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# Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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# Orientation of Liquid-Crystal Molecules at the Nematic-Isotropic Interface and the Nematic Free Surface

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ORIENTATION OF LIQUID-CRYSTAL MOLECULES AT THE NEMATIC-ISOTROPIC INTERFACE AND THE NEMATIC FREE SURFACE

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Abstract Using the generalized Kirkwood-Buff formula for a surface tension we study the interfacial properties of liquid crystals. Surface tension,  $\chi$ , is calculated for the dilute hard rod system in the sharp interface approximation as a function of a tilt angle,  $\Theta_{\mathbf{t}}$ , measured from the normal to the flat interface. This function has a minimum at  $\Theta_{\mathbf{t}}^{\mathbf{u}}$  corresponding to the preferred orientation of liquid crystal molecule at the nematic-isotropic interface and in our case  $\Theta_{\mathbf{t}}^{\mathbf{u}} = 60^{\circ}$ . We also argue that hard-core repulsion favours perpendicular alignment at the nematic free surface i.e  $\Theta_{\mathbf{t}}^{\mathbf{u}} = 0^{\circ}$ .

#### INTRODUCTION

The direction of the alignment of liquid-crystal molecules in the bulk nematic is arbitrary because the free energy of the system is rotationally invariant, i.e. it does not depend on the nematic director  $\widehat{\mathbf{n}}$ . This rotational symmetry of the system is broken by the presence of limiting surface. Then the molecules in the region adjacent to such a surface are aligned in a definite manner. This alignment can be described by the tilt angle,  $\Theta_{\mathbf{t}}$ , of the nematic director with respect to the normal to the surface. Recently there have been performed measurments of  $\Theta_{\mathbf{t}}$  at the nematic-isotropic (N-I) interface  $\mathbf{t}$  for ncB (n=5,6,7,8)|(4-n-alkyl-4´-cyano)biphenyl|; they give  $\mathbf{t}$  in the range 50°-70°. In this paper we present a simple model for the N-I interface and calculate the tilt angle.

## SURFACE TENSION

The N-I surface tension is given by the well known generalized Kirkwood-Buff formula  $^{2}$ 

$$\chi_{N-1} = \int dz_1 \int dr_{12} \int d\omega_1 \int d\omega_2 \int g^{(2)}(z_1, r_{12}, \omega_1, \omega_2) \\
\times (x_{12} \frac{\partial}{\partial x_{12}} + y_{12} \frac{\partial}{\partial y_{12}} - 2z_{12} \frac{\partial}{\partial z_{12}}) u(r_{12}, \omega_1, \omega_2), \tag{1}$$

where  $oldsymbol{g}^{(2)}(z_1,\ r_{12}, \omega_1, \omega_2)$  is the two-particle reduced distribution function in the system inhomogeneous in the z-direction,  $oldsymbol{\omega}_1$  and  $oldsymbol{\omega}_2$  denote the orientations of the particles, and  $\mathbf{u}(\mathbf{r}_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$  is the intermolecular potential. We assume that our system consists of very long hard rods and take the Onsager limit  $\mathbf{z}$ . In this approximation

$$\varsigma^{(2)}(z_{1},r_{12},\omega_{1},\omega_{2}) = \varsigma^{(1)}(z_{1}+z_{12},\omega_{2})e^{-u(r_{12},\omega_{1},\omega_{2})}$$

$$\times \varsigma^{(1)}(z_{1},\omega_{1}),$$
(2)

where  $\mathbf{p}^{(1)}(\mathbf{z}_1, \mathbf{\omega}_1)$  is the one-particle reduced distribution function. We also assume the sharp-interface approximation for the N-I interface i.e.  $\mathbf{p}^{(1)}(\mathbf{z}, \mathbf{\omega})$  has the following form:

$$\mathbf{g}^{(1)}(z,\omega) = \begin{cases}
\mathbf{g}_{1}/4\pi & \text{if } z < 0 \\
\mathbf{g}_{N}f(\omega) & \text{if } z > 0
\end{cases}$$
(3)

where  $Q_I$ ,  $Q_N$  denote the bulk densities of the isotropic and the nematic phase, respectively, and  $f(\omega)=f(\widehat{n}\,\widehat{\omega})$  is the orientational distribution function for the bulk nematic. Combining equations (1), (2) and (3) we find the following expression for  $\chi_{N-I}$  in a system of hard rods:

$$\begin{split} \gamma_{N-1} &= \frac{1}{2} \int d\omega_{1} \int d\omega_{2} \ v_{1}(\omega_{1}, \omega_{2}) (2 \frac{\rho_{N} \rho_{F}}{4\pi} \ f(\omega_{1}) \\ &- \rho_{N}^{2} f(\omega_{1}) f(\omega_{2}) - \rho_{1}^{2} / (4\pi)^{2}), \\ v_{1}(\omega_{1}, \omega_{2}) &= - \int dz_{12} z_{12} \int dx_{12} \int dy_{12} (e^{-u(r_{12}, \omega_{1}, \omega_{2})} - 1). \end{split}$$

The surface tension  $\chi_{N-1}$  depends on the director orientation  $\, \Theta_{\, t} \,$  because  $\, {
m f}(\omega) = {
m f}({
m \hat{n}} \, {
m \hat{\omega}} \,)$  and the kernel  ${f V}_1^{}(\omega_1^{},\omega_2^{})$  does not posses full rotational symmetry. The the minimum of  $\chi_{\mathsf{N-T}}(\Theta_{\mathsf{t}}).$  We note that Eq (4) has also been derived in the Onsager model generalized to inhomogeneous systems  $^4$ . We find  $9^{eq}_{t}=60^{\circ}\pm4^{\circ}$ . This compares well with the experimental results $^{1}$ . Application of Eqs(1-4) vapour density leads to the conclusion that the hard-core potential prefers the perpendicular alignment of molecules at the nematic-air interface i.e.  $\Theta_{ ext{t}}$ =0°4. We conclude that the hard-core potential is sufficient to explain the alignment of liquid-crystal molecules at the N-I interface and at the nematic free surface.

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