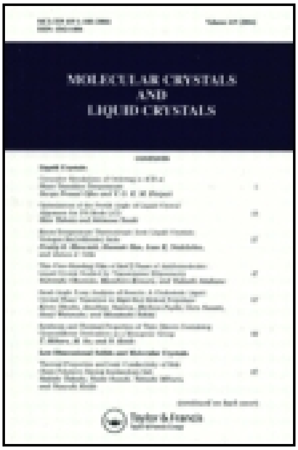

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Density-Functional Theory of Liquid Crystal Surfaces

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Version of record first published: 24 Sep 2006.

To cite this article: Yashwant Singh & Jokhan Ram (1996): Density-Functional Theory of Liquid Crystal Surfaces, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 288:1, 143-152

To link to this article: http://dx.doi.org/10.1080/10587259608034591

Mol. Cryst. Liq. Cryst., 1996, Vol. 288, pp. 143–152
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DENSITY-FUNCTIONAL THEORY OF LIQUID CRYSTAL SURFACES

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Abstract We develop a density-functional theory based on weighted density formalism to describe the surfaces of liquid crystals. The expression for the surface free energy is written in terms of order parameters characterizing the nature and amount of ordering in the interface and the structural parameters which involve the spherical harmonic coefficients of the direct pair correlation function of an effective isotropic fluid the density of which is determined using a criterion of the weighted density-functional formalism. We report preliminory results of our calculations for nematic/vapour and nematic/isotropic liquid interfaces.

INTRODUCTION

The influence of a surface on a system of molecules which exhibits liquid crystalline phases at appropriate conditions can be separated into two aspects : First the presence of a surface induces a perturbation of the liquid crystalline order over a thickness ξ_s near the surface. When the system is far from any phase transition of the bulk, ξ_s is of the order of a few molecular lengths ranging from 20 Å to 100 Å, and defines the thickness of the transition region, or interface between the bulk liquid crystal phase and the other phase (solid, liquid and vapour) which has been placed in contact with the liquid crystal to create a surface. Depending on the nature of the constituent molecules of the liquid crystal and the surface creating phase, the induced ordering in the interface may include enhanced or supressed orientational ordering, biaxiality and smectic ordering[1,2]. When the liquid crystal approaches a bulk phase transition the thickness. ξ_s can increase and reach macroscopic values. This behaviour known as critical adsorption or wetting is similar to the behaviour of any other system.

The second aspect of the surface effect is a macroscopic effect on the bulk liquid crystal phase whose order is recovered at a distance from the surface greater than ξ_s. Close to the interface the liquid crystal molecules take a fixed mean orientation $\underline{\hat{n}}$ which is called the anchoring direction of the liquid crystal at the interface. In the absence of any other orienting field this orientation is imposed on the bulk via the elastic forces which tend to orient all molecules parallel to each other. This phenomena of orientation of liquid crystal by an interface, called anchoring is very similar to epitaxy of solids on substrates. The main issue of anchoring of nematic liquid crystals is to relate the observed anchoring with the structure of the interfaces and to find the microscopic interactions responsible for the orientation of these phases by surfaces.

There has been efforts to calculate the interfacial properties of nematic liquid crystals by several authors using either the phenomenological Landau-de Gennes theory[3] or the molecular-statistical theory based on various approximations[4-9]. While the phenomenological theory is physically appealing and mathematically convenient, it has many drawbacks, including lack of quantiitative predictive power about the interface structure and phase diagram. In the molecular-field theories too many simplifying approximations are made - in the choice of models for intermolecular interactions, in the statistical mechanical approximation schemes, and in the evaluation of the correlation functions and interfacial properties. As a consequence, results vary from one author to the other. For example, the angle which the director makes with the normal to the interface (known as tilt angle) at the nematic-isotropic interface has been reported to have value equal to 90° [4], 0° [5] and 60° [6] although in all cases rod-like molecules are considered. Similar discrepancies are found to exist in the reported results for other cases also.

In this article we develop a theory based on the weighted density-functional formalism for the interfacial properties of liquid crystals. We give explicit results for the free nematic surfaces and the nematic-isotropic interfaces. In these cases there is no interaction with the substrate. The interfacial behaviour is mainly due to the disordering effect of the spatial delocalization across the interface and a surface torque field.

THEORY

We consider a system of nonuniform liquid crystal described by a single particle density distribution or singlet distribution $\rho(\underline{r},\underline{\Omega})$, where $\underline{r}$ indicates the location of centre of a molecule and $\underline{\Omega}$ its relative orientation described by Euler angles θ, ϕ and ψ. For a nonuniform system one may write $\rho(\underline{r},\underline{\Omega}) = \rho(\underline{r})\ f(\underline{r},\underline{\Omega})$ where $\rho(\underline{r})$ is the mean number density of the centre of mass of molecules at point $\underline{r}$ and the function $f(\underline{r},\underline{\Omega})$ describes the local ordering. While for a uniform isotropic fluid, $\rho(\underline{r},\underline{\Omega})$ is constant independent of positions and orientations i.e. $\rho(\underline{r}) = \rho_f$ and $f(\underline{r},\underline{\Omega}) = 1$, for a uniform liquid crystal phase $\rho(\underline{r}) = \rho_n$ and $f(\underline{r},\underline{\Omega})$ describes the nature and amount of ordering which characterize the phase.

It is often convenient to express $f(\underline{r},\underline{\Omega})$ in terms of the Fourier series and the Wigner rotation matrices. Thus[10]

$$f(\underline{r},\underline{\Omega}) = \sum_{G}\sum_{\ell mn} Q_{\ell mn}(\underline{G},\underline{r})\ \exp[i\underline{G}.\underline{r}]\ D^{\ell}_{mn}(\underline{\Omega}) \tag{1a}$$

where

$$Q_{\ell mn}(\underline{G},\underline{r}) = (2\ell+1)\ \langle \exp[i\underline{G}.\underline{r}']\ D^{\ell *}_{mn}(\underline{\Omega}') \rangle . \tag{1b}$$

Here $Q_{\ell mn}(\underline{G},\underline{r})$ are the order parameters which measure the nature and strength of ordering at point $\underline{r}$ in the system and $< --- >$ represents the ensemble average over the primed variables. $\{\underline{G}\}$ are the reciprocal lattice vectors describing the nature of position ordering. All the angles in Eq. (1) refer to a local space-fixed (SF) coordinate frame with its Z-axis along the direction of the local director $\hat{\underline{n}}(\underline{r})$.

The interface between bulk liquid crystal and fluid (coexisting isotropic liquid or vapour) takes the singlet distribution $\rho(\underline{r},\underline{\Omega})$ which minimize the excess grand potential $\Delta\Omega$ (Ω = -PV),

$$\Delta\Omega = \int d\underline{r}_1[\rho(\underline{r}_1)\ \{k_B T \int d\underline{\Omega}_1\ f(\underline{r}_1,\underline{\Omega}_1)\ \big(\ell n(\rho(\underline{r}_1,\underline{\Omega}_1)\Lambda)-1\big) + \Delta a(\underline{r}_1)-\mu\}+P] \tag{2}$$

subject to the constraint of fluid $\rho(\underline{r},\underline{\Omega}) = \rho_f$ and bulk $\rho(\underline{r},\underline{\Omega}) = \rho_n\ f(\underline{\Omega})$ singlet distribution asymptotically on either side of the interface. In Eq. (2) the first term is the ideal gas entropy, Λ the cube of thermal wave length of a molecule, μ the chemical potential and $\Delta a(\underline{r}_1)$ the excess Helmholtz free energy per particle at point $\underline{r}_1$. $\Delta a(\underline{r}_1)$ is functional of $\rho(\underline{r},\underline{\Omega})$. The interfacial free energy γ is precisely the excess free energy per unit area at the minimum $\gamma = \Delta\Omega/L^2|_{\min}$ (L^2 being the area of the surface) and so the structure and surface energy are obtained simultaneously and inseparably.

From a weighted density-functional theory of a nonuniform system one finds[10,11]

$$\beta\Delta a(\underline{r}) = -\int d\underline{r}_2 \int d\underline{\Omega}_1 \int d\underline{\Omega}_2 \, f(\underline{r}_1,\underline{\Omega}_1)\, c^{(2)}(\underline{r}_{12},\underline{\Omega}_1,\underline{\Omega}_2;\bar{\rho}(r))\, \rho(\underline{r}_2) f(\underline{r}_2,\underline{\Omega}_2) \qquad (3a)$$

where $c^{(2)}\,(\underline{r}_{12},\underline{\Omega}_1,\underline{\Omega}_2;\bar{\rho}(r))$ is the direct pair correlation function of an "effective" isotropic fluid of density $\bar{\rho}(r)$. The effective density $\bar{\rho}(r)$ is found from the relation

$$\bar{\rho}(r) = \int d\underline{r}'\, \rho(\underline{r}') \int d\underline{\Omega} \int d\underline{\Omega}'\, f(\underline{r},\underline{\Omega})\, \omega(|\underline{r}-\underline{r}'|,\underline{\Omega},\underline{\Omega}')\, f(\underline{r}',\underline{\Omega}') \qquad (3b)$$

where the weight factor ω is chosen in a way that the functional relationship between the DPCF and the excess Helmholtz free energy remains preserved.

We now separate from $\beta\Delta a(\underline{r})$ the part which correspond to free-energy per particle of a uniform system of density $\rho(\underline{r})$ and the surface term. Thus

$$\beta\Delta a(\underline{r}) = \beta\Delta a_u(\underline{r}) + \beta\Delta a_s(\underline{r}) \qquad (4a)$$

where

$$\beta\Delta a_u(\underline{r}) = -\frac{1}{2}\rho(\underline{r}_1) \int d\underline{r}_{12} \int d\underline{\Omega}_1 \int d\underline{\Omega}_2 \, f(\underline{r}_1,\underline{\Omega}_1)\; c^{(2)}\,(\underline{r}_{12},\underline{\Omega}_1,\underline{\Omega}_2;\bar{\rho}(r))\, f(\underline{r}_1,\underline{\Omega}_2) \qquad (4b)$$

and

$$\beta\Delta a_s(\underline{r}) = -\frac{1}{2}\int d\underline{r}_{12} \int d\underline{\Omega}_1 \int d\underline{\Omega}_2 \, f(\underline{r}_1,\underline{\Omega}_1)\, c^{(2)}\,(\underline{r}_{12},\underline{\Omega}_1,\underline{\Omega}_2;\bar{\rho}(r))\; [\rho(\underline{r}_2)\, f(\underline{r}_2,\underline{\Omega}_2) - \rho(\underline{r}_1)\, f(\underline{r}_1,\underline{\Omega}_2)] \qquad (4c)$$

We choose a SF coordinate frame with its Z-axis along the normal to the interface and expand all angle dependent functions of above equations in spherical harmonics. Assuming that the molecules are cylindrically symmetric and that the director is pointing uniformly along a direction in the interface (i.e. we neglect the distortion in the interface region) we find

$$\beta\Delta a_s(r) = -\frac{1}{2}\sum_{G}\sum_{\ell_1\ell_2\ell}\sum_{m_1'm_2'm'm}\frac{C_g(\ell_1\ell_2\ell\ :\ m_1'm_2'm')}{\left[(4\pi)^2(2\ell_1+1)(2\ell_2+1)\right]^{1/2}}D^{\ell\,*}_{m'm}(\hat{\underline{n}}(r))$$

$$Q_{\ell_1 m_1'}(\underline{G},\underline{r}_1)\int d\underline{r}_{12}\left[\rho(\underline{r}_2)\ Q_{\ell_2 m_2'}(\underline{G},\underline{r}_2) - \rho(\underline{r}_1)\ Q_{\ell_2 m_2'}(\underline{G},\underline{r}_1)\right]$$

$$\exp\left[i\underline{G}.\underline{r}_{12}\right]\ c_{\ell_1\ell_2\ell}(r_{12})\ y^{*}_{\ell m}(\hat{\underline{r}}_{12}) \qquad (5)$$

Where $C_g(\ell_1\ell_2\ell:m_1m_2m)$ are the Clebsch-Gordon coefficients, $c_{\ell_1\ell_2\ell}(r_{12})$ the spherical harmonic coefficients of the DPCF in the SF frame, $\hat{\underline{r}}_{12} = \underline{r}/|\underline{r}|$ is a unit vector along the intermolecular axis and $\hat{\underline{n}}(\underline{r})$ is a unit vector along the direction of the alignment of molecules in the interface. Thus the surface energy depends on the orientation of the director.

Eq. (5) is a general expression of the surface free energy in a sense that it takes into account various kind of surface ordering which can in principle, be found by minimizing Eq. (2) or (5). Formally, the minimum of Eq. (2) can be found by solving the Euler-Lagrange equation $\delta(\Delta\Omega)/\delta\rho(r) = 0$ and $\delta(\Delta\Omega)/\delta Q_{\ell m}(G,r) = 0$. Alternatively, one may perform a direct numerical minimization of $\Delta\Omega$ with respect to parameters of appropriately chosen trial functions for the density $\rho(\underline{r})$ and the order parameters $Q_{\ell m}(\underline{G},\underline{r})$. A practical obstacle to this method, however, is the actual parametrization of the trial function with modest number of parameters. Furthermore, one should also be careful in finding an equilibrium phase diagram using the density-functional theory in the same form as used in the study of interface, in order to determine the boundary conditions for minimization of Eq. (2). This is necessary to make the theory self-consistent.

In writing Eq. (5) we neglected the contribution arising due to distortions. While this may be a reasonable approximation for a one-dimensional interface, the distortion free energy may play crucial role in determining the behaviour of liquid crystals in confined geometries (droplets, films and capilaries). In such situations, both the order parameters and the director field may show large spatial variations at equilibrium. The expression for the distortion free energy per particle in the interface region is given as

$$\beta\Delta a_s^{(d)} = -\frac{1}{2}\sum_{G}\sum_{\ell_1\ell_2\ell}\sum_{m_1m_2m}\sum_{m_1'm_2'm'}\sum_{\ell''\lambda} C_g(\ell_1\ell_2\ell:m_1m_2m)$$

$$C_g(\ell_1\ell_2\ell'':m_1'\underline{\lambda}m')\; C_g(\ell_1\ell_2\ell'':m_1m_2'm'')\; \frac{Q_{\ell_1m_1'}(\underline{G},\underline{r}_1)}{4\pi\big((2\ell_1+1)(2\ell_2+1)\big)^{1/2}}$$

$$\int d\underline{r}_{12}\,\left[\rho(\underline{r}_2)\,Q_{\ell_2m_2'}(\underline{G},\underline{r}_2) - \rho(\underline{r}_1)\,Q_{\ell_2m_2'}(\underline{G},\underline{r}_1)\right]$$

$$\left[D^{\ell_2}_{-\lambda,m_2}(\Delta\chi) - \delta_{-\lambda,m_2}\right] y^{*}_{\ell m}(\hat{\underline{r}}_{12})\; c_{\ell_1\ell_2\ell}(r_{12})$$

Here $\Delta\chi$ is angle between directors at $\underline{r}_1$ and $\underline{r}_2$. A density functional theory of elastic constants of the liquid crystals bulk has already been developed[12,13]. The interfacial structure will depends on the competition of the surface and elastic free energies and therefore has to be included in Eq. (2) before its minimization.

RESULT AND DISCUSSIONS

In this article we, however, take a simplified view and calculate the interfacial properties in three limiting cases. In the first case we take a step function interface, i.e., ρ and $Q_{\ell m}$ remains constant till the surface where they suddenly go to zero. The second case is that of a very diffused interface so that the second gradient approximation in the expansion of the density and order parameters be reasonable. In these two cases we consider only nematic ordering. In the third case we consider a diffused interface with smectic ordering. In all the cases a planar interface in the XY plane is taken. The axis Z is taken perpendicular to the interface. The system is rotationally invariant in the plane of interface and therefore without loss of generality we can choose the director to be in the XZ plane.

The Case of a Sharp Interface

In this case, as stated above, we restrict ourselves to orientational ordering and therefore choose G = 0. The surface is taken at z = 0. We also assume that the nematic ordering remains constant till the surface at which both the density and order parameters jump to zero. For this case Eq. (5)

reduces to

$$\beta \Delta A_s/L^2 = a_{0n} + a_{2n}\, P_2(\cos\psi) + a_{4n}\, P_4(\cos\psi) \tag{6a}$$

where ΔA_s is total surface free energy,

$$a_{in} = \frac{1}{2}\rho^2 \sum_{\ell_1 \ell_2 m} \frac{C_g(\ell_1\, \ell_2 \ell\, :\, m\underline{m}0)}{4\big((2\ell_1+1)(2\ell_2+1)\big)^{1/2}}\, Q_{\ell_1 m} Q_{\ell_2 \underline{m}}\, I_{\ell_1 \ell_2 i}. \tag{6b}$$

Here

$$I_{\ell_1 \ell_2 0} = \bar{C}_3(\ell_1 \ell_2 0)\, \delta_{\ell_1 \ell_2} \tag{6c}$$

$$I_{\ell_1 \ell_2 2} = \sqrt{\frac{5}{16}}\, \bar{C}_3(\ell_1 \ell_2 2) \tag{6d}$$

$$I_{\ell_1 \ell_2 4} = -\sqrt{\frac{1}{64}}\, \bar{C}_3(\ell_1 \ell_2 4) \tag{6e}$$

and

$$\bar{C}_p(\ell_1 \ell_2 \ell) = \frac{1}{\sqrt{4\pi}} \int_0^\infty dr\, r^p\, c_{\ell_1 \ell_2 \ell}(r) \tag{6f}$$

For a simple case of uniaxial ordering for which $m = 0$ and $Q_\ell = (2\ell+1)\bar{P}_\ell$ where

$$\bar{P}_\ell = \frac{1}{2} \int P_\ell\, (\cos\theta)\, f(\Omega)\, d(\cos\theta) \tag{7}$$

we get

$$\beta \Delta A_s/L^2 = b_0 + b_2\, P_2(\cos\psi) + b_4 P_4\, (\cos\psi) \tag{8a}$$

where

$$b_0 = \frac{1}{8}\rho^2\big[C_3(000) + \sqrt{5}\, \bar{P}_2^2\, \bar{C}_3(220)\big] \tag{8b}$$

$$b_2 = \frac{5}{16}\rho^2\big[P_2 C_3(202) - \sqrt{\frac{5}{14}}\, P_2^2\, C_3(222)\big] \tag{8c}$$

$$b_4 = -\frac{3}{64}\sqrt{\frac{10}{7}}\, \rho^2\, P_2^2\, C_3(224) \tag{8d}$$

The tilt angle ψ is found by minimizing Eq. (8a) with respect to cos ψ. This leads to

$$\psi = \pi/2 \qquad \text{for } b_2 > \frac{5}{2} b_4$$

$$\cos^2 \psi = \frac{3}{35} \frac{5b_4 - 2b_2}{b_4} \qquad \text{for } \frac{5}{2} b_4 > b_2 > -\frac{10\, b_4}{3}$$

$$\psi = 0 \qquad \text{for } b_2 < -\frac{10}{3} b_4 \tag{9}$$

The Case of a Diffused Interface

If the interface is so broad that the variance of $\rho(z)$ and $Q_{\ell m}(G,z)$ is large compared to the range of pair correlation function, then we can make a gradient expansion in Eq. (5) and neglect the term beyond the second gradient. The square gradient approximation (SGA) leads to the following expression for the surface free energy for the case of uniaxial nematic surface ordering

$$\beta \Delta A_s / L^2 = \int dz\, \beta \Delta a_s(z)$$

where

$$\beta \Delta a_s(z) = b_{od}(z) + b_{2d}(z)\, P_2(\cos \psi) \tag{10a}$$

with

$$b_{od}(z) = \frac{1}{12}\Big[\rho'(z)^2\big(\bar{C}_4(000) + \rho(z)\, \bar{C}'_4(000)\big) + \sqrt{5}\, \psi'(z) \\ \big(\psi'(z)\, \bar{C}_4(220) + \psi(z)\, \rho'(z)\, \bar{C}'_4(220)\big)\Big] \tag{10b}$$

$$b_{2d}(z) = \frac{1}{3}\Big[\Big\{\psi'(z)\, \rho'(z)\, \bar{C}_4(202) + \frac{1}{2}\, \rho'(z)\, \big(\rho'(z)\, \psi(z) + \rho(z)\, \psi'(z)\big) \\ \bar{C}'_4(202)\Big\} - \sqrt{\frac{5}{14}}\, \psi'(z)\, \{\psi'(z)\, \bar{C}_4(222) + \psi(z)\, \rho'(z)\, \bar{C}'_4(222)\}\Big]. \tag{10c}$$

Here

$$\psi(z) = \rho(z)\, \bar{P}_2(z);\ \rho'(z) = d\rho(z)/dz;\ \psi'(z) = d\psi(z)/dz$$

and $\bar{C}'_4(\ell_1 \ell_2 \ell) = d\, \bar{C}_4(\ell_1 \ell_2 \ell)/d\rho(z)$.

It is therefore clear that for this case one gets either parallel or homeotropic anchoring but not oblique one. The parallel anchoring will be preferred for $b_{2d} > 0$ and homeotropic for $b_{2d} < 0$. For $b_{2d} = 0$ the surface energy will be independent of the tilt angle ψ.

The Case of Diffused Interface with Smectic Ordering

In the SGA approximation the expression for the surface free energy for an interface with smectic ordering is found to be

$$\beta \Delta a_s(z) = b_{0s}(z) + b_{2s}(z)\, P_2(\cos\psi) + b_{4s}(z)\, P_4(\cos\psi) \tag{11a}$$

where

$$b_{0s}(z) = \frac{1}{12} \sum_G \sum_{\ell_1 \ell_2 \ell} \sum_L (i)^L \frac{C_g(\ell_1\, \ell_2 \ell : 000)}{\left[(2\ell_1+1)(2\ell_2+1)\right]^{1/2}} \frac{2L+1}{\sqrt{4\pi}}$$
$$\left[\delta_{\ell L} + 2|C_g(2L\ell{:}000)|^2\right] \frac{d}{dz}\left[\psi_{\ell_1}(G,z)\, A^L_{\ell_1 \ell_2 \ell}(G,\bar{\rho}(z))\right]$$
$$\frac{d}{dz}\, \psi_{\ell_2}(z) \tag{11b}$$

where $\ell = 0, 2, 4$, $G = \frac{2\pi n}{d}$, n being positive integer and d the inter layer spacing in a smectic ordering, and $\psi_\ell(G,z) = \rho(z)\, Q_\ell(G,z)$. Here

$$A^L_{\ell_1 \ell_2 \ell}\left(\bar{\rho}(z)\right) = \int dr\, r^4\, c_{\ell_1 \ell_2 \ell}\left(r,\bar{\rho}(z)\right) j_L(G,r) \tag{11c}$$

The condition for the tilt angle are, therefore, same as given in Eq. (9) with b_{2s}, b_{4s} for b_2 and b_4, respectively.

Our preliminary calculations for the modified Gay-Berne potential[14] with length to width ratio $x_0 = 3$ and well depth ratio $k' = 5$ (see refs 15 and 16 for notations and for the values of spherical harmonics of DPCF) we find that for the sharp interface the anchoring is homeotropic. However near the triple point when $\bar{P}_2 \sim 1$ or for nematogens with large value of quadrupole moments ($Q \sim 50 \times 10^{-26}$ esu cm^2) the anchoring may be oblique. On the other hand, for a diffused interface we again find for both the nematic/vapour and nematic/isotropic liquid interfaces the anchoring is homeotropic. If the nematogens have large quadrupole moments the nematic/isotropic interface may have parallel anchoring.

A systematic study of the structure and thermodynamics of different interfaces based on Eqs. (2) and (5) is in progress and results of this study will be reported in a separate publication.

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