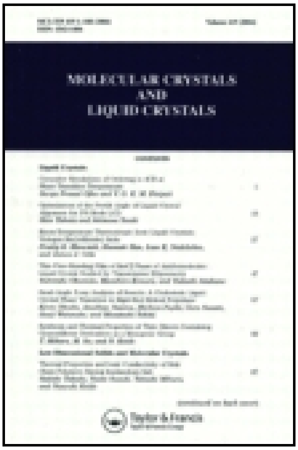

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Theoretical Studies of the Isotropic-Nematic Interface

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Theoretical Studies of the Isotropic-Nematic Interface

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We discuss phenomenological and molecular theoretical approaches to the thermodynamics of isotropic-nematic interfaces. Traditional square-gradient theories are inconsistent with the observed anisotropy of the isotropic-nematic surface tension unless the liquid crystal molecules possess up-down symmetry which they manifest as interfacial polar order. Using the Onsager functional for the nonideal free energy of hard spherocylinders, we show that for short spherocylinders, the fourth and higher-order terms in the gradient expansion of the order parameter profiles may also account for the anisotropy of the surface tension. However, these terms have a negligible effect on the isotropic-nematic interfaces of very long spherocylinders to which the Onsager approximation applies asymptotically.

Keywords: interface, surface tension, tilt angle, nematic ordering

I. INTRODUCTION

During the past twenty years, molecular theories of liquid crystal phase diagrams have placed considerable emphasis on the isotropic-nematic phase transition,[1] and a well-accepted picture has emerged for the molecular mechanisms that lead to spontaneous orientational ordering. As for many other phase coexistences, there have been comparatively few attempts[2–7] to describe the inhomogeneous region separating the equilibrium isotropic and nematic phases. Nevertheless, a number of considerations make the isotropic-nematic (I-N) interface problem a natural candidate for extensive study. First of all, it provides one of the simplest examples of an interface that separates a condensed isotropic phase from a state of broken symmetry. In this instance, the symmetries of the coexisting phases (see Figure 1) dictate the interfacial thermodynamics in terms of a single orientational parameter—usually chosen as the angle between the *bulk* nematic director $\hat{n}$ and the interfacial normal $\hat{z}$. Secondly, experimental techniques can be employed to measure this dependence over a substantial range of the tilt angle = $\cos^{-1}$ $(\hat{n} \cdot \hat{z})$. Thus, experimental studies of 4-methoxybenzilidene-4′-(n-butyl)aniline (MBBA)[8] and the homologous series 4-cyano-4′-(n-alkyl)biphenyl (nCB)[9] now supply us with a detailed qualitative picture of I-N interfaces. Finally, the large body of theoretical research focusing on the bulk thermodynamics of liquid crystals provides a helpful foundation on which to base molecular theories of their interfaces.

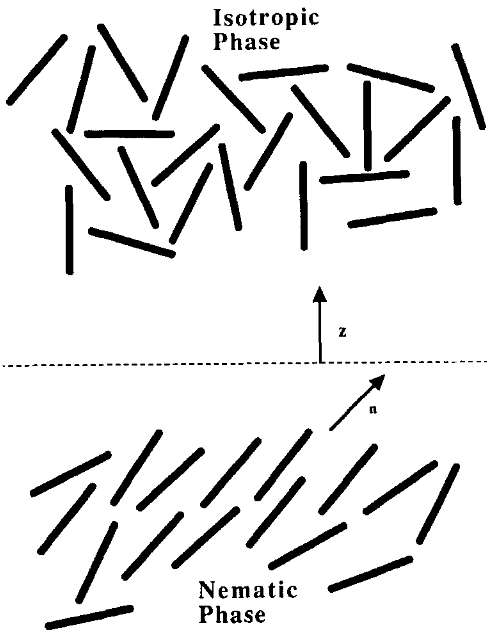

FIGURE 1 Schematic of the isotropic-nematic interface. The director in the bulk nematic is $\hat{n}$, the normal to the surface is $\hat{z}$.

For the purposes of discussion, it proves convenient to introduce the tilt angle θ_t defined as the angle between the bulk nematic director $\hat{n}$ and the interfacial normal $\hat{z}$. For molecules in the nCB series,[9] θ_t ranges between 50 and 70° while its value for MBBA[8] is less certain but appears to lie within 10 or 15° of $\hat{n} \cdot \hat{z} = 0$. The width of the I-N interface is several hundred angstroms and the interfacial tension γ_{IN} of the order 0.01 erg/cm^2. Calculations derived from a successful theory of the interface should account for the observed values of the tilt angles and reproduce the interfacial width and surface tension to within, say, an order of magnitude. Phenomenological approaches to the problem can achieve this goal at the cost of introducing some parameters into the theory that are difficult to quantify. In contrast, a completely satisfactory model has yet to be introduced upon which to base a molecular theory. However, molecular theories can be systematically improved and require fewer assumptions about the nature of the I-N interface for their implementation.

The next section reviews some aspects of the phenomenological and molecular theories of the I-N interface with emphasis on the factors that affect the tilt angle. Symmetry considerations show that conventional square-gradient treatments of the interfacial profile cannot account for tilt angles other than 0 and 90°. This leaves several explanations for the θ_t's observed for molecules like the nCB's. If the molecules possess a strong, permanent dipole moment, our analysis demonstrates that linear terms in the gradient expansion of the inhomogeneous free energy (usually discarded on the basis of the symmetry of the bulk phases) favor $\theta_t = 0°$. This contribution competes with other molecular factors (for instance, the excluded volume interactions) which may favor a parallel ($\theta_t = 90°$) orientation of the nematic director relative to the interface, and can lead to a compromise θ_t between the 0 and 90° extremes. Self-consistent solutions to integral-equations for the density profiles of $D_{\infty h}$ models may also lead to oblique tilt angles if the calculations employ sufficiently general forms for the intermolecular potentials. [Note that too simple an intermolecular or effective potential may predict an isotropic I-N surface tension. See Reference (3) for such an example.] However, the generally diffuse nature of experimental[8,9] I-N interfaces suggests that conventional square-gradient expansions should, in most cases, adequately describe the interfacial density profiles. In this article, we present some new results for hard spherocylinders that demonstrate how a square-gradient treatment of the I-N interface may yield reasonable values for the interfacial widths and tension but fail to account for the tilt angle. For moderately short spherocylinders, we find that the orientational dependences which arise from the square-gradient parts of the surface free energy become vanishingly small. Then small, fourth-order gradient terms primarily determine the anisotropy of the surface tension. We conclude the article with a few brief comments about our results and make some suggestions for future research.

II. THEORY

A. Phenomenological Approach

A Landau[2,12,13] expansion of the inhomogeneous free energy about the isotropic phase affords a reasonable qualitative picture of the I-N interface. The free energy density consists of two parts: a local contribution F_L that stabilizes the coexisting bulk phases in regions far from the interface, and an inhomogeneous term F_g that stems from the inherent nonlocality of the free energy functional. From a physical point of view, the existence of a microscopically diffuse interface requires the presence of F_g or another function like it. Let Q be the conventional P_2 order parameter defined as the thermal average

$$Q = \langle P_2(\cos \theta_{\hat{n}})\rangle \tag{1}$$

where $\theta_{\hat{n}}$ is measured relative to the bulk nematic director $\hat{n}$. We also introduce a polar order parameter μ as

$$\mu = \langle \cos \theta_{\hat{n}} \rangle \tag{2}$$

that indicates the extent of local polar ordering. For ordinary nematics, $Q > 0$ and $\mu = 0$. The simplest possible form for F_L is[2,7]

$$F_L = \frac{a}{2} Q^2 - \frac{b}{3} Q^3 + \frac{c}{4} Q^4 + \frac{d}{2} \mu^2 \tag{3}$$

with all four parameters a, b, c, and d functions of the temperature but positive definite and independent of Q and μ. The conditions on the homogeneous phases

$$\frac{\partial F_L}{\partial \mu} = 0 \tag{4a}$$

and

$$\frac{\partial F_L}{\partial Q} = 0 \tag{4b}$$

determine the coexistence conditions for the nematic phase as

$$Q = Q^* = \frac{2b}{3c} \tag{5a}$$

and

$$\mu = 0. \tag{5b}$$

By definition, both order parameters vanish in the isotropic phase.

Construction of all second-order invariant combinations of the order parameters and their derivatives leads to[7] the square-gradient form

$$\begin{aligned} F_g = {} & [\alpha + \beta P_2(\hat{n} \cdot \hat{z})] \left[\frac{dQ}{dz}\right]^2 - E(\hat{n} \cdot \hat{z})\mu(z)\frac{dQ}{dz} \\ & + [\lambda + \nu P_2(\hat{n} \cdot \hat{z})] \left[\frac{d\mu}{dz}\right]^2 \end{aligned} \tag{6}$$

with α, β, λ, ν, and E temperature-dependent, phenomenological constants. The $-$ sign on the term linear in the gradient of $Q(z)$ guarantees that $E > 0$. The surface tension follows as

$$\gamma_{IN} = \int_{-\infty}^{\infty} dz[F_L(Q(z), \mu(z)) + F_g(Q(z), \mu(z))] \tag{7}$$

with boundary conditions imposed on Q and μ so that when $z \to \infty$, the order parameters approach their bulk nematic values while as $z \to -\infty$, they vanish. For molecules that possess up-down symmetry, $E = 0$. The functional minimization of Equation (7) with respect to Q and μ shows that $\mu(z)$ is identically zero unless both E and $\hat{n} \cdot \hat{z} \neq 0$. Of course, each different choice of $\hat{n} \cdot \hat{z}$ leads to a different value of γ_{IN}. The global minimum for γ_{IN} occurs at the equilibrium value of $\hat{n} \cdot \hat{z}$. If $0 < \hat{n} \cdot \hat{z} < 1$, the molecules in the bulk nematic *tilt* compared to the I-N interfacial normal. Within the context of the phenomenological model discussed here, such behavior results from polar ordering within the interface. In the absence of this effect, the minimum must occur at either $\hat{n} \cdot \hat{z} = 0$ or 1. The usual assumption that $\mu(z) = 0$ everywhere provides an upper bound on γ_{IN}. However, by allowing $\mu(z)$ to differ from 0 in the interface, the inhomogeneous I-N system may realize an even lower interfacial free energy.

Upon first examination, it may seem that by extending our phenomenological arguments to include higher-order nematic order parameters, we can obtain a nontrivial tilt angle within a square-gradient approximation (SGA) without invoking the concept of a polar order parameter. However, applications of the SGA to most[10] explicit functional forms for the nonideal free energy result in expressions of the form

$$\gamma_{IN} = F_L + F_g P_2(\hat{n} \cdot \hat{z}) \tag{8}$$

with F_L a local functional of the one-molecule density and F_g a quadratic functional of the order parameters and their spatial derivatives. The second Legendre polynomial $P_2(\hat{n} \cdot \hat{z})$ has extrema at $\hat{n} \cdot \hat{z} = 0$ and 1. It follows that the global minimum of γ_{IN} must occur at one of these endpoints regardless of the form of F_L and F_g.

B. Molecular Theory

As an alternative to the phenomenological approach outlined in the previous subsection, we now consider a molecular theory of the I-N interface and its application to a liquid crystal model. The quantity of central interest is the grand potential difference betweeen an inhomogeneous I-N system with density $\rho(\mathbf{r}, \omega)$ and a uniform isotropic phase of density ρ_0. In the absence of external fields, this difference has the form[11,6] (in units of Boltzmann's constant times the temperature)

$$\Delta\Omega[\rho(\mathbf{r}, \omega)] = -\int d\mathbf{r} \int d\omega \left[\rho(\mathbf{r}, \omega) - \frac{\rho_0}{4\pi}\right] + \int d\mathbf{r} \int d\omega \rho(\mathbf{r}, \omega) \ln\left[\frac{4\pi\rho(\mathbf{r}, \omega)}{\rho_0}\right] - \Delta\Phi[\rho(\mathbf{r}, \omega)]. \tag{10}$$

The same functional applies to the I-N nematic phase coexistence when ρ_0 is chosen so that $\Delta\Omega = 0$ at its minimum. For the inhomogeneous system, the minimized $\Delta\Omega$ divided by the interfacial area equals γ_{IN}. A knowledge of the nonideal functional $\Delta\Phi[\rho(\mathbf{r}, \omega)]$ reduces the task of determining the I-N interfacial properties to a large numerical computation.

An exact expression for $\Delta\Phi[\rho(\mathbf{r}, \omega)]$ is, of course, unavailable for any realistic model of a nematic-forming liquid crystal. Nevertheless, some of the formal properties of $\Delta\Phi[\rho(\mathbf{r}, \omega)]$ have made it possible to construct approximate functionals that predict nematic ordering. Perhaps the most well-known example of this type is Onsager's lowest-order virial expansion of the hard-spherocylinder free energy.[1] Although it displays a too strongly first-order phase transition and applies, in principle, only to extremely long spherocylinders, this functional provides a rudimentary basis for more thorough studies of I-N interfaces. Onsager's functional is

$$\Delta\Phi[\rho(\mathbf{r},\omega)] \approx -\frac{1}{2}\int d\mathbf{r}_1 \int d\omega_1 \int d\mathbf{r}_2 \int d\omega_2 \Delta\rho(\mathbf{r}_1,\omega_1)\Delta\rho(\mathbf{r}_2,\omega_2) \times f(\mathbf{r}_{21},\omega_1,\omega_2) \tag{11}$$

where the Mayer function $f(\mathbf{r}_{21},\omega_1,\omega_2)$ equals -1 if spherocylinders (having center-of-mass and angular coordinates $\mathbf{r}_1$, ω_1 and $\mathbf{r}_2$, ω_2) overlap and 0 if they do not. Near a planar interface separating the coexisting phases, the density varies according to

$$\rho(\mathbf{r},\omega) = \frac{\rho_0}{4\pi}\left[1 + \sum_l \mu_l(z)P_l(\cos\theta)\right] \tag{12}$$

with θ measured relative to the bulk nematic director $\hat{n}$. Substituting Equation (12) into Equation (11) and rotating the Legendre polynomials in Equation (12) to a coordinate frame that has the interfacial normal $\hat{z}$ parallel to its z axis yields[6]

$$\Delta\Phi[\rho(\mathbf{r},\omega)] = \text{terms independent of } \hat{n}\cdot\hat{z} + \sum_{l_1,l_2,l}\int dz\mu_{l_1}(z) \times \int d\mathbf{R}[\mu_{l_2}(z+Z) - \mu_{l_2}(z)]F_{l_1l_2l}(R)P_l(\cos\theta_R)P_l(\hat{n}\cdot\hat{z}). \tag{13}$$

Some of the properties of the $F_{l_1l_2l}(R)$'s have been derived in Reference (6). For the present, it suffices to observe that $\Delta\Phi[\rho(\mathbf{r},\omega)]$ depends on $\hat{n}\cdot\hat{z}$ in an apparently complex way. There is no a priori reason to believe that $\hat{n}\cdot\hat{z} = 0$ or 1 will minimize γ_{IN}. However, upon expanding the order parameter $\mu_{l_2}(z+Z)$ to second order in Z, we recover the square-gradient result

$$\Delta\Phi[\rho(\mathbf{r},\omega)] = F_L[\{\mu_l(z)\}] + \frac{2}{15}\sum_{l_1,l_2}\int dz\frac{d\mu_{l_1}}{dz}\frac{d\mu_{l_2}}{dz} \times \int d\mathbf{R}R^2F_{l_1l_22}(R)P_2(\hat{n}\cdot\hat{z}) \tag{14}$$

since l odd does not occur in the sum for the spherocylinder model. In the limit that the $\mu_l(z)$'s vary slowly enough, Equation (14) applies and we reach the same conclusion as in subsection A—namely that $\hat{n}\cdot\hat{z} = 0$ or 1 minimizes γ_{IN}.

In order to carry out the minimization of the inhomogeneous grand potential functional, we initially make the ansatz

$$\mu_l(z) = \frac{\mu_l}{2}[1 + \tanh(z/\lambda)] \tag{15}$$

in which the order parameters each vary according to the same length scale λ. Although more sophisticated trial functions could be chosen for the $\mu_l(z)$'s, this single-parameter variation illustrates most of the salient features of the interface problem. It also enables a comparison of the full numerical integration[6] (Equation (13)) to the SGA. We first solve for the coexistence conditions using Equations (10) and (11). The explicit forms of Equations (13) and (14) and the ideal free energy functional (the first two terms in Equation (10)) yield the plots shown in Figure 2. For L (= the length of the cylindrical part of a spherocylinder)/D (= the diameter of the spherocylinder) greater than about 15, the SGA and the numerical integration produce qualitatively identical results for the tilt angle. Figure 2 shows the curve for $L/D = 20$. For shorter spherocylinders, the differences between the two calculations become more apparent. As an example, when $L/D = 5$ (the lower plot in Figure 2), the minimum in $\hat{n} \cdot \hat{z}$ occurs when $\theta_t = 58°$, but the SGA continues to predict $\theta_t = 90°$. The small curvature of the square-gradient curve indicates that the coefficient of $P_2(\hat{n} \cdot \hat{z})$ in Equation (14) has nearly vanished. For L/D still smaller, the P_2 term favors $\hat{n} \cdot \hat{z} = 1$. Under most circumstances, the P_2 term dominates the inhomogeneous free energy (see Equation (13)), but the P_4 term emerges as the most important contribution to the orientationally dependent surface tension of short spherocylinders. While P_4 has a minimum at $\theta_t = 49°$ that clearly manifests itself when $L/D = 5$, the actual minimum of the surface tension versus θ_t is a compromise between the P_2 and P_4 terms. An important difference between our findings and earlier calculations,[5] based on the assumption of a step-function profile for the I-N interface, is the somewhat sensitive dependence of θ_t on the aspect ratio. For comparison to the $L/D = 5$ case, we note that when $L/D = 10$, $\theta_t = 75°$.

A more general variational calculation involves the trial functions

$$\mu_0(z) = \frac{\mu_0}{2}\left[1 + \tanh(z - z_0)/\lambda_0\right] \tag{16a}$$

and

$$\mu_{l\neq 0}(z) = \frac{\mu_l}{2}\left[1 + \tanh z/\lambda_1\right]. \tag{16b}$$

We note that the SGA limits our ability to obtain information about $\mu_0(z)$ because the coefficient of

$$\int dz \left(\frac{d\mu_0}{dz}\right)^2 \tag{17}$$

in the expression for the surface tension is negative. In the one-parameter calculation, we constrain $\lambda_0 = \lambda_1$ and $z_0 = 0$. However, a calculation starting with Equations (16ab) would trivially lead to $\lambda_0 = 0$ since the resulting delta functions in Equation (17) are not quadratically integrable. On the other hand, Equation (14) is bounded as $\lambda_0 \rightarrow 0$. Table I summarizes the results of several variational

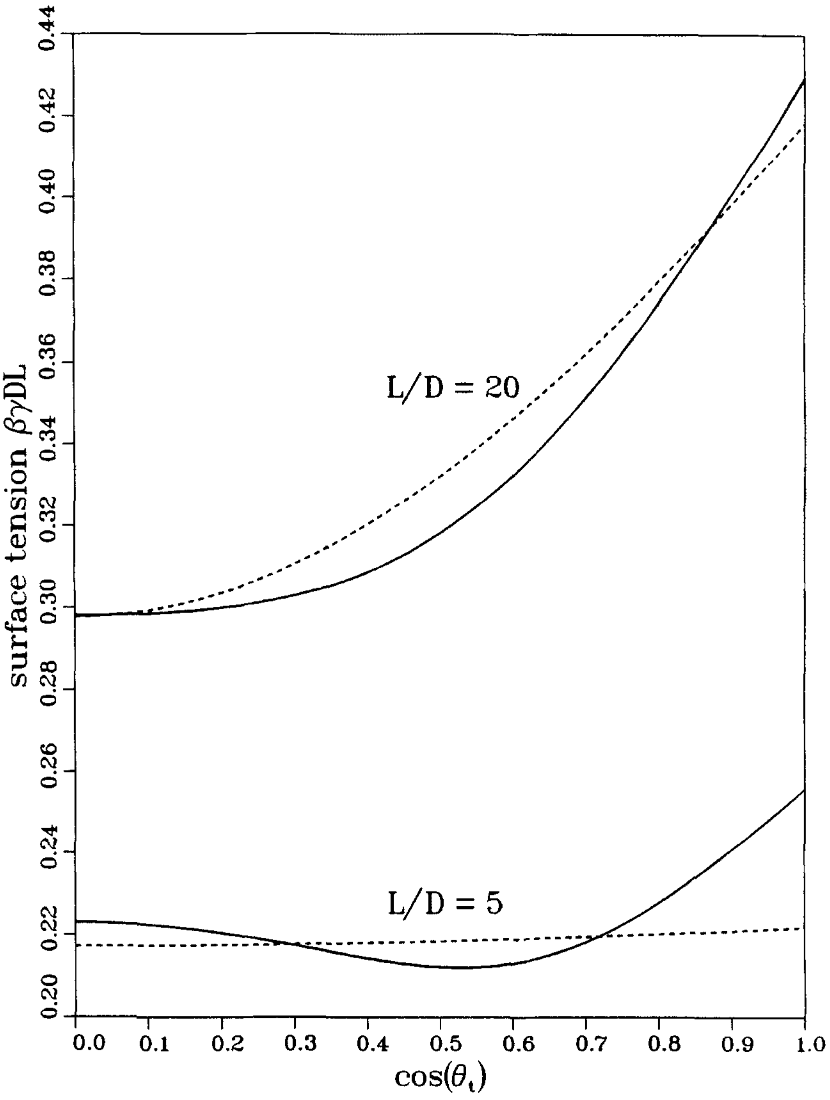

FIGURE 2 Isotropic-nematic surface tensions as functions of the cosine of the tilt angle, $\hat{n} \cdot \hat{z}$. The upper set of curves are for the aspect ratio of $L/D = 20$, the lower ones for $L/D = 5$. The square-gradient results are represented by the dashed lines, the numerical method results by the solid lines.

calculations within the SGA and the full numerical integration. For $L/D = 20$, the SGA agrees quite well with the full calculation. When $L/D = 5$, the agreement is poor for θ_t but reasonable for the surface tension and interfacial width. The more complete calculations based on Equations (16ab) show that a substantial decrease in the surface tension accompanies a shift in the $\mu_0(z)$ profile relative to that of the remaining order parameters. Thus, the growth in the number density lags behind the increase in orientational order upon passing from the isotropic to the nematic phase. In units of the length of the spherocylinders, the 10–90 width (the distance

TABLE I

Surface tensions and tilt angles

Aspect Ratio L/D = 20

Case	λ_1/L	λ_0/L	z_0/L	$\beta\gamma_{min}DL$	θ_t
1	0.310			0.298041	90°
1(SGA)	0.316			0.297766	90°
2	0.466	0.311		0.290375	90°
3	0.340		0.248	0.263405	90°
4	0.340	0.327	0.250	0.263383	90°

Aspect Ratio L/D = 5

Case	λ_1/L	λ_0/L	z_0/L	$\beta\gamma_{min}DL$	θ_t
1	0.409			0.211886	58°
1(SGA)	0.448			0.217239	90°
2	0.514	0.413		0.211777	61°
3	0.437		0.293	0.200672	62°
4	0.429	0.265	0.272	0.200033	58°

Description of cases in Table I: in case 1, λ_1 is varied ($\lambda_0 = \lambda_1$ and $z_0 = 0$); in case 2, λ_0 and λ_1 are allowed to vary ($z_0 = 0$); in case 3, λ_1 and z_0 are allowed to vary ($\lambda_0 = \lambda_1$); in case 3, λ_0, λ_1 and z_0 are varied. SGA indicates the square-gradient results.

over which the order parameters vary from 10 to 90 percent of their bulk nematic values) is less than 1 in all the calculations. As noted above, real I-N interfaces extend over hundreds of angstroms (10–100 times the lengths of typical nematic liquid crystal molecules). This deficiency stems from large discontinuities that accompany the hard-spherocylinder I-N transition and the short range of interactions between the model molecules.

III. DISCUSSION AND CONCLUSIONS

We have outlined two theoretical approaches to the I-N interface. The phenomenological theory accounts for the experimental observations by invoking the concept of interfacial polar ordering. This adds a term linear in $\hat{n} \cdot \hat{z}$ to the second-order gradient expansion of the inhomogeneous free energy and may shift the $P_2(\hat{n} \cdot \hat{z})$ parabola from its $\hat{n} \cdot \hat{z} = 0$ minimum. However, some of the parameters in this theory (especially d and E in Equations (3) and (6)) are difficult to obtain—either experimentally or theoretically. The molecular-based calculations for hard spherocylinders account for the tilt angles of I-N interfaces only when the $P_2(\hat{n} \cdot \hat{z})$ component ceases to dominate the surface tension. In our calculations, this occurs when $L/D < 10$, but the Onsager functional ignores terms in this range of aspect ratios that could affect these results. At this stage, the available experimental evidence fails to suggest whether or not the theoretically observed dependence of θ_t on L/D is a weakness or strength of the model. The tilt angles observed in the studies of Reference (9) are somewhat insensitive to the length of the alkyl chains pendant to the core aromatic groups of the *n*CB's. However, lengthening these groups does not simply translate into increasing of the aspect ratio of the hard-spherocylinder model. On the other hand, the MBBA[8] and *n*CB[9] studies, taken collectively, all but rule out a universal behavior of I-N tilt angles. Additional experimental effort directed toward understanding the roles that molecular symmetry and aspect ratios play in determining the I-N tilt angle seem warranted.

The theoretical machinery exists to improve the molecular theory in a variety of ways. Alternative approaches to the I-N transition can provide the basis for an inhomogeneous free energy functional applicable to dense isotropic and nematic phases. We have recently extended Tarazona's smoothed-density approximation[14] to restricted-orientation rods[15] and obtained good agreement with high-order virial and y-expansion[15] treatments of the I-N transition. The generalization to an inhomogeneous I-N interface proceeds straightforwardly. Similar calculations based on the scaled-particle theory of nematic liquids[16] or the Pynn approximation[17] for the direct correlation function would also constitute worthwhile studies.

The numerical calculations based on the variational principle and Equations (15) or (16ab) are, of course, grossly oversimplified. One could adapt the integral-equation scheme employed in Reference (3) to analyze the density profiles more carefully. This would surely lead to a lower value for the surface tension and a more accurate picture of the interfacial density profile. However, the main conclusions of our numerical work concerning the tilt angle in the short spherocylinder and Onsager $L/D \to \infty$ limits would almost certainly survive. These result not so much from the parametrized forms chosen for the density profiles as from the magnitudes of the harmonics $F_{l_1 l_2 l}(R)$ that appear in the orientational part of the interfacial free energy (see Equation (13)). In particular, we find that harmonics with $l = 2$ tend to dominate the inhomogeneous free energy. Those with $l = 4$ or higher make comparatively minor contributions to the surface tension. The outstanding exception to this observation occurs when $L/D \leq 10$ for which considerable cancellation occurs among the $P_2(\hat{n} \cdot \hat{z})$ terms. Over the range of aspect ratios $1 < L/D \leq 10$, the hard-spherocylinder model (within the Onsager approximation) is undergoing a transition from $\hat{n} \cdot \hat{z} = 0$ to 1. As the prefactors of the $P_2(\hat{n} \cdot \hat{z})$ terms change sign from positive ($L/D \approx 10$) to negative ($L/D < 5$) they cross zero, and the $l = 4$ contributions determine the orientational dependence of γ_{IN}.

Besides accounting for an oblique tilt angle, a successful molecular model must also account for a diffuse I-N interface and provide realistic estimates of γ_{IN} ($\gamma_{IN}LD \approx 0.002kT$). Softer I-N transitions generally lead to broader I-N interfaces and smaller interfacial tensions. The hard-spherocylinder model predicts too narrow an interface and large interfacial free energies ($\gamma_{IN}LD \approx 0.2kT$). In this regard, it would be interesting to investigate the I-N interface of a hard-particle model displaying a weakly first-order I-N transition. For such systems, we would expect a smaller surface tension and a commensurate broadening of the density profile. By adjusting the dimensions of restricted-orientation, biaxial parallelipipeds,[15] it is possible to observe arbitrarily weak I-N transitions within a theoretical model. Our continuing studies of I-N interfaces will, in part, emphasize models like this that undergo almost continuous I-N transitions.

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