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Director orientation at the nematic-phase–isotropic-phase interface for the model of hard spherocylinders

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A fluid of hard spherocylinders is studied in the Onsager model adapted to a nonuniform system. The interfacial properties at nematic-phase–isotropic-phase coexistence are considered. It is found that the angle between the director and the normal to the interface is approximately 60° and does not depend on the length-to-width ratio L/D of the spherocylinder. The nematic-phase–isotropic-phase surface tension, however, tends linearly to zero as $D/L \to 0$. It is also argued that the anisotropic hard-core repulsion favors the perpendicular alignment at the nematic free surface. The results concerning the tilt angle are in good agreement with experimental studies for nCB ($n=5,6,7,8$)[(4-n-alkyl-4′-cyano)biphenyl].

I. INTRODUCTION

It was shown by Onsager[1] in 1949 that a system of a hard elongated particles can undergo a first-order phase transition from the disordered (isotropic) phase to the orientationally ordered (nematic) phase. The density change is responsible for the transition, as for hard interactions temperature is an irrelevant variable.

At the other extreme, there exists the Maier-Saupe theory[2] which entirely neglects the hard-core anisotropic repulsion but instead takes into account long-range attractive anisotropic interactions in a mean-field fashion. Modern theories of liquid crystals[3,4] try to deal with both anisotropic hard-core repulsions and long-range attractions. Although the attractive forces acting between liquid-crystal molecules should not be underestimated (they provide the temperature dependence of physical quantities), recent computer simulations[5–7] have convinced us that anisotropic hard-core interactions alone explain the essential physics of liquid crystals. Not only has the formation of the nematic phase been observed in those simulations but also the smectic and columnar phases have been observed.

In the present paper we study the problem of the director orientation at the nematic-phase–isotropic-phase interface using the Onsager model of a nematogen adapted to a nonuniform system. When the nematic and isotropic phases coexist, the interface breaks both translational and orientational symmetry. Though the bulk free energy of the nematic phase is independent of the director $\hat{\mathbf{n}}$, the surface tension does depend on $\hat{\mathbf{n}}$. The system will adopt the orientation for which the surface tension is minimized.

The problem of the preferred orientation near liquid-crystal surfaces has received much attention during the last few years. We quickly review the main results.

Telo da Gama[8] has assumed that outside the effective spherical hard core[9] of radius R the liquid-crystal particles interact via long-range attractive potential of the Maier-Saupe type:

$$V_{\rm att}(\mathbf{r},\hat{\omega}_1,\hat{\omega}_2)=\begin{cases}-A(R/r)^6-B(R/r)^6P_2(\hat{\omega}_1\cdot\hat{\omega}_2) & \text{for } r>R\\ 0 \quad \text{for } r<R\ ,\end{cases} \tag{1}$$

where A and B are constants and $\hat{\omega}_1$ and $\hat{\omega}_2$ are the orientations of the interacting molecules. This model exhibits no preferred orientation at the nematic-phase–isotropic-phase interface, due to the lack of coupling between the orientational and translational degrees of freedom in the potential. This result is contradicted by experiments which show that $\hat{\mathbf{n}}$ is obliquely tilted at the nematic-phase–isotropic-phase interface.[10,11] The tilt angle, measured from the normal to the interface, has been found for different substances (nCB, $n=5,6,7,8$) to lie in the range of 50°–70°.

The problem in this theory has been remedied[12,13] by the inclusion of quadrupolar interactions and anisotropic repulsions. This leads to an obliquely tilted director, as was shown by Sullivan.[12] However, the Sullivan calculations are based on an expansion in spherical harmonics which converges slowly for hard-core interactions, so neglecting terms higher than P_4 in the surface tension seems unjustified. Kimura and Nakano[13] have found that hard-core interactions should favor parallel alignment of the molecules relative to the interface. Their result is not very convincing, however, because of geometrical oversimplifications concerning excluded-volume effects. On the other hand, those authors do take into account the anisotropic attractive potential which can produce a tilted director at the interface.

In this paper we provide evidence that a system of hard spherocylinders exhibits an obliquely tilted director at the nematic-phase–isotropic-phase interface, with a tilt angle of $\theta_t \cong 60°$. This angle turns out to be insensitive, within the numerical accuracy of our computations, to changes in the length-to-width ratio of the spherocylinder in the range $L/D=5-100$.

The paper is organized as follows. In Sec. II we specify the model and the applied approximations. In Sec. III we present the main results of calculations for the nematic-phase–isotropic-phase interface and also make some comments concerning the role of hard-core interactions in the case of the free nematic surface. And finally, Sec. IV is devoted to the discussion. All details of analytical calculations have been relegated to the Appendix.

II. THE MODEL

To study the nematic-phase–isotropic-phase interface we employ the grand potential Ω in a form applicable to inhomogeneous systems[14,15] and use a lowest-order virial expansion of its nonideal part. Then

$$\Omega\{\rho(\mathbf{r},\omega)\}/k_BT=\int d\mathbf{r}_1 d\omega_1 \rho(\mathbf{r}_1,\omega_1)\{\ln[\Lambda^3\rho(\mathbf{r}_1,\omega_1)]-1\}-\tfrac{1}{2}\int d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 f_2(\mathbf{r}_{12},\omega_1,\omega_2)\rho(\mathbf{r}_1,\omega_1)\rho(\mathbf{r}_2,\omega_2)$$
$$-(\mu/k_BT)\int d\mathbf{r}_1 d\omega_1 \rho(\mathbf{r}_1,\omega_1)\ , \qquad (2)$$

where $\rho(\mathbf{r},\omega)$ stands for the one-particle distribution function, $\mathbf{r},\omega$ denoting the positional and orientational coordinates; μ is the chemical potential and Λ comes from the kinetic energy of the system. We model the nematogen by a system of hard spherocylinders for which the Mayer function f_2 equals -1 if two spherocylinders overlap and 0 otherwise. It was shown by Onsager that the truncation of the virial expansion (2) is justified at low density and when the higher virial coefficients are small, as is the case for large L/D. To find the equilibrium $\rho(\mathbf{r},\omega)$ we should minimize Ω and then solve the resulting integral equation with the proper boundary conditions. This would be a rather difficult numerical problem; thus we seek an alternative approach. We follow Sullivan[12] and assume the interface to be a sharp, flat surface located at $z=0$ and dividing the uniform isotropic ($z<0$) and nematic ($z>0$) phases. In this approximation $\rho(\mathbf{r},\omega)$ reads as follows:

$$\rho(\mathbf{r},\omega)=\rho(z,\omega)=\begin{cases}\rho_I/4\pi & \text{for } z<0\\ \rho_N f(\omega) & \text{for } z>0\ ,\end{cases} \qquad (3)$$

where ρ_I and ρ_N are the densities of the isotropic and nematic phases, respectively. $f(\omega)$ stands for the orientational distribution function of the bulk nematic phase at the coexistence conditions. It is understood that $f(\omega)$ depends on $\hat{\mathbf{n}}$, which is uniform throughout the nematic phase. Substitution of (3) into (2) and subtraction of the bulk terms results in the following expression for the surface tension, which is equal to the surface grand potential per unit area:[16]

$$\gamma(\hat{\mathbf{n}})=\gamma_1(\hat{\mathbf{n}})+\gamma_2(\hat{\mathbf{n}})+\gamma_3\ , \qquad (4)$$

where

$$\gamma_1(\hat{\mathbf{n}})/k_BT=(\rho_N\rho_I/4\pi)\int d\omega_1 d\omega_2 V_1(\omega_1,\omega_2)f(\omega_1)\ , \qquad (5)$$

$$\gamma_2(\hat{\mathbf{n}})/k_BT=-\tfrac{1}{2}\rho_N^2\int d\omega_1 d\omega_2 V_1(\omega_1,\omega_2)f(\omega_1)f(\omega_2)\ , \qquad (6)$$

$$\gamma_3/k_BT=-\tfrac{1}{2}(\rho_I/4\pi)^2\int d\omega_1 d\omega_2 V_1(\omega_1,\omega_2)\ , \qquad (7)$$

$$V_1(\omega_1,\omega_2)=-\int_0^\infty z_{12}dz_{12}\int d\mathbf{r}_{12}^{\perp} f_2(\mathbf{r}_{12},\omega_1,\omega_2)\ , \qquad (8)$$

and $\mathbf{r}_{12}^{\perp}$ is the projection of $\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1$ onto the plane parallel to the interface. Equations (4)–(8) appear in Sullivan's paper[12] but we outline the derivation in the Appendix. The dependence of γ_1 and γ_2 on $\hat{\mathbf{n}}$ follows from the fact that $V_1(\omega_1,\omega_2)$ does not have full rotational symmetry and γ_3 is independent of $\hat{\mathbf{n}}$ as it contains only the isotropic-phase distribution function $1/4\pi$. Having γ as a function of $\hat{\mathbf{n}}$ we can find the tilt angle θ_t at the nematic-phase–isotropic-phase interface by a minimization procedure. We interpret the contributions to γ as follows. γ_2 and γ_3 are due to the increase of the translational entropy of molecules at the surface if only a half space is filled with either the nematic or the isotropic phase and the other half space is empty. A molecule at the surface enjoys greater translational freedom than the molecules in the bulk because of the lack of near neighbors on the other side of the surface. At least qualitatively, these terms can be considered as the contribution of hard-core interactions to the nematic-phase–vapor and the isotropic-phase–vapor surface tension, respectively. The negative contributions of γ_2 and γ_3 to γ are compensated by the positive term γ_1. The latter comes from the direct interaction between molecules of the isotropic and nematic phases. To calculate $V_1(\omega_1,\omega_2)$ one has to perform the integration of z_{12} over a half of the solid of excluded volume, defined by $-f_2(\mathbf{r}_{12},\omega_1,\omega_2)$, for fixed ω_1 and ω_2 (see Fig. 1). The orientation of the solid with respect to the interface is determined by ω_1 and ω_2. The calculation of V_1 for the whole solid would be a rather tedious task; thus we make some approximation to perform the integral. One can easily see from Fig. 1 that for large L/D the contribution of the cylindrical and spherical parts of the solid of excluded volume to V_1 is negligible unless the angle θ_{12} between the long axes of two spherocylinders is very small. If θ_{12} is close to zero these parts give the main contribution to V_1. These cases are rather rare, however, unless the orientational distribution function $f(\omega)$ is sharply peaked around $\hat{\mathbf{n}}$. Thus in our calculations we take into account only the inside part of the solid of excluded volume which is a rectangular prism with a rhombus in its base [see the unshadowed area in Fig. 1(a)]. It is worth noting that making this approximation, we do not lose any symmetries of the full solid of excluded volume. Moreover, it is consistent with the Onsager low-density approximation for the free energy which is justified in the large L/D limit. The calculation of V_1 is presented in the Appendix.

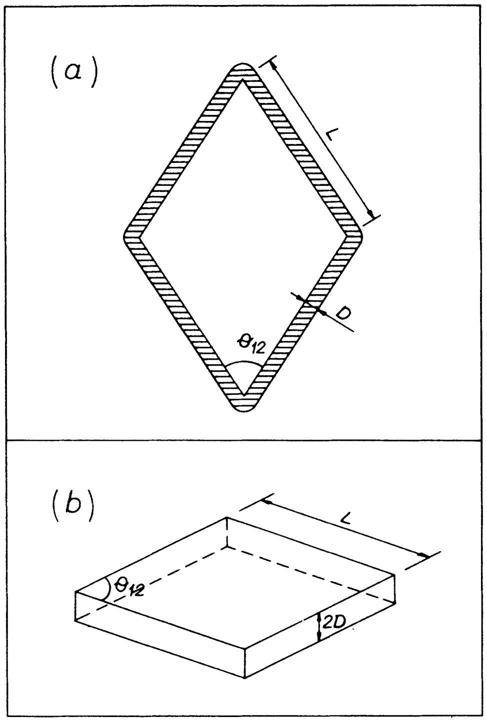

FIG. 1. Perpendicular projection of the solid of excluded volume onto the plane parallel to its base. θ_{12} is the angle between the long axes of two spherocylinders of length L and width D. The hatched area represents the projection of spherical and cylindircal parts. (b) The rectangular prism with the rhombus in its base, obtained from the solid of excluded volume after rejection of the spherical and cylindrical parts.

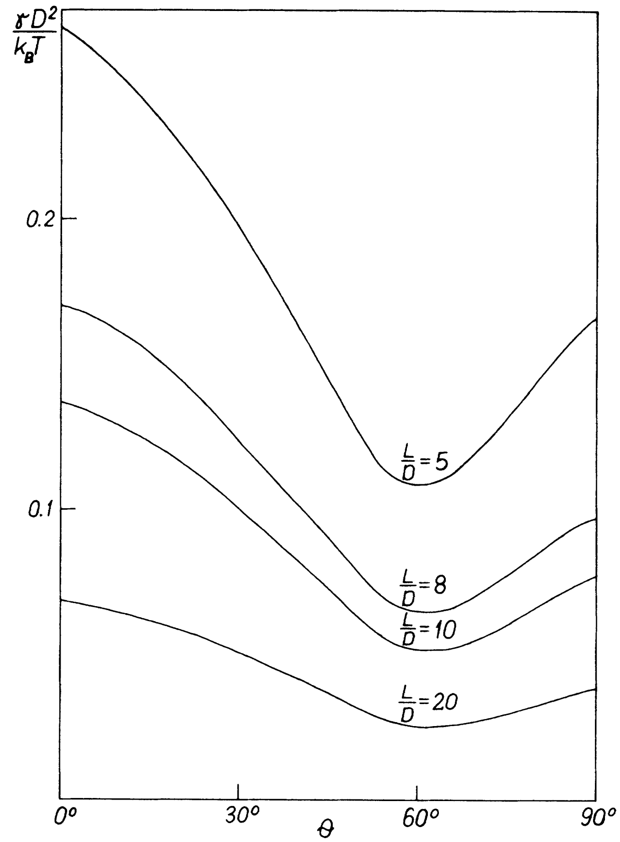

FIG. 2. Nematic-phase–isotropic-phase surface tension γ (in units of $k_B T/D^2$) as a function of the angle θ between the director and the normal to the interface for $L/D=5,8,10,20$. γ is minimal for $\theta=\theta_t=60°$ for all L/D.

III. RESULTS

The integrals (5)–(7) over the angular variables ω_1 and ω_2 have been calculated numerically by the Monte Carlo method. The explicit form of $V_1(\omega_1,\omega_2)$ is given in the Appendix and the orientational distribution function $f(\omega)$ and the densities ρ_I,ρ_N at nematic-phase–isotropic-phase coexistence have been taken from Lasher's paper.[17] The function $f(\omega)$, obtained by Lasher, is parameterized by the dimensionless parameter $\lambda=2\rho_N DL^2$. At nematic-phase–isotropic-phase coexistence, $\lambda=10.6$ and $\rho_N/\rho_I=1.26$. $f(\omega)$ is given in the form of an expansion in Legendre polynomials P_l, $l=2,4,\ldots,14$

$$f(\omega)=\frac{1}{4\pi}\left[1+\sum_{l=2,4,\ldots,14} a_l P_l(\hat{\mathbf{n}}\cdot\hat{\omega})\right], \tag{9}$$

where $\hat{\omega}$ is the unit vector along the long axis of a spherocylinder. The calculations have been done for $L/D=5,8,10,15,20,25,100$. Figure 2 shows the dependence of the nematic-phase–isotropic-phase surface tension γ on the angle θ between $\hat{\mathbf{n}}$ and the normal to the interface for $L/D=5,8,10,20$. The equilibrium value of γ corresponds to the minimum which occurs at $\theta=\theta_t=60\pm4°$ for all values of L/D, including $L/D=15$, 25 and 100 not shown in Fig. 2. The minimum is rather flat, especially for large values of L/D, and this is the reason of the large uncertainty in the location of the tilt angle θ_t. In Fig. 3 we show the equilibrium value of the surface tension $\gamma(\theta_t)$ as a function of D/L. For $D/L<0.1$ the dependence is practically linear and $\gamma(\theta_t)\to 0$ as $D/L\to 0$. This is not surprising as the density measured in units of the volume of a spherocylinder, $\rho^*=\rho LD^2=\frac{1}{2}\lambda D/L$, tends to zero with $D/L\to 0$ as λ is constant at the coexistence. The two contributions to the surface tension, γ_1 and γ_2, are presented in Figs. 4 and 5, respectively, as functions of θ for $L/D=5,8,10,20$. The positive contribution γ_1, describing the direct interaction between molecules belonging to the different phases, has a minimum at $\theta=90°$ for all values of L/D. On the contrary, γ_2 is minimal for $\theta=0°$, also for all L/D. This behavior can be explained as follows. When one half space is empty and the other is filled with the nematic phase (see γ_2), then the more freedom of translation the molecules at the surface have, the more they stick out from the surface. Thus on entropic grounds γ_2 prefers the perpendicular ($\theta=0°$) alignment. On the other hand, when the other half space is filled with the isotropic phase, greater freedom of translation is admitted to those molecules of the nematic phase that keep close to the surface

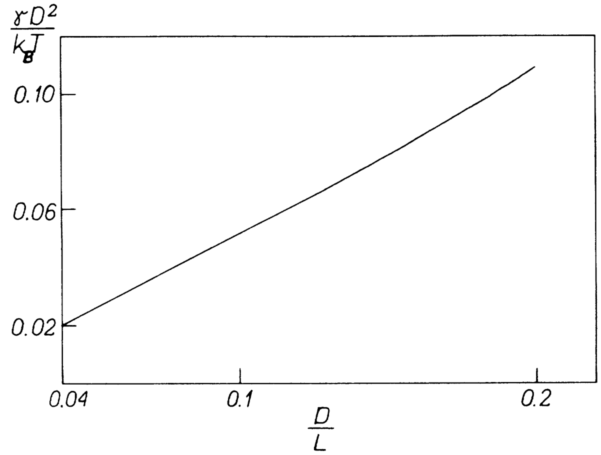

FIG. 3. Equilibrium nematic-phase–isotropic-phase surface tension γ ($\theta=60°$) as a function of the width-to-length ratio D/L. For $D/L \leq 0.1$ the dependence is linear and $\gamma \to 0$ as $D/L \to 0$.

and do not stick out. This means that γ_1 is minimal for the parallel alignment ($\theta=90°$). These opposite tendencies lead to the obliquely tilted director at the nematic–phase-isotropic-phase interface.

As we have already mentioned, γ_2 can be considered as the main contribution of hard-core interactions to the

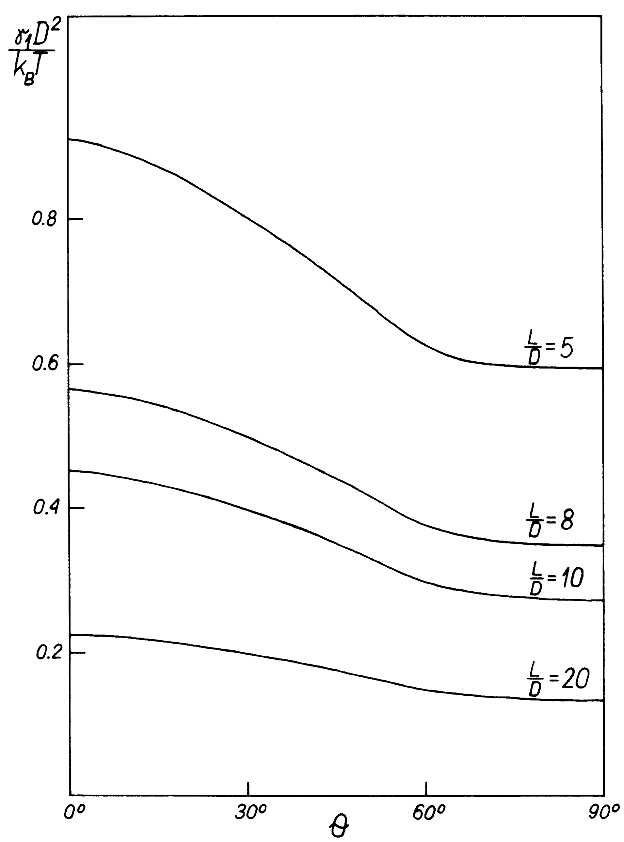

FIG. 4. γ_1 [see Eq. (5)] as a function of the angle θ for $L/D=5,8,10,20$.

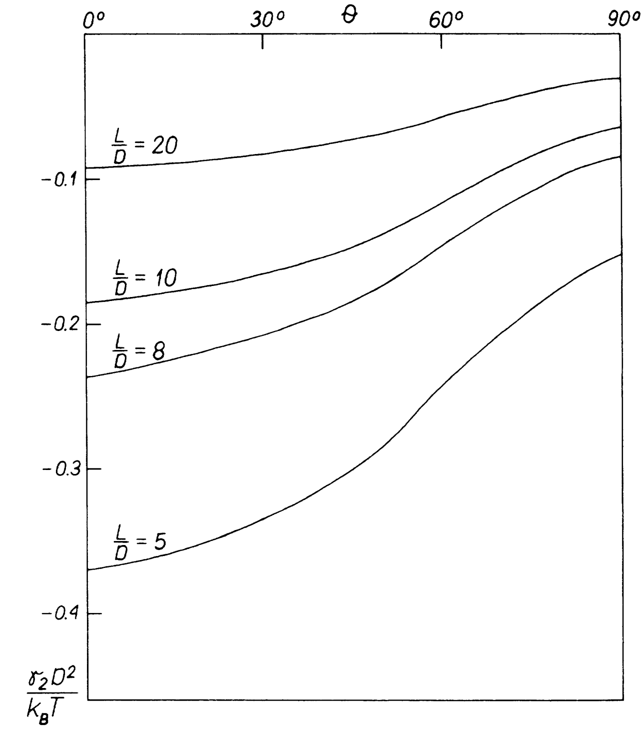

FIG. 5. γ_2 [see Eq. (6)] as a function of the angle θ for $L/D=5,8,10,20$.

nematic-phase–vapor surface tension γ_{NV} because $\rho_V \ll \rho_N$ [see Eqs. (5)–(7) with ρ_I replaced by ρ_V (Ref. 12)]. Of course, the free nematic-phase surface can exist only if the attractive forces are taken into account; nevertheless it would be useful to have some hints concerning the hard-core contribution. First of all we expect that the hard-core interactions will favor the perpendicular alignment ($\theta=0°$) at the free surface. Indeed, this behavior has been observed for 8CB [(4-*n*-octy(-4′-cyano)biphenyl], 5CB [(4-*n*-pentyl-4′-cyano) biphenyl] (Ref. 18), and also for MBBA [*N*-(4-*n*-methoxy)benzylidene-4′-(*n*-butyl) airiline] and EBBA [*N*-(4-*n*-ethoxy)benzylidene-4′-(*n*-butyl) airiline] at temperatures close to the nematic-phase–isotropic-phase transition temperature.[19,20] Secondly, we can estimate from our model the jump in the liquid-vapor surface tension, $\Delta\gamma_{LV}=\gamma_{NV}-\gamma_{IV}$, at the nematic-phase–isotropic-phase transition. For the hard-core contribution to $\Delta\gamma_{LV}$ we have $\Delta\gamma_{LV}^{HC}=\gamma_2-\gamma_3$, and we find that $\Delta\gamma_{LV}^{HC}<0$ for the perpendicular alignment ($\theta=0°$), which is in agreement with the experiment for 8CB, 5CB, and MBBA.[18] Finally we note that Kimura and Nakano[21] also concluded that hard-core interactions should favor the perpendicular alignment at the nematic free surface.

IV. DISCUSSION

In this paper we have studied the nematic-phase–isotropic-phase interface using the Onsager model of the nematogen. We conclude that hard-core interactions alone are capable of explaining the tilt of the director at the interface. The tilt angle obtained, $\theta_t=60°$, is in a very good agreement with the experimental results for many liquid crystals. In our model, θ_t does not depend on L/D but this may be the result of our approximations. The neglect of the round parts in the solid of excluded volume is justified in the limit of large L/D. Therefore, for smaller L/D, the inclusion of those parts could change θ_t but this remains to be investigated. Our calculations were also based on the sharp-interface approximation which disagrees with both experiment[10] and theoretical studies.[8] It has been found that the interface is far from being sharp; its thickness varies for different substances from 400 to 750 Å, while the typical length of a liquid-crystal molecule is around 20 Å. The diffusive nature of the interface is due to the fact that the nematic-phase–isotropic-phase transition is weakly first order. It would be interesting to investigate the effect of the interfacial thickness on the average orientation of the director in the interface.

We would like also to mention some other factors that have not been studied in this paper but could affect the tilt angle at the nematic-phase–isotropic-phase interface and at the nematic free surface. These are as follows: anisotropic attractive forces,[12,13,21–24] polar ordering,[25] biaxiality,[26] and flexible chains. Finally we note that because hard-core interactions favor the perpendicular alignment at the nematic free surface, it may result in the formation of smectic order near the surface, which has been recently observed in experiment.[18,27–29]

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APPENDIX

1. Derivation of the expression for $\gamma(\hat{\mathbf{n}})$

Because of the sharp-interface approximation, only the nonideal part of the grand potential, Ω, contributes to the surface tension. Thus after subtracting the bulk terms we find from (2) that

$$\begin{aligned}\gamma/k_BT=&\tfrac{1}{2}\int_{-\infty}^{0}dz_1\left[\int_{-\infty}^{+\infty}dz_2d\omega_1d\omega_2V(|z_{12}|,\omega_1,\omega_2)\rho(z_1,\omega_1)\rho(z_2,\omega_2)-\int d\omega_1d\omega_2V_0(\omega_1,\omega_2)\rho(-\infty,\omega_1)\rho(-\infty,\omega_2)\right]\\&+\tfrac{1}{2}\int_{0}^{+\infty}dz_1\left[\int_{-\infty}^{+\infty}dz_2d\omega_1d\omega_2V(|z_{12}|,\omega_1,\omega_2)\rho(z_1,\omega_1)\rho(z_2,\omega_2)\right.\\&\qquad\left.-\int d\omega_1d\omega_2V_0(\omega_1,\omega_2)\rho(+\infty,\omega_1)\rho(+\infty,\omega_2)\right],\end{aligned}\tag{A1}$$

where

$$V(|z_{12}|,\omega_1,\omega_2)=-\int d\mathbf{r}_{12}^{\perp}f_2(\mathbf{r}_{12},\omega_1,\omega_2)\ ,\tag{A2}$$

$$V_0(\omega_1,\omega_2)=-\int d\mathbf{r}_{12}f_2(\mathbf{r}_{12},\omega_1,\omega_2)\ .\tag{A3}$$

Using (3) we transform (A1) as follows:

$$\begin{aligned}\gamma/k_BT=\tfrac{1}{2}\int d\omega_1d\omega_2\Bigg[&-(\rho_I/4\pi)^2\int_{-\infty}^{0}dz_1\left[\int_{-\infty}^{0}dz_2V(|z_{12}|,\omega_1,\omega_2)-V_0(\omega_1,\omega_2)\right]\\&-\rho_N^2\int_0^{+\infty}dz_1\left[\int_0^{+\infty}dz_2V(|z_{12}|,\omega_1,\omega_2)-V_0(\omega_1,\omega_2)\right]f(\omega_1)f(\omega_2)\\&+2\rho_N(\rho_I/4\pi)\int_{-\infty}^{0}dz_1\int_0^{+\infty}dz_2V(|z_{12}|,\omega_1,\omega_2)f(\omega_1)\Bigg]\ .\end{aligned}\tag{A4}$$

All integrals over z_1 and z_2 appearing in (A4) transform to

$$\begin{aligned}\int_0^{+\infty}dz_1\int_{z_1}^{+\infty}dz_{12}V(|z_{12}|,\omega_1,\omega_2)&=\int_0^{+\infty}dz_{12}z_{12}V(|z_{12}|,\omega_1,\omega_2)\\&=V_1(\omega_1,\omega_2)\ ,\end{aligned}\tag{A5}$$

and we recover Eqs. (4)–(7).

2. Derivation of the expression for $V_1(\omega_1,\omega_2)$

To calculate the function $V_1(\omega_1,\omega_2)$ in the approximation neglecting the cylindrical and spherical parts in the solid of excluded volume, we rewrite Eq. (8) as follows:

$$V_1(\omega_1,\omega_2)=\int d\mathbf{r}_{12}(\hat{\mathbf{k}}\cdot\mathbf{r}_{12})\Theta(\hat{\mathbf{k}}\cdot\mathbf{r}_{12})\chi(\mathbf{r}_{12},\omega_1,\omega_2)\ ,\tag{A6}$$

where $\chi(\mathbf{r}_{12},\omega_1,\omega_2)$ is the characteristic function of the rhomboidal prism ($\chi=1$ inside and $\chi=0$ outside the prism), $\Theta(\hat{\mathbf{k}}\cdot\mathbf{r}_{12})$ stands here for the Heaviside step function, and $\hat{\mathbf{k}}$ denotes the vector normal to the interface cutting the prism through its center at $\mathbf{r}_{12}=0$. The prism can be defined by three vectors: $\mathbf{a}=L\hat{\omega}_1/2$, $\mathbf{b}=L\hat{\omega}_2/2$, and $\mathbf{c}=D\hat{\omega}_1\times\hat{\omega}_2/|\hat{\omega}_1\times\hat{\omega}_2|$, where $\hat{\omega}_1,\hat{\omega}_2$ are the unit vectors along the symmetry axes of two spherocylinders. Each vector $\mathbf{r}_{12}$ belonging to the prism has the following form:

$$\mathbf{r}_{12}=r\mathbf{a}+s\mathbf{b}+t\mathbf{c}\ ,\tag{A7}$$

with $-1 \le r,s,t \le +1$. It is convenient to change the integration variable $\mathbf{r}_{12}$ to r,s,t, which gives

$$V_1(\omega_1,\omega_2)=\tfrac{1}{8}V_0\int_{-1}^{1}ds\int_{-1}^{1}dt\int_{-1}^{1}dr\,\Theta(rA+sB+tC)\times(rA+sB+tC)\ , \tag{A8}$$

where $V_0=2L^2D\sin\theta_{12}$ is the volume of the prism and $A=\mathbf{a}\cdot\hat{\mathbf{k}}$, $B=\mathbf{b}\cdot\hat{\mathbf{k}}$, and $C=\mathbf{c}\cdot\hat{\mathbf{k}}$. Without loss of generality we can assume that $A\ge B\ge C\ge 0$. Then we find that

$$V_1=(V_0/8A)\int_{-1}^{1}ds\int_{-1}^{1}dt\int_{-A+sB+tC}^{A+sB+tC}dz\,z\Theta(z)\ , \tag{A9}$$

where $z=rA+sB+tC$. Two separate cases have to be considered: 1, $A\ge B+C$ and 2, $A\le B+C$.

Case 1

In this case the integration over z in (A9) is from $z=0$ to $z=A+sB+tC$ because $-A+sB+tC\le -A+B+C\le 0$ and $A+sB+tC\ge A-B-C\ge 0$; hence

$$V_1=V_0(3A^2+B^2+C^2)/12A\ . \tag{A10}$$

Case 2

When $A\le B+C$ we calculate the integral over z as follows:

$$\int_{-A+sB+tC}^{A+sB+tC}dz\,z\Theta(z)=\tfrac{1}{2}(A+sB+tC)^2\Theta(A+sB+tC)-\tfrac{1}{2}(-A+sB+tC)^2\times\Theta(-A+sB+tC)\ . \tag{A11}$$

To integrate the first term in (A11) over s and t we substitute $y=A+sB+tC$, $ds=dy/B$, hence

$$\begin{aligned}\tfrac{1}{2}\int_{-1}^{1}dt\int_{-1}^{1}ds(A+sB+tC)^2\Theta(A+sB+tC)&=\frac{1}{2B}\int_{-1}^{1}dt\int_{A-B+tC}^{A+B+tC}dy\,y^2\Theta(y)\\&=\frac{1}{6B}\left[\int_{-1}^{1}dt(A+B+tC)^3-\int_{-1}^{1}dt(A-B+tC)^3\Theta(A-B+tC)\right]\\&=\frac{1}{6BC}\left[\int_{A+B-C}^{A+B+C}dx\,x^3-\int_{A-B-C}^{A-B+C}dx\,x^3\Theta(x)\right]\\&=\frac{1}{24BC}[(A+B+C)^4-(A+B-C)^4-(A-B+C)^4]\end{aligned} \tag{A12}$$

because $A-B-C<0$. One easily finds that the second term in (A11) gives

$$-\tfrac{1}{2}\int_{-1}^{1}dt\int_{-1}^{1}ds(-A+sB+tC)^2\Theta(-A+sB+tC)=-(-A+B+C)^4/24BC\ . \tag{A13}$$

Substitution of (A12) and (A13) into (A9) leads to the expression for V_1. For arbitrary signs and relations between A,B,C we can summarize the two cases as follows:

$$V_1=\tfrac{1}{12}V_0\frac{\{2[\max(|A|,|B|,|C|)]^2+A^2+B^2+C^2\}}{\max(|A|,|B|,|C|)} \tag{A14}$$

if $|A|,|B|,|C|$ do not satisfy the triangle inequality and

$$\begin{aligned}V_1=\tfrac{1}{192}V_0[(|A|+|B|+|C|)^4&-(|A|+|B|-|C|)^4\\&-(|A|-|B|+|C|)^4\\&-(-|A|+|B|+|C|)^4]/|A|\,|B|\,|C|\ ,\end{aligned} \tag{A15}$$

if $|A|,|B|,|C|$ satisfy the triangle inequality.

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