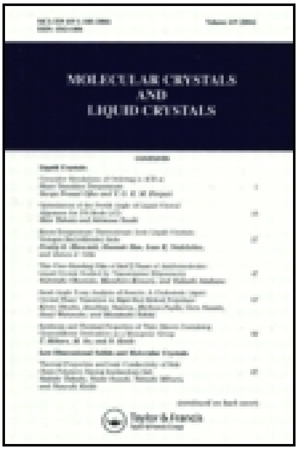

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A Molecular Theory of Surface Tension in Nematic Liquid Crystals

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A Molecular Theory of Surface Tension in Nematic Liquid Crystals

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Starting with a model intermolecular potential that includes $\vec{e}\cdot\vec{R}/R$ terms (to account for anisotropic steric interactions) a statistical mechanical calculation of the surface tension at the free surface of a nematic liquid crystal is carried out. The effect of the transition zone on the surface tension is examined. The expressions for surface tension are obtained from the extended Fowler-Kirkwood-Buff formulas for the cases of linear, cubic and exponential density profiles.

Keywords: nematic liquid crystals, surface tension, pair distribution

INTRODUCTION

We have observed experimentally several interesting effects at the surface regions of liquid crystals.

In the absence of external perturbations, the orientation of the liquid crystal molecules at the surface layer has cylindrical symmetry around an axis normal to the surface. Thus, the director $\vec{n}(\theta)$ has a conical degeneracy;[1] if $\theta = \pi/2$, the molecules are parallel to the surface, the anchorage being planely degenerate. From this point of view, the free surface is analogous to the liquid-liquid (or liquid-liquid crystal) interface. In most cases the surface and the interfacial tensions have similar values (20 ~ 50 dyn/cm). The orientation of the liquid crystal molecules at the interface has been studied experimentally. D. Langevin[2] showed that the molecules of PAA tend to lie in the plane of the nematic-air free surface whereas those of MBBA are inclined at an angle to the normal which varies with temperature from a few degrees to 15°. In other cases a homeotropic structure occurs with the molecules normal to the surface.[3] The behaviour of the surface tension at the nematic isotropic transition temperature has been studied for a variety of materials using a variety of techniques, and the results obtained have been inconsistent in many respects.[2,7] Some workers have found the temperature dependence of γ to be normal (in the sense that $d\gamma/dT$ is negative throughout the range investigated) others have found that just above or just below the clearing point T_c, (or both) $d\gamma/dT$ is positive. Some authors have observed a discontinuity in the surface tension γ at T_c.[4,7]

From a theoretical point of view, the study of the surface regions has developed along two major directions. Firstly there is the phenomenological approach, based on the Landau-de Gennes theory.[1,8] Such a theory is physically reasonable, mathematically convenient, and gives qualitatively sound results. Quantitatively however, it encounters difficulties because of the oversimplifications necessary.[9,10] The second approach is the molecular theory which starts from the general equivalent expressions obtained independently from the surface tension for polyatomic fluids.[11,12] Using this approach Parsons[13] and Murakami[14] have calculated the nematic surface tension, but the work of both authors contain certain lacunae and these are extensively discussed in References 6 and 15.

Gray and Gubbins[11] have extended the statistical formalism of the surface tension for simple liquids[16] to the polyatomic fluids, obtaining the following form for the surface tension:

$$\gamma = \gamma_R + \gamma_\theta \tag{1}$$

where

$$\gamma_R = -\frac{1}{2}\int_{-\infty}^{\infty} dz_1 \int d\vec{R} P_2(\cos\theta) R \left\langle P^{(2)}(z_1,\vec{R},\vec{e}_1,\vec{e}_2)\,\frac{\partial u(\vec{R},\vec{e}_1,\vec{e}_2)}{\partial R}\right\rangle_{\vec{e}_1,\vec{e}_2} \tag{2}$$

$$\gamma_\theta = \frac{3}{4}\int_{-\infty}^{\infty} dz_1 \int d\vec{R}\,\sin\theta\,\cos\theta \left\langle P^{(2)}(z_1,\vec{R},\vec{e}_1,\vec{e}_2)\,\frac{\partial u(\vec{R},\vec{e}_1,\vec{e}_2)}{\partial \theta}\right\rangle_{\vec{e}_1,\vec{e}_2} \tag{3}$$

where $\langle\ \rangle_{\vec{e}_1,\vec{e}_2}$ denotes an unweighted averaging over the orientations $\vec{e}_1$ and $\vec{e}_2$, $\vec{R} = \vec{r}_2 - \vec{r}_1$ is the center of mass vector, $\vec{R} = (R,\theta,\varphi)$, $\vec{e}_i(\theta_i,\varphi_i,x_i)$ denotes the Euler angles specifying the orientation of each molecule (which we assume to be rigid) P_2 is the second Legendre polynomial. $P^{(2)}(\vec{r}_1,\vec{r}_2,\vec{e}_1,\vec{e}_2)$ is the pair distribution function given by:

$$P^{(2)}(\vec{r}_1,\vec{r}_2,\vec{e}_1,\vec{e}_2) = \frac{N(N-1)}{Q}\int e^{-U/kT}\{d\vec{r}_3^{\,N}\}\{d\vec{e}_3^{\,N}\} \tag{4}$$

Q being the configurational partition function. In (2) and (3) the z axis is chosen to be normal to the free surface, which we shall conveniently fix at $z = 0$. Since the system is assumed to be homogeneous in the x and y directions, we can write:

$$P^{(2)}(\vec{r}_1,\vec{r}_2,\vec{e}_1,\vec{e}_2) = P^{(2)}(z_1,\vec{R},\vec{e}_1,\vec{e}_2) \tag{5}$$

For a system with inhomogeneity in the z direction one can replace the pair distribution function $P^{(2)}(z_1,\vec{R},\vec{e}_1,\vec{e}_2)$ by a pair correlation function $g(z_1,\vec{R},\vec{e}_1,\vec{e}_2)$ which is normalized to unity at large R:

$$P^{(2)}(z_1,\vec{R},\vec{e}_1,\vec{e}_2) = P^{(1)}(z_1,\vec{e}_1)P^{(1)}(z_2,\vec{e}_2)g(z_1,\vec{R},\vec{e}_1,\vec{e}_2) \tag{6}$$

where $P^{(1)}(z_i,\vec{e}_i)$ is the single particle distribution function. In the mean field approximation, local correlations in orientation are ignored; so Eq. (6) becomes:

$$P^{(2)}(z_1,\vec{R},\vec{e}_1,\vec{e}_2) = \rho^{(1)}(z_1)\rho^{(1)}(z_2)f(z_1,\vec{e}_1)f(z_2,\vec{e}_2)g(z_1,\vec{R}) \tag{7}$$

where $f(z_i,\vec{e}_i)$ is the orientational single particle distribution function.

In this work we shall ignore the dependence of the orientational single particle distribution function on z and we will assume that the order parameter η has the bulk value up to the surface. This approximation contradicts the boundary condition on η at the free surface which can be derived from free energy arguments. The detailed qualitative picture of the form of $\eta(z)$ through the surface region was obtained by a self-consistent treatment.[17]

With these considerations, the pair distribution function becomes:

$$P^{(2)}(z_1,\vec{R},\vec{e}_1,\vec{e}_2) = \rho^{(1)}(z_1)\rho^{(1)}(z_2)f(\vec{e}_1)f(\vec{e}_2)g(z_1,\vec{R}) \tag{8}$$

POTENTIAL MODEL

In a statistical theory of nematic liquid crystals, in principle one need only be given the potential that describes the interaction between a pair of cylindrically symmetrical nonchiral molecules. We use a potential model[18]:

$$V(1,2) = V_0(R) + V_2(R)P_2(\vec{e}_1\cdot\vec{e}_2) + f\left(R, \frac{\vec{e}_1\cdot\vec{R}}{R}, \frac{\vec{e}_2\cdot\vec{R}}{R}\right) \tag{9}$$

The first two terms in (9) represent the McMillan form of the potential.[19] The last term couples spatial and orientational variables. In expressing the last term in (9) we have followed Berne and Pechukas[20] who have proposed a Gaussian overlap model in which the overlap between two ellipsoidal charge distributions is calculated.

We have obtained the potential model in the form:[18]

$$V(1,2) = V_0(R) + V_2(R)P_2(\vec{e}_1\cdot\vec{e}_2) + v_2(R)\left[P_2\left(\frac{\vec{R}\cdot\vec{e}_1}{R}\right) + P_2\left(\frac{\vec{R}\cdot\vec{e}_2}{R}\right)\right] \tag{10}$$

where the last term includes anisotropic steric interactions.

STATISTICAL FORMALISM

In order to calculated the averages which appear in the expressions (2) and (3) we introduce a spherical coordinate system with polar axis $\vec{n}$ and express $\vec{e}_1,\vec{e}_2$ and $\vec{R}$ accordingly

$$\vec{e}_i = \begin{pmatrix} \sin\theta_i\cos\varphi_i \\ \sin\theta_i\sin\varphi_i \\ \cos\theta_i \end{pmatrix}; \frac{\vec{R}}{R} = \begin{pmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{pmatrix} \tag{11}$$

Since the nematic state has cylindrical symmetry and the molecules are uniaxial, all azimuthal angles $\varphi_1,\varphi_2,\varphi$ are equally probable. The average $V(1,2)$ over these angles then becomes:

$$\langle V(1,2)\rangle_{\varphi_1,\varphi_2} = V_0(R) + V_2(R)\left[\left(\frac{3}{2}\cos^2\theta_1 - \frac{1}{2}\right)\left(\frac{3}{2}\cos^2\theta_2 - \frac{1}{2}\right)\right] + v_2(R)\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)\left(\frac{3}{2}\cos^2\theta_1 - \frac{1}{2} + \frac{3}{2}\cos^2\theta_2 - \frac{1}{2}\right) \tag{12}$$

Next, we average Eq. (12) over the polar angles θ_1,θ_2, the distribution function $f(\vec{e})$ being connected to the order parameter η by:

$$\eta = \int_0^{\pi/2} \frac{1}{2}(3\cos^2\theta - 1)\sin\theta\, f(\vec{e})d\theta \tag{13}$$

With the approximation (6), the interaction averaged over all orientations of the two molecules, becomes:

$$\langle V(1,2)\rangle_{\vec{e}_1,\vec{e}_2} = V_0(R) + V_2(R)\eta^2 + v_2(R)(3\cos^2\theta - 1)\eta \tag{14}$$

One can observe that, in addition to the term in η^2, associated with the mean field theory, there is a term in η which is characteristic of the third term in the potential (10).

Thus, the expressions (2) and (3) become:

$$\gamma_R = -\frac{1}{2}\int_{-\infty}^{\infty} dz_1\rho(z_1)\int d\vec{R}\rho(z_2)\, R\,\frac{3\cos^2\theta - 1}{2}\, g(z_1,z_2,\vec{R})\,\frac{\partial\langle V(1,2)\rangle_{\vec{e}_1,\vec{e}_2}}{\partial R} \tag{15}$$

$$\gamma_\theta = \frac{3}{4}\int_{-\infty}^{\infty} dz_1\rho(z_1)\int d\vec{R}\rho(z_2)\sin\theta\cos\theta\, g(z_1,z_2,\vec{R})\,\frac{\partial\langle V(1,2)\rangle_{\vec{e}_1,\vec{e}_2}}{\partial\theta} \tag{16}$$

where:

$$\frac{\partial\langle V(1,2)\rangle_{\vec{e}_1,\vec{e}_2}}{\partial R} = \frac{dV_0}{dR} + \eta^2\frac{dV_2}{dR} + (3\cos^2\theta - 1)\eta\frac{dv_2}{dR} \tag{17}$$

$$\frac{\partial\langle V(1,2)\rangle_{\vec{e}_1,\vec{e}_2}}{\partial\theta} = -6\cos\theta\sin\theta\eta\, v_2(R) \tag{18}$$

If all the angles θ are equally probable (complete rotational symmetry), $\langle\cos^2\theta\rangle = 1/3$ (the Maier-Saupe assumption[21]) the linear term in η from the equation (14) disappears, and the equation (14) is reduced to:

$$\langle V(1,2)\rangle_{\hat{e}_1,\hat{e}_2} = V_0(R) + V_2(R)\eta^2 \tag{19}$$

a potential characteristic for the mean field. With this potential (19), $\gamma_\theta = 0$. But for a fluid of non-spherical molecules γ_θ does not in general vanish because the part of the potential energy (the third term in (10)), which determines γ_θ is significant if anisotropic physical properties are taken into consideration.

THE FKB MODEL

The FKB assumptions[16] are: a) the transition layer has zero thickness, and b) the vapour density is negligible. With these approximations Eqs. (15) and (16) reduce to:

$$\gamma_R = \frac{\pi\rho_L^2}{8}\int_0^\infty R^4 g_1(R)\left[\frac{dV_0}{dR} + \eta^2\frac{dV_2}{dR} + 2\eta\frac{dv_2}{dR}\right]dR \tag{20}$$

and

$$\gamma_\theta = \frac{3\pi\rho_L^2}{4}\int_0^\infty R^3 g_1(R)\eta v_2(R)dR \tag{21}$$

EXTENSIONS OF FOWLER-KIRKWOOD-BUFF FORMULA

We extend the algebraic procedure used for simple fluids[22] to the case of nematic liquid crystals. We shall take the vapour-phase density occupying $z \leq 0$ to be effectively zero. The density of the nematic phase is taken to be a constant ρ_1 for $z \geq d$. As the $\rho(z)$ and the radial distribution function $g(z_1,z_2,R)$ are unknown in the transition zone, three alternative representations of $\rho(z)$ will be used.

The simplest form, other than Fowler's step-function profile, is the linear profile for a transition zone of width d:

$$\rho(z) = \rho_L\frac{z}{d}, \qquad 0 \leq z \leq d \tag{22}$$

A slightly more complicated form is the cubic profile:

$$\rho(z) = \rho_{\mathrm{L}}\left(\frac{3z^2}{d^2} - \frac{2z^2}{d^3}\right), \qquad 0 \le z \le d \tag{23}$$

A somewhat more realistic profile is given by the exponential expression:

$$\rho(z) = \rho_{\mathrm{L}}\left[1 - \frac{e^{-\omega(z-d/2)}}{2}\right], \qquad 0 \le z \tag{24}$$

where $\omega \sim 1/d$.

In addition to the assumed profiles, we also need the specific values of $g(z_1,z_2,R)$. It is clear that the term $g(z_1,z_2,R)$ tends to $g_{\mathrm{L}}(R)$ when both z_1 and z_2 are in the bulk liquid crystal phase, and tends to $g_v(R)$ when both z_1 and z_2 are in the bulk vapor phase. When z_1 and/or z_2 are in the transition zone, the value of $g^{(2)}$ is, however, uncertain. It is tempting to represent the $g(z_1,z_2,R)$ in the transition zone as an interpolation between $g_{\mathrm{L}}(R)$ and $g_b(R)(g_b(R) = \exp[-V(R)/kT])$. But this kind of interpolation is not accurate for most of the regions in the transition zone, where $\rho(z)$ is substantially larger than ρ_v. In the following discussion we shall use $g_{\mathrm{L}}(R)$ only for $g(z_1,z_2,R)$ with no consideration of any mixing between $g_{\mathrm{L}}(R)$ and $g_b(R)$.

The final expressions, which can be readily evaluated, are then:

$$\begin{aligned}\gamma_R = {} & \frac{\pi}{2}\int_0^\infty dR\cdot g_{\mathrm{L}}(R)\left(\frac{dV_0}{dR} + \eta^2\frac{dV_2}{dR}\right) \\ & \times \int_0^{R+d} dz_1\rho(z_1)\int_{\max(0,z_1-R)}^{z_1+R} dz_2[R^2 - 3(z_2 - z_1)^2]\rho(z_2) \\ & - \frac{\pi}{2}\int_0^\infty dR\cdot\frac{g_{\mathrm{L}}(R)}{R^2}\eta\frac{dv_2}{dR} \\ & \times \int_0^{R+d} dz_1\rho(z_1)\int_{\max(0,z_1-R)}^{z_1+R} dz_2[9(z_2 - z_1)^4 \\ & - 6(z_2 - z_1)^2R^2 + R^4]\rho(z_2)\end{aligned} \tag{25}$$

$$\gamma_\theta = -9\pi \int_0^\infty dR \, \frac{g_L(R)}{R^3} \, \eta v_2(R)$$

$$\times \int_0^{R+d} dz_1 \rho(z_1) \int_{\max(0, z_1 - R)}^{Z_1 + R} dz_2 [(z_2 - z_1)^2 R^2 - (z_2 - z_1)^4] \rho(z_2) \tag{26}$$

In these equations the integration over z_1 and z_2 can be carried out explicitly. We shall omit all the lengthy algebra and simply state the resultant formulas:

a) for linear profile:

$$\gamma_R = \pi\rho_L^2 \int_d^\infty dR g_L(R) \left[\left(\frac{dV_0}{dR} + \eta^2 \frac{dV_2}{dR} \right) \left(\frac{d^4}{120} - \frac{R^2 d^2}{24} + \frac{R^4}{8} \right) + \right.$$

$$\left. + 2\eta \frac{dv_2}{dR} \left(\frac{3}{1120} \frac{d^6}{R^2} - \frac{d^4}{120} + \frac{R^2 d^2}{48} - \frac{1}{5} R^3 d + \frac{R^4}{8} \right) \right]$$

$$+ \pi\rho_1^2 \int_0^d dR g_1(R) \left[\left(\frac{dV_0}{dR} + \eta^2 \frac{dV_2}{dR} \right) \left(\frac{2}{15} \frac{R^5}{d} - \frac{1}{24} \frac{R^6}{d^2} \right) \right.$$

$$\left. + 2\eta \frac{dv_2}{dR} \left(-\frac{2}{15} R^3 d + \frac{11}{105} \frac{R^5}{d} - \frac{1}{32} \frac{R^6}{d^2} \right) \right] \tag{27}$$

$$\gamma_\theta = \pi\rho_L^2 \int_d^\infty dR g_L(R) 2\eta v_2 \left(-\frac{3}{560} \frac{d^6}{R^3} + \frac{1}{40} \frac{d^4}{R} - \frac{3}{5} R^2 d + \frac{3}{8} R^3 \right) +$$

$$+ \pi\rho_L^2 \int_0^d dR g_L(R) 2\eta v_2 \left(-\frac{2}{5} R^2 d + \frac{9}{35} \frac{R^4}{d} - \frac{1}{16} \frac{R^5}{d^2} \right) \tag{28}$$

b) for cubic profile:

$$\gamma_R = \pi\rho_L^2 \int_d^\infty dR g_L(R) \left[\left(\frac{dV_0}{dR} + \eta^2 \frac{dV_2}{dR} \right) \left(\frac{9}{2800} d^4 - \frac{1}{40} R^2 d^2 + \frac{R^4}{8} \right) \right.$$

$$\left. + 2\eta \frac{dv_2}{dR} \left(\frac{1}{1400} \frac{d^6}{R^2} - \frac{9}{2800} d^4 + \frac{1}{80} R^2 d^2 - \frac{1}{5} R^3 d + \frac{R^4}{8} \right) \right]$$

$$+\pi\rho_{\mathrm{L}}^2\int_0^d dRg_{\mathrm{L}}(R)\left[\left(\frac{dV_0}{dR}+\eta^2\frac{dV_2}{dR}\right)\left(\frac{4}{25}\frac{R^5}{d}-\frac{8}{70}\frac{R^7}{d^3}+\frac{R^8}{16d^4}-\frac{R^{10}}{200d^6}\right)\right.$$

$$+\,2\eta\,\frac{dv_2}{dR}\left(-\frac{26}{175}R^3d+\frac{22}{175}\frac{R^5}{d}-\frac{5}{8}\frac{R^6}{d^2}\right.$$

$$\left.\left.-\frac{3}{35}\frac{R^7}{d^3}-\frac{19}{400}\frac{R^8}{d^2}-\frac{11}{2800}\frac{R^{10}}{d^6}\right)\right] \tag{29}$$

$$\gamma_\theta=\pi\rho_{\mathrm{L}}^2\int_d^\infty dRg_{\mathrm{L}}(R)2\eta v_2\left(-\frac{1}{700}\frac{d^6}{R^3}+\frac{27}{2800}\frac{d^4}{R}-\frac{3}{5}R^2d+\frac{3}{8}R^3\right)$$

$$+\,\pi\rho_{\mathrm{L}}^2\int_0^d dRg_{\mathrm{L}}(R)2\eta v_2\left(-\frac{78}{175}R^2d+\frac{54}{175}\frac{R^4}{d}\right.$$

$$\left.+\frac{1}{7}\frac{R^6}{d^3}+\frac{27}{400}\frac{R^7}{d^4}-\frac{132}{175}\frac{R^9}{d^6}\right) \tag{30}$$

c) for exponential profile:

$$\gamma_R=\pi\rho_{\mathrm{L}}^2\int_0^\infty dRg_{\mathrm{L}}(R)\left(\frac{dV_0}{dR}+\eta^2\frac{dV_2}{dR}\right)$$

$$\cdot\left\{\frac{R^4}{8}+e^{-\omega R}\left[\left(\frac{R^2}{\omega^2}+\frac{3R}{\omega^3}+\frac{3}{\omega^4}\right)(e^{-\omega d/2}-e^{\omega d/2})+\right.\right.$$

$$+\left(-\frac{R^2}{4\omega^2}-\frac{3R}{4\omega^3}-\frac{3}{4\omega^4}\right)(e^{-\omega d}-e^{\omega d})$$

$$+\left(\frac{R^2}{2\omega^2}-\frac{3}{\omega^4}\right)(e^{-\omega d/2}-e^{\omega d/2})+$$

$$\left.+\left(-\frac{R^2}{8\omega^2}+\frac{3}{4\omega^4}\right)(e^{-\omega d}-e^{\omega d})\right\}$$

$$+\,\pi\rho_{\mathrm{L}}^2\int_0^\infty dRg_{\mathrm{L}}(R)2\eta\,\frac{dv_2}{dR}\left\{\frac{R^4}{8}-\frac{2}{5}R^3d+\right.$$

$$+\,e^{-\omega R}\left[\left(\frac{R^2}{\omega^2}+\frac{6R}{\omega^3}+\frac{24}{\omega^4}+\frac{54}{R^2\omega^5}+\frac{54}{R^2\omega^6}\right)(e^{-\omega d/2}-e^{\omega d/2})+\right.$$

$$+ \left(\frac{R^2}{4\omega^2} + \frac{3R}{2\omega^3} + \frac{6}{\omega^4} + \frac{26}{2R\omega^5} + \frac{27}{2R^2\omega^6}\right)\left(e^{\omega d} - e^{-\omega d}\right)\Bigg] +$$

$$+ \left(\frac{1}{5}\frac{R^3}{\omega} + \frac{R^2}{4\omega^2} + \frac{3}{\omega^4} + \frac{54}{R^2\omega^6}\right)\left(e^{\omega d/2} - e^{-\omega d/2}\right) +$$

$$+ \left(\frac{R^2}{16\omega^2} - \frac{3}{4\omega^4} + \frac{27}{R^2\omega^6}\right)\left(e^{-\omega d} - e^{\omega d}\right)\Bigg\} \quad (31)$$

$$\gamma_\theta = \pi\rho_L^2 \int_0^\infty dR g_L(R) 2\eta v_2(R) \left\{\frac{3}{8}R^3 - \frac{6}{5}R^2 d + \right.$$

$$+ e^{-\omega R}\Bigg[\left(-\frac{9}{\omega^3} - \frac{45}{R\omega^4} - \frac{108}{R^2\omega^5} - \frac{108}{R^3\omega^6}\right)\left(e^{-\omega d/2} - e^{\omega d/2}\right) +$$

$$+ \left(\frac{9}{4\omega^3} + \frac{45}{4R\omega^4} + \frac{27}{R^2\omega^5} + \frac{27}{R^3\omega^6}\right)\left(e^{-\omega d} - e^{\omega d}\right)\Bigg] +$$

$$+ \left(-\frac{3}{5}\frac{R^2}{\omega} - \frac{9}{R\omega^4} + \frac{108}{R^3\omega^6}\right)\left(e^{-\omega d/2} - e^{\omega d/2}\right)$$

$$\left. + \left(\frac{9}{4R\omega^4} - \frac{27}{R^2\omega^6}\right)\left(e^{-\omega d} - e^{\omega d}\right)\right\} \quad (32)$$

When $d = 0$ of these expressions reduce to the result of the FKB approximation (20) and (21).

CONCLUSIONS

In order to show the Eq. (27) and (32) explicitly, the form of the radial distribution function must be known.

For simple liquids, there are experimental values for $g(R)$. For liquid crystals, such data are not available and the only possibility is to determine $g(R)$ theoretically, starting from the generalized hierarchy of equations (BBGKY). The way this hierarchy is truncated and the physical involvements of these approximations have been rigorously discussed previously.[23]

The expressions (27) and (32) were obtained by making the approximation that the order parameter η is constant within the transition zone. But, like the density, the order parameter must vary within the surface layer and because of this, the contributions of this change to the surface tension shall be calculated. We intend to tackle these problems more completely in a future study.

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