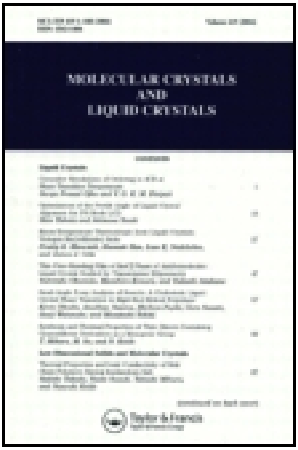

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Density-Functional Theory of Nematics Near Surfaces

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Density-Functional Theory of Nematics Near Surfaces

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A density-functional theory for the growth of a nematic wetting layer near surfaces is presented. The theory predicts complete wetting at a high enough value of the surface field. The phenomenon is examined for *p*-azoxyanisole (PAA) in the framework of random-phase approximation (RPA).

Keywords: Nematic liquid crystal, pair distribution, density function theory

1. INTRODUCTION

Many molecular fluids consisting of elongated, rod-like particles exhibit one or more liquid crystalline phases[1] between the isotropic liquid state and the crystalline solid state. The nematic phase, the simplest of all liquid crystalline phases, is characterized by long-range orientational order, i.e., the long molecular axes tend to align along a preferred direction (the director $\vec{n}$).

Two mechanisms that can bring about such alignment have been proposed.[2,3] Maier and Saupe[4] have initiated an approach which ascribes the phenomenon of nematic ordering to the anisotropy of the attractive forces. The intermolecular repulsions are assumed to be isotropic, and serve to provide a positive pressure. This model fails to predict the correct density dependence of the order parameter.[5] At the other extreme, there exists the Onsager theory[6] in which the nematic order results primarily from the short-range highly anisotropic repulsive forces between rod-like molecules (excluded volume effects). The density change is responsible for the transition and so the hard-rods models are athermal. Efforts[7–12] to reconcile the two extreme points of view by incorporating both anisotropic intermolecular repulsions and attractions have also appeared in the liquid-crystal literature as have lattice theories,[7,13] discrete-orientation models[14] and scaled-particle theory.[12] More recently, density-functional theories[15,17] have been extended to the nematic-isotropic transitions[18–26] providing a more general framework from which to construct theories of model nematogens.

Frenkel and co-workers[27] have carried out a number of simulations of hard anisotropic model for liquid crystals, furnishing additional evidence that steric forces alone may account for most liquid-crystalline phases.

Comparatively less is known about the way molecular interactions affect the inhomogeneous surface region of a liquid crystal.[28,29] In this connection there are two phenomena which are closely related but which are not always treated together: the problem of the preferred director orientation and the problem of wetting. A discussion of the connection between these two phenomena is made in Reference 30, in the framework of Landau-de Gennes theory.[1,3] The mechanism of alignment of liquid crystal molecules at various limiting surfaces has received much theoretical attention (the nematic free surface,[31,32] the nematic-isotropic interface[32,33] and the solid substrate-liquid crystal interfaces.[34])

The phenomenon of wetting is concerning with enhanced (or diminished) order near an interface.[28] Order in a liquid crystal depends on direction as well, but in wetting transitions it is the magnitude of the surface order which undergoes a transition. The problem of wetting has received a great deal of both experimental and theoretical attention. Surface birefringence and ellipsometry experiments[35] show the growth of nematic order near the surface of 5CB [(4-pentyl-4′-cyano)biphenyl] as the system approaches the bulk isotropic-nematic transition temperature (T_{IN}). The theory of nematic wetting has been developing in three major directions: the continuum point of view,[36–38] the molecular point of view[39,40] and lattice models.[41,42] Firstly, Sheng[36] used a Landau-de Gennes[1,3] free energy and surface free energy of the form $-GS_0 = -GS(z=0)$. By minimizing the free energy, he has shown that the nematic phase can completely or incompletely wet the surface, depending on the surface ordering field. Secondary, taking a molecular point of view, Telo da Gama has minimized a thermodynamic grand potential of a model with short-range, hard-core repulsions and long-range intermolecular isotropic and anisotropic attractions. She has also found that the nematic phase can completely wet the surface. Thirdly, Luckhurst *et al.*[41] and Pawlowska *et al.*[42] have carried out Monte Carlo simulations and mean-field calculations for a non-uniform lattice nematic model. They found that the nematic phase completely wets the surface when the value of the surface field is sufficiently high.

This paper presents a density-functional theory for non-uniform nematic system. This is a molecular-field theory[2] of the Ramakrishnan-Yussouff type[15] in which the direct pair correlation function (DPCF)[43] plays the role of a two-particle potential. An approximate scheme, which is equivalent to the random-phase approximation (RPA) for the structure factor[43] is proposed to estimate the values of DPCF of the isotropic liquid, required as an input for the theory. This model is solved for a semi-infinite system with a surface field in the case of PAA.

The plan of the remaining part of this paper is as follows. In Sec. 2 the density-functional theory of uniform nematics is presented and in Sec. 3 the extension of the nematic theory to nonuniform systems and the results obtained for PAA are presented. The paper is concluded in Sec. 4.

2. BULK NEMATIC PHASE

The basis for the Ramakrishnan–Yussouff[15,16] density-functional theory is an expansion for the adimensional grand-canonical thermodynamic potential functional W for a nonuniform density $\rho(\vec{r},\hat{\Omega})$ (the average density of molecules at the point $\vec{r}$ with orientation $\hat{\Omega}$),

$$W - W_l = -\int d\vec{r}\int d\hat{\Omega}[\rho(r,\hat{\Omega}) - \rho_l] + \frac{1}{2}\int d\vec{r}_1\int d\hat{\Omega}_1\int d\vec{r}_2\int d\hat{\Omega}_2 \\ \times[\rho(\vec{r}_2,\hat{\Omega}_2) - \rho_l][\rho(\vec{r}_1,\hat{\Omega}_1) + \rho_l]c(\vec{r}_1,\vec{r}_2,\hat{\Omega}_1,\hat{\Omega}_2)\cdots \tag{1}$$

Here W_l is the adimensional grand-canonical potential of the uniform, isotropic liquid of density ρ_l and $c(\vec{r}_1,\vec{r}_2,\hat{\Omega}_1,\hat{\Omega}_2)$ is the DPCF of the isotropic liquid which is given by:

$$c(\vec{r}_1,\vec{r}_2,\hat{\Omega}_1,\hat{\Omega}_2) = -\frac{\delta^2 H}{\delta\rho(\vec{r}_1,\hat{\Omega}_1)\delta\rho(\vec{r}_1,\hat{\Omega}_2)} \tag{2}$$

where H is the excess reduced Helmholtz free energy arising from the interparticle interactions. Translational invariance yields:

$$c(\vec{r}_1,\vec{r}_2,\hat{\Omega}_1,\hat{\Omega}_2) = c(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2) \tag{3}$$

where $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$.

The minimization of $(W - W_l)$ with respect to $\rho(\vec{r},\hat{\Omega})$ leads to

$$\ln\frac{\rho(\vec{r}_1,\hat{\Omega}_1)}{\rho_l} = \int d\vec{r}_2 d\hat{\Omega}_2[\rho(\vec{r}_2,\hat{\Omega}_2) - \rho_l]c(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2) \tag{4}$$

The only input quantity of this theory is the DPCF of the isotropic liquid. The solutions of integral equations[43] are difficult to obtain even in the case of axially symmetric rigid molecules. Another method that can be applied to anisotropic fluids with relative ease is a perturbation scheme.

In developing such a perturbation scheme, one begins by writing the pair potential interaction $U(\vec{r}_1,\hat{\Omega}_1,\vec{r}_2,\hat{\Omega}_2)$ as a sum of two parts: one part of this division is known as a reference potential $U_0(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)$ and the other is the perturbation potential $U_p(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)$, i.e.,

$$U(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2) = U_0(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2) + U_p(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)$$

Here $U_0(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)$ represents the repulsion between hard ellipsoids parametrized by the length-to-width ratio $X_0 = a/b$, where $2a$ and $2b$ denote, respectively, the length of the major axis and minor axis of the ellipsoids

$$U_0(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2) = U_0(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2) = \begin{cases}\infty & \text{for } r_{12} < D(\hat{r}_{12},\hat{\Omega}_{12})\\ 0 & \text{for } r_{12} \geq D(\hat{r}_{12},\hat{\Omega}_{12})\end{cases} \tag{6}$$

$D(\hat{\Omega}_{12})$ is the distance of closest approach of two molecules with relative orientation $\hat{\Omega}_{12}$, which in the Gaussian overlap model[44] has the expression

$$D(\hat{\Omega}_{12}) = 2b\left[1-\chi\frac{(\hat{r}_{12}\cdot\hat{e}_1)^2+(\hat{r}_{12}\cdot\hat{e}_2)^2-2(\hat{r}_{12}\cdot\hat{e}_1)(\hat{r}_{12}\cdot\hat{e}_2)(\hat{e}_1\cdot\hat{e}_2)}{1-\chi^2(\hat{e}_1\cdot\hat{e}_2)^2}\right]^{-1/2} \tag{7}$$

where χ is the eccentricity parameter $\chi = (X_0^2-1)/(X_0^2+1)$, $\hat{r}_{12}$ is a unit vector along the intermolecular axis and $\hat{e}_1$, $\hat{e}_2$ are unit vectors along symmetry axes of two interacting hard ellipsoids.

The $U_p(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2)$ represents the intermolecular attraction and is assumed to have the following form:

$$\begin{aligned} U_p(\vec{r}_1,\hat{\Omega}_1;\vec{r}_2,\hat{\Omega}_2) = U_p(r_{12},\Omega_{12}) = &-V_0'\exp\left[-\left(\frac{r_{12}}{D(\hat{\Omega}_{12})}\right)^2\right] \\ &-V_2'\exp\left[-\left(\frac{r_{12}}{D(\hat{\Omega}_{12})}\right)^2\right]P_2(\cos\theta_{12}) \end{aligned} \tag{8}$$

where V_0' and V_2' are constants related to the isotropic and anisotropic attractive interactions. θ_{12} is the angle between the symmetry axes of the two molecules and P_2 is the second order Legendre polynomial.

In the RPA for the structure factor,[45] the DPCF for the system interacting via a pair potential U is

$$c(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2) = c_0(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2) - \beta U_p(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2) \tag{9}$$

where $c_0(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2)$ is the DPCF for the reference system. Using the decoupling approximation[19,21]

$$c_0(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2) = c_0(r_{12}/D(\hat{\Omega}_{12})) = c_0(r) \tag{10}$$

and fitting the compressibility factor $\partial(\beta p)/\partial\rho$ with Carnahan–Starling[46] expression, one obtains

$$\begin{aligned} \frac{\partial(\beta p)}{\partial\rho} &= 1-\rho\int d\vec{r}_{12}d\hat{\Omega}_1 d\hat{\Omega}_2 c_0(\vec{r}_{12},\hat{\Omega}_1,\hat{\Omega}_2) \\ &= 1-24\eta F_1(\chi)I(\eta) \end{aligned} \tag{11}$$

where $\eta = \rho v_0$, $v_0 = 4\pi/3b^2a$; $F_1(\chi) = 1/2\cdot[1+(\arcsin\chi)/(\chi(1-\chi^2)^{1/2})]$ and

$$I(\eta) = \int_0^\infty dr\, r^2 c_0(r;\eta) = \frac{\eta-4}{12(1-\eta)^4} \tag{12}$$

In writing (11), use has been made of the excluded volume

$$V_{exc} = \frac{1}{3}\int d\hat{\Omega}_{12}D^3(\hat{r}_{12},\hat{\Omega}_{12}) = 8v_0(1-\chi^2)^{-1/2}(1-\chi^2\cos^2\theta_{12})^{1/2} \tag{13}$$

Since at constant pressure, the isotropic-nematic transition is accompanied by change in density, the following expression for singlet distribution is used

$$\rho(\vec{r},\hat{\Omega}) = \rho_l[\Delta\rho + f(\hat{\Omega})] \tag{14}$$

where $\Delta\rho = (\rho_n - \rho_l)/\rho_l$ is the fractional change in density due to constant pressure transition, ρ_n is the mean number density of the nematic phase, and $f(\hat{\Omega})$ is the orientational single distribution truncated at the second term:

$$f(\hat{\Omega}) = f(\cos\theta) = f(m) = 1 + 5SP_2(m) \tag{15}$$

where S is the orientational order parameter.

When (8)–(15) are substituted in (1) and (4) we get[26]

$$\begin{aligned}
&-\Delta\rho + \tfrac{1}{2}\Delta\rho(2+\Delta\rho)f_1(\chi,\eta) + S^2F_2(\chi,\eta) = 0\\
&1+\Delta\rho = \exp[\Delta\rho f_1(\chi,\eta)]\int_0^1 dm\,\exp[Sf_2(\chi,\eta)P_2(m)]\\
&S = \exp[\Delta\rho f_1(\chi,\eta)]\int_0^1 dm P_2(m)\exp[Sf_2(\chi,\eta)P_2(m)]
\end{aligned} \tag{16}$$

where

$$f_1(\chi,\eta) = \frac{2\eta^2 - 8\eta}{(1-\eta)^4} + \eta\frac{V_0}{T}F_1(\chi) - \eta\frac{V_2}{T}F'_1(\chi)$$

$$f_2(\chi,\eta) = \frac{8\eta - 2\eta^2}{(1-\eta)^4} - \eta\frac{V_0}{T}F_2(\chi) + \eta\frac{V_2}{T}F'_2(\chi)$$

with

$$F_2(\chi) = \tfrac{1}{3}\chi^2(1-\chi^2)^{-1/2}(1 + \tfrac{3}{14}\chi^2 + \tfrac{5}{56}\chi^4 + \tfrac{25}{528}\chi^6)$$

$$F'_1(\chi) = -\tfrac{1}{5}F_2(\chi)$$

$$F'_2(\chi) = (1-\chi^2)^{-1/2}(1 - \tfrac{11}{21}\chi^2 - \tfrac{3}{56}\chi^4 - \tfrac{85}{3696}\chi^6)$$

$V_i = V'_i/k$ $(i = 0, 2)$; k-Boltzmann's constant.

The molecular volume v_0 for PAA was taken to be[47] 230 Å^3. At a constant pressure of one atmosphere, the isotropic-nematic transition temperature for PAA is 408 K, and so $\beta p/\rho = 0.00414$. The interaction constants V_0 and V_2 were chosen so as to reproduce the isotropic-nematic transition temperature ($T_{IN} = 408$ K) and the parameter of Alben,[7] which for PAA[5] is $\gamma = 4$. So, the equations for V_0 and V_2 are the following

$$\beta p v_0 = \eta + \left[\frac{4\eta^2 - 2\eta^3}{(1-\eta)^3} - \frac{1}{2}\eta^2\frac{V_0}{T}\right]F_1(\chi) + \frac{1}{2}\eta^2\frac{V_2}{T}F'_1(\chi) = 0.00414 \tag{17}$$

$$\frac{\eta}{T}\left(\frac{\partial T}{\partial\eta}\right)_S = \frac{(8 + 20\eta - 4\eta)^2F_2(\chi)}{(1-\eta)^5\left[\frac{V_2}{T}F'_2(\chi) - \frac{V_0}{T}F_2(\chi)\right]} - 1 = 4$$

Thus, we get[26]:

$$f_1(\chi,\eta)=\frac{2\eta^2-8\eta}{(1-\eta)^4}F_1(\chi)+\frac{8\eta-4\eta^2}{(1-\eta)^3}F_1(\chi)-\frac{0.00828}{\eta}$$

$$f_2(\chi,\eta)=\frac{8\eta-2\eta^2}{(1-\eta)^4}F_2(\chi)+\frac{4\eta}{3}\frac{2+5\eta-\eta^2}{(1-\eta)^5}F_2(\chi) \qquad (18)$$

Extensive numerical calculations of this model are published elsewhere.[26] Here we give only the transition properties of the model with $V_0=39362\,\mathrm{K}$, $V_2=2430\,\mathrm{K}$ and $X_0=1.163$ ($\chi=0.15$): $S_C=0.4357$; $\eta_C=0.6093$; $\Delta\rho_C=0.0036$. The corresponding experimental results for PAA are: $S_C=0.4$; $\eta_C=0.62$; $\Delta\rho_C=0.0035$. The agreement is very good with one exception; $X_0=1.163$ while for PAA, $X_0\approx 4$. This fact can be explained by the neglect of the experimentally established flexibility of molecules.[26]

3. NON-UNIFORM NEMATIC

The density-functional theory described in Sec. 2 can be extended to non-uniform nematic systems. In general, the surface behaviour of the nematic is different from the bulk behaviour. This may be because the order parameter is enhanced near the wall, sometimes sufficiently so to cause the growth of a wetting layer of nematic (above T_{IN}) between the isotropic phase and the wall. Under other circumstances the order parameter is reduced near the wall, and the reduction may be sufficient to cause an isotropic wetting layer between the nematic phase and the wall, below T_{IN}. The growth of wetting layers near T_{IN} is governed by the competition between the surface interaction and the energy of the nematic-isotropic interface.[35]

For simplicity the surface is considered flat and the system is semi-infinite. One takes $z=0$ to be the position of the centers of mass of the molecules right at the surface, with z increasing into the bulk.

To model the effects of the surface, we suppose that it induces an external potential of the form:

$$U^e(z,\cos\theta)=-V'_{S_1}\exp\left[-\left(\frac{z}{D(\hat{\Omega}_{12})}\right)^2\right]-V'_{S_2}\exp\left[-\left(\frac{z}{D(\hat{\Omega}_{12})}\right)^2\right]P_2(\cos\theta) \qquad (19)$$

The first term in (19) favours the growth of a isotropic phase (below T_{IN}) near the wall and the second term causes the growth of a nematic phase (above T_{IN}) between the isotropic phase and the wall.

We consider that the surface does not affect the excluded volume. This effect is not important in studying the wetting layers but it becomes essential in studying the orientation of liquid crystal molecules.

With this external potential, using (8)–(15), the minimum grand-canonical potential occurs when (see eq. (4)):

$$1+\Delta\rho(z)=\frac{V_{S_1}}{T}\exp(-z^2)+\exp[\Delta\rho(z)f_1(\chi,\eta)]\int_0^1 dm\exp[S(z)f_2(\chi,\eta)P_2(m)]$$

$$S(z)=\frac{V_{S_2}}{T}\exp(-z^2)+\exp[\Delta\rho(z)f_1(\chi,\eta)]\int_0^1 dmP_2(m)\exp[S(z)f_2(\chi,\eta)P_2(m)] \tag{20}$$

where z is expressed in $D(\hat{\Omega}_{12})$ units. One attempts to find solutions of $\Delta\rho(z)$ and $S(z)$ for (20). To do so, we *discretize* z into a fine lattice of points z_i with spacing 0.1D.

We first consider the case where $z=0$. In this case one obtains the behaviour of the PAA sample near the wall. The isotropic-anisotropic attraction of the wall (i.e., V_{S_1}, V_{S_2}) phase diagram for PAA at $T=T_{IN}=408$ K is plotted in Figure 1. In region I the isotropic phase wets the wall, while in region II the nematic phase wets the wall. There is a first-order wetting transition. A qualitative difference emerges between this result of this theory and the continuum theory.[38] There is no prewetting transition for the values of V_{S_1} and V_{S_2} plotted in Figure 1. Thus, the wetting transition is located as a function of the strengths of the isotropic and anisotropic attraction of the wall. The "propagation" of the transition curve with temperature is shown in Figure 2. For constant V_{S_2}, with increasing temperature, the isotropic phase wets the wall to greater values of V_{S_1}. The

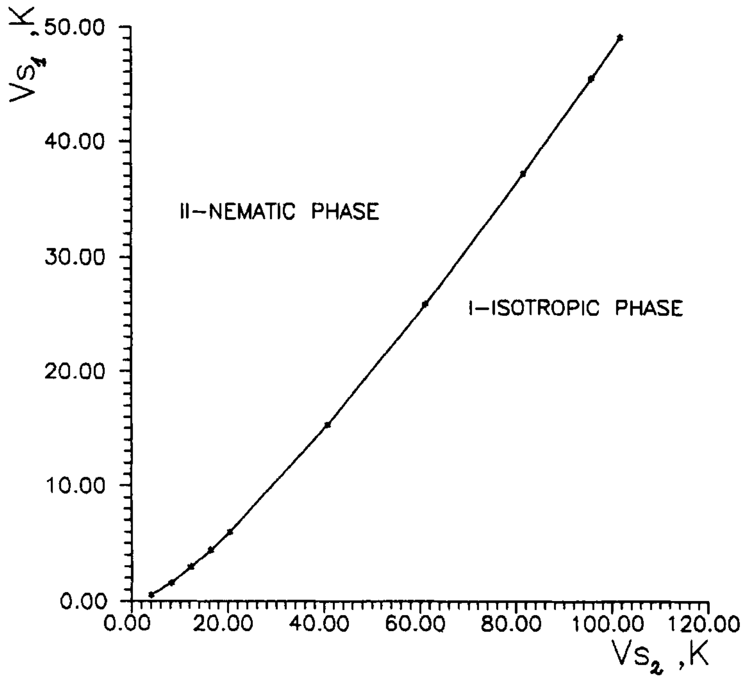

FIGURE 1 The (V_{S_1}, V_{S_2}) phase diagram for PAA at $T=T_{IN}=408$ K.

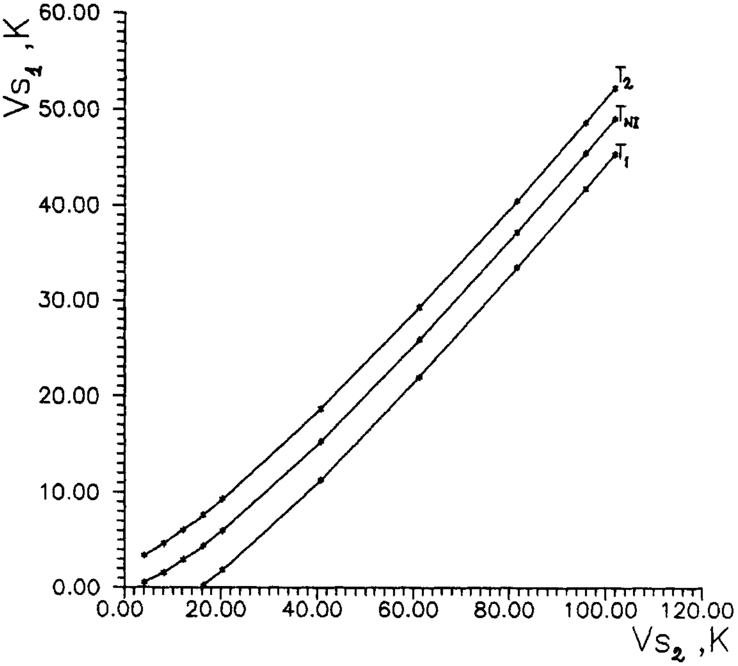

FIGURE 2 The (V_{S_1}, V_{S_2}) phase diagram for PAA at $T_1 = 403.92$ K, $T_{NI} = 408$ K and $T_2 = 412.08$ K.

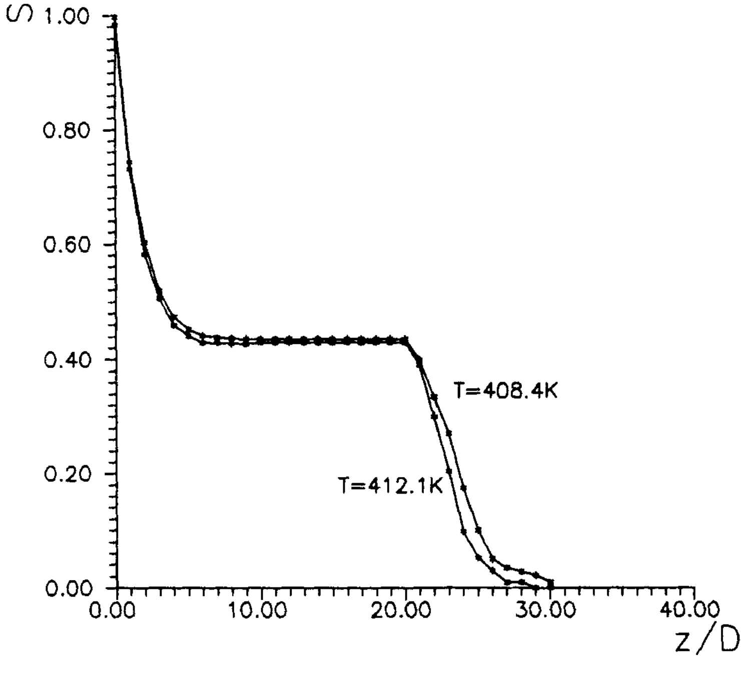

FIGURE 3 Profiles of $S(z)$ for $V_{S_1} = 95.88$ K at $T_1 = 408.4$ K and $T_2 = 412.1$ K ($V_{S_2} = 0$).

variation of the order parameter S as a function of distance z/D away from the surface is plotted in Figure 3, for two different temperatures $T_1 = 408.4$ K and $T_2 = 412.1$ K. Because of the surface field $S(z = 0)$ is almost saturated at 1. Away from the surface $S(z)$ quickly decays to a value close to the bulk nematic value. It stays there for a long distance and then decays to the bulk isotropic value of 0.

4. CONCLUSIONS

The density-wave theory of Ramakrishnan and Yussouff[15,16] has been used to formulate an approximate theory of the isotropic-nematic transition. The direct pair correlation function is expressed in terms of the random-phase approximation perturbative scheme, in which the reference system is one of hard ellipsoids of revolution. The mathematical implementation of the theory has been kept as simple as possible by resorting to a one-order-parameter angular distribution (15) in order to minimize the grand-canonical thermodynamic potential. Further simplifications are provided by using an approximate analytic form of the pair excluded volume (13) together with the Carnahan–Starling[46] compressibility equation and with the decoupling approximation (10). This approximation firstly suggested by Pynn[48] decouples the orientational and positional degrees of freedom. The main drawback of Pynn's model is that it predicts an isotropic DPCF at the origin and at contact, which is unphysical.[21,49] The results of the theory reproduce well the thermodynamic properties of the isotropic-nematic phase transition (see also References 25 and 26) except for the length to width ratio for the PAA molecule. This is so because of the assumption that the molecules are rigid is not realistic. Further, the Carnahan–Starling equation describes a fluid of hard spheres and breaks down at $\eta = 0.5$ when the fluid solidifies, whereas long, non-spherical molecules solidify at higher densities. It may therefore be coincidental that Carnahan–Starling equation can be used at higher η.

We than applied this model to the growth of nematic wetting layers near surfaces. The surface induces an external potential of the form (19) with two attractive terms so the wetting transition is the result of the competition between the strengths of the isotropic (V_{S_1}) and anisotropic (V_{S_2}) attraction of the wall. The drawback of this model is that it does not predict a prewetting transition.

It were interesting to use this model to study the smectic A order induced by a free surface in the isotropic phase of compounds that have direct transitions from isotropic to smectic A phases.[21]

In conclusion, with the main hypothesis of this model (the short-range anisotropic intermolecular repulsions play a major role in stabilizing the nematic phase) we can satisfactory describe, at least qualitatively, the wetting transitions in nematics (see also Reference 25).

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