

## Biaxial effect at an isotropic-nematic interface

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A numerical solution is obtained for the generalized Onsager problem for the isotropic-nematic interface of rigid rods, which accounts for the biaxial effect that was ignored in previous calculations. It is found that the biaxial effect on interfacial tension is indeed weak, as previously expected. The biaxiality becomes significant only near the isotropic side of the interface.

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Many simple models in statistical physics can be used to understand underlying fundamental mechanisms of much more complicated, real systems. One good example is the Onsager theory for a dilute solution of rigid rods, which serves as a basis for understanding the isotropic-nematic phase transitions in liquid crystals [1]. Frenkel and co-workers presented a series of Monte Carlo studies of systems composed of rigid, anisotropic molecules [2]. These numerical simulations clearly demonstrate that the anisotropic, repulsive interactions are responsible for the formation of the nematic ordering in liquid crystals. The Onsager theory is based on a second-virial-coefficient approximation, which is, in principle, only valid for dilute fluids. Other theories have been developed to account for more realistic features of the nematic phase; however, the basic idea remains the same [3]. The Onsager theory can be further extended to describe isotropic-nematic transitions in semiflexible polymer systems [4,5].

It is of fundamental importance to study the role played by the excluded-volume interactions in determining the isotropic-nematic interfacial properties. Accounting for spatial inhomogeneity, the generalized Onsager theory of rigid rods has been used by several authors as a simple model for this purpose. One of the most interesting features, which does not occur at interfaces of isotropic systems such as the liquid-vapor interface, is the property of the tilt angle between the bulk nematic director  $\hat{n}$  and the interfacial normal. There are disagreements in the literature regarding the value of this tilt angle. The question is whether or not the excluded-volume interactions alone can produce a nontrivial tilted director at the interface. While Kimura and Nakano [6] found that a tilt angle of  $\theta_i = \pi/2$  is preferred at the interface by the excluded-volume interactions, Holyst and Poniewierski [7] discovered a nontrivial tilt angle close to  $\pi/3$  which does *not* depend on the length-to-width ratio based on a similar, step-function approximation for the density profile at the interface. Using a variational method that allows for a smooth interpolation of the interfacial profiles while keeping a few parameters of the profile as variational parameters, Moore and McMullen obtained an estimate for the value of the interfacial tension [8]. In an earlier publication, McMullen [9] also presented a square-gradient theory that only includes a

Legendre polynomial of the tilt angle up to rank 2; this theory is not capable of being used to examine the nontrivial tilt-angle effect [8]. In an effort to resolve this theoretical discrepancy, we presented a numerical solution of the generalized Onsager problem for long rigid rods, which shows that the interfacial tension has a lowest value at a  $\pi/2$  tilt angle; moreover, we found that the numerical solution of the interfacial tension is 50% lower than the best variational calculation [10]. When the nematic director is parallel to the plane of the interface, the rotational symmetry of the distribution function about the director is destroyed as a result of the presence of the interface; however, this biaxial effect is expected to be weak. As an approximation in the previous calculation, the biaxial effect on the distribution function was neglected [10]. In this Brief Report, I present the results of incorporating the biaxial effect in the interfacial problem at a  $\pi/2$  tilt angle. The results here confirm the previous expectation of a weak biaxial effect on the interfacial tension.

The convention for the coordinate system in this Brief Report is shown schematically in Fig. 1. The normal to the interface has been chosen to be in the  $y$  direction. The averaged number density  $C$ , the spatial variables  $x$ ,  $y$ , and  $z$ , and the number density per unit solid angle at  $\mathbf{r}$ ,  $\rho(\mathbf{r}, \Omega)$ , are made dimensionless with the aid of the length  $L$  and diameter  $d$  of the rods:  $\bar{x} = x/L$ ,  $\bar{y} = y/L$ ,

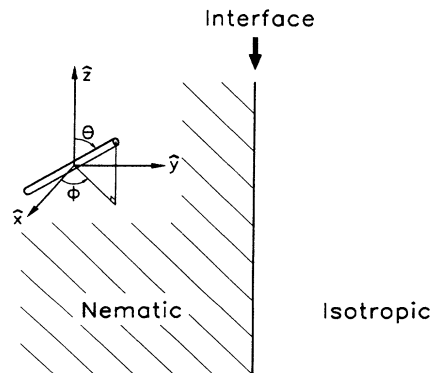


FIG. 1. The coordinate system used in this Brief Report. The nematic director is along the  $z$  direction, and the interfacial normal is along the  $y$  direction.

$\bar{z}=z/L$ ,  $\bar{C}=CL^2d$ , and  $\bar{\rho}=\rho L^2d$ . The interfacial tension can then be written as a functional of the number-density distribution  $\rho(\mathbf{r},\Omega)$ :

$$\begin{aligned} \frac{\sigma Ld}{k_B T} = & \int_{-\infty}^{\infty} d\bar{y} d\Omega \bar{\rho}(\bar{y},\Omega) \{ \ln[4\pi\bar{\rho}(\bar{y},\Omega)] - \bar{\mu} \} \\ & + \frac{1}{2} \int_{-\infty}^{\infty} d\bar{y} d^3\bar{r}' d\Omega' \bar{w}(\bar{y},\bar{r}',\Omega,\Omega') \\ & \times \bar{\rho}(\bar{y},\Omega) \bar{\rho}(\bar{y}',\Omega'), \end{aligned} \quad (1)$$

where  $\bar{\mu}$  is the dimensionless bulk chemical potential at the phase transition. Here a rescaled function  $\bar{w}=wL/d$  has been defined; for steric interactions, the function  $w$  is assumed to have value 1 when two rods overlap, and 0 otherwise. The number-density distribution function  $\rho(\bar{y},\Omega)$  is a function of  $y$ , the polar angle  $\theta$ , and the azimuthal angle  $\phi$  (see coordinate system in Fig. 1). The interfacial profile is determined by minimizing the dimensionless interfacial tension in Eq. (1) with respect to  $\rho(\mathbf{r},\Omega)$ :

$$\begin{aligned} \frac{\delta(\sigma Ld/k_B T)}{\delta\bar{\rho}(\bar{y},\Omega)} = & 1 + \ln[4\pi\bar{\rho}(\bar{y},\Omega)] \\ & + \int d^3\bar{r}' d\Omega' \bar{w}(\bar{y},\bar{r}',\Omega,\Omega') \bar{\rho}(\bar{y}',\Omega') - \bar{\mu} \\ = & 0, \end{aligned} \quad (2)$$

where the bulk chemical potential  $\bar{\mu}$  at the phase transition has the value

$$\bar{\mu} = 9.010. \quad (3)$$

A more accurate numerical solution for the bulk phase gives  $\bar{\mu}=9.0134$ , but the above value is used here for the consistency of keeping the number of finite grid points the same in computing.

The numerical method used to solve the equilibrium condition, Eq. (2), is somewhat different from that used in Ref. [10]. The interface is arbitrarily assumed to be within  $y=[-5,5]L$ ; this interval is broken into  $n_y=40$  subintervals with a mesh size  $\Delta y=L/4$ . There is no reason why the subintervals must all have equal length, but it is found that this simplifies the actual calculation. At each grid point, a number-density distribution function is defined, and a trapezoidal approximation is used to carry out the integral involving  $\mathbf{r}'$  in Eq. (2); the number-density distribution function itself is further represented by specifying values at  $n_\theta=20$  equally spaced points in  $(0,\pi/2)$  for the variable  $\theta$ , and at  $n_\phi=40$  equally spaced points in  $(0,\pi)$  for the variable  $\phi$ . Simpson's rule is used for the integration over the variables  $\theta'$  and  $\phi'$ .

The distribution function obtained in Ref. [10], in which the  $\phi$  dependence was ignored, is chosen to be the initial approximation. At each step of the numerical iteration, a Newton algorithm for solving a system of  $(n_\theta+1)\times(n_\phi+1)=861$  nonlinear equations is used to solve Eq. (2) for a given  $y$  grid point. The solution is then used at the next step of the iteration. At the next step, the program proceeds to the next  $y$  grid point; and returns to the first grid point in  $y$  after all  $y$  grid points are updated once. The iteration finishes when Eq. (2) is satisfied within 0.005% of the value for the bulk chemical

potential in Eq. (3).

It is customary to define an order parameter  $S_2$  corresponding to the average of the second-rank Legendre polynomial of the polar variable with respect to the orientation distribution function. Here this average is taken for a fixed  $y$ :

$$S_2(y) = \langle P_2(\cos\theta) \rangle_y. \quad (4)$$

A biaxiality  $\Delta S$  is also defined for the interfacial profile:

$$\Delta S(y) = \frac{3}{2} \langle \sin^2\theta(\cos^2\phi - \sin^2\phi) \rangle_y. \quad (5)$$

Figure 2 shows the variations of the number density, order parameter, and biaxiality crossing the interface. The profiles of  $C(y)$  and  $S_2(y)$  remain almost the same as in

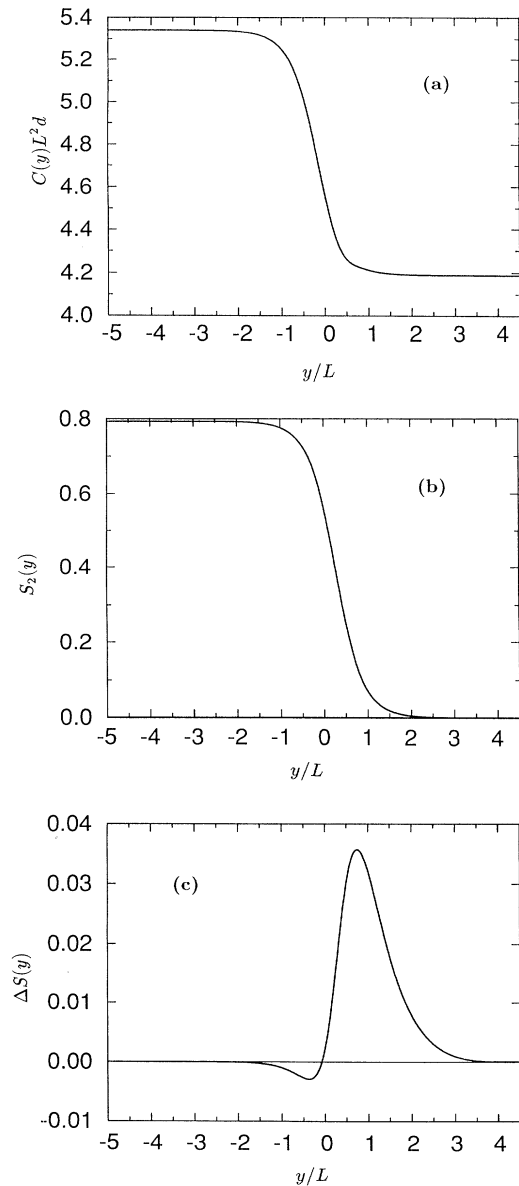


FIG. 2. (a) Density profile  $C(y)$ , (b) order parameter profile  $S_2(y)$ , and (c) biaxiality profile  $\Delta S(y)$  at the nematic-isotropic interface.

our previous calculation [10]. Figure 2(c) demonstrates that the biaxial effect only appears significant near the isotropic side of the interface, where the nematic ordering, as characterized by the order parameter  $S_2$ , is relatively small. The width of the effect is roughly  $2L$ .

The interfacial tension  $\sigma$  deduced from the present calculation is

$$\frac{\sigma L d}{k_B T} = (0.181 \pm 0.002), \quad (6)$$

which agrees with the previous result [10]  $\sigma L d / k_B T = (0.183 \pm 0.002)$ . Within the uncertainty of the calculation, the interfacial tension calculated with the biaxial effect is indistinguishable from the interfacial tension calculated ignoring biaxiality.

Different tilt angles were also chosen for the initial ap-

proximation of the distribution function. It is observed in the process of solving Eq. (2) that the interface induces a rotation of the tilt angle until it becomes  $\pi/2$  or 0. Therefore Eq. (2) has two true solutions only, one ( $\theta_i = \pi/2$ ) for which the interfacial tension reaches a minimum, and one ( $\theta_i = 0$ ) for which the interfacial tension reaches a maximum.

In summary, the solution of the generalized Onsager model for the isotropic-nematic interface shows a weak biaxiality. It would be interesting to incorporate other effects, such as the end effect, flexibility, and attractions, in the model.

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