

Surface tension of the isotropic-nematic interface

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We present calculations of the pressure tensor profile in the vicinity of the planar interface between isotropic liquid and nematic liquid crystal, using Onsager's density functional theory and computer simulation. When the liquid crystal director is aligned parallel to the interface, the situation of lowest free energy, there is a large tension on the nematic side of the interface and a small compressive region on the isotropic side. By contrast, for perpendicular alignment, the tension is on the isotropic side. There is excellent agreement between theory and simulation both in the forms of the pressure tensor profiles, and the values of the surface tension.

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The nematic liquid crystal phase is distinguished from the isotropic liquid by the existence of long-range orientational ordering of the constituent molecules [1]. The structure of the planar interface between coexisting nematic (N) and isotropic (I) phases is of fundamental interest: along with the liquid-vapor surface, it is one of the simplest fluid-fluid interfaces. Molecular-scale interactions, capillary-wave fluctuations, and the coupling between translational and rotational degrees of freedom may all influence the interface properties. The surface excess free energy, or interfacial tension γ , is a key parameter. The variation of this quantity with the direction of molecular ordering in the liquid crystal, the so-called *director*, dictates the molecular alignment which will be preferred by the surface: the phenomenon of *anchoring*, an essential feature of liquid crystal physics [2]. Determining the surface tension of the N - I interface for a given molecular model by computer simulation, and predicting it from first principles by theoretical methods, is clearly desirable. For a planar interface, γ may be calculated by integrating the difference between normal P_N and transverse P_T pressure tensor components with respect to position [3,4]: $\gamma = \int_{-\infty}^{\infty} dz [P_N(z) - P_T(z)]$.

In this Rapid Communication, we present a discussion of the pressure tensor profile through the nematic-isotropic interface in the framework of a simple density functional theory in the Onsager approximation [5], modeling the molecules as freely rotating and translating rodlike rigid bodies. We shall show that there is a significant difference between the two situations of most interest, when the director is oriented respectively parallel to, and normal to, the interface. Previous studies [6–9] calculating the surface tension from free energy differences have indicated that, in the limit of infinite rod elongation, the minimum surface free energy is obtained when the rods lie parallel to the N - I interface; in other words, this interface favors *planar* anchoring. We provide additional insight into this result, through an examination of the normal and transverse pressure.

We back up these predictions by carrying out computer simulations to give the pressure tensor profiles for equilibrium N - I interfaces, confined between parallel walls under different anchoring conditions, using the same molecular models as in the theory. Our results are further supported by computer simulations of free standing nematic films in coexistence with the isotropic phase. From the simulation viewpoint, this study is much more challenging than determining the surface tension of the liquid-vapor interface [10], since the densities and other properties of the two phases are very similar. To our knowledge, the only other such studies have involved two phases maintained out of thermodynamic equilibrium [11,12].

We employ two very similar molecular models in this work, in both simulation and theory. Both models are axially symmetric, with molecular orientations represented by unit vectors \mathbf{u}_i and center-of-mass positions by vectors \mathbf{r}_i . In the first model, the molecules are taken to be hard ellipsoids of revolution of axial ratio $\kappa = A/B = 15$, where A is the length of the symmetry axis and B that of the transverse axes; the bulk phase diagram of this model is well known [13], and the interfacial structure has been recently reported by one of us [14]. For hard particle models, the temperature enters only trivially into the thermodynamics, and we define units of energy by setting $k_B T = 1$ in this work. Length units are fixed by taking $B = 1$, mass units by setting particle mass $M = 1$, and the moment of inertia was fixed at $I/MB^2 = 50$. In the second “soft ellipsoid” model, a continuous pair potential $v_{12} = 4\epsilon(s_{12}^{-12} - s_{12}^{-6}) + 1$, for $s_{12} < 2^{1/6}$, $v_{12} = 0$ otherwise, was used. Here, $s_{12} = (r_{12} - \sigma_{12} + B)/B$ is a scaled and shifted separation where the “diameter” $\sigma_{12} = \sigma(\hat{\mathbf{r}}_{12}, \mathbf{u}_1, \mathbf{u}_2; A, B)$ is a standard approximation [15,16] to the contact distance of two ellipsoids (again with $A/B = 15$ here) at given relative orientations; $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, $r_{12} = |\mathbf{r}_{12}|$ and $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/r_{12}$. The potential is purely repulsive and varies quite strongly over a short range of interparticle separation. We choose an energy parameter $\epsilon = 1$, again take $k_B T = 1$, and set other parameters as for the hard ellipsoids.

In planar geometry, with translational invariance in the x and y directions, we adopt the Irving-Kirkwood convention [17] so as to write components of the pressure tensor in the form [3,10,18]

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$$\begin{aligned}
P_{\alpha\alpha}(z) &= k_B T \rho(z) - \frac{1}{2} \int d\mathbf{r}_{12} \int d\mathbf{u}_1 \int d\mathbf{u}_2 \left(r_{12}^\alpha \frac{\partial v_{12}}{\partial r_{12}^\alpha} \right) \\
&\times \int_0^1 d\xi \varrho^{(2)}[\mathbf{r}_{12}, z - \xi z_{12}, z \\
&+ (1 - \xi)z_{12}; \mathbf{u}_1, \mathbf{u}_2], \quad \alpha = x, y, z. \quad (1)
\end{aligned}$$

Here, $\rho(z) = \int d\mathbf{u} \varrho^{(1)}(z, \mathbf{u})$ is the number density, $\varrho^{(1)}(z, \mathbf{u})$ the (position- and orientation-dependent) single-particle density, and $\varrho^{(2)}(\mathbf{r}_{12}, z_1, z_2; \mathbf{u}_1, \mathbf{u}_2)$ the pair density. The normal component $P_N(z) = P_{zz}(z) = P$ is independent of z throughout the system, while the transverse component $P_T(z) = P_{xx}(z) = P_{yy}(z)$ is not. Far from the interface, the pressure tensor becomes isotropic, $P_N(z) = P_T(z) = P$.

For simulations of the soft-ellipsoid system, the pressure tensor was routinely computed from Eq (1) via the intermolecular forces [3,10,18]. For the hard-ellipsoid system, it was calculated by identifying nearly contacting pairs of ellipsoids [19,20]. Such pairs are defined as those which would overlap if their dimensions are uniformly scaled by a factor λ , very slightly larger than unity. Tests were carried out with several choices of λ : all of the results here are obtained with $\lambda = 1.01$, the smallest value to give acceptable statistics, which was also found to be satisfactory in Ref [19].

The construction and minimization of the Onsager free-energy functional followed closely the procedure described before [21,14]. The excess part of the Helmholtz free energy $\mathcal{F} = \mathcal{F}^{\text{id}} + \mathcal{F}^{\text{ex}}$ is expressed in terms of $\varrho^{(1)}(\mathbf{r}, \mathbf{u})$,

$$\begin{aligned}
\mathcal{F}^{\text{ex}}[\varrho^{(1)}] &= -\frac{1}{2} k_B T \int d\mathbf{r}_1 \int d\mathbf{u}_1 \int d\mathbf{r}_2 \int d\mathbf{u}_2 \\
&\times \varrho^{(1)}(\mathbf{r}_1, \mathbf{u}_1) \varrho^{(1)}(\mathbf{r}_2, \mathbf{u}_2) f(\mathbf{r}_{12}, \mathbf{u}_1, \mathbf{u}_2), \quad (2)
\end{aligned}$$

where $f(\mathbf{r}_{12}, \mathbf{u}_1, \mathbf{u}_2) = \exp(-v_{12}/k_B T) - 1$; this is the leading term in a low-density virial expansion. Fluctuation effects, which come in through higher-order terms, were neglected. The most important fluctuations are capillary waves, which only slightly broaden the profiles in small systems, and do not affect the interfacial tension. Since $\varrho^{(1)}$ is independent of x and y , f may be integrated over these coordinates. The logarithm of the density is expanded in spherical harmonics, on a discrete grid in z with an interval $\delta z = B/5 = A/75$: $\ln \varrho^{(1)}(z_i, \mathbf{u}) = \sum_{lm} C_{i;lm} Y_{lm}(\mathbf{u})$. Periodic boundary conditions apply in the z direction. In the current application, this expansion was taken to fourth order in the $Y_{lm}(\mathbf{u})$ (restricting to second order was found to change the coexistence pressure and densities by $\sim 1\%$). All relevant orientational integrals were expressed in terms of spherical harmonic coefficients of the density up to order 10 (reducing to order 8 was found to change the coexistence pressure and densities by $\sim 0.01\%$). The parameters $C_{i;lm}$ were varied to minimize the grand potential $\beta\Omega[\varrho^{(1)}] \equiv \beta\mathcal{F}[\varrho^{(1)}] - \beta\mu N$ of an I - N film system at the coexistence value of the chemical potential μ , determined by a preliminary bulk calculation.

The normal pressure is constant through the system, and equal to $-\Omega/V$ in both bulk phases at coexistence. The transverse pressure tensor profile was calculated directly

from the minimized density profiles. The definition consistent with Onsager's approximation and the use of the Irving-Kirkwood convention in the simulations is easily derived from Eq. (1), by inserting the low-density form

$$\begin{aligned}
&\varrho^{(2)}(\mathbf{r}_{12}, z_1, z_2; \mathbf{u}_1, \mathbf{u}_2) \\
&\approx \varrho^{(1)}(z_1, \mathbf{u}_1) \varrho^{(1)}(z_2, \mathbf{u}_2) \exp(-v_{12}/k_B T)
\end{aligned}$$

and carrying out an integration by parts. The result is

$$\begin{aligned}
P_T(z) &= k_B T \rho(z) - \frac{1}{2} k_B T \int d\mathbf{r}_{12} \int d\mathbf{u}_1 \int d\mathbf{u}_2 f(\mathbf{r}_{12}, \mathbf{u}_1, \mathbf{u}_2) \\
&\times \int_0^1 d\xi \varrho^{(1)}(z - \xi z_{12}, \mathbf{u}_1) \varrho^{(1)}[z + (1 - \xi)z_{12}, \mathbf{u}_2]. \quad (3)
\end{aligned}$$

All simulations were carried out at constant volume. A cuboidal simulation box was employed in all cases, with periodic boundaries in the x and y directions. Conventional, microcanonical ensemble molecular dynamics (MD) simulations of soft ellipsoids employed periodic boundaries also in the z direction, and used a reduced time step $\delta t = 0.002$. Several systems of $N = 7200$ particles in boxes of size $L_x/A = L_y/A = 2.5, L_z/A \approx 20$ were studied. At average number densities $0.24 \leq \rho A B^2 \leq 0.255$, from an initially isotropic configuration, one or several nematic films were observed to assemble spontaneously, with planar interfaces normal to the z direction and, in every case, the director lying parallel to the interface. In addition, from an initially nematic configuration aligned in the z direction, a similar two-phase system nucleated with the nematic director turned through 90° to lie parallel to the interface, within roughly 1 million time steps.

One of the systems at density $\rho A B^2 = 0.255$, containing a nematic film of width $\sim 13B$, was further equilibrated over 7 million time steps, monitoring the pressure tensor profiles; run averages were then accumulated over 4.7 million steps. In the absence of walls, the interfacial tension can be calculated simply from the difference between the system averages of P_N and P_T . This has been done independently using the transverse component P_{yy} , which happens to be roughly parallel to the director, and the transverse component P_{xx} , which is perpendicular, giving respectively $\gamma B^2/k_B T = 0.022 \pm 0.01, 0.015 \pm 0.01$. Thus, the free film simulations yielded clear evidence that the anchoring at the interface is planar, provided a rough estimate of the interfacial tension, and indicated an unexpected difference between the transverse stress components P_{xx} and P_{yy} . To provide more convenient control of the director orientation relative to the interface, a more systematic study was therefore conducted in a confined geometry.

Both hard and soft ellipsoids were simulated using conventional constant- NVT Monte Carlo (MC) [22] using $N \approx 8000$ particles in a box of dimensions $L_x/A = L_y/A = 2.22, L_z/A = 22.73$. Flat walls with a short-range orienting field at the box ends allowed nematic films of width approximately $8A$ to be stabilized in a desired director orientation, separated by a central isotropic region of width approxi-

TABLE I. Coexistence parameters for hard (HE) and soft (SE) ellipsoids. We report coexistence pressure P_{NI} , coexisting number densities ρ_N and ρ_I , nematic order parameter S_N , and the surface tensions γ_{NI} for normal and parallel director alignment.

	$P_{NI}B^3/k_B T$	$\rho_N B^3$	$\rho_I B^3$	S_N	$\gamma_{NI}B^2/k_B T$ (normal)	$\gamma_{NI}B^2/k_B T$ (planar)
HE (Onsager)	0.118221	0.029645	0.025008	0.731952	0.016	0.010
HE (simulation)	0.099	0.0225	0.0188	0.71	0.014 ± 0.003	0.006 ± 0.005
SE (Onsager)	0.083528	0.022446	0.018556	0.745852	0.015	0.010
SE (simulation)	0.076	0.0180	0.0149	0.74	0.015 ± 0.004	0.011 ± 0.004

mately 7A. Full details of the system, together with a description of the film structure, have been given elsewhere [14]. In this paper we focus on the cases of normal (along z) and in-plane (along y) orientation of the director relative to the interface. For each model, and each director alignment, we report the results of averaging over eight independent runs. For the hard ellipsoids, more than 10^6 Monte Carlo sweeps were allowed for equilibration, and the averages were accumulated over a further 7.5×10^5 sweeps (one sweep is one attempted move per particle). For the soft ellipsoids, the corresponding figures are 3.5×10^5 sweeps and 6.25×10^5 sweeps. Profiles of number density $\rho(z)$, orientational order parameter $S(z)$ (the largest eigenvalue of the second rank order tensor [14]) and the pressure tensor were accumulated. To facilitate the precise comparison between simulation profiles and theoretical predictions, a correction was made for the fluctuations in the interface position, as described elsewhere [14]. Error bars were estimated by assuming a normal distribution of the results of the eight separate runs. For the in-plane cases of director alignment along y we detected (as for the free films) an extremely small discrepancy $P_{zz} = P_{xx} \neq P_{yy}$ in the nematic phase far from the

interface. We ascribe this to correlations of aligned molecules across the periodic box: to eliminate this finite-size effect from the very sensitive surface tension calculation we set $P_T(z) = P_{xx}(z)$ in these cases. For normal alignment, we found the x and y directions to be equivalent and set $P_T(z) = [P_{xx}(z) + P_{yy}(z)]/2$.

Coexistence parameters from theory and simulation are compared in Table I. As is well known [13], for elongation $A/B = 15$ the Onsager theory overestimates the coexistence pressures and densities by up to 30%. Profiles in the vicinity of the interface are compared in Figs. 1 and 2. To help locate the interface, we show the number density curves for both simulation and theory, scaled by the bulk coexistence values ρ_I, ρ_N thus: $\rho^*(z) = [\rho(z) - \rho_I]/(\rho_N - \rho_I)$, and similarly for the nematic order parameter $S^*(z)$. The zero of z is taken at the point of inflection of $S^*(z)$; as discussed elsewhere [14], the density profile lies at $z \approx -A/3$ relative to this (on the nematic side). In the figures we show both the pressure tensor difference $P_N - P_T(z)$ and the running integral $\int_{z_0}^z dz P_N - P_T(z)$ taken from a point z_0 in the bulk nematic phase far from the interface. The results, for the two different director alignments, are dramatically different. For parallel, in-plane alignment, there is a large tension (low transverse pressure) on the nematic side of the interface, followed by a small compressive region (high transverse pressure) on the

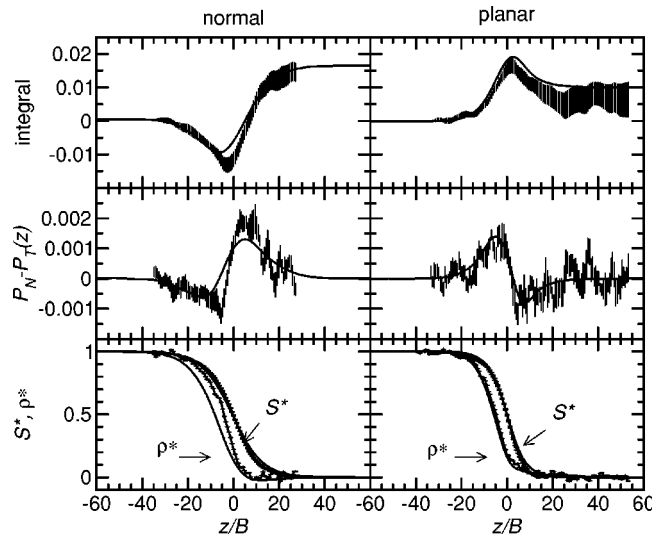


FIG. 1. Profiles near the N - I interface for hard ellipsoids. Top: surface tension integral $\int_{z_0}^z dz P_N - P_T(z)$. Middle: pressure tensor difference $P_N - P_T(z)$. Bottom: reduced density $\rho^*(z)$ and order parameter $S^*(z)$. Simulation results are points with error bars, predictions of Onsager theory represented as lines.

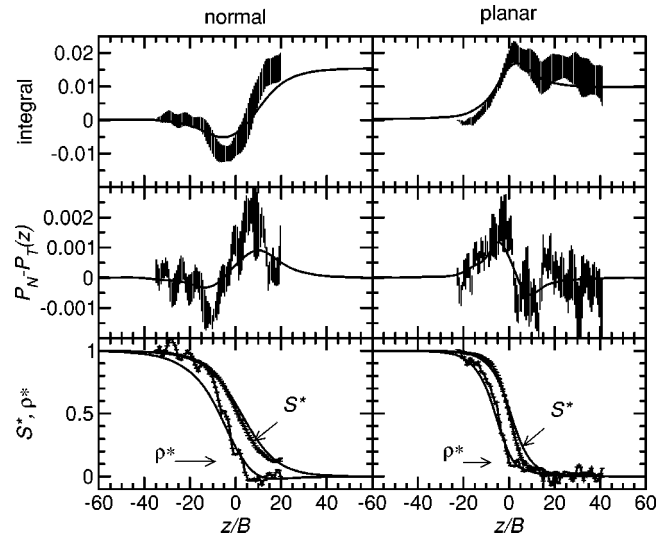


FIG. 2. Profiles near the N - I interface for soft ellipsoids. Notation is the same as in Fig. 1.

isotropic side, as seen in simulations of the liquid-vapor interface of a simple fluid [23,10]. The *surface of tension* defined by the first moment of $P_N - P_T(z)$ [4] lies on the *denser* side of the interface. For normal alignment, there is a compressive region on the nematic side, and a region under tension on the isotropic side: the surface of tension lies on the side of the less dense phase. Such behavior is seen in the idealized penetrable sphere model of the liquid vapor interface [4] but has been observed here for a molecular model with realistic interactions. The step change in the running integrals gives estimates of the surface tension, which are reported in Table I. We find that the planar orientation is favored, as it has the lower excess free energy; the same result was obtained by Onsager theory in the infinite elongation limit [9], although the corresponding surface tensions in that case (appropriately scaled by A and B) are about 40% larger than here.

Although the simulation results are subject to significant error bars, we have succeeded in resolving the variation of transverse pressure through the interface, and the profiles are very similar, both in form and magnitude, to those predicted by theory. Indeed, the level of agreement between theory and

simulation results is remarkable, bearing in mind the absence of adjustable parameters in the Onsager theory. In principle, the location of the surface of tension depends on the convention adopted for the transverse stress, e.g., Irving-Kirkwood versus Harasima [4], but in the current study we find that the profiles are only slightly dependent on this choice; moreover, the results for such molecular shapes should be indicative of the behavior for more elongated particles, so we expect them to be rather generally applicable.

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