Numerical solution of the Onsager problem for an isotropic-nematic interface

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The interfacial profile of the isotropic-nematic interface of a rigid-rod system is solved numerically based on a generalized Onsager model. For long rigid rods, the surface tension has the lowest value at a $\pi/2$ tilt angle between the nematic director and the normal to the interface. The density and order parameter are found to have different interfacial widths and interfacial positions. We find a dip in the density profile near the isotropic phase when the nematic director is almost parallel to the interfacial normal. The surface tension obtained here is 50% lower than the best variational calculation.

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In 1949, Onsager considered a system of rigid rodlike molecules interacting with each other through steric, excluded-volume interactions [1]; he demonstrated that at sufficiently high density, the system exhibits a first-order, disorder (isotropic) to orientation-ordered (nematic) phase transition. Subsequent models and numerical simulations have confirmed Onsager's picture, which is now commonly regarded as the main mechanism for the formation of the nematic ordering in liquid crystals [2]. The interfacial properties between the isotropic and nematic phases, however, have received less attention until recently [3–8]. In particular, the role played by anisotropic steric excluded-volume interactions in determining the interfacial properties is still unsatisfactorily explained.

Because of difficulties in solving this interfacial problem analytically, the existing theories propose either an artificially imposed interface profile (sharp or smooth) [4,5(a),6], or a square-gradient expansion [5(b)] which cannot be used to account for the effect of a nontrivial tilt angle between the nematic director and interfacial normal [5(a)]. These theories have arrived at different answers regarding the possibilities of the existence of a nontrivial tilt angle. While Holyst and Poniewierski [4] claim that a tilt angle of $\pi/3$ between the director and interfacial normal exists as a result of the excluded-volume interactions of hard rods with a large aspect ratio L/d, other authors found that the excluded-volume interaction favors a $\pi/2$ tilt angle for large aspect ratio [5,6]. An open question is whether or not these discrepancies are caused by the approximations mentioned above. In this paper we report a numerical solution of the generalized Onsager model for the isotropic-nematic interface of long rigid rods that avoids the pitfalls of these approximations. We conclude that, for long rigid rods, the surface tension has the lowest value at a $\pi/2$ tilt angle.

Based on a second-viral-coefficient approximation for a spacially inhomogeneous system, we can express the free energy of molecules with anisotropic shapes as [1]

$$\frac{F}{k_B T}=\int d^3r\, d\Omega\, \rho(\mathbf{r},\Omega)\ln 4\pi\rho(\mathbf{r},\Omega)+\frac{1}{2}\int d^3r\, d^3r'\, d\Omega\, d\Omega'\, w(\mathbf{r},\mathbf{r}',\Omega,\Omega')\rho(\mathbf{r}',\Omega')\rho(\mathbf{r},\Omega)\ . \tag{1}$$

Here the number density per unit solid angle, $\rho(\mathbf{r},\Omega)$, is a function of the position $\mathbf{r}$ and solid angle Ω. For steric interactions the function w is assumed to have value 1 when two rods overlap and 0 otherwise.

For a homogeneous system, i.e., for the bulk phases, $\rho(\mathbf{r},\Omega)$ becomes independent of the position $\mathbf{r}$ and the free-energy model (1) reduces to the Onsager model for the isotropic-nematic phase transition [1]. The minimum of the free energy is found by a variation with respect to the angular distribution function $f(\theta)$, which leads to an integral equation for $f(\theta)$:

$$\ln[f(\theta)]=\lambda-\bar{C}\int W(\gamma)f(\theta')d\Omega'\ . \tag{2}$$

In Eq. (2), $W(\gamma)$ is the excluded volume of two rods of orientations Ω and Ω', having a relative angle γ, and λ is a normalization constant. Dividing the region $(0,\pi)$ for the variable θ into $n_\theta=40$ equal segments and using a Simpson's rule to approximate the integral, we discretize Eq. (2) into $n_\theta+1$ equations with $n_\theta+1$ variables $f(\theta_i)$, $(i=1,\ldots,n_\theta+1)$. Neglecting end effects for long rigid rods (i.e., taking the length-to-diameter ratio $L/d\gg 1$) and solving this set of nonlinear equations, we confirm that a first-order athermal phase transition exists at sufficiently high density. At the phase-transition point, the isotropic phase has a number density C_i with the value

$$\bar{C}_i\equiv C_i L^2 d=4.188\pm 0.001\ , \tag{3}$$

and the nematic phase has a number density C_n and a order parameter S with the values

$$\bar{C}_n\equiv C_n L^2 d=5.341\pm 0.005\ , \tag{4a}$$

$$S \equiv \langle P_2(\cos\theta) \rangle = 0.7935 \pm 0.001 , \tag{4b}$$

where L and d are the length and diameter of the rigid rods, respectively. Using appropriate units, one can write the chemical potential at the phase transition as

$$\bar{\mu} = 1 + \ln \bar{C}_i + \frac{\pi}{2} \bar{C}_i = 9.010 \pm 0.002 . \tag{5}$$

The average in Eq. (4b) is performed using the angular distribution function of the rigid rods. These values can be compared with the results $\bar{C}_i = 4.190$, $\bar{C}_n = 5.377$, and $S = 0.796$ from a bifurcation analysis of Kayser and Raveché [9] and the results $\bar{C}_i = 4.189$, $\bar{C}_n = 5.336$, and $S = 0.792$ by Stroobants, Lekkerkerker, and Odijk [10]. In our numerical procedure, the Onsager trial solution [1] for the distribution function of the nematic phase provides an initial guess, and at each iteration step, the distribution function is updated using a Newton algorithm for solving a coupled equation set of $n_\theta + 1$ variables.

The inhomogeneous interfacial problem is more complicated; the free-energy model (1) must be solved taking into account the spacial variable $\mathbf{r}$. Assuming a flat isotropic-nematic interface normal to the z direction and using the rescaled variables $\bar{x} = x/L$, $\bar{y} = y/L$, $\bar{z} = z/L$, $\bar{\rho} = \rho L^2 d$, and $\bar{w} = Lw/d$, we can rewrite the free energy (1) in the form

$$\frac{FLd}{Ak_BT} = \int_{-\infty}^{\infty} d\bar{z}\, d\Omega\, \bar{\rho}(z,\Omega) \ln 4\pi \bar{\rho}(\bar{z},\Omega) + \frac{1}{2} \int d\bar{z}\, d^3\bar{r}'\, d\Omega\, d\Omega'\, \bar{w}(\bar{z},\bar{\mathbf{r}}',\Omega,\Omega') \bar{\rho}(\bar{z},\Omega) \bar{\rho}(\bar{z}',\Omega') , \tag{6}$$

where A is the interfacial area. The interfacial profile is determined by requiring the quantity $\bar{\mu}(z)$ identical to the bulk value $\bar{\mu}$, where

$$\bar{\mu}(z) = \frac{\delta(F/Ak_BT)}{\delta \bar{\rho}(\bar{z},\Omega)} = 1 + \ln 4\pi \bar{\rho}(\bar{z},\Omega) + \int d^3\bar{r}'\, d\Omega'\, \bar{w}(\bar{z},\bar{\mathbf{r}}',\Omega,\Omega') \bar{\rho}(\bar{z}',\Omega') , \tag{7}$$

with the boundary conditions $\bar{\rho}(-\infty,\theta) = \bar{C}_n f_n(\theta)$ and $\bar{\rho}(\infty,\theta) = \bar{C}_i/4\pi$. Here $f_n(\theta)$ is the bulk nematic angular distribution function.

Because of the rather sharp interface found below, it is not adequate to expand the last term in the right-hand side of Eq. (6) in a square-gradient approximation. Furthermore, as recently pointed out by Moore and McMullen [5], a square-gradient theory only includes a Legendre polynomial of the tilt angle up to rank two and thus is not suitable for examining the nontrivial tilt-angle effect. Therefore, it is desirable to obtain a solution of Eq. (6) beyond the square-gradient approximation.

We have developed a numerical procedure in order to solve the nonlocal integral equation (7). For simplicity, we assume that the number density $\bar{\rho}(\bar{z},\Omega)$ is only a function of $\bar{z}$ and the polar angle θ, where θ is measured from the director of the nematic phase. In general, since the rotational symmetry about the director is destroyed as a result of the presence of the interface for an arbitrary tilt angle, the number density $\bar{\rho}$ at the interface should also be a function of the azimuthal variable ϕ; it is generally expected that this dependence is weak. We have observed in our numerical solution that the introduction of the ϕ dependence amounts to a 1% change in the final results for surface tension, which is within the error of the numerical procedure. In order to evaluate the integral in Eq. (7), the $\bar{z}$ coordinate is divided into n pieces of slabs with width $\Delta\bar{z}$ bounded by planes at ($\bar{z} = \bar{z}_1$, $\bar{z}_1 + \Delta\bar{z}$, $\bar{z}_1 + 2\Delta\bar{z}$, ..., $\bar{z}_1 + n\Delta\bar{z}$). Inside each slab bounded by $(\bar{z}_i, \bar{z}_{i+1})$, we calculate analytically the integral

$$\int_{-\infty}^{\infty} d\bar{x}'\, d\bar{y}' \int_{\bar{z}_i}^{\bar{z}_{i+1}} d\bar{z}'\, \bar{w}(\bar{z},\bar{\mathbf{r}}',\Omega,\Omega') \bar{\rho}(\bar{z}',\theta') ,$$

by assuming that the function $\bar{\rho}(\bar{z}',\theta')$ can be approximated by a linear interpolation between the number density at $\bar{z}_i$, $\bar{\rho}(\bar{z}_i,\theta')$, and at $\bar{z}_{i+1}$, $\bar{\rho}(\bar{z}_{i+1},\theta')$. For each $\bar{z}_i$, in order to solve the nonlinear problem (7), we further divide the range $(0,\pi)$ for the angle θ into n_θ equally spaced segments and carry out the angular part of the integral using a Simpson's rule as for the homogeneous case. The interface is arbitrarily assumed to be within $z/L = [-5,5]$, and this interval is divided into $n = 40$ sections of slab with a mesh size $\Delta z/L = 0.25$. This as-

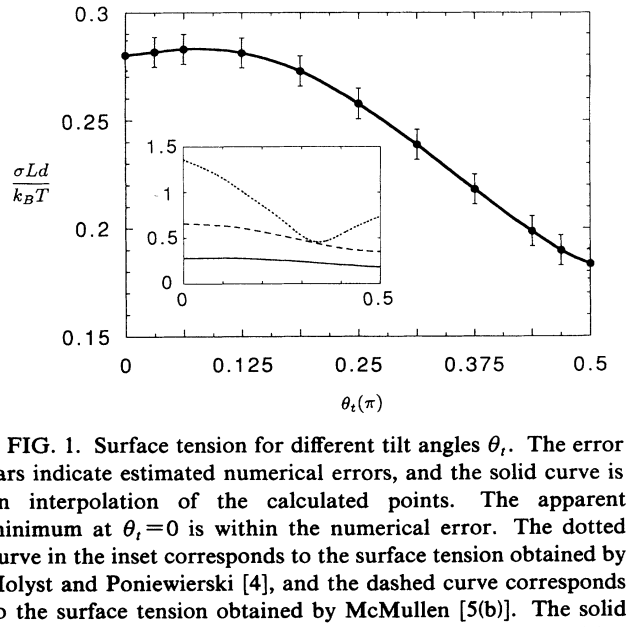

FIG. 1. Surface tension for different tilt angles θ_t. The error bars indicate estimated numerical errors, and the solid curve is an interpolation of the calculated points. The apparent minimum at $\theta_t = 0$ is within the numerical error. The dotted curve in the inset corresponds to the surface tension obtained by Holyst and Poniewierski [4], and the dashed curve corresponds to the surface tension obtained by McMullen [5(b)]. The solid curve in the inset is the same as the one in the larger plot with a different vertical scale.

sumption is justified below by the fact that the interfacial width is found to be of order $2L$. A step-function form is assumed for the initial guess of the interfacial profile. By requiring the chemical potential (7) at every mesh point to be the same as the bulk value (5), we obtain an updated interfacial profile using a Newton algorithm for solving a system of $(n_\theta+1)\times n=1640$ equations with $(n_\theta+1)\times n=1640$ variables. This interfacial profile is then used to determine the next one and so on. The iteration is assumed to converge when the local chemical potential $\bar{\mu}(z)$ deviates less than 0.01% from the bulk value in (5).

In order to study the effect of the tilt angle θ_t, we numerically solve Eq. (7) for given values of θ_t. No variation of the tilt angle is assumed across the interface. The surface tensions determined for different tilt angles are shown in Fig. 1, which clearly shows a minimum at $\theta_t=\pi/2$. (The solid curve in Fig. 1 is a spline fitting to the points calculated.) Therefore, we conclude that for the nematic-isotropic interface consisting of long rigid rods, the tilt angle between the nematic director and normal to the interface is $\pi/2$. The surface tension $\sigma(\theta_t)$ determined here can be compared with the surface tension found by McMullen [5(b)], as shown in the inset of Fig. 1 (long-dashed curve). McMullen has obtained the surface tension using a variational method with an artificially imposed hyperbolic profile; his result is almost twice as large as from this study. Holyst and Poniewierski [4] have also determined the surface tension using a step-function density profile. Their function $\sigma(\theta_t)$ determined for the aspect ratio $L/d=20$ shows a minimum near $\theta_t=\pi/3$, which is clearly an artifact arising from their approximation, since the corresponding surface tension is greatly overestimated, as shown by the dotted curve in the inset of Fig. 1.

In Figs. 2(a) and 2(b), we show the order-parameter profile $S(z)$ and density profile $C(z)$, respectively, for different values of the tilt angles. Three interesting features can be found. First, the centers of the profiles for $C(z)$ and $S(z)$ are different, where a center of a profile is defined as the position in the interface at which the profile decreases 50% of the bulk-value difference from the nematic value. The distance δ between the centers of these two quantities is plotted in Fig. 3. A typical value of this quantity is of order $0.5L$, which can be compared with $0.25L$ from a variational analysis [5]. When one goes from the nematic to the isotropic phase, there is a "phase shift" for the order-parameter profile toward the isotropic phase compared to the density profile. Physically, this is reasonable since it takes approximately one rod length for isotropic rods to interact with the ordered ones. Although the present model is based on a second-virial-coefficient approximation, this effect should be generally valid.

Second, the interfacial width at $\theta_t=\pi/2$ is narrower than those of other tilt angles. This can be shown by defining an interfacial width Δ as the distance over which the profiles decrease from 90% to 10% of their bulk-value difference. Figure 3 shows the interfacial widths for the density and order-parameter profiles.

Finally, it is surprising to find a shallow dip in the density profile near the isotropic phase for tilt angles smaller than $\pi/4$. It can be seen from Fig. 2 that in the region of the dip, the order parameter still does not approach zero. For $\theta_t=0$ the dip persists as long as one rod length. The total free energy (1) contains two terms, an entropy term that prefers isotropic distribution and an excluded-volume interaction term that prefers a nematic phase. The nematic-isotropic phase transition, and therefore the

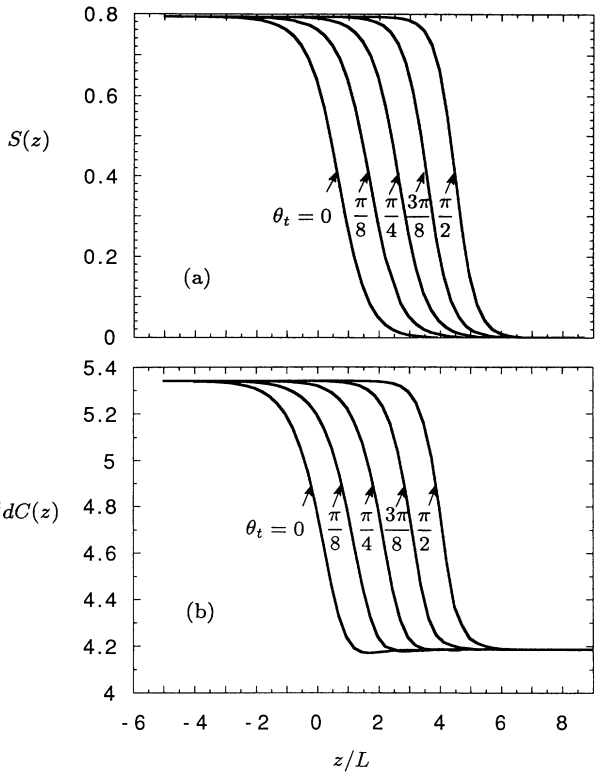

FIG. 2. (a) Order-parameter profile $S(z)$ and (b) density profile $C(z)$ at the interface. The centers of the density profiles are shifted by L in order to clearly display the profiles for different tilt angles. The relative differences between the centers of the order-parameter and density profiles are retained in this plot.

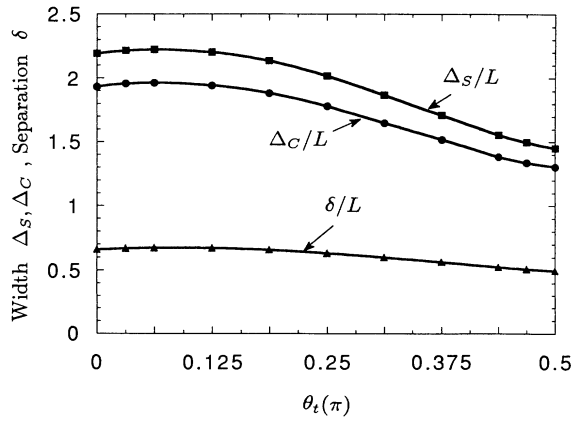

FIG. 3. Interfacial widths of the density profile Δ_C, of the order-parameter profile Δ_S, and distance δ between the centers of the density and order-parameter profiles.

nematic-isotropic interface, is a result of the competition of these two terms. This dip is related to the substantially finite value of the order parameter at this point, which encourages the system to exclude disordered rods from this region in order to decrease the total excluded-volume interactions at the expense of some entropy.

For the nematic-isotropic interface of 4-methoxybenzilidene-4′−(*n*-butyl)aniline (MBBA), the optical-reflectometry experiments by Langevin and Bouchiat indicate a nearly $\pi/2$ tilt angle, confirming our analysis [7]. However, Faetti and Palleschi [8] have discovered that the interface in 4-cyano-4′-(*n*-alkil)biphenyl (*n*CB) displays a tilt angle close to $\pi/3$. It has been argued by some authors that this nontrivial tilt angle is caused by the end effect of the excluded-volume interactions of rigid rods [5]. A numerical solution of a nematic-isotropic interfacial problem accounting for the end effect is currently under investigation.

In conclusion, the numerical procedure developed here to solve a generalized Onsager model for a nematic-isotropic interface has provided information about the interfacial properties that can be used for further understanding of the excluded-volume effect in this class of problems.

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