Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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

Robert Holyst [a] & Andrzej Poniewierski [a]

[a] Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warsaw, POLAND

Version of record first published: 22 Sep 2006.

To cite this article: Robert Holyst & Andrzej Poniewierski (1990): Orientation of Liquid-Crystal Molecules at the Nematic-Isotropic Interface and the Nematic Free Surface, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 192:1, 65-67

To link to this article: http://dx.doi.org/10.1080/00268949008035607

Mol. Cryst. Liq. Cryst. 1990, Vol. 192, pp. 65–67
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

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

ROBERT HOŁYST AND ANDRZEJ PONIEWIERSKI
Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, POLAND.

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

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 $\hat{n}$. 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, Θ_t, of the nematic director with respect to the normal to the surface. Recently there have been performed measurments of Θ_t at the nematic-isotropic (N-I) interface[1] for ncB (n=5,6,7,8)|(4-n-alkyl-4´-cyano)biphenyl|; they give Θ_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]

$$\gamma_{N-I} = \int dz_1 \int dr_{12} \int d\omega_1 \int d\omega_2 \; \rho^{(2)}(z_1, r_{12}, \omega_1, \omega_2) \times \left(x_{12} \frac{\partial}{\partial x_{12}} + y_{12} \frac{\partial}{\partial y_{12}} - 2 z_{12} \frac{\partial}{\partial z_{12}} \right) u(r_{12}, \omega_1, \omega_2), \tag{1}$$

where $\rho^{(2)}(z_1, r_{12}, \omega_1, \omega_2)$ is the two-particle reduced distribution function in the system inhomogeneous in the z-direction, ω_1 and ω_2 denote the orientations of the particles, and $u(r_{12}, \omega_1, \omega_2)$ is the intermolecular potential. We assume that our system consists of very long hard rods and take the Onsager limit[3]. In this approximation

$$\rho^{(2)}(z_1, r_{12}, \omega_1, \omega_2) = \rho^{(1)}(z_1 + z_{12}, \omega_2) e^{-u(r_{12}, \omega_1, \omega_2)} \times \rho^{(1)}(z_1, \omega_1), \tag{2}$$

where $\rho^{(1)}(z_1, \omega_1)$ is the one-particle reduced distribution function. We also assume the sharp-interface approximation for the N-I interface i.e. $\rho^{(1)}(z, \omega)$ has the following form:

$$\rho^{(1)}(z, \omega) = \begin{cases} \rho_I / 4\pi & \text{if } z < 0 \\ \rho_N f(\omega) & \text{if } z > 0, \end{cases} \tag{3}$$

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

$$\gamma_{N-I} = \frac{1}{2}\int d\omega_1 \int d\omega_2\, V_1(\omega_1,\omega_2)\left(2\frac{\rho_N\rho_I}{4\pi}\, f(\omega_1) - \rho_N^2 f(\omega_1)f(\omega_2) - \rho_I^2/(4\pi)^2\right), \tag{4}$$

$$V_1(\omega_1,\omega_2) = -\int_0^\infty dz_{12} z_{12}\int dx_{12}\int dy_{12}\left(e^{-u(r_{12},\omega_1,\omega_2)}-1\right).$$

The surface tension γ_{N-I} depends on the director orientation θ_t because $f(\omega)=f(\hat{n}\hat{\omega})$ and the kernel $V_1(\omega_1,\omega_2)$ does not posses full rotational symmetry. The equilibrium value of the tilt angle, θ_t^{eq}, corresponds to the minimum of $\gamma_{N-I}(\theta_t)$. We note that Eq (4) has also been derived in the Onsager model generalized to inhomogeneous systems[4]. We find $\theta_t^{eq}=60^\circ \pm 4^\circ$. This compares well with the experimental results[1]. Application of Eqs(1-4) to the nematic free surface i.e. with ρ_I replaced by the vapour density leads to the conclusion that the hard-core potential prefers the perpendicular alignment of molecules at the nematic-air interface i.e. $\theta_t=0^\circ$[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[5].

REFERENCES

1. S. Faetti and V. Palleschi, Phys. Rev. A 30, 3241 (1984).
2. J. P. R. B. Walton and K. E. Gubbins, Molec. Phys., 55, 679 (1985).
3. L. Onsager, Ann. N. Y. Acad. Sci., 51, 627 (1949).
4. R. Hołyst and A. Poniewierski, Phys. Rev. A, 38, 1527 (1988).
5. M. G. Gannon and T. E. Faber, Philos. Mag. 37A, 117 (1978).