difficulty in understanding the bulk properties of nematics, the understanding of the liquid-vapour surface tension of a nematic liquid crystal in terms of the interaction potential between the constituent molecules present a formidable problem. Nonetheless some progress has been made. The problem has been tackled emphasising the role of excess surface order, i.e. the different magnitude and type of order at the interface [4,10,11]. Other approaches have drawn on ideas from liquid state theory [12] originally proposed by Kirkwood and Buff [13] and extended to fluids of anisotropic molecules [14]. This connects the surface tension to the molecular correlation functions in the interface, although these are difficult quantities to obtain both theoretically and experimentally. Perhaps the most significant progress has been made in a recent set of papers by Telo da Gama [15] and Thurtell, Telo da Gama and Gubbins [16]. These authors, using a model in which the anisotropic intermolecular interactions are short-ranged, find, in a van der Waals like theory of the interface, some of the observed behaviours. However, in all cases they were not able to account for the anomalous behaviour in the surface tension, $d\gamma/dT > 0$.

The interfacial phenomena of liquid crystals on a substrate is another interesting problem which has a resemblance with the liquid crystal free surface. This problem has attracted several workers due to its immediate application in display devices [3,17,18]. Recently Sluckin and Poniewreski [3] have extended Shengs [17] model of the liquid crystal interface on a substrate and studied in the presence of an external magnetic field and predicted the possibility of surface wetting by both paranematic and nematic phases.

In this work we study the liquid crystal free surface, i.e. in the absence of both external magnetic field and substrate potential. We have employed the Landau - de Gennes theory with the appropriate boundary conditions. Phenomenological parameters of two nematogens known to show anomalous properties are used to test the theoretical predictions. The theory is outlined in the following section. We then present, in section 3, the results and discussion of our investigation.

THE MODEL

The nematic liquid crystal free surface is defined to be at $z = 0$, and the sample is assumed to be uniform in the x- and y-directions. The bulk extends to the positive z direction. To study the thermodynamic consequence of such a model, we start with the Landau - de Gennes free energy density ϕ [11]

$$\phi = f(\eta) + L\left[\frac{d\eta}{dz}\right]^2, \qquad (2.1)$$

$$f(\eta) = a(T - T^\circ)\eta^2 + B\eta^3 + C\eta^4,$$

where $\eta = \langle P_2(\cos\beta)\rangle$ is the second rank orientational order parameter, β is the angle between the molecular symmetry axis and the director, which is assumed to be parallel to the z-axis, T is the temperature, a, T°, B, C, and L are material parameters which can be determined from thermodynamic and fluctuation measurements [19]. Given ϕ, the total free energy Φ is obtained directly by integration over z:

$$\Phi = A\left\{\int_0^\infty \left[f(\eta) + L\left[\frac{d\eta}{dz}\right]^2\right] dz\right\}, \qquad (2.2)$$

where A is the surface area. To determine the equilibrium form of the local order parameter $\eta(z)$, we employ the condition of minimum free energy. Equation (2.2) is minimized variationally with respect to $\eta(z)$. This leads to Euler equation

$$f'(\eta) = 2L\left[\frac{d^2\eta}{dz^2}\right], \tag{2.3}$$

which can be integrated to yield

$$\int f'(\eta)d\eta = 2L\int\left[\frac{d^2\eta}{dz^2}\right]dz, \tag{2.4}$$

$$= L\int\frac{d}{dz}\left(\frac{d\eta}{dz}\right)^2 dz\ . \tag{2.5}$$

$$K + f(\eta) = L\left(\frac{d\eta}{dz}\right)^2. \tag{2.6}$$

The constant K is determined by the condition as $z \to \infty$, the bulk liquid crystal is uniform, therefore,

$$\left.\frac{d\eta}{dz}\right|_{z\to\infty} = 0, \tag{2.7}$$

which directly implies

$$K = -f(\eta_b). \tag{2.8}$$

Therefore

$$L\left(\frac{d\eta}{dz}\right)^2 = f(\eta) - f(\eta_b), \tag{2.9}$$

where η_b is the bulk order parameter. The elastic constant L is related to the correlation legth ξ by

$$\xi = (L/aT^o)^{1/2}. \tag{2.10}$$

Let

$$F(\eta) = f(\eta)/aT^o$$

then

$$\xi^2\left(\frac{d\eta}{dz}\right)^2 = F(\eta) - F(\eta_b). \tag{2.11}$$

Substituting equation (2.9) into equation (2.2) yields

$$\Phi = A\left\{\int_0^\infty\left[f(\eta_b) + 2L\left[\frac{d\eta}{dz}\right]^2\right]dz\right\}, \tag{2.12}$$

$$= f(\eta_b)V + 2AL\int_0^\infty\left[\frac{d\eta}{dz}\right]^2 dz, \tag{2.13}$$

$$\frac{\Phi}{aT^{o}} = F(\eta_b)V + \frac{2AL}{aT^{o}} \int_0^{\infty} \left[\frac{d\eta}{dz}\right]^2 dz, \qquad (2.14)$$

where $F(\eta_b) = f(\eta_b)/aT^{\circ}$.

Changing integration variables and substituting equation (2.9) into equation (2.14) yields

$$\frac{\Phi}{aT^{o}} = F(\eta_b)V + 2\xi A \int_{\eta(z=0)}^{\eta_b} \sqrt{F(\eta) - F(\eta_b)}\, d\eta, \qquad (2.15)$$

The first term, the bulk free energy, is proportional to the volume of the sample. The second term, due to the free surface, can be picked out by its proportionality to ξ to give

$$\gamma^{*} = 2 \int_{\eta(z=0)}^{\eta_b} \sqrt{F(\eta) - F(\eta_b)}\, d\eta, \qquad (2.16)$$

where γ^{*} ($\equiv \gamma/\xi$) is the scaled surface tension.

The bulk order parameter η_b is obtained via

$$F(\eta_b) = \min F(\eta) \qquad (2.17)$$

and $\eta(z)$ profile can be obtained by integrating equation (2.11),

$$\xi \frac{d\eta}{dz} = \sqrt{F(\eta) - F(\eta_b)}, \qquad (2.18)$$

at constant temperature to yield

$$z^{*} = \pm \int_{\eta(z=0)}^{\eta(z)} \left[\sqrt{F(\eta) - F(\eta_b)} \right]^{-1} d\eta, \qquad (2.19)$$

where $z^{*} = z/\xi$. The sign is taken in such a way that z^{*} is positive.

Within the molecular field approximation a boundary phase of vapour, isotropic liquid or a hard wall are all equivalent, i.e. $\eta(z=0) = 0$. This approximation definitely has a second order effect on the predictions of the theory. However, it does not change the essential physics of the problem [2,15,16].

RESULTS AND DISCUSSION

Here, we begin by presenting the results predicted for two nematic liquid crystals, 4-n-pentyl-4'-cyanobiphenyl (5CB) and 4-methoxybenzylidene-4'-n-butylaniline(MBBA). In the calculation, experimental values for a, B, C, and T° (given in Table 1) were used. The order parameter profile obtained via equation (2.19) for MBBA is presented in Fig. 1 for four different scaled temperatures. The model predicts that the transition from the vapour to the nematic region is continuous A similar result is obtained for 5CB. This is in contrast to the results reported in ref. [2] via molecular field theory and computer simulation on a finite system. The model predicts that close to the nematic-isotropic transition the layer is always covered with thin isotropic layer. This isotropic layer thickness grows as the nematic isotropic transition temperature is approached.

Table 1. Experimental parameters used for numerical calculations.

Compound	$a/(\mathrm{J/cm^3K})$	$B/(\mathrm{J/cm^3})$	$C/(\mathrm{J/cm^3})$	T°/K
5CB[17]	0.086	2.12	1.742	307.14
MBBA[19]	0.042	0.64	0.35	320

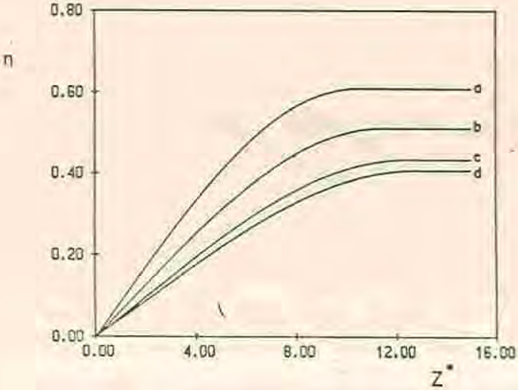

Fig. 1. The order parameter profile of MBBA for four selcted reduced temperatures T^* ($\equiv T/T^0$),

a) 1.0000 b) 1.0020 c) 1.0030 and d) 1.0032.

The decrease in the order parameter from its value in the bulk nematic to that in the surface may be expressed more compactly through the quantity Γ defined as

$$\Gamma = -(1/2)\int_0^\infty \left[\frac{(\eta(z)-\eta_b)}{\eta_b}\right]dz. \quad (3.1)$$

Using equation (2.18) into (3.1) yields

$$\Gamma^* = -(1/2)\int_{\eta(z=0)}^{\eta_b}\left[\frac{(\eta(z)-\eta_b)}{\eta_b\sqrt{F(\eta)-F(\eta_b)}}\right]d\eta, \quad (3.2)$$

where Γ^* ($\equiv\Gamma/\xi$) represents the effective scaled thickness of the isotropic layer in the inerface. The variation of Γ^* with temperature is shown in Fig. 2. The thickness of the isotropic layer is found to diverge as the transition to the isotropic phase is approached. The values of Γ^* are available only over a relatively narrow temperature range, in consequence, it is possible to fit the data to a variety of empirical functions. For example, the function

$$\Gamma^* = a/(T_d^* - T^*), \qquad (3.3)$$

where a and $T_d^*(\equiv T_d/T^\circ)$ are adjustable parameters, often used to represent pre-transitional behaviour in the isotropic phase. The scaled divergence temperatures T_d^*, are found to be 1.0141 and 1.0121 for 5CB and MBBA respectively. These are somewhat higher than the respective scaled nematic-isotropic transition temperatures, $T_{NI}^*(\equiv T_{NI}/T^\circ)$, 1.00359 and 1.00324. This appears to suggest that the isotropic phase only partially wets the nematic-vapour interface since Γ^* remains finite, although large, at T_{NI}.

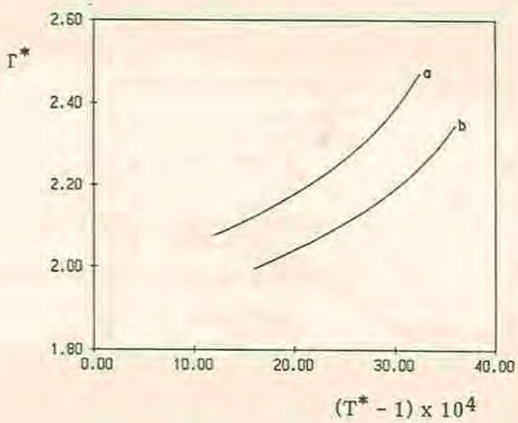

Fig. 2. The dependence of the scaled layer thickness Γ^* $(\equiv \Gamma/\xi)$, on the reduced temperature, $T^*(\equiv T/T^0)$, a) MBBA and b) 5CB.

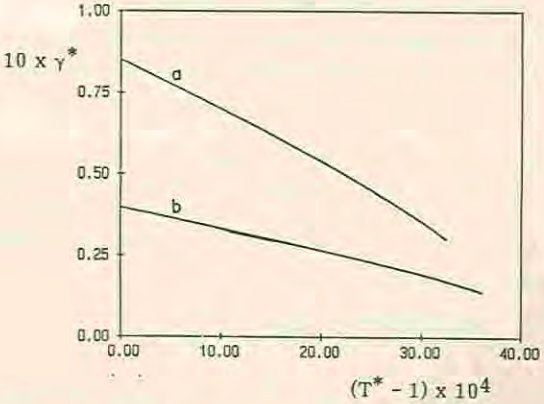

Fig. 3 The dependence of the scaled surface tension $\gamma^*(\equiv \gamma / \xi)$, on the reduced temperature, T^* $(\equiv T/T^0)$, a) MBBA and b) 5CB.

We turn next to the surface tension. The results predicted for the surface tension of both compounds is shown in Fig. 3. For both compounds $d\gamma/dT < 0$ close to the transition and $\Delta\gamma > 0$, which is known to be normal behaviour. Eventhough we used empirical parameters in the model the results predicted for both compounds is in marked contrast with experimental findings. Considering the complicating experimental factors, the chemical instabilitiy of many nematogens, which results in slow formation of an adsorbed layer of impurity at the liquid-vapour interface we would like to think that the pre- and post-transitional anomaly in the surface tension is caused by surface reactions.

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