

## Nematic alignment at a solid substrate: The model of hard spherocylinders near a hard wall

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(Received 1 March 1988)

A system of hard spherocylinders near an impenetrable wall is studied in the low-density Onsager approximation. Using a simple local approximation for the one-particle distribution function, we show that the preferred orientation of the nematic director is parallel to the wall. The density and order-parameter profiles are calculated. The nematic main order parameter  $Q$  is enhanced near the wall even though the density is reduced. The wall-induced biaxiality  $P$  is small in the interfacial region. We find that wetting by the nematic phase should occur at the nematic-isotropic coexistence.

### I. INTRODUCTION

The properties of liquid crystals are very sensitive to boundary conditions. Even a weak interaction with a limiting surface can change the structure of a liquid crystal in the layer adjacent to that surface. Therefore it is very important for practical applications of liquid crystals to study the effect of boundaries on their properties. Thus it is not surprising that the problem of liquid crystal surfaces received both experimental<sup>1-6</sup> and theoretical<sup>7-10</sup> attention.

One of the interesting and rather poorly understood problems is the mechanism of alignment of liquid crystal molecules at various limiting surfaces. One such surface is the nematic free surface. The experimental results<sup>1,11-13</sup> show that the preferred orientation of the nematic director at this surface is, in almost all cases,<sup>14</sup> normal or close to normal to the surface, especially for temperatures close to the nematic-isotropic transition temperature. On the other hand, in the case of the nematic-isotropic interface, the director is usually tilted with respect to the normal and the tilt angle is in the range of  $50^\circ$ – $70^\circ$ .<sup>2,15,16</sup>

We have shown recently,<sup>17</sup> studying the Onsager model of a nematogen,<sup>18</sup> that anisotropic hard-core interactions favor perpendicular alignment of molecules at the nematic free surface and also a tilted director at the nematic-isotropic interface. The tilt angle has been found to be close to  $60^\circ$  independently of the length-to-width ratio of a molecule. Of course, to explain the variations of the tilt angle with temperature<sup>11-13</sup> one must take into account attractive forces.<sup>19-23</sup> Nevertheless the results obtained for anisotropic hard-core interactions alone suggest that the short-range repulsion plays an important role in the mechanism of the director orientation at both the free surface and  $N-I$  interface. Thus one can expect that also in the case of liquid crystal alignment at solid surfaces the short-range fluid-fluid and substrate-fluid anisotropic repulsion is very important.

Numerous experiments have been performed to study solid substrate-liquid crystal interfaces.<sup>3-6,24-33</sup> Often the substrates have been treated by special techniques like rubbing, buffing, oblique evaporation, and others.<sup>3,4</sup> They are thought to produce a desired director orienta-

tion at the surface. They do not, however, always lead to unique results<sup>3,4</sup> and in some sense hide the true mechanism of the alignment of liquid crystal molecules. An insufficient purity of the liquid crystal may also lead to confusing results. For example, impurities produced by hydrolysis of the liquid crystal can change the director orientation from homogeneous to homeotropic. Such a behavior has been observed for MBBA [*N*-(4-*n*-methoxy)benzylidene-4'-(*n*-butyl) aniline] and 5CB [(4-*n*-pentyl-4'-cyano) biphenyl] in a remarkable experiment by Ohgawara *et al.*<sup>26</sup> The authors show that if they remove the impurities and deal only with clean inorganic surfaces, then the alignment of all nematic liquid crystals of Schiff base, biphenyl, ester, PCH, and azoxy compounds is parallel to the surface. This fact cannot apparently be explained by van der Waals forces<sup>34</sup> nor by polar ordering.<sup>26</sup> Thus the short-range anisotropic repulsion seems to be responsible for the liquid crystal alignment, at least for some kind of solid substrates.

In this paper we study the nematic-wall and the isotropic-wall interfaces assuming that liquid crystal molecules interact with one another and with the wall only via hard-core repulsion. The Onsager model of a nematogen adapted to a nonuniform system is assumed. We find that if the nematic phase is in contact with the wall, the minimum of the nematic-wall surface tension occurs for the director lying on the wall. The main order parameter increases near the wall even though the density decreases. Close to the wall the system is biaxial but the amount of biaxiality is small.

The paper is organized as follows. In Sec. II we specify the model and derive the expressions for the surface tension, and for the density and the order-parameter profiles. In Sec. III we present the results of numerical calculations and Sec. IV is devoted to the discussion. Some details of analytical calculations are presented in the Appendix.

### II. THEORY

#### A. The liquid crystal-wall surface tension

We consider the system of hard spherocylinders of length  $L$  and diameter  $D$  in the presence of a hard wall. The position and orientation of a spherocylinder are

determined by  $\mathbf{r}$  and  $\omega = (\theta, \varphi)$ , respectively. The  $z$  axis is chosen to be perpendicular to the wall. The system is athermal as only hard-core interactions are taken into account and the only parameters appearing in the problem are the ratio  $L/D$  and the density of the fluid  $\rho_b$  at  $z = +\infty$ . The grand thermodynamical potential  $\Omega$  as a functional of the one-particle distribution function  $\rho(\mathbf{r}, \omega)$  has the following general form:

$$\begin{aligned} \Omega\{\rho(\mathbf{r}, \omega)\} = & \mathcal{F}^{\text{id}}\{\rho(\mathbf{r}, \omega)\} + \mathcal{F}^{\text{ex}}\{\rho(\mathbf{r}, \omega)\} \\ & - \beta\mu \int d\mathbf{r} d\omega \rho(\mathbf{r}, \omega) \\ & + \beta \int d\mathbf{r} d\omega \rho(\mathbf{r}, \omega) V_{\text{ext}}(\mathbf{r}, \omega), \end{aligned} \quad (2.1)$$

where

$$\mathcal{F}^{\text{id}} = \int d\mathbf{r} d\omega \rho(\mathbf{r}, \omega) \{ \ln[\Lambda^3 \rho(\mathbf{r}, \omega)] - 1 \}, \quad (2.2)$$

$\mu$  is the chemical potential,  $\beta = 1/k_B T$  is the Boltzmann factor,  $V_{\text{ext}}$  stands for the external potential, and  $\Lambda^3$  comes from the kinetic energy.  $\mathcal{F}^{\text{ex}}$  is the excess part of the free energy corresponding to the interactions between molecules. We assume the low density Onsager approximation for  $\mathcal{F}^{\text{ex}}$ , i.e.,

$$\begin{aligned} \mathcal{F}^{\text{ex}} = & -\frac{1}{2} \int d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 f_2(\mathbf{r}_{12}, \omega_1, \omega_2) \\ & \times \rho(\mathbf{r}_1, \omega_1) \rho(\mathbf{r}_2, \omega_2), \end{aligned} \quad (2.3)$$

where  $f_2$  stands for the Mayer function which is equal to  $-1$  when two molecules overlap and  $0$  otherwise. The expression for the external potential exerted on a molecule by the hard wall reads as follows:

$$V_{\text{ext}}(\mathbf{r}, \omega) = \begin{cases} +\infty & \text{if } z < z_m(\theta) \\ 0 & \text{if } z > z_m(\theta), \end{cases} \quad (2.4)$$

where  $\theta$  is the angle between the  $z$  axis and the symmetry axis of a molecule, and  $z_m(\theta) = \frac{1}{2}(L |\cos\theta| + D)$  stands for the minimal distance between the wall and a molecule of orientation  $\omega$ . The minimization of  $\Omega$  with respect to  $\rho(\mathbf{r}, \omega)$  leads to the integral equation for  $\rho(\mathbf{r}, \omega)$ ,

$$\begin{aligned} \rho(\mathbf{r}_1, \omega_1) = & \frac{e^{\beta\mu}}{\Lambda^3} \exp \left[ -\beta V_{\text{ext}}(\mathbf{r}_1, \omega_1) \right. \\ & \left. + \int d\mathbf{r}_{12} d\omega_2 f_2(\mathbf{r}_{12}, \omega_1, \omega_2) \right. \\ & \left. \times \rho(\mathbf{r}_2, \omega_2) \right]. \end{aligned} \quad (2.5)$$

In the absence of an external potential Eq. (2.5) has a spatially uniform solution  $\rho(\mathbf{r}, \omega) = \rho_b f(\omega)$ , where  $f(\omega)$  is the orientational distribution function normalized to unity. For the isotropic phase  $f(\omega) = 1/4\pi$  and for the nematic phase  $f(\omega) = f(\hat{\mathbf{n}} \cdot \hat{\boldsymbol{\omega}})$ , where  $\hat{\mathbf{n}}$  is the nematic

director and  $\hat{\boldsymbol{\omega}}$  is the unit vector along the symmetry axis of a molecule. When the wall is present, instead of solving Eq. (2.5) we approximate  $\rho(z, \omega)$  as follows:

$$\rho(z, \omega) = \rho_b e^{-\beta V_{\text{ext}}(z, \omega)} f(\omega), \quad (2.6)$$

which means that molecules "feel" the wall only through the direct molecule-wall interaction. This approximation can be also seen as the first step in the iterative procedure of solving of Eq. (2.5) if we start from the uniform solution. Of course, such an approximation would be trivial for a fluid of hard spheres but it is by no means trivial in our case because of the coupling between the orientational and translational degrees of freedom. We also assume that the director orientation does not change throughout the sample. This assumption is reasonable provided we do not take into account the nematic-isotropic interface which favors director orientation other than the wall.<sup>17</sup>

Substitution of (2.6) into (2.1)–(2.3) and subtraction of the bulk term leads to the expression for the liquid crystal-wall surface tension  $\gamma$ . For hard-core interactions only entropic terms contribute to the free energy; thus  $\gamma$  can be expressed as follows:

$$\frac{\gamma}{k_B T} = -\frac{S}{k_B} - \frac{\Delta\mu}{k_B T} \Gamma, \quad (2.7)$$

where  $S$  is the surface entropy per unit area,

$$\Delta\mu = \mu - kT \ln(\Lambda^3 \rho_b / 4\pi), \quad (2.8)$$

$$\Gamma = \int_0^\infty dz d\omega [\rho(z, \omega) - \rho_b f(\omega)] = -\rho_b \langle z_m(\omega) \rangle_{f(\omega)} \quad (2.9)$$

stands for the adsorption, and  $\langle \dots \rangle_{f(\omega)}$  means averaging over orientations with angular distribution  $f(\omega)$ .  $S$  contains contributions from both translational and orientational degrees of freedom, i.e.,  $S = S_{\text{rot}} + S_{\text{tr}}$ . The rotational entropy comes only from the ideal term in the free energy

$$S_{\text{rot}} / k_B = \rho_b \langle z_m(\omega) \ln[4\pi f(\omega)] \rangle_{f(\omega)}. \quad (2.10)$$

The effect of the wall is twofold: it restricts the rotational freedom of a molecule and reduces the number of molecules close to the wall. For the isotropic phase the distinction between  $S_{\text{rot}}$  and the contribution to the translational entropy,  $S_{\text{tr}}$ , from the ideal term is the matter of convention. Thus we have defined  $S_{\text{rot}}$  in such a way that it vanishes for the isotropic phase. Both the ideal and the excess term contribute to  $S_{\text{tr}}$ , i.e.,

$$S_{\text{tr}} = S_{\text{tr}}^{\text{id}} + S_{\text{tr}}^{\text{ex}}, \quad (2.11)$$

where

$$S_{\text{tr}}^{\text{id}} / k_B = -\rho_b \langle z_m(\omega) \rangle_{f(\omega)}, \quad (2.12)$$

$$\begin{aligned} S_{\text{tr}}^{\text{ex}} / k_B = & \frac{1}{2} \rho_b^2 \int d\omega_1 d\omega_2 f(\omega_1) f(\omega_2) z_m(\omega_1) V_0(\omega_1, \omega_2) \\ & + \frac{1}{2} \rho_b^2 \int d\omega_1 d\omega_2 f(\omega_1) f(\omega_2) \int_{z_m(\omega_1) - z_m(\omega_2)}^\infty dz_{12} [z_{12} - z_m(\omega_1) + z_m(\omega_2)] V(|z_{12}|, \omega_1, \omega_2), \end{aligned} \quad (2.13)$$

$$V(|z_{12}|, \omega_1, \omega_2) = - \int dx_{12} dy_{12} f_2(\mathbf{r}_{12}, \omega_1, \omega_2), \quad (2.14)$$

and

$$V_0(\omega_1, \omega_2) = - \int d\mathbf{r}_{12} f_2(\mathbf{r}_{12}, \omega_1, \omega_2) \quad (2.15)$$

is the excluded volume for two spherocylinders. The derivation of Eq. (2.13) is given in the second part of the Appendix.  $S_{tr}^{id}$  is always negative because the wall restricts the translational freedom of molecules.  $S_{tr}^{ex}$  is the correction to  $S_{tr}$  due to the interactions between pairs of molecules. Both terms contributing to  $S_{tr}^{ex}$  are positive. The first one takes into account the pairs of molecules one of which interacts directly with the wall whereas the other does not. The second term takes into account all pairs in which both molecules interact directly with the wall. The reduction in the number of molecules near the wall is given by  $\Gamma$ , which is always negative, like  $S_{tr}^{id}$ .

The nematic-wall surface tension  $\gamma_{NW}$  is a function of  $\hat{\mathbf{n}}$  as the director enters through  $f(\omega) = f(\hat{\mathbf{n}} \cdot \hat{\omega})$ . Thus  $\gamma_{NW}(\hat{\mathbf{n}})$  should be minimized with respect to  $\hat{\mathbf{n}}$  in order to find the equilibrium value of the tilt angle  $\theta_t$  between  $\hat{\mathbf{n}}$  and the normal to the wall.

The orientations preferred by each of the terms contributing to  $\gamma_{NW}(\hat{\mathbf{n}})$  are discussed in Sec. III.

### B. The density and the order-parameter profiles

In our approximation (2.6) for the one-particle distribution function  $\rho(z, \omega)$ , the thickness of the interfacial region,  $l$ , is equal to the range of  $V_{ext}$ , i.e.,  $l = \frac{1}{2}(L + D)$ . For  $z > l$  the density and the order parameters are equal to their bulk values. Thus only the range  $\frac{1}{2}D \leq z \leq \frac{1}{2}(L + D)$  is interesting. For  $z < \frac{1}{2}D$ ,  $\rho(z) = 0$  and the order parameters are undefined. Integrating  $\rho(z, \omega)$  over the angular variables, we find that

$$\begin{aligned} \rho(z) &= \rho_b \langle e^{-\beta V_{ext}(z, \omega)} \rangle_{f(\omega)} \\ &= \rho_b \int_0^{2\pi} d\varphi \int_{\theta_m(z)}^{\pi - \theta_m(z)} \sin\theta d\theta f(\omega), \end{aligned} \quad (2.16)$$

where  $\theta_m(z) = \arccos(2\Delta z/L)$ ,  $\Delta z = z - \frac{1}{2}D$ . The orientational distribution function is equal to  $f(z, \omega) = \rho(z, \omega)/\rho(z)$  in the interfacial region and the tensor order parameter is given by

$$\begin{aligned} Q_{ij}(z) &= \frac{1}{2} \langle 3\omega_i \omega_j - \delta_{ij} \rangle_{f(z, \omega)} \\ &= \frac{\frac{1}{2} \langle e^{-\beta V_{ext}(z, \omega)} (3\omega_i \omega_j - \delta_{ij}) \rangle_{f(\omega)}}{\langle e^{-\beta V_{ext}(z, \omega)} \rangle_{f(\omega)}}. \end{aligned} \quad (2.17)$$

If the wall is in contact with a stable isotropic phase we find all profiles immediately substituting  $f(\omega) = 1/4\pi$  into (2.16) and (2.17), which gives

$$\rho(z) = \rho_b \frac{2\Delta z}{L}, \quad (2.18)$$

$$Q_{zz}(z) = \frac{1}{2} \left[ \frac{2\Delta z}{L} \right]^2 - \frac{1}{2}, \quad (2.19)$$

$$Q_{xx}(z) = Q_{yy}(z) = -\frac{1}{2} Q_{zz}(z) \quad (2.20)$$

for  $0 \leq \Delta z \leq \frac{1}{2}L$ . In the interfacial region the density is reduced and tends to zero as  $z \rightarrow 0$ .  $Q_{zz}(z)$  is negative,

which means that the molecules tend to lie on the wall but the symmetry in the  $xy$  plane is not broken. If the bulk nematic phase is in contact with the wall then all profiles depend on the director orientation. Disregarding the problem of the equilibrium orientation of  $\hat{\mathbf{n}}$  we study here two extreme cases: the perpendicular and the parallel orientation. If  $\hat{\mathbf{n}}$  is perpendicular to the wall then the nematic phase is uniaxial also in the interfacial region and we find that

$$Q_{zz}(z) = \frac{\int_{\theta_m(z)}^{\pi - \theta_m(z)} \sin\theta d\theta P_2(\cos\theta) f(\cos\theta)}{\int_{\theta_m(z)}^{\pi - \theta_m(z)} \sin\theta d\theta f(\cos\theta)}. \quad (2.21)$$

Close to the wall  $\theta_m(z) \sim (\pi/2) - (2\Delta z/L)$  and hence  $Q_{zz}(z) < 0$ . Thus for the perpendicular alignment,  $Q_{zz}(z)$  decreases from a positive bulk value to  $Q_{zz} = -\frac{1}{2}$  at  $\Delta z = 0$ . This means that in a thin layer adjacent to the wall the molecules order in a similar way as in the isotropic phase, close to the wall. If  $\hat{\mathbf{n}}$  is parallel to the wall then the nematic phase in the interfacial region is biaxial. In this case the main order parameter  $Q$  and the biaxiality  $P$  are given by

$$Q(z) = Q_{xx}(z) = \frac{1}{2} \langle 3 \sin^2\theta \cos^2\varphi - 1 \rangle_{f(z, \omega)} \quad (2.22)$$

and

$$\begin{aligned} P(z) &= \frac{1}{2} [Q_{zz}(z) - Q_{yy}(z)] \\ &= \frac{3}{4} \langle \cos^2\theta - \sin^2\theta \sin^2\varphi \rangle_{f(z, \omega)}, \end{aligned} \quad (2.23)$$

respectively. Hence, for  $\Delta z = 0$  we find that

$$Q_0 = \int_0^{2\pi} d\varphi P_2(\cos\varphi) f(\cos\varphi) / \int_0^{2\pi} d\varphi f(\cos\varphi), \quad (2.24)$$

and

$$\begin{aligned} P_0 &= -\frac{3}{4} \int_0^{2\pi} d\varphi \sin^2\varphi f(\cos\varphi) / \int_0^{2\pi} d\varphi f(\cos\varphi) \\ &= -\frac{1}{2} (1 - Q_0). \end{aligned} \quad (2.25)$$

Thus Eq. (2.25) gives the relation between the main order parameter and the biaxiality at the wall.

### III. RESULTS

We calculate the nematic-wall surface tension  $\gamma_{NW}(\mathbf{n})$  and the isotropic-wall surface tension  $\gamma_{IW}$  for the chemical potential  $\mu$  corresponding to the nematic-isotropic coexistence, using Eqs. (2.7)–(2.15). We take  $f(\omega)$  for the nematic phase and the values of the nematic and isotropic densities at coexistence from the paper by Lasher.<sup>35</sup> The key function in our model is  $V(|z_{12}|, \omega_1, \omega_2)$ . To calculate this function we neglect the spherical and cylindrical parts of the excluded volume solid for two spherocylinders. This approximation, described in more detail elsewhere,<sup>17</sup> is consistent with the low-density Onsager approximation. It also retains all symmetries of the full solid of excluded volume. The details of calculations are given in the Appendix.

All integrals appearing in the problem have been performed numerically by the Monte Carlo method. We have found that  $S_{rot}$  and each of both terms in  $S_{tr}^{ex}$  prefer

the perpendicular orientation of  $\hat{n}$ . On the other hand  $S_{tr}^{id}$  and  $(\Delta\mu)\Gamma$  prefer the parallel alignment because then the volume inaccessible for molecules is the smallest. The effect of restricted freedom of translation of molecules caused by the wall, and described by  $S_{tr}^{id}$  and  $(\Delta\mu)\Gamma$ , turns out to be dominant.

In Fig. 1 the dependence of the nematic-wall surface tension on the tilt angle  $\theta_t$  is shown for  $L/D = 5, 8, 10, 20$ . In all cases the minimum of  $\gamma_{NW}$  occurs at  $\theta_t = 90^\circ$ , i.e., for the parallel alignment. Figure 1 agrees qualitatively with the experimental results of Yokoyama and van Sprang.<sup>6</sup> The equilibrium surface tension  $\gamma_{eq} = \gamma_{NW}(\theta_t = 90^\circ)$  as a function of  $D/L$  is presented in Fig. 2. Its decay to zero with  $D/L \rightarrow 0$  results from the fact that at constant  $\mu$  the fraction of the volume occupied by spherocylinders tends to zero when  $D/L \rightarrow 0$ . Having calculated the nematic-wall and isotropic-wall surface tensions for the nematic-isotropic coexistence we can compare them with the nematic-isotropic surface tension  $\gamma_{NI}$  obtained in our previous paper.<sup>17</sup> We find that the following inequality holds:  $\gamma_{NW}(90^\circ) + \gamma_{NI}(\theta_t) < \gamma_{IW}$  for  $0 \leq \theta_t \leq 90^\circ$ . Even though our simple model does not take into account director distortions we can conclude that the wetting by the parallel aligned nematic phase should occur. It is also worth mentioning that for the perpendicular alignment the opposite inequality holds, i.e.,  $\gamma_{NW}(0^\circ) > \gamma_{NI}(\theta_t) + \gamma_{IW}$ . In Figs. 3–5 we have plotted the density  $\rho(z)$ , the main order parameter  $Q(z)$ , and the biaxiality  $P(z)$ , respectively, for the equilibrium parallel alignment.  $Q(z)$  is strongly enhanced near the

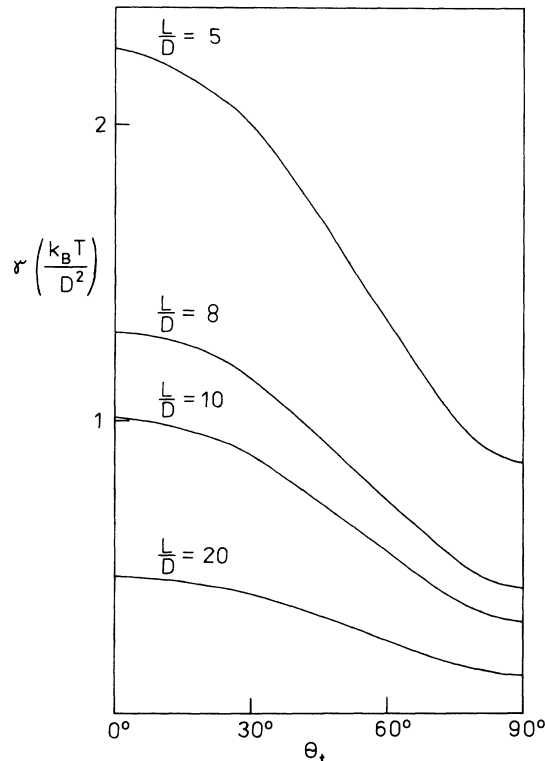


FIG. 1. Nematic-wall surface tension (in  $k_B T/D^2$  units) as a function of the tilt angle  $\theta_t$  for  $L/D = 5, 8, 10, 20$ .

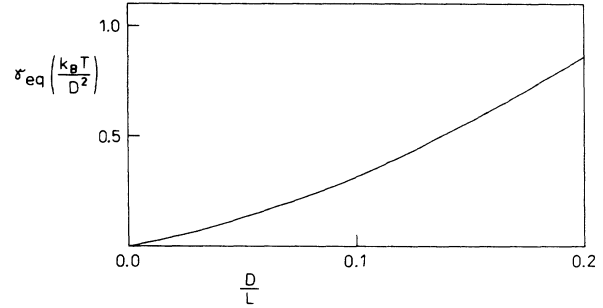


FIG. 2. Equilibrium nematic-wall surface tension  $\gamma_{eq}(\theta_t = 90^\circ)$  as a function of  $D/L$ .

wall.  $P(z)$  is also enhanced but its value is rather small in the whole interfacial region. All profiles do not depend on the ratio  $L/D$ . This is the consequence of applied approximations which lead to  $f(\omega)$  independent of  $L/D$ .

#### IV. DISCUSSION

There is a growing evidence<sup>17,36–41</sup> that the essential physics of liquid crystals stems from the anisotropic short-range repulsive forces. The long-range attractive interactions should serve as an auxiliary factor responsible for the density change when a change in temperature occurs. Our results obtained for the model of hard spherocylinders interacting with a hard wall confirm this point of view. The main result is that the hard wall prefers the parallel alignment of the nematic phase. It has been obtained for the nematic-isotropic coexistence but it can be extended beyond the coexistence conditions. This finding is in line with the simple intuitive picture based on consideration of the translational entropy of the system.<sup>42</sup> It also results from our model that for the parallel alignment the main order parameter  $Q(z) = Q_{xx}(z)$  is enhanced near the wall. On the other hand  $Q_{zz}(z) = -\frac{1}{2}Q(z) + P(z)$  is negative.  $Q_{zz}(z)$  is also negative for the isotropic phase, which is in line with some experimental results.<sup>30</sup>

We have found that the wall should be wetted by the nematic phase. This has not been observed experimentally so far, however. The experimental results indicate that

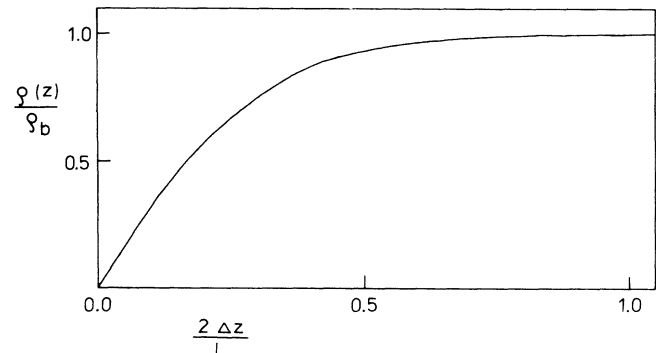


FIG. 3. Density profile  $\rho(z)/\rho_b$  for the nematic phase (parallel alignment) in the interfacial region.

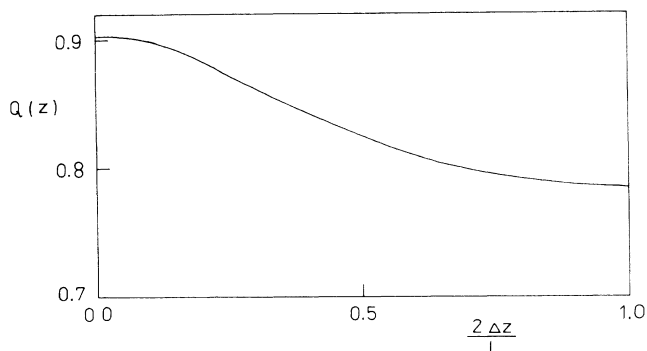


FIG. 4. Nematic main order parameter  $Q(z)$  in the interfacial region for the parallel alignment.

rather complete or partial wetting by the isotropic phase occurs for the random planar boundary conditions but this behavior is not entirely universal.<sup>8,30</sup> Certainly our approximation for the one-particle distribution function is rather crude and we intend to improve our model in the future work.

#### ACKNOWLEDGMENTS

We would like to thank Professor J. Stecki for his interest in this work. This work has been carried out under the Research Project C.P.B.P. 01.12.12.1.

#### APPENDIX

When the solid of excluded volume for two spherocylinders of orientations  $\hat{\omega}_1$  and  $\hat{\omega}_2$ , respectively, is cut with a plane parallel to the wall and distant from the centre of the solid by  $|z_{12}|$ , then the area of the cross section is equal to  $V(|z_{12}|, \hat{\omega}_1, \hat{\omega}_2)$ . To calculate the function  $V(|z_{12}|, \hat{\omega}_1, \hat{\omega}_2)$  we make use of the following identity:

$$V(|z_{12}|, \hat{\omega}_1, \hat{\omega}_2) = \int d\mathbf{r}'_{12} \chi(\mathbf{r}'_{12}, \hat{\omega}_1, \hat{\omega}_2) \delta(\hat{\mathbf{k}} \cdot \mathbf{r}'_{12} - |z_{12}|), \quad (\text{A1})$$

where  $\chi$  is the characteristic function of the excluded volume solid and equals 1 inside and 0 outside the solid,  $\hat{\mathbf{k}}$  is the unit vector normal to the wall, and  $\delta$  is the Dirac  $\delta$  function. In our approximation<sup>17</sup> we integrate only over the inside part of the excluded volume solid, which is a rectangular prism, and neglect the contributions from the cylindrical and spherical parts. The prism has a rhombus of the side  $L$  and the angle  $\theta_{12}$  in its base, and the thickness of the prism is  $2D$ .

A vector belonging to the prism can be represented in the following form:

$$\mathbf{r}'_{12} = r\mathbf{a} + s\mathbf{b} + t\mathbf{c}, \quad -1 < r, s, t \leq 1 \quad (\text{A2})$$

where  $\mathbf{a} = \frac{1}{2}L\hat{\omega}_1$ ,  $\mathbf{b} = \frac{1}{2}L\hat{\omega}_2$ , and  $\mathbf{c} = D\hat{\omega}_1 \times \hat{\omega}_2 / |\hat{\omega}_1 \times \hat{\omega}_2|$  are the three vectors on which the prism is spanned. We change the integration variable  $\mathbf{r}'_{12}$  for  $r, s, t$ , which gives

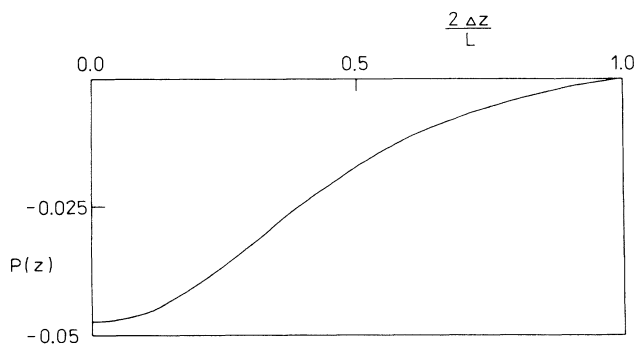


FIG. 5. Biaxiality  $P(z)$  in the interfacial region for the parallel alignment.

$$V(|z_{12}|, \hat{\omega}_1, \hat{\omega}_2) = \frac{1}{8}V_0 \int_{-1}^1 dr \int_{-1}^1 ds \int_{-1}^1 dt \delta(rA + sB + tC - |z_{12}|), \quad (\text{A3})$$

where  $V_0 = 2L^2D \sin\theta_{12}$  is the volume of the prism and  $A = \mathbf{a} \cdot \hat{\mathbf{k}}$ ,  $B = \mathbf{b} \cdot \hat{\mathbf{k}}$ ,  $C = \mathbf{c} \cdot \hat{\mathbf{k}}$ . It is obvious from (A3) that  $V$  is symmetric in  $A, B, C$  and depends only on their absolute values. To calculate the integral in (A3) we make use of the following two identities:

$$\int_{z_1}^{z_2} \delta(z) dz = \Theta(z_2) - \Theta(z_1) \quad (\text{A4})$$

and

$$\int_{z_1}^{z_2} f(z) \Theta(z) dz = F(z_2) \Theta(z_2) - F(z_1) \Theta(z_1) \quad (\text{A5})$$

for  $z_2 > z_1$  and  $F(z) = \int_0^z f(z') dz'$ , where  $f(z)$  is an arbitrary integrable function. The function  $\Theta(z)$  stands here for the Heaviside step function. Let us assume first that  $A, B, C \neq 0$ . Then one easily finds, using (A4) and (A5) and changing properly the integration variables, that

$$V(|z_{12}|, \hat{\omega}_1, \hat{\omega}_2) = \frac{V_0}{16|ABC|} \sum_{\substack{i,j,k=0,1 \\ i+j+k < 3}} (-1)^{i+j+k} (z_{ijk} - |z_{12}|)^2 \times \Theta(z_{ijk} - |z_{12}|), \quad (\text{A6})$$

where  $z_{ijk} = (-1)^i |A| + (-1)^j |B| + (-1)^k |C|$ . As  $V$  is symmetric in  $|A|, |B|, |C|$  we can assume that  $|A| \geq |B| \geq |C|$ . Then we have the following possibilities.

$$(1) |z_{12}| \geq |A| + |B| + |C|,$$

$$V = 0. \quad (\text{A7})$$

(2)

$$|A| + |B| - |C| \leq |z_{12}| \leq |A| + |B| + |C| \quad (\text{triangle}),$$

$$V = \frac{V_0}{16|ABC|} (|A| + |B| + |C| - |z_{12}|)^2.$$

(A8)

(3)  $|A| - |B| + |C| \leq |z_{12}| \leq |A| + |B| - |C|$   
(trapezoid),

$$V = \frac{V_0}{4|AB|} (|A| + |B| - |z_{12}|). \quad (\text{A9})$$

(4)  $|A| - |B| - |C| \leq |z_{12}| \leq |A| - |B| + |C|$   
(pentagon),

$$V = \frac{V_0}{16|ABC|} [ (|A| + |B| + |C| - |z_{12}|)^2 - (|A| + |B| - |C| - |z_{12}|)^2 - (|A| - |B| + |C| - |z_{12}|)^2 ], \quad (\text{A10})$$

(5)  $|z_{12}| \leq ||A| - |B| - |C||$ : (a)  $|A| > |B| + |C|$  (parallelogram),

$$V = V_0/2 |A|; \quad (\text{A11})$$

(b)  $|A| \leq |B| + |C|$  (hexagon),

$$V = \frac{V_0}{16|ABC|} [ (|A| + |B| + |C| - |z_{12}|)^2 - (|A| + |B| - |C| - |z_{12}|)^2 - (|A| - |B| + |C| - |z_{12}|)^2 - (-|A| + |B| + |C| - |z_{12}|)^2 ]. \quad (\text{A12})$$

In parentheses we have indicated the plane figures corresponding to the given cross sections that follow each possibility. If  $|A|, |B| \neq 0$  and  $|C| = 0$  only the possibilities (1), (3), and 5(a) remain. If  $|A| \neq 0$  and  $|B| = |C| = 0$  only (1) and 5(a) can be satisfied.

### 1. Derivation of the expression for $S_{\text{tr}}^{\text{ex}}$

Subtracting the bulk term from  $\mathcal{F}^{\text{ex}}$  [see Eq. (2.3)] and making use of the approximation (2.6) and the definitions (2.14) and (2.15) we arrive at the following expression:

$$S_{\text{tr}}^{\text{ex}}/k_B = -\frac{1}{2} \int d\omega_1 d\omega_2 \int_0^\infty dz_1 \left[ \int_0^\infty dz_2 \rho(z_1, \omega_1) \rho(z_2, \omega_2) V(|z_{12}|, \omega_1, \omega_2) - \rho_b^2 V_0(\omega_1, \omega_2) f(\omega_1) f(\omega_2) \right] \\ = \frac{1}{2} \rho_b^2 \int d\omega_1 d\omega_2 f(\omega_1) f(\omega_2) z_m(\omega_1) V_0(\omega_1, \omega_2) \\ - \frac{1}{2} \rho_b^2 \int d\omega_1 d\omega_2 f(\omega_1) f(\omega_2) \int_{z_m(\omega_1)}^\infty dz_1 \left[ \int_{z_m(\omega_2)}^\infty dz_2 V(|z_{12}|, \omega_1, \omega_2) - V_0(\omega_1, \omega_2) \right], \quad (\text{A13})$$

where the lower limits of the integrals over  $z_1$  and  $z_2$  come from the presence of the hard-wall potential. We transform these integrals as follows:

$$\int_{z_m(\omega_1)}^\infty dz_1 \left[ \int_{z_m(\omega_2)}^\infty dz_2 V(|z_{12}|, \omega_1, \omega_2) - V_0(\omega_1, \omega_2) \right] \\ = \int_{z_m(\omega_1) - z_m(\omega_2)}^\infty dz_1 \left[ \int_0^\infty dz_2 V(|z_{12}|, \omega_1, \omega_2) - V_0(\omega_1, \omega_2) \right] \\ = - \int_{z_m(\omega_1) - z_m(\omega_2)}^\infty dz_1 \int_{z_1}^\infty dz_{12} V(|z_{12}|, \omega_1, \omega_2) \\ = - \int_{z_m(\omega_1) - z_m(\omega_2)}^\infty dz_{12} V(|z_{12}|, \omega_1, \omega_2) \int_{z_m(\omega_1) - z_m(\omega_2)}^{z_{12}} dz_1 \\ = - \int_{z_m(\omega_1) - z_m(\omega_2)}^\infty dz_{12} [z_{12} - z_m(\omega_1) + z_m(\omega_2)] V(|z_{12}|, \omega_1, \omega_2). \quad (\text{A14})$$

Substituting (A14) and (A13) we recover Eq. (2.13).

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