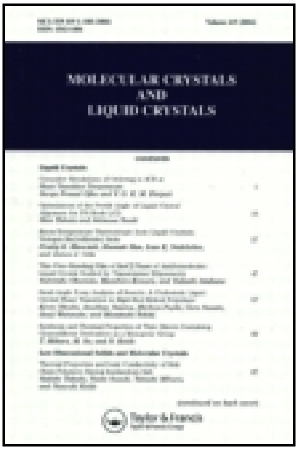

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Hard Ellipsoids in an Anisotropic Mean Field: Surface Effects on the Isotropic-Nematic Phase Transition

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Hard Ellipsoids in an Anisotropic Mean Field: Surface Effects on the Isotropic-Nematic Phase Transition

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The surface effects on the isotropic-nematic phase transition are analyzed using a functional form of the surface energy which contains two terms: one linear term in the order parameter and the second proportional to the square of the order parameter. The first-order nematic-paranematic phase transition is found to take place only in limited ranges of substrate potential strengths. This transition is examined for p-azoxy-anisole (PAA) in the framework of "the hard ellipsoids in an anisotropic mean field" model.

Keywords: nematic liquid crystal, pair distribution

1. INTRODUCTION

Liquid crystals constitute a state of matter that is intermediate in symmetry between isotropic liquid phases, which are rotationally and translationally invariant, and ordered solid phases with full crystalline symmetry. Nematic mesophases are the simplest of all liquid crystalline phases. In the bulk region of a nematic liquid crystal the molecular centers of gravity are disordered as in a liquid, but the long organic molecules tend to align parallel to one another along a direction specified by a unit vector **n** (the director). The degree of ordering is given by an orientational order parameter[1] S such that $0 \leq S \leq 1$. $S = 1$ refers to perfect order and $S = 0$ is for an isotropic liquid with no long-range orientational order. If there are no applied fields, the nematic phase has complete rotational symmetry and all orientations of the director **n** are equivalent.

The behaviour of nematic liquid crystals near an interface is very different from the bulk behaviour, because the properties of nematics are very sensitive to boundary conditions. Even a weak interaction with a boundary surface can change the structure of a nematic in the layer adjacent to that surface. The effect of boundaries on the properties, more precisely, on the surface alignment, of nematics has been widely used to obtain the desired director configurations in liquid-crystal cells made for display or measurement purposes. Due to the these practical applications it is not surprising that the problem of nematic liquid crystal surfaces has received both experimental and theoretical attention.[2] This study has been developing in two major directions. One of these is the study of the mechanism of alignment of nematic molecules at various boundary surfaces. One such surface is the nematic free surface. The experimental results[3,4] show that the preferred orientation of the nematic director at this surface is, in almost all cases, normal to the surface, expecially for temperatures close to the bulk first-order isotropic to nematic transition temperature (T_{IN}). But, in the case of the nematic-isotropic interface, the director is usually tilted with respect to the normal and the tilt angle is in the range of 50°–70°.[5,6] The theoretical results[7-9] show that anisotropic hard-core interactions favour perpendicular alignment of molecules at the nematic free surface and a tilted director at the nematic-isotropic interface. Numerous experiments have been performed to study solid substrate-liquid crystal interfaces.[10-16] The substrates have been treated by special techniques[2] such as chemical etching, adsorption of organic surfactant additives, rubbing, oblique evaporation or coating with lecithin. Poniewierski and Holyst[17] studying the Onsager model of a nematogen, found that the preferred orientation of the nematic director is parallel to the wall. However, regardless of the technique, the surface alignment always produces an enhancement of the order parameter near the wall that is sometimes sufficient to cause the growth of a wetting layer of nematic or smectic above T_{IN} between the isotropic phase and the wall. Thus, the second direction is the study of this phenomenon, known as wetting. It has attracted a great deal of recent experimental and theoretical interest. Several experiments[2,15,18] have used surface birefringence and ellipsometry to study the growth of nematic order near the surface of pentylcyanobiphenyl (5CB) as the system approaches T_{IN}. These experiments have shown that the surface induces perpendicular alignment of the director near the wall that penetrates into the bulk, and that the penetration length diverges logarithmically as $T \rightarrow T_{IN}$.

The theory of these orientational wetting transitions has been developing in three directions: Landau-de Gennes theories,[19,20] molecular continuum theories[21-23] and lattice models.[24,25] First, Sheng[19] wrote the Landau-de Gennes free energy as a functional of the nematic order parameter profile $S(z)$. By minimizing the free energy, he found that the nematic phase can completely or incompletely wet the surface, depending on the surface ordering field, and that there can be a special surface prewetting transition before complete wetting. Second, Telo de Gama[21] minimized the thermodynamic grand potential of a model with short-range hard-sphere repulsions and long-range intermolecular isotropic and anisotropic attractions. She also found that the nematic phase can completely wet the surface. Third, Luckhurst *et al.*[24] and Pawlowska *et al.*[25] have done Monte Carlo simulations and mean-field calculations for a nonuniform lattice nematic model without and with an aligning field at the surface. They found that the nematic phase completely wets the surface at high enough value of the surface field.

In this paper we present a study of the wetting transitions in nematics in the framework of the "hard ellipsoids in an anisotropic mean field" model. In this model, presented in Section 2, the short-range intermolecular repulsions are represented by repulsions between hard ellipsoids and the anisotropic intermolecular attractions are treated in the mean field approximation. For the pure repulsive system we use the uniform liquid as a reference system.[26-32] For a nonuniform system (liquid-vapor interface,[26] uniform solid,[27] solid-liquid interface,[28] liquid crystal[29-32]) the grand-canonical thermodynamic potential may be represented as a functional series of the single-particle density distribution. A functional series expansion may be related to the direct correlation function of the liquid. Numerical calculations are reported and compared with experimental data for p-azoxyanisole (PAA). Its application to the orientational wetting transitions in nematics is described in Section 3. In Section 4 some conclusions of the paper are drawn.

2. HARD ELLIPSOIDS IN AN ANISOTROPIC MEAN FIELD

The grand-canonical thermodynamic potential difference between the ordered state with single distribution function $\rho(x) = \rho(\mathbf{r}, \Omega)$ and the isotropic phase with number density ρ_0 is[26-32] (note that W is defined with the same sign convention as in Reference 26 and 29):

$$-\Delta W = -\int dx \delta\rho(x) + \frac{1}{2}\iint dx_1\, dx_2 \delta\rho(x_2)[\rho(x_1) + \rho_0]c(x_1, x_2; \rho_0) \qquad (1)$$

where $\delta\rho(x_i) = \rho(x_i) - \rho_0$ and $c(x_1, x_2; \rho_0)$ is the direct correlation function (DCF) of the isotropic phase.

In the grand canonical ensemble we can obtain also another nonlinear equation which relates the single-particle distribution function $\rho(x)$ of the ordered phase to the DCF of the coexisting isotropic liquid:

$$\ln \frac{\rho(x_1)}{\rho_0} = \int dx_2 \delta\rho(x_2) c(x_1, x_2; \rho_0) \qquad (2)$$

One attempts to find solution $\rho(x)$ of (2) which have the symmetry of the nematic phase. These solutions inserted in (1) give the grand potential difference between the nematic and isotropic liquid phases. The phase with the lowest grand potential is the stable one. Phase coexistence occurs when $-\Delta W = 0$. The only input quantity of this theory is the DCF of the isotropic liquid.

We assume (in the spirit of the perturbation theories of simple liquids[33,34]) that the detailed structure of a nematic liquid crystal is determined primarily by short-ranged intermolecular repulsions (which may be approximated by hard-ellipsoid repulsions), while the role of the long-ranged intermolecular attractions is, to a first approximation, merely to provide a spatially uniform mean field in which the molecules move.[35,36]

The pure repulsive system is composed of hard ellipsoids of revolution parametrized by the length-to width ratio $X_0 = a/b$ where a and b denote the lengths of major and minor semi-axes of the ellipsoids. The potential energy of interaction of a pair of hard ellipsoids of revolution is represented as

$$U(r_{12}, \Omega_1, \Omega_2) = \begin{cases} \infty & \text{for} \quad r_{12} < D(\hat{r}_{12}, \Omega_{12}) \\ 0 & \text{for} \quad r_{12} \geq D(\hat{r}_{12}, \Omega_{12}) \end{cases} \tag{3}$$

where $D(\hat{r}_{12}, \Omega_{12})$ is the distance of closest approach of two molecules. For $D(\hat{r}_{12}, \Omega_{12})$ we use the expression given by the Gaussian overlap model,[37]

$$D(\hat{r}_{12}, \Omega_{12}) = 2b$$

$$\left[1 - \chi \frac{(\hat{r}_{12}\cdot\hat{e}_1)^2 + (\hat{r}_{12}\cdot\hat{e}_2)^2 - 2(\hat{r}_{12}\cdot e_1)(\hat{r}_{12}\cdot\hat{e}_2)(\hat{e}_1\cdot\hat{e}_2)}{1 - \chi^2(\hat{e}_1\cdot\hat{e}_2)^2}\right]^{-1/2} \tag{4}$$

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

Because of the translational invariance in the isotropic phase, the DCF depends only on the relative distance vector $\mathbf{r}_{12}$, i.e.,

$$c(x_1, x_2, \rho_0) = c(\mathbf{r}_{12}, \Omega_1, \Omega_2; \rho_0) \tag{5}$$

We approximate the DCF for this system by

$$c(\mathbf{r}_{12}, \Omega_1, \Omega_2) = c(\mathbf{r}_{12}/D(\hat{r}_{12}, \Omega_{12})) = c(r) \tag{6}$$

This approximation[30,32] decouples the orientational and positional degrees of freedom. It is exact at very low density but cannot be exact at liquid density.

With this "decoupling" approximation the Carnahan-Starling[33] compressibility is

$$\frac{\partial(\beta p)}{\delta\rho} = 1 - \rho \int d\mathbf{r}_{12}\, d\Omega_1\, d\Omega_2 c(\mathbf{r}, \Omega_1, \Omega_2) = 1 - 24\eta F_1(\chi) I(\eta) \tag{7}$$

where $\eta = \rho v_0$, $v_0 = (4\pi/3)b^2a$ is the molecular volume and

$$\begin{aligned} F_1(\chi) &= (1 - \chi^2)^{-1/2}\left(1 - \frac{1}{6}\chi^2 - \frac{1}{40}\chi^4 - \frac{1}{112}\chi^6\right) \\ I(\eta) &= \int_0^\infty dr\cdot r^2 c(r; \eta) = \frac{\eta - 4}{12(1 - \eta)^4} \end{aligned} \tag{8}$$

In writing equations (7) use has been made of the excluded volume,[38]

$$V_{\text{exc}} = \frac{1}{3}\int d\mathbf{r}_{12} D^3(\mathbf{r}_{12}, \Omega_{12}) = 8v_0(1 - \chi^2)^{-1/2}(1 - \chi^2\cos^2\theta_{12})^{1/2} \tag{9}$$

For this system we have determined the constant volume and constant pressure isotropic-nematic transition properties.[39] The main deficiency of this model is that the system is athermal. But it constitutes a simple reference system for the investigation of more realistic systems by considering the intermolecular attractions.

The expression for the total attractive interaction energy is[35,40]

$$\overline{U_a} = -\tfrac{1}{2}N\rho(V_0' + SV_2') \tag{10}$$

N being the number of molecules.

For a uniaxial nematic phase with cylindrically symmetric molecules the singlet distribution function is[30]

$$\rho(r, \Omega) = \rho_0[\Delta\rho + f(\Omega)] \tag{11}$$

where $\Delta\rho = (\rho_n - \rho_0)/\rho_0$ is the fractional density change due to the constant pressure transition, ρ_n is the mean number density of the nematic phase and ρ_0 is the number density of the isotropic liquid. $f(\Omega)$ is the orientational singlet distribution function normalized to unity. A completely general parametrization of $f(\Omega)$ is provided by

$$f(\Omega) = f(w) = 1 + \sum_{L\geq 2} (2L + 1)\overline{P_L}P_L(w); \quad w = \cos\theta \tag{12}$$

where $P_L(w)$ are the Legendre polynomials and

$$\overline{P_L} = \frac{1}{2\rho_0}\int d\theta \sin\theta\rho(r, \Omega)P_L \cos\theta) \tag{13}$$

is the orientational order parameter of the nematic phase. Note that this expression has the disadvantage that the positivity of $f(\Omega)$ cannot be guaranteed a priori once the series (12) is truncated. Here, our purpose however is not to determine $f(\Omega)$ accurately but instead to use $f(\Omega)$ in the expressions (1) and (2) where many of the detailed features of $f(\Omega)$ are integrated out. For the present purpose it will therefore be sufficient to approximate (12) by

$$f(w) = 1 + 5SP_2(w); \quad S = \overline{P_2} \tag{14}$$

Using the "decoupling" approximation (6), with the total attractive energy (10), equations (1) and (2) become

$$\begin{aligned}
-\frac{\Delta W}{N} &= -\Delta\rho + \frac{1}{2}\Delta\rho(2 + \Delta\rho)c_{2,0} + \frac{1}{2}S^2\left(c_{2,2} + \eta\frac{V_2}{T}\right) = 0 \\
\frac{\beta_p}{\rho} &= 1 + \frac{4\eta - 2\eta^2}{(1 - \eta)^3}F_1(\chi) - \frac{1}{2}\eta\frac{V_0}{T} \\
S &= \exp(\Delta\rho c_{2,0})\int_0^1 dw\, P_2(w)\exp\left[S\left(c_{2,2} + \eta\frac{V_2}{T}\right)P_2(w)\right] \\
1 + \Delta\rho &= \exp(\Delta\rho c_{2,0})\int_0^1 dw \exp\left[S\left(c_{2,2} + \frac{V_2}{T}\right)P_2(w)\right]
\end{aligned} \tag{15}$$

where

$$V_i = \frac{V_i'}{kV_0}; \quad i = 0, 2;$$

k is the Boltzmann's constant

$$c_{2,0} = \frac{-8\eta + 2\eta^2}{(1 - \eta)^4} F_1(\chi) \qquad c_{2,2} = \frac{8\eta - 2\eta^2}{(1 - \eta)^4} F_2(\chi)$$

$$F_2(\chi) = \frac{1}{3}\chi^2(1 - \chi^2)^{-1/2}\left(1 + \frac{3}{14}\chi^2 + \frac{5}{56}\chi^4\right)$$

and $P_2(w) = \frac{1}{2}(3w^2 - 1)$ is the second-order Legendre polynomial.

The interaction constants V_0 and V_2 are chosen so as to reproduce the nematic-isotropic transition temperature for PAA($T_{IN} = 408$ K) and the parameter $\gamma(T_{IN}) = 4$. The parameter γ, first introduced by Alben[41] measures the relative sensitivity of the order parameter to density changes (at constant T) versus temperature changes (at constant ρ)

$$\gamma = \frac{V}{T}\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V} = \left(\frac{\partial \ln T}{\partial \ln \eta}\right)_S \tag{16}$$

For PAA, the experimental value[42] of γ is 4. The properties of this model with $V_0 = 30437.94$ K, $V_2 = 2184.62$ K and $X_0 = 1.225$ ($\chi = 0.2$) are given and compared with experimental data for PAA in Table I.

3. SURFACE EFFECTS ON THE NEMATIC-ISOTROPIC PHASE TRANSITION

Consider a sample of nematic liquid crystal bounded on one side by a solid substrate. The solid-liquid-crystal interface is defined as $z = 0$, and the sample is assumed

TABLE I

Comparison of the nematic-isotropic phase transition in PAA and in the model

Quantity	Theoretical value	PAA-exp
T_{IN}	408 K	408 K[42]
S_c	0.4419	0.40[43]
η_c	0.568	0.62[44]
$\Delta\rho$	0.0039	0.0035[45]
$\Delta\Sigma/Nk$	0.443	0.218[40]
$\gamma(T_{IN})$	4.0	4[42]
dT_{IN}/dp	138.2 K/kb	43 K/kb[45]

S_C is the order parameter in the nematic phase at T_{IN}, $\eta_C = \rho_n v_0$; $\Delta\Sigma/Nk$ is the entropy difference between the two phases.

to be uniform in the x and y directions. The total grand potential (per unit area) of the nematic sample is

$$\Phi[\{S(z)\}] = \int_0^\infty dz \left[f(S) + L \left(\frac{dS}{dz} \right)^2 \right] - G_1 S_0 - \frac{1}{2} G_2 S_0^2, \tag{17}$$

where S_0 denotes the value of S at $z = 0, f(S)$ is the grand thermodynamic potential per particle; i.e.,

$$f(S) = \frac{1}{\beta} \rho w(S) = -\frac{1}{\beta} \rho \frac{W}{N}; \quad \beta = \frac{1}{kT} \tag{18}$$

with

$$w(S, \Delta\rho) = -\Delta\rho + \frac{1}{2} \Delta\rho(2 + \Delta\rho)c_{2,0} + \frac{1}{2} S^2 \left(c_{2,2} + \eta \frac{V_2}{T} \right) \tag{19}$$

G_1 and G_2 are the surface contributions to Φ coming from the interaction between the nematic and the substrate[46] and $L = \frac{3}{2} L_1 + \frac{1}{2} L_2$ is an average elastic constant.

Minimizing variationally the functional (17) with respect to $S(z)$ one finally obtains[19]

$$\xi_0^2 \left(\frac{dS}{dz} \right)^2 = w(S) - w(S_b) \tag{20}$$

where $\xi_0 = (\beta L/\rho)^{1/2}$ is a correlation length of the order of molecular dimensions and S_b is the bulk value of the order parameter. The orientationally-dependent (boundary layer) part of the grand thermodynamic potential (or surface tension) is obtained from (17) using Equation (20):

$$\frac{\beta \Phi_{\mathrm{BL}}}{\rho \xi_0} = 2 \int_{S_b}^{S_0} \sqrt{w(S) - w(S_b)}\, dS - g_1 S_0 - \frac{1}{2} g_2 S_0^2 \tag{21}$$

where $g_i = \beta G_i/\xi_0 \rho$ ($i = 1, 2$) are the dimensionless parameters characterizing the substrate potential. The equilibrium value of S_0 is determined by the condition $d\Phi_{\mathrm{BL}}/dS_0 = 0$, i.e.,

$$w(S_0) = w(S_b) + \tfrac{1}{4}(g_1 + g_2 S_0)^2 \tag{22}$$

We first consider the case $g_2 = 0$. In Figure 1 we show the calculated results for S_0 for the nematic liquid crystal p-azoxyanisole (PAA). For $g_1 < 0.08$, S_0 exhibits a discontinuous transition in its value at the bulk-transition temperature T_{IN}. For $0.08 < g_1 < g_{1c} = 0.134$ the transition in S_0 occurs at a temperature higher than T_{IN}. For $g_1 > g_{1c}$, the discontinuous transition disappears and S_0 becomes a con-

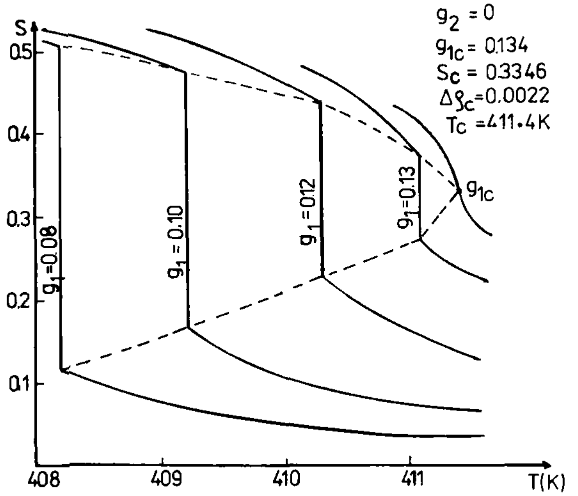

FIGURE 1 The PAA order-parameter value at the substrate-nematic interface plotted as a function of temperature. The value of the substrate potential parameter g_1 is given beside each curve. $g_2 = 0$ for all the curves.

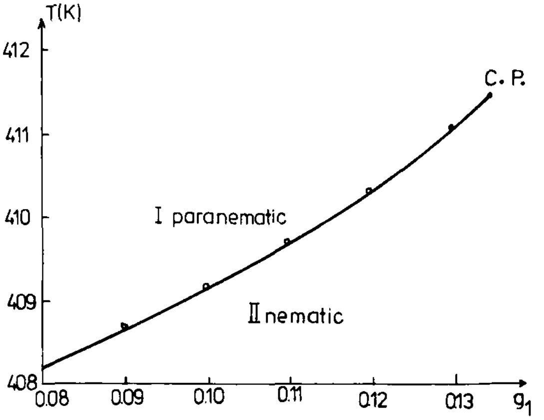

FIGURE 2 The substrate potential parameter g_1-temperature phase diagram for $g_2 = 0$.

tinuous function of temperature. For $g_1 < g_{1c}$ we have a first-order boundary layer phase transition in S_0 that possesses a critical point (T_c, g_{1c}) at which it becomes second order. This critical value g_{1c} is a very dependent model; e.g., Sheng[19] obtains $g_{1c} = 0.012$.

Figure 2 shows the one substrate potential parameter g_1-temperature phase diagram for a semi-infinite PAA sample. In region I the paranematic phase wets the wall, while in region II the nematic phase wets the wall.

The results using two substrate potential parameters are given in Figure 3 and Table II. In Figure 3 we present the substrate potential parameter g_2-temperature phase diagram at $g_1 = 0.10$. For this value of g_1, we obtain $g_{2c} = 0.240$. From Table II we see that the effect of increasing g_2 is to increase the transition tem-

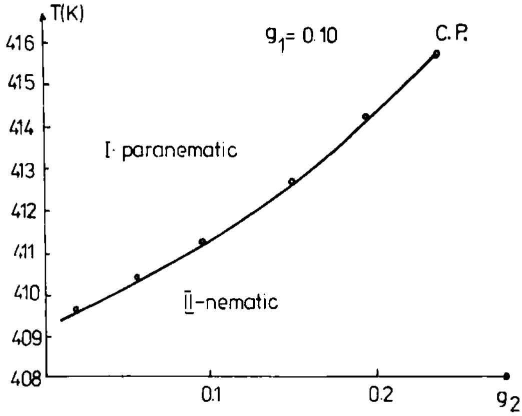

FIGURE 3 The substrate potential parameter g_2-temperature phase diagram for $g_1 = 0.10$.

TABLE II

The results using two substrate potential parameters

g_1	g_2	T_c(K)	S_0	$\delta\rho_0$	S'_0	$\Delta\rho'_0$	ΔS
0.08	0	408.2	0.5051	0.0051	0.1152	0.0003	0.3898
	0.01	408.4	0.5019	0.0051	0.1169	0.0003	0.3851
	0.02	408.6	0.4990	0.0050	0.1185	0.0003	0.3805
	0.10	409.8	0.4956	0.0049	0.1367	0.0004	0.3589
	0.20	412.2	0.4713	0.0044	0.1630	0.0005	0.3084
	0.30	415.4	0.4395	0.0038	0.1996	0.0008	0.2399
	0.411 (g_{2c})	420.0	0.2927	0.0017	0.2927	0.0017	0
0.10	0	409.2	0.4756	0.0046	0.1152	0.0005	0.3151
	0.01	409.4	0.4735	0.0045	0.1622	0.0005	0.3113
	0.02	409.6	0.4719	0.0045	0.1655	0.0005	0.3064
	0.10	411.2	0.4525	0.0041	0.1972	0.0008	0.2553
	0.20	414.1	0.4033	0.0032	0.2650	0.0014	0.1382
	0.240 (g_{2c})	415.6	0.3060	0.0018	0.3060	0.0018	0
0.12	0	410.3	0.4395	0.0039	0.2273	0.0040	0.2122
	0.01	410.5	0.3292	0.0039	0.2362	0.0011	0.2030
	0.02	410.7	0.4334	0.0038	0.2432	0.0012	0.1902
	0.09 (g_{2c})	412.7	0.3215	0.0020	0.3215	0.0020	0
0.13	0	411.1	0.3755	0.0028	0.2713	0.0015	0.1042
	0.01	411.3	0.3771	0.0028	0.2991	0.0018	0.0781
	0.02 (g_{2c})	411.6	0.3381	0.0023	0.3381	0.0023	0
0.134 (g_{1c})	0	411.4	0.3346	0.0022	0.3346	0.0022	0

T_c is the nematic-paranematic transition temperature, ΔS is the difference between the order parameters of the nematic phase S_0 and paranematic phase S'_0, $\Delta\rho_0 = (\rho_n - \rho_0)/\rho_0$ and $\Delta\rho'_0 = (\rho_p - \rho_0)/\rho_0$ where $\rho_n(\rho_p)$ is the nematic (paranematic) density and ρ_0 is the isotropic phase density.

perature and decrease the difference between the order parameters of the nematic and paranematic phases.

4. CONCLUSIONS

In this paper we presented a model for a nematic liquid crystal in which the short-range intermolecular repulsions are represented by repulsions between hard ellipsoids of revolution and the intermolecular attractions are treated in the mean field approximation. The mathematical implementation of the theory has been kept as simple as possible by resorting to a one-order-parameter angular distribution in order to minimize the grand-canonical thermodynamic potential. Further simplifications are provided by using an approximate analytic form for the pair excluded volume[38] together with the Carnahan-Starling compressibility equation. The results of this model were compared with experimental data for PAA. The model reproduces well the thermodynamic properties of the nematic-isotropic phase transition excepting the length to width ratio for the PAA molecule. This is so because the assumption that the molecules are rigid is not realistic.

We then applied this model to the orientational wetting transitions in nematics. We wrote the total grand thermodynamic potential (Equation (17)) adding two terms for the surface contribution. It must be noted that the inclusion in Φ of the term $\frac{1}{2}L(dS/dz)^2$ means that a part of the surface energy has been taken into account, because, even in the case in which the director is fixed on the surface (strong anchoring), a surface energy exists, due to the S variation. Our hypothesis that the surface terms can be of the form (17) is supported by experimental data.[20] The model encompasses wetting by both the paranematic and nematic phases for certain values of g_1 and g_2. Also, for some values of g_1 and g_2, there is a first-order transition between the nematic and paranematic phases (called the boundary-layer phase transition[19]). The first-order transition in S_0 should possess a critical point at which the transition becomes second order. This transition can be explained by the competition between the elastic force, which connects the surface molecules with the bulk, and the substrate aligning force. We analyzed only the surface effects on the isotropic-nematic phase transition. In this model we assumed that the fluid density does not change near the solid substrate; this assumption may be seriously incorrect at low pressure. We considered here only the case of a semi-infinite sample. The finite thickness sample problem will be considered in a future paper.

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46. For a detailed discussion of the surface free energy see Reference 2.