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Influence of permanent molecular dipoles on surface anchoring of nematic liquid crystals

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We consider the ordering of molecular dipoles at a nematic surface and the influence of this ordering on the equilibrium director orientation and the anchoring energy. Both phenomenological and molecular approaches are used. We show that a thin, spontaneously polarized layer will appear even at a structureless nematic surface without any charged impurities or gradients of the order parameter. The ordering of molecular dipoles in this layer is determined by strong dipole-quadrupole interactions, modified by the presence of the surface. Surface polarization gives a significant contribution to the anchoring energy of nematic liquid crystals composed of strongly polar molecules. The estimates indicate that in such systems the dipolar contribution is very large and could even be predominant, for example, at a free surface of some nematic liquid crystals. We show also that in the case of large longitudinal dipoles the equilibrium director orientation at a free surface is homeotropic. In the case of large transverse dipoles the alignment is planar. The principal results of this study are consistent with experimental observations on ferroelectric layers at nematic interfaces and with data on the orientation of typical polar nematics at a free surface. [S1063-651X(97)01801-1]

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I. INTRODUCTION

Surface properties of nematic liquid crystals attract much attention for both fundamental and technological reasons. On the one hand, a liquid-crystal interface poses several interesting problems in the general theory of anisotropic nonuniform fluids. Experimentally, one observes various kinds of surface ordering and surface transitions (see [1] for a review) that are far from being understood completely. On the other hand, the surface anchoring of nematic liquid crystals plays a vital role in the fabrication of liquid-crystal display devices, which make use of thin nematic cells. The delicate control of the surface parameters of such cells is impossible without an understanding of the general microscopic mechanisms that determine the surface anchoring of nematic liquid crystals.

The phenomenological theory of the surface properties of nematic liquid crystals was developed by Sluckin and Poniewierski [2] and by Sen and Sullivan [3]. This approach has been complemented by microscopic theories developed by several authors using different approximations [4–9]. In spite of some discrepancies between the results of different authors, it has been found that short-range steric and van der Waals interactions result in the equilibrium planar orientation of a nematic at a free surface. By contrast, long-range quadrupole-quadrupole interactions can compete with short-range potentials, and for sufficiently large quadrupoles there is the possibility of a tilted orientation or a temperature-induced planar-homeotropic surface transition [5,6].

In real liquid crystals one also finds some strong intermolecular interactions that have not been taken into account in the existing microscopic theory [4–9]. In particular, many nematic liquid crystals used in experimental studies and applications possess large longitudinal or transverse dipoles. Symmetry considerations permit molecular dipoles to be ordered at a surface, and indeed spontaneous polarization in a thin boundary layer of a nematic liquid crystal has been observed experimentally [10–13]. This surface polarization can make an important contribution to the surface free energy of a nematic liquid crystal because the dipole-dipole interaction energy is very strong in the case of large molecular dipoles. We shall see below that the ‘‘dipolar’’ contribution is at least comparable to all other contributions or even can be predominant for some nematic liquid crystals (such as cyanobiphenyls) with very large dipoles.

The only attempt to take the surface dipolar effects into account of which we are aware was made by Parsons [14] many years ago. Later McMullen [15] also considered the dipolar gradient terms in the free-energy expansion specific to the diffuse nematic-isotropic interface. According to Parsons, the free energy of the nematic surface can be written as

$$F_s = a\cos\vartheta + b\cos^2\vartheta, \tag{1}$$

where ϑ is the tilt angle of the nematic director with respect to the surface normal. The first term in Eq. (1) comes from the coupling between the surface polarization **P** and the surface electric field **E**, while the second term is claimed to be determined by quadrupolar interactions.

The simple surface free energy (1) was used by Parsons to describe planar to homeotropic transitions at the nematic surface. In this description, the two terms in (1) compete with each other and possess a different temperature dependence, thus leading naturally to the possibility of temperature-induced anchoring transitions. The essence of this argument is as follows. Dipolar and quadrupolar contributions to the surface energy can be qualitatively (and obviously) distinguished using symmetry criteria; dipolar terms are of the form $\cos\vartheta$, whereas quadrupolar terms take the form $\cos^2\vartheta$. The problem with this approach is that in equilibrium the absolute value of surface polarization can also depend on

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the tilt angle ϑ. In fact, we shall see below that the component of polarization parallel to the director is always proportional to $\cos\vartheta$. Now the two terms on the right-hand side of Eq. (1) possess the same general structure after minimization and surprisingly one cannot single out the dipole contribution using the naive symmetry categorisation suggested by Parsons.

In this paper we consider the appearance of surface polarization and its influence on the surface anchoring of nematic liquid crystals using both phenomenological and density-functional approaches. The phenomenological description will be developed in Sec. II and the molecular theory in Sec. III. In Sec. III we investigate the microscopic origin of the dipolar ordering in a thin boundary layer of a nematic liquid crystal near a flat, structureless, charge-free surface. In Sec. IV there is a brief discussion of the significance of our results. Some more mathematical details have been relegated to the Appendixes.

In Sec. III we have developed a microscopic statistical-mechanical approach to the problem of surface dipolar interactions in a nematic liquid crystal. We show that the spontaneous polarization in such a boundary layer is caused by the interaction between permanent molecular dipoles and quadrupoles. This interaction is averaged out in the bulk, but gives a significant contribution when the interacting molecules are close to a flat surface. In this case the surface polarization is induced by an inhomogeneous distribution of molecular dipoles and quadrupoles at the surface.

The simple molecular theory permits estimates of the dipolar contribution to the total anchoring strength of a nematic at a flat surface. It will be shown that this contribution is rather large and could even be predominant, for example, at a free surface of cyanobiphenyl-type nematic liquid crystals. We shall also see that large molecular dipoles have a strong tendency to be normal to the surface. Thus, in the case of large longitudinal dipoles the director orientation at a free surface is expected to be homeotropic, whereas in the case of large transverse dipoles it must be planar.

In addition to the effects we discuss in detail, we mention two other possible electric-field effects at the nematic surface. The first is related to the field caused by charged impurities adsorbed at the surface [16]. The other is the so-called order electric effect, which involves the appearance of a polarization proportional to the gradient of the average quadrupole density near the surface [17,18]. We discuss briefly the relative importance of these effects in Sec. IV.

II. PHENOMENOLOGICAL DESCRIPTION OF SURFACE POLARIZATION

Let us consider a nematic liquid crystal in contact with a structureless flat surface lying in the xOy plane. The free energy of such surface for nonpolar nematics has been considered in detail by Sluckin and Poniewierski [2] and Sen and Sullivan [3]. In the case of nematic liquid crystals composed of polar molecules one also has to take into account the surface polarization $\mathbf{P}$, which is an independent thermodynamic quantity. In all calculations in this paper $\mathbf{P}$ is a quantity per unit *volume* and is supposed to be constant over the dipolar layer of thickness ξ. A related quantity, which might turn out to be more easily measurable in some experiments, would be the integrated polarization per unit *area* $\mathbf{P}^*=\mathbf{P}\xi$. Although there have been speculations about the existence of a spontaneously ordered polar nematic phase, in real nematic liquid crystals the polarization is confined to a very thin boundary layer of microscopic thickness. We shall consider only systems that (a) possess zero polarization in the bulk and (b) are not close to a ferroelectric phase transition. In these cases the typical length scale of the polarization decay must be of the order of the molecular length. This means that all polarization is concentrated in a very thin layer of thickness ξ and contributes only to the surface free energy f_s, which actually comes from averaging over this thin boundary layer [3]. However, we note that this conclusion is invalid for a broad nematic-isotropic interface. In this case the dipolar effects are determined by the slow gradients of the polarization [15]. By contrast, the length scale of the nematic order parameter variations near the surface is generally much larger than the molecular length because it is inversely proportional to $\alpha(T-T^*)$, where T^* is the nematic-isotropic transition temperature [19].

Now the free energy of the polar nematic surface can be expanded in powers of the polarization

$$f_s=f_s^0(\mathbf{Q})+(\mathbf{M}\cdot\mathbf{P})+\frac{1}{2}(\mathbf{P}\cdot\mathbf{W}\cdot\mathbf{P}), \tag{2}$$

where $f_s^0(\mathbf{Q})$ is the free energy of the nonpolar nematic surface discussed in detail in [2,3]. In Eq. (2) $\mathbf{M}$ has the meaning of some effective surface field and the tensor $\mathbf{W}$ is the inverse surface dielectric susceptibility. In the simplest case the vector $\mathbf{M}$ is just the electric field due to surface charges [20,21], i.e., $\mathbf{M}=-\mathbf{E}_0$. On the other hand, it will be shown in Sec. III that there is an effective surface field $\mathbf{M}$ even in the simple case of a structureless charge-free flat wall. This effective field is determined by the discontinuity in the average molecular quadrupole density at the flat surface.

The general expression (2) follows by symmetry; any surface must produce some polarity since the symmetry plane parallel to it is removed. The parameters $\mathbf{M}$ and $\mathbf{W}$ in (2) also can be expanded in powers of the nematic order parameter $\mathbf{Q}$ by exact analogy with the case of a nonpolar nematic surface [2,3]. In the general case the tensor order parameter $Q_{\alpha\beta}$ is biaxial near the surface, but this biaxiality appears to be small [22] and, like previous authors [4–9], we shall neglect it here. Now the tensor order parameter can be written in the form $Q_{\alpha\beta}=S[\hat{n}_\alpha\hat{n}_\beta-(1/3)\delta_{\alpha\beta}]$, where $\hat{\mathbf{n}}$ is the nematic director and S is the scalar order parameter. In this case the surface field $\mathbf{M}$ and the tensor $\mathbf{W}$ depend only on the surface normal $\hat{\mathbf{e}}$ and the nematic tensor $\hat{n}_\alpha\hat{n}_\beta$ and can readily be written in the general form. For example, there are only two independent contributions to the surface field $\mathbf{M}$ that can be composed from $\hat{\mathbf{e}}$ and $\hat{n}_\alpha\hat{n}_\beta$: $m_1\hat{\mathbf{e}}$ and $m_2\hat{\mathbf{n}}(\hat{\mathbf{e}}\cdot\hat{\mathbf{n}})$. In the general case the coefficients m_1 and m_2 can depend on $\cos^2\vartheta=(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})^2$.

From symmetry reasons the effective surface field $\mathbf{M}$ and the inverse susceptibility $\mathbf{W}$ can now be written as

$$\mathbf{M}=m_1\hat{\mathbf{e}}+m_2\hat{\mathbf{n}}(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}}) \tag{3}$$

and

$$W_{\alpha\beta}=g_1\delta_{\alpha\beta}+g_2\hat{e}_\alpha\hat{e}_\beta+g_3\hat{n}_\alpha\hat{n}_\beta+g_4(\hat{e}\alpha\hat{n}_\beta+\hat{e}_\beta\hat{n}_\alpha)(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}}), \tag{4}$$

where $(\hat{\mathbf{n}}\cdot\hat{\mathbf{e}})=\cos\vartheta$ and ϑ is the tilt angle of the director $\hat{\mathbf{n}}$ with respect to the surface normal $\hat{\mathbf{e}}$. We emphasize that in the general case the effective surface field $\mathbf{M}$ is not parallel to the surface normal $\hat{\mathbf{e}}$ and the main axes of the inverse surface susceptibility $W_{\alpha\beta}$ are not parallel to either $\hat{\mathbf{e}}$ or $\hat{\mathbf{n}}$. Only in the case of homeotropic alignment $\hat{\mathbf{e}}\|\hat{\mathbf{n}}$ is the nematic surface characterized by a symmetry axis parallel to the surface normal.

Substituting Eqs. (3) and (4) into Eq. (2), we obtain the expression for the surface free energy

$$\begin{aligned}\Delta F_s(\mathbf{P})&=(m_1+m_2)P_\|\cos\vartheta+m_1P_\perp\sin\vartheta+\frac{1}{2}g_1(P_\|^2+P_\perp^2)\\&\quad+\frac{1}{2}g_\|P_\|^2+\frac{1}{2}g_2\sin^2\vartheta P_\perp^2\\&\quad+(g_2+g_4)\sin\vartheta\cos\vartheta P_\|P_\perp,\end{aligned} \tag{5}$$

with

$$g_\|=g_2\cos^2\vartheta+g_3+2g_4\cos^2\vartheta. \tag{6}$$

Here $P_\|=(\mathbf{P}\cdot\hat{\mathbf{n}})$ is the component of the surface polarization along the director and $P_\perp=|\mathbf{P}-\hat{\mathbf{n}}(\mathbf{P}\cdot\hat{\mathbf{n}})|$ is the component perpendicular to it. Minimization of this free energy then yields the expressions for the components of the equilibrium surface polarization

$$\begin{aligned}P_\|=\cos\vartheta[&-(m_1+m_2)(g_1+g_2\sin^2\vartheta)\\&+m_1(g_2+g_4)\sin^2\vartheta]\sigma(\vartheta),\end{aligned} \tag{7}$$

$$P_\perp=\sin\vartheta[-m_1(g_1+g_\|)+(m_1+m_2)(g_2+g_4)\cos^2\vartheta]\sigma(\vartheta), \tag{8}$$

with

$$\begin{aligned}\sigma(\vartheta)=[&-(g_1+g_2\sin^2\vartheta)(g_\|+g_1)\\&-(g_2+g_4)^2\sin^2\vartheta\cos^2\vartheta]^{-1}.\end{aligned} \tag{9}$$

Note that $P_\|\propto\cos\vartheta$ and $P_\perp\propto\sin\vartheta$. This means that the first two terms in Eq. (5) give similar contributions to the surface free energy, which now have the symmetry of $\cos^2\vartheta$.

Substituting Eqs. (7)–(9) into Eq. (5), one can obtain an expression for the surface free energy $\Delta F_s(\vartheta)$, which appears to be a complicated function of the tilt angle ϑ. This expression, however, can be simplified if we assume that the main axes of the inverse surface susceptibility tensor $W_{\alpha\beta}$ are determined mainly by the director $\hat{\mathbf{n}}$. This assumption is obviously correct in the bulk. By making it also for the susceptibility of the surface layer we assume, in fact, that the susceptibility is affected only weakly by the surface. In this case (which corresponds to high values of the nematic order parameter and to large longitudinal dipoles) the coefficients g_1 and g_3 are much larger then g_2 and g_4. In this case one obtains

$$P_\|\approx-m(g_1+g_3)^{-1}\cos\vartheta,\quad P_\perp\approx-m_1g_1^{-1}\sin\vartheta, \tag{10}$$

and

$$\Delta F_s(\vartheta)\approx-W_0\cos^2\vartheta+\text{const},$$

where

$$W_0=\frac{m^2}{2(g_1+g_3)}-\frac{m_1^2}{2g_1}. \tag{11}$$

We note that the sign of the anchoring strength W_0 is determined by the balance between the two terms in Eq. (11). The first term is proportional to the coefficient m, which determines the surface polarization $\mathbf{P}_\|$ parallel to the director. The second term in Eq. (11) is proportional to the coefficient m_1, which determines the transverse polarization $\mathbf{P}_\perp$. Thus the anchoring strength W_0 appears to be positive or negative depending on the balance between the tendencies of longitudinal and transverse molecular dipoles to be perpendicular to the surface, respectively. In the case of large longitudinal dipoles the polarization $P_\perp\ll P_\|$ and $m\gg m_1$. Then the anchoring strength W_0 is positive with $W_0\approx m^2/2(g_1+g_2)$. We thus conclude that the ordering of permanent molecular longitudinal dipoles at a flat nematic surface promotes homeotropic director alignment.

In this section we have developed an elementary phenomenological theory. It indicates that, at a flat structureless surface, a net surface polarization due to the ordering of permanent longitudinal molecular dipoles promotes homeotropic director alignment. However, at this stage we are not yet able to predict the magnitude of this effect. To calculate how large the dipolar contribution to the total anchoring strength of a nematic liquid crystal is, as compared to other contributions, we must resort to a molecular theory. This theory must be able to predict the coefficients of the phenomenological theory in terms of molecular model parameters. This theory will be developed in Sec. III.

III. MICROSCOPIC APPROACH

A. Preliminary comments

In the general case the polar nematic liquid crystal is described by the one-particle distribution function $f_1(\omega,\mathbf{r})$, which depends on molecular position $\mathbf{r}$ and orientation ω. In this paper we use the simple model of a uniaxial molecule with the longitudinal dipole $\mu_\|$. In this case the distribution function depends on the unit vector $\hat{\mathbf{a}}$ in the direction of the long molecular axes. The nematic ordering is characterized by the tensor order parameter $Q_{\alpha\beta}=\langle[a_\alpha a_\beta-(1/3)\delta_{\alpha\beta}]\rangle$, where the angular brackets denote the statistical average. The polar ordering is described by the polar order parameter $\mathbf{p}=\langle\hat{\mathbf{a}}\rangle$ and the polarization is given by $\mathbf{P}=\rho\mu_\|\langle\hat{\mathbf{a}}\rangle$, where ρ is the number density. If the polarization is weak, the distribution function can be approximately expressed as

$$f_1(\mathbf{r},\hat{\mathbf{a}})=f_0(\mathbf{r},\hat{\mathbf{a}})+3(\hat{\mathbf{a}}\cdot\mathbf{p})+\cdots, \tag{12}$$

where $f_0(1)$ is the distribution function of the nonpolar state.

The description of the polar nematic liquid crystal is particularly simple in the limiting case of the perfect ordering of the long molecular axes. In this approximation $a_\alpha a_\beta = \hat{\mathbf{n}}_\alpha \hat{\mathbf{n}}_\beta$ and the distribution function depends only on the classical spin-like variable $\eta = \pm 1$ specifying the direction of the longitudinal dipole $\vec{\mu}_\parallel$ along the nematic axis. Thus $\hat{\mathbf{a}} = \eta \hat{\mathbf{n}}$ and $f_1(\mathbf{r}, \hat{\mathbf{a}}) = f_1(\mathbf{r}, \eta)$. For small homogeneous polarization

$$f(\eta) = 1 + \frac{1}{2} \eta \langle \eta \rangle + \cdots, \tag{13}$$

where the average $\langle \eta \rangle$ is related to the polarization

$$\mathbf{P} = \rho \mu_\parallel \langle \eta \rangle \hat{\mathbf{n}}. \tag{14}$$

B. General results

The microscopic theory of the nematic surface uses the density-functional approach [23,7] to the theory of liquids. The density-functional theory of liquid crystals relies on the representation of the free energy as a functional of the one-particle distribution function $f_1(\mathbf{r}, \omega)$, which depends on the position $\mathbf{r}$ and on the orientation ω of the molecule [23]. The general structure of this functional is not known, but the functional derivatives of the free energy are related to the direct correlation function of the medium. The expression for the free energy of the nematic phase can then be obtained by means of an expansion of the free energy of the nematic liquid crystal around its value in the isotropic phase [23]. This expansion is, in fact, a generalization of the usual Landau–de Gennes expansion in terms of the order parameter.

In the case of a flat structureless surface the nematic can be assumed to be homogeneous in the (x,y) plane parallel to the surface. In this case the one-particle distribution function depends only on the distance from the surface z: $f_1(\mathbf{r}, \omega) = f_1(\omega, z)$. The free energy of a semi-infinite nematic sample at density ρ and temperature T can now be written approximately as

$$\begin{aligned} F_N/\sigma = {} & F_I/\sigma + \rho k_B T \int d\omega \int_0^\infty dz f_1(\omega,z) \ln f_1(\omega,z) \\ & - \frac{1}{2} \rho^2 k_B T \int d\omega_1 d\omega_2 \int_0^\infty dz_1 \int_0^\infty dz_2 \\ & \times \int dx_{12} dy_{12} C_2(\omega_1, \omega_2, \mathbf{r}_{12}) \Delta f_1(\omega_1, z_1) \\ & \times \Delta f_1(\omega_2, z_2) + \cdots, \end{aligned} \tag{15}$$

where $x_{12} = x_1 - x_2$, $y_{12} = y_1 - y_2$, F_I is the free energy of the isotropic phase, σ is the surface area, $\Delta f_1(\omega_1, z_1) = f_1(\omega_1, z_1) - 1/4\pi$, $C_2(1,2)$ is the two-particle direct correlation function of the isotropic phase, and the $\mathbf{z}$ axis is normal to the plane of the surface. The higher-order terms in Eq. (15) depend on higher-order direct correlation functions.

The general free energy (15) can be used in the description of surface effects if one can separate between the bulk and surface parts of the total free energy of the sample. Tjipto-Margo and Sullivan [4] and Teixeira and Sluckin [5] have performed this separation with the help of the Fowler approximation [24], which assumes that the density and the nematic order parameter near the surface are equal to their bulk values. In the case of a polar nematic surface, however, one has to take into account that near the surface the one-particle distribution function $f_1(\omega, z)$ depends also on the polarization $\mathbf{P}$, which is confined to a thin boundary layer. In this case we shall make a simple generalization of the Fowler approximation. We assume that density and nematic order parameter are still equal to their bulk values, but there exists in addition a thin surface layer of thickness ξ with homogeneous average polarization $\mathbf{P}$. In this model the one-particle distribution function $f_1(\omega, z) = f_{1s}(\omega)$ when $0 < z < \xi$ and $f_1(\omega, z) = f_{1b}(\omega)$ when $\xi < z$. Here $f_{1b}(\omega)$ is the bulk orientational distribution function of a nematic and $f_{1s}(\omega)$ is the orientational distribution within the surface polar layer. We note that $f_{1b}(\omega)$ is different from $f_{1s}(\omega)$ because the latter depends on the surface polarization $\mathbf{P}$.

The total free energy (15) can now be represented as a sum of two terms

$$F_N = F_b + F_s. \tag{16}$$

Here F_b is the bulk free energy of the sample, which is given by

$$F_b = \int d^3\mathbf{r} f_b(\mathbf{r}), \tag{17}$$

with

$$\begin{aligned} f_b(\mathbf{r}) = {} & \rho k_B T \int d\omega \int d\omega f_b(\omega) \ln f_b(\omega) \\ & - \frac{1}{2} \rho^2 k_B T \int d^3\mathbf{r}_{12} \int d\omega_1 d\omega_2 C_2(\omega_1, \omega_2, \mathbf{r}_{12}) \\ & \times f_b(\omega_1) f_b(\omega_2). \end{aligned} \tag{18}$$

In the thermodynamic limit the bulk free energy F_b is proportional to the sample volume.

The second term in Eq. (16) is the free energy associated with the nematic surface. As shown in Appendix A, it can be written approximately as

$$
\begin{aligned}
F_s/\sigma = {} & \rho k_B T\xi \int d\omega_1 [f_{1s}(\omega_1)\ln f_{1s}(\omega_1) - f_{1b}(\omega_1)\ln f_{1b}(\omega_1)] + \frac{1}{2}\rho^2 k_B T \int d\omega_1 d\omega_2 \widetilde{C}_2(\omega_1,\omega_2,\mathbf{r}_{12}) f_{1b}(\omega_1) f_{1b}(\omega_2) \\
& + \rho^2 k_B T \int d\omega_1 d\omega_2 \widetilde{C}_2(\omega_1,\omega_2,\mathbf{r}_{12})[f_{1s}(\omega_1) - f_{1b}(\omega_1)] f_{1b}(\omega_2) - \rho^2 k_B T\xi \int d\omega_1 d\omega_2 \widetilde{C}_0(\omega_1,\omega_2,\mathbf{r}_{12})[f_{1s}(\omega_1) \\
& - f_{1b}(\omega_1)] f_{1b}(\omega_2) - \frac{1}{2}\rho^2 k_B T \int d\omega_1 d\omega_2 \widetilde{C}_2(\omega_1,\omega_2)[f_{1s}(\omega_1) - f_{1b}(\omega_1)][f_{1s}(\omega_2) - f_{1b}(\omega_2)] \\
& - \frac{1}{2}\rho^2 k_B T\xi \int d\omega_1 d\omega_2 \widetilde{C}_0(\omega_1,\omega_2)[f_{1s}(\omega_1) - f_{1b}(\omega_1)][f_{1s}(\omega_2) - f_{1b}(\omega_2)], \qquad (19)
\end{aligned}
$$

with

$$\widetilde{C}_2(\omega_1,\omega_2) = \int d\mathbf{r}_{12}\Theta(\mathbf{r}_{12}\cdot\hat{\mathbf{e}})(\mathbf{r}_{12}\cdot\hat{\mathbf{e}}) C_2(\omega_1,\omega_2,\mathbf{r}_{12}) \qquad (20)$$

and

$$\widetilde{C}_0(\omega_1,\omega_2) = \int d\mathbf{r}_{12} C_2(\omega_1,\omega_2,\mathbf{r}_{12}), \qquad (21)$$

where $\xi > r_c^0$ is the thickness of the surface polar layer, with r_c^0 the direct correlation radius. Here $\Theta(\mathbf{r}_{12}\cdot\hat{\mathbf{e}})$ is a step function: $\Theta(x)=0$ if $x<0$ and $\Theta(x)=1$ if $x>0$.

Note that the last four terms in Eq. (19) depend on the difference between surface and bulk one-particle distributions $f_{1s}(\omega) - f_{1b}(\omega)$, where the surface distribution function $f_{1s}(\omega)$ depends on the surface polarization $\mathbf{P}$. In a nematic liquid crystal composed of uniaxial molecules with longitudinal dipoles, the one-particle distribution function in the polar surface layer $f_{1s}(\omega_1) = f_1((\hat{\mathbf{a}}_1\cdot\hat{\mathbf{n}})^2, (\hat{\mathbf{a}}_1\cdot\mathbf{P}))$. By contrast, the bulk distribution $f_{1b}(\omega_1) = f_1((\hat{\mathbf{a}}_1\cdot\mathbf{n})^2)$.

The free energy of a nonpolar nematic surface is represented by the second term in Eq. (19). This contribution, which depends only on the nematic order parameter $Q_{\alpha\beta}$, was first derived by Tijpto-Margo and Sullivan [4] and has been discussed extensively before [7]. The first term and the last four terms in Eq. (19) represent the polarization-dependent part of the free energy that is under consideration in the present paper. At small polarization the difference $f_{1s}(\omega) - f_{1b}(\omega) \propto \mathbf{P}$ and the third and the fourth terms in Eq. (19) are linear in $\mathbf{P}$. These terms correspond to the second term $(\mathbf{M}\cdot\mathbf{P})$ in the phenomenological expression (2). The first, the fifth, and the sixth terms in Eq. (19) are quadratic in polarization $\mathbf{P}$ and correspond to the second term in (2).

Different terms in Eq. (19) have slightly different origin. We note that the first, the fourth, and the sixth terms are proportional to the thickness of the surface layer ξ. These terms have the meaning of an extra free-energy density in the surface layer multiplied by the volume of the layer. By contrast, the second, the third, and the fifth terms are not proportional to the layer thickness. These contributions are, in fact, nonlocal as they cannot be represented as an integral over the surface layer volume. As a result, they contain an extra power of r_{12} under the integral.

The polarization-dependent contribution to the surface free energy must be determined by some polar intermolecular interaction. We shall see later that the most important such interaction is between permanent molecular dipoles and quadrupoles. However, the electrostatic dipole-dipole and dipole-quadrupole interactions are long range. These terms produce well-known difficulties in statistical theory of fluids (see, for example, [25]). In the present case one finds formal difficulties in evaluating the integral in Eq. (20).

At large intermolecular separation the asymptotic expression for the direct correlation function is $C_2(1,2) = -V_l(1,2)/k_B T$, where $V_l(1,2)$ is the long-range part of the pair interaction potential. Then at large r_{12} the integral in Eq. (20) is convergent only conditionally (i.e., the result depends on the order of integration) when $V(1,2)$ is the dipole-quadrupole interaction potential proportional to r_{12}^{-4}. Similar problems appear in the calculation of lattice sums in the dielectric theory of polar crystals [26], and the general method to overcome these difficulties was proposed by Ewald long ago [27]. In the context of the statistical theory of polar fluids this method corresponds to the separation between the short-range and long-range parts of the electrostatic potential before applying the formal density-functional theory [18,28]. Then the short-range part of the potential can be taken into account in the usual way. The long-range part of the electrostatic interaction determines the energy of the average electric field, which depends on the shape of the sample. These questions, together with the actual separation procedure for the present case, are discussed in more detail in Appendix B. The energy of the average electric field (which is related to the polarization by Maxwell equations) in the surface layer can be written as [see Eq. (B9)]

$$U_{\mathrm{el}} = 2\pi \int d\mathbf{k}(\mathbf{P}_{\mathbf{k}}\cdot\mathbf{k})(\mathbf{P}_{-\mathbf{k}}\cdot\mathbf{k})k^{-2}. \qquad (22)$$

In the case of a flat nematic surface the surface polarization $\mathbf{P}$ depends only on the distance z along the surface normal $\hat{\mathbf{e}}$. Hence $\mathbf{k} = \hat{\mathbf{e}}k$ and Eq. (22) can be simplified, yielding

$$U_{\mathrm{el}} = 2\pi \int d\mathbf{k}(\mathbf{P}_k\cdot\hat{\mathbf{e}})(\mathbf{P}_{-k}\cdot\hat{\mathbf{e}}).$$

This electrostatic energy, located in the surface polar layer, makes an additional contribution to surface free energy and must be added to Eq. (19), which presents a contribution from short-range forces.

C. Perfect orientational order

A general expression for the surface free energy of a nematic has been presented in Sec. II. By performing an expansion in powers of the surface polarization, one can use these expressions to estimate the quantities **M** and $W_{\alpha\beta}$ in Eq. (1) for the phenomenological surface free energy. We make these estimates for the simple case of a nematic liquid crystal composed of molecules with longitudinal dipoles. In order to simplify the calculations, we suppose that the long molecular axes in the surface region are perfectly ordered. This approximation will have only a minor quantitative, and no qualitative, inaccuracy [7].

In this approximation the one-particle distribution function of the surface layer is given by Eq. (13). Substituting Eq. (13) into the general expression (19) yields the equation for the polarization contribution to the surface free energy

$$F_d/\sigma=(\mathbf{M}\cdot\mathbf{P})+(\mathbf{P}\cdot\mathbf{W}\cdot\mathbf{P}), \tag{23}$$

with

$$\mathbf{M}=\frac{1}{8}k_BT\mu_\parallel^{-1}\hat{\mathbf{n}}\sum_{\eta_1,\eta_2}\eta_1[\widetilde{C}_2(\hat{\mathbf{n}},\eta_1,\eta_2)-\xi\widetilde{C}_0(\hat{\mathbf{n}},\eta_1,\eta_2)], \tag{24}$$

$$W_{\alpha\beta}=-\frac{1}{8}k_BT\mu_\parallel^{-2}\hat{n}_\alpha\hat{n}_\beta\sum_{\eta_1,\eta_2}\eta_1\eta_2[\widetilde{C}_2(\hat{\mathbf{n}},\eta_1,\eta_2)-\xi\widetilde{C}_0(\hat{\mathbf{n}},\eta_1,\eta_2)]+\frac{1}{8}k_BT\xi\rho^{-1}\mu_\parallel^{-2}, \tag{25}$$

where

$$\widetilde{C}_2(\hat{\mathbf{n}},\eta_1,\eta_2)=\int d\mathbf{r}_{12}\Theta(\mathbf{r}_{12}\cdot\hat{\mathbf{e}})(\mathbf{r}_{12}\cdot\hat{\mathbf{e}})C_2(\hat{\mathbf{a}}_1,\hat{\mathbf{a}}_2,\mathbf{r}_{12}) \tag{26}$$

and

$$\widetilde{C}_0(\hat{\mathbf{n}},\eta_1,\eta_2)=\int d\mathbf{r}_{12}C_2(\hat{\mathbf{a}}_1,\hat{\mathbf{a}}_2,\mathbf{r}_{12}) \tag{27}$$

for $\hat{\mathbf{a}}_1=\hat{\mathbf{n}}\eta_1$ and $\hat{\mathbf{a}}_2=\hat{\mathbf{n}}\eta_2$. The last term in Eq. (25) is proportional to the thickness of the surface polar layer ξ. This term has the meaning of the ''bulk'' dielectric susceptibility multiplied by ξ, while the first term in (25) is a surface correction to the susceptibility.

We note that the polarization **P** vanishes if $\mathbf{M}=\mathbf{0}$. One can readily see from Eq. (24) that any nonzero contribution to **M** can come only from the direct correlation function (and hence from the corresponding interaction potential that has the same symmetry) that is odd in η_1 and even in η_2. This is equivalent to being polar with respect to $\hat{\mathbf{a}}_1$ and nonpolar with respect to $\hat{\mathbf{a}}_2$. On the other hand, the inverse susceptibility $W_{\alpha\beta}$ is determined by the correlation function that is odd in both η_1 and η_2.

D. Dipolar contribution to the surface free energy

Now let us estimate the quantities **M** and $W_{\alpha\beta}$ in the molecular field approximation using some simple intermolecular interactions. In this approximation the direct correlation function

$$C_2(1,2)=-(k_bT)^{-1}V(1,2)\Theta(r_{12}-\kappa_{12}),$$

where $V(1,2)$ is the pair intermolecular potential and $\Theta(r_{12}-\kappa_{12})$ is the steric cutoff factor that depends on the molecular shape via the function $\kappa_{12}(1,2)$. The function $\kappa_{12}(\hat{\mathbf{a}}_1,\hat{\mathbf{a}}_2,\hat{\mathbf{u}}_{12})$ depends on the relative orientation of the two molecules and appears to be rather complicated. Fortunately, there exists a simple interpolation expression proposed by van der Meer and Vertogen [29]

$$\kappa_{12}=D+\frac{1}{2}(L-D)[(\hat{\mathbf{a}}_1\cdot\hat{\mathbf{u}}_{12})^2+(\hat{\mathbf{a}}_2\cdot\hat{\mathbf{u}}_{12})^2]. \tag{28}$$

This expression is exact for two specific relative orientations of the two molecules, i.e., when $\hat{\mathbf{a}}_1\|\hat{\mathbf{a}}_2\|\hat{\mathbf{u}}_{12}$ and $\hat{\mathbf{a}}_1\|\hat{\mathbf{a}}_2\perp\hat{\mathbf{u}}_{12}$, where $\hat{\mathbf{u}}_{12}=\mathbf{r}_{12}/r_{12}$.

In a nematic liquid crystal composed of uniaxial molecules with longitudinal dipoles the interaction potential $V(1,2)=V(\hat{\mathbf{a}}_1,\mathbf{r}_{12},\hat{\mathbf{a}}_2)$ depends on the unit vectors $\hat{\mathbf{a}}_1$ and $\mathbf{a}_2$ and on the intermolecular vector $\mathbf{r}_{12}$. In the case of perfect nematic ordering $\hat{\mathbf{a}}_1=\eta_1\hat{\mathbf{n}}$, $\hat{\mathbf{a}}_2=\eta_2\hat{\mathbf{n}}$, and the pair potential depends only on the director $\hat{\mathbf{n}}$, intermolecular vector $\mathbf{r}_{12}$, and the spinlike variables η_1,η_2: $V(1,2)=V(\hat{\mathbf{n}},\mathbf{r}_{12},\eta_1,\eta_2)$.

As discussed at the end of Sec. III C, a consequence of Eq. (24) is that the vector **M** is nonzero only if the potential $V(\hat{\mathbf{a}}_1,\mathbf{r}_{12},\hat{\mathbf{a}}_2)$ is polar with respect to $\hat{\mathbf{a}}_1$ and nonpolar with respect to $\hat{\mathbf{a}}_2$ (i.e., it must be odd in η_1 and even in η_2). In a system of anisotropic noncharged molecules with large permanent dipoles the predominant interaction of this kind is the electrostatic dipole-quadrupole interaction. In the case of perfect nematic order this can be written as

$$V_{Qd}(\eta_1,\eta_2,\mathbf{r}_{12})=-Q\mu_\parallel\eta_1\eta_2^2(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})\left[P_2(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12})-\frac{2}{5}\right], \tag{29}$$

where Q is the molecular quadrupole. At the same time the inverse surface susceptibility tensor $W_{\alpha\beta}$ is determined mainly by the electrostatic dipole-dipole interaction potential

$$V_{dd}(\eta_1,\eta_2,\mathbf{r}_{12})=-\frac{2}{r_{12}^3}\mu_\parallel^2\eta_1\eta_2P_2(\hat{\mathbf{n}}\cdot\hat{\mathbf{u}}_{12}).$$

Now dipole-dipole and dipole-quadrupole interactions are long range. Thus it is necessary to separate the long-range parts of these electrostatic interaction potentials (see Appendix B) and to use the effective short-range potentials in Eqs. (26) and (27):

$$V_{dq}^{\mathrm{eff}}=V_{dq}(1,2)[\Theta(r_{12}-\kappa_{12})-1],$$

$$V_{dd}^{\mathrm{eff}}=V_{dd}(1,2)[\Theta(r_{12}-\kappa_{12})-1].$$

We note that the effective dipole-dipole and dipole-quadrupole potentials are nonzero only within the excluded volume for the two molecules, which is determined by the inequality $r_{12} < \kappa_{12}$. At the same time, the excluded volume is isotropic for $r_{12} < D$ and therefore the corresponding contribution vanishes after integration over $\hat{\mathbf{u}}_{12}$ in Eqs. (26) and (27). Thus the quantities $\mathbf{M}$ and $W_{\alpha\beta}$ are determined by the dipole-dipole and dipole-quadrupole interaction potentials for $D < r_{12} < \kappa_{12}$. As shown in Appendix B, the contribution from the long-range parts of the electrostatic interaction potential determines the energy of the average electromagnetic field (see also [38]) and will be added to the final expression for the surface free energy.

Substitution of the effective dipole-dipole and dipole-quadrupole interaction potentials into Eqs. (25) and (26) yields the expressions for the functions $\widetilde{C}_2(1,2)$ and $\widetilde{C}_0(1,2)$,

$$\widetilde{C}_2(\hat{\mathbf{n}}, \eta_1, \eta_2) = -(k_B T)^{-1} \int d\hat{\mathbf{u}}_{12} \left(2\Theta(\hat{\mathbf{u}}_{12} \cdot \hat{\mathbf{e}}) \ln(\kappa_{12}/D) Q \mu_\parallel \eta_1 \eta_2^2 (\hat{\mathbf{e}} \cdot \mathbf{u}_{12}) \left[P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_{12}) - \frac{2}{5} \right] - 2\kappa_{12} \mu_\parallel^2 \eta_1 \eta_2 P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_{12}) \right) \tag{30}$$

and

$$\widetilde{C}_0(\hat{\mathbf{n}}, \eta_1, \eta_2) = -(k_B T)^{-1} \int d\hat{\mathbf{u}}_{12} [\ln(\kappa_{12}/D) - 2\mu_\parallel^2 \eta_1 \eta_2 P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_{12}) - \kappa_{12}^{-1} Q \mu_\parallel \eta_1 \eta_2^2 (\hat{\mathbf{e}} \cdot \hat{\mathbf{u}}_{12})] \left[P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_{12}) - \frac{2}{5} \right], \tag{31}$$

where D is the molecular diameter. Equations (30) and (31) depend on the function $\ln(\kappa_{12}/D)$. This function can be approximated similarly to Eq. (28),

$$\ln \xi_{12}/D \approx \ln(L/D)(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_{12})^2.$$

Substituting this expression into Eqs. (30) and (31) and then into the general equations (24) and (26), one obtains, after the summation over η_1 and η_2,

$$\mathbf{M} = -\frac{5}{6} \rho Q \ln(L/D) \hat{\mathbf{n}} A_1, \tag{32}$$

$$W_{\alpha\beta} = -\hat{n}_\alpha \hat{n}_\beta \left[\frac{L-D}{2} A_2 + \xi \ln(L/D) A_3 \right] + \frac{\xi}{8} \left(\frac{k_B T}{\rho \mu^2} \right) \delta_{\alpha\beta}, \tag{33}$$

where

$$A_1 = \int d\hat{\mathbf{u}} \Theta(\hat{\mathbf{u}} \cdot \hat{\mathbf{e}})(\hat{\mathbf{u}} \cdot \hat{\mathbf{e}})(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}})^3 \left[\frac{2}{5} + P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}) \right],$$

$$A_2 = \int d\hat{\mathbf{u}} \Theta(\hat{\mathbf{u}} \cdot \hat{\mathbf{e}})(\hat{\mathbf{u}} \cdot \hat{\mathbf{e}})(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}})^2 P_2(\hat{\mathbf{n}} \cdot \mathbf{u}),$$

$$A_3 = \int d\hat{\mathbf{u}} (\hat{\mathbf{n}} \cdot \hat{\mathbf{u}})^2 P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}). \tag{34}$$

The coefficients A_1, A_2, and A_3 can readily be estimated for small tilt angles $\vartheta^2 \ll 1$. In this case one obtains

$$A_1 \approx \frac{68\pi}{175} + o(\vartheta^2), \quad A_2 \approx \frac{\pi}{4} + o(\vartheta^2), \quad A_3 \approx \frac{4\pi}{15} + o(\vartheta^2). \tag{35}$$

We note that all coefficients A_1, A_2, and A_3 are of the order of unity. Therefore we present simple estimates for the quantities $\mathbf{M}$ and $W_{\alpha\beta}$ omitting all numerical coefficients of the order of one:

$$\mathbf{M} \approx -\rho Q \ln(L/D) \hat{\mathbf{n}} (\hat{\mathbf{n}} \cdot \hat{\mathbf{e}}), \tag{36}$$

$$W_{\alpha\beta} \approx -\hat{n}_\alpha \hat{n}_\beta \left[\frac{L-D}{2} + \xi \ln(L/D) \right] + \frac{\xi}{8} \frac{kT}{\rho \mu_\parallel^2} \delta_{\alpha\beta}. \tag{37}$$

E. Final estimates

Comparing Eqs. (37) and (38) with the phenomenological expressions (3) and (4), we obtain $m_2 = -\rho Q \ln(L/D)$ and $g_1 = \xi kT / 8\rho\mu_\parallel^2$. The term $m_1 \hat{\mathbf{e}}$ in Eq. (37), the surface field $\mathbf{M}$, is absent and therefore $m_1 = 0$ in the present simple theory. Accordingly, the terms $g_2 \hat{\mathbf{e}}_\alpha \hat{\mathbf{e}}_\beta$ and $g_4(\hat{\mathbf{e}}_\alpha \hat{\mathbf{n}}_\beta + \hat{\mathbf{e}}_\beta \hat{\mathbf{n}}_\alpha)(\hat{\mathbf{n}} \cdot \hat{\mathbf{e}})$ are absent in Eq. (38) and thus $g_2 = g_4 = 0$ here. In the case of perfect nematic ordering and zero transverse dipole the transverse polarization $\mathbf{P}_\perp$ vanishes. Then the dipolar contribution to the surface free energy can be written as [see Eq. (5)]

$$\Delta F_s = m_2 P_\parallel \cos\vartheta + \frac{1}{2}(g_1 + g_3) P_\parallel^2,$$

with the equilibrium polarization

$$P_\parallel = -\frac{m_2}{g_1 + g_3} \cos\vartheta.$$

Finally, the dipolar contribution to the surface free energy reads

$$\Delta F_s = -\frac{1}{2} \frac{m_2^2}{g_1 + g_3} \cos^2\vartheta. \tag{38}$$

Substituting the expressions for the coefficients m_2, g_1, and g_3, obtained above, we obtain the estimate for the dipolar contribution to the total

$$\Delta F_s = -\frac{1}{2} \frac{\rho^2 Q^2 \ln^2(L/D) \gamma_D}{[L + 2\xi \ln(L/D)] \gamma_D + \xi/8} \cos^2\vartheta, \tag{39}$$

where the dimensionless parameter $\gamma_D = \rho\mu_\|^2/kT$.

Equation (39) shows that the dependence of the anchoring strength on the value of molecular dipole is determined by the dimensionless parameter $\gamma_d = \rho\mu_\|^2/k_BT$. This parameter is of the order of unity in the case of large molecular dipoles ($\mu_{||} \approx 4-5$ D) characteristic of cyanobiphenyl liquid crystals. For very large dipoles the dipolar contribution to the anchoring strength no longer depends on the value of the dipole and reaches a saturation value that is approximately given by $W_d \sim [\rho Q \ln(L/D)]^2/2[L+2\xi\ln(L/D)]$. Setting $\rho = 2\times10^{21}$ cm^{-1}, $L = 3\times10^{-7}$ cm, $L = 4D$, $\xi = 2L$, and $Q = 10^{-25}$ esu [30], we obtain $W_d \sim 10^{-1}$ erg cm^{-2}. This estimate shows that the dipole contribution to the surface free energy can be very large if the nematic liquid crystal consists of molecules with large longitudinal dipoles. Indeed, this estimate of W_d is comparable to, or even larger than, the typical anchoring strength of various nematic liquid crystals ($W_0 \sim 10^{-2}-10^{-3}$ erg cm^{-2}) [31–33]. Even if we have overestimated it in the context of the present qualitative theory, this is still an indication that the effect is strong; the longitudinal dipoles have a very strong tendency to align perpendicular to the structureless surface.

We note that the above numerical estimates for W_d are valid in the case of large molecular dipoles. In the case of weakly polar molecules, by which we mean $\gamma_d \ll 1$, Eq. (39) reduces to $W_d \sim [\rho Q \ln(L/D)]^2 \rho\mu_\|^2/Lk_BT$. This contribution vanishes when $\mu_\| \to 0$.

IV. DISCUSSION

Both the phenomenological and the microscopic theories presented in this paper predict that a spontaneously polarized layer will always be found at a nematic surface. This layer exists even at a structureless flat surface, in the absence of electric fields, charged impurities, or gradients of the order parameter. The appearance of the surface polar layer is a formal consequence of the fact that a boundary between two different media destroys reflection symmetry with respect to the surface plane. This symmetry, by contrast, is unbroken in the bulk system. The surface is not a mirror plane of the system and thus a surface spontaneous polarization may (and usually will) exist even when the polarization is absent in the bulk, a fact pointed out by Petrov and Derzhanski [40]. This simple symmetry argument is almost obvious. The details of the actual microscopic mechanisms that induce the ordering of dipoles at the flat surface, however, are not similarly obvious. In the molecular theory developed in this paper the surface polarization is caused by the electrostatic interaction between permanent molecular dipoles and quadrupoles. The average dipole-quadrupole interaction vanishes in the bulk of a simple fluid. By contrast, because a part of the interaction sphere is cut off by the surface plane, this contribution to the intermolecular potential gives a nonzero (and large) contribution near the surface; this phenomenon is sometimes known as the incomplete interaction at an interface. The average dipole-quadrupole interaction potential then becomes a function of the angle between the average dipole and the surface normal. In this way the terms linear in the polarization appear in the free energy expansion and, when the surface energy is minimized, one finds a spontaneous surface polarization. This result is confirmed by experimental data obtained by Guyot-Sionnest *et al.* [10], Jérôme *et al.* [12,13], and Mochizuki *et al.* [11], who have observed a polar layer at the nematic surface with a thickness of few molecular lengths. There is, in addition, indirect evidence of the existence of surface polarization in nematics. For example, Lavrentovich *et al.* [20] have observed some surface electrooptic effects that have been interpreted as arising from surface polarization and not from the flexoelectric effect.

Surface polarization gives a significant contribution to the anchoring strength of a nematic liquid crystal composed of strongly polar molecules. For large longitudinal dipoles the dipolar contribution favors homeotropic director alignment at the surface. The dipoles have a strong tendency to be perpendicular to a structureless surface. The estimates performed in Sec. III B indicate that the dipolar contribution is very large ($W_d \sim 10^{-1}$ erg cm^{-2}) and is comparable to, or even larger than, the typical values of the anchoring strength measured for various nematic liquid crystals. Thus the dipolar contribution may even predominate, for example, at the free surface of liquid crystals that possess strongly polar terminal groups. The experimental data indicate indeed that cyanobiphenyl and oxycyanobiphenyl liquid crystals (which have a strongly polar CN group) align homeotropically at the free surface [34–36].

In the case of purely longitudinal dipoles the minimum of the surface free energy (39) corresponds to homeotropic alignment of the nematic director. By analogy one may suppose that for purely transverse dipoles the equilibrium orientation of the director will be planar (i.e., again the dipoles are perpendicular to the surface). This conclusion is also not in contradiction with the existing experimental data. For example, the nematic para-azoxyanisole, with a moderate molecular transverse dipole, has a planar orientation at the free surface [34], in contrast to cyanobiphenyls whose large dipole seems to force a homeotropic orientation. Detailed calculations for this case, however, are more difficult.

We have presented numerical estimates for W_d. Our qualitative conclusions are valid as long as the molecular dipoles are sufficiently large. If the molecular dipoles are small, the problem is more complicated and cannot be described completely using the model we have developed in this paper. Now the molecular polarizability gives a substantial contribution to the susceptibility of a liquid crystal and the polar part of the surface free energy cannot be calculated by considering only the ordering of permanent molecular dipoles. However, in this case the dipolar contribution to the total anchoring strength is relatively unimportant.

In this paper we have considered an interaction between permanent molecular dipoles and the structureless surface on a two-body level. Clearly, some many-body effects can also make a contribution to the surface energy. Some of these many-body effects are represented on the macroscopic level by an interaction of the dipole with its image. At a free surface the permanent dipole $\vec{\mu}_1$, which makes an angle θ with the surface normal, creates the image dipole $\mu_2 \approx \mu_1(\epsilon-1)/(\epsilon+1)$, where ϵ is the dielectric constant of the medium. The image dipole makes an angle of $\pi-\theta$ with the surface normal. As a result, the interaction of the dipole with its image can be estimated as U_{dd}

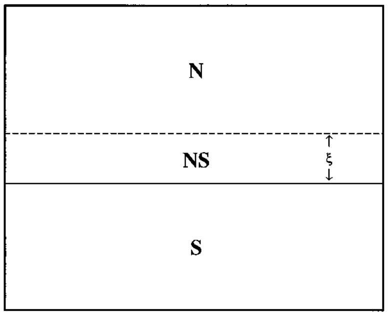

FIG. 1. Schematic division of space into the half plane N containing the bulk liquid crystal, the surface plane NS containing a polar liquid crystal, and the region S without a liquid crystal.

$\approx \mu^2(\epsilon-1)/(\epsilon+1)z^{-3}\cos 2\theta$, where z is the distance from the surface. This interaction will contribute to the total anchoring energy of the liquid crystal if we assume that the direction of the dipole is parallel to that of the director $\hat{\mathbf{n}}$. Considering the dominant contribution from the dipoles in the first molecular layer, we can estimate this contribution to the surface free energy to be $\Delta W \sim \rho\mu^2 l^{-2}(\epsilon-1)/(\epsilon+1)$, where l is a molecular length $L \sim 2\times 10^{-7}$ cm.

For large dipoles this contribution can be of the order of 1 erg cm $^{-2}$, i.e., it is very large. We note, however, that in this way one strongly overestimates the corresponding contribution. In fact, the concept of an image dipole is valid only for a macroscopic dipole embedded in a medium at a relatively large distance from the surface. In other words, there must be some ''continuous medium'' between the dipole and the surface. This requires that distance $z \gg a$, where a is the typical dimension of the particles that compose that medium. Thus one cannot apply this concept to dipoles in the first or second molecular layers. Furthermore, at distances $z \gg L$ the interaction with the image dipole appears to be much weaker and can be neglected in comparison with other contributions.

Finally, we discuss the relation between the phenomena discussed in this paper and other polar effects at a nematic surface. First, the nematic order parameter at the surface is not equal to that in the bulk and there is some spatial variation of the order parameter in a thin boundary layer. Nematic liquid crystals are anisotropic and possess a nonzero quadrupole density $\langle Q_{\alpha\beta}\rangle \propto S$ in the ground state. Then the spatial variation of the nematic order parameter near the surface results in the nonzero average polarization proportional to the gradient of the quadrupole density $\mathbf{P} = -\boldsymbol{\nabla}\cdot\mathbf{Q}$. This effect, known as order electricity [16], has been discussed in detail elsewhere [18,37]. The order electric effect favors a tilted director orientation at the free surface. However, according to the estimates of Ref. [38], the order electric contribution to the anchoring strength is of the order of 2×10^{-3} erg cm^{-2} and should be much weaker than the contribution from the ordering of permanent dipoles. We conclude that the contribution from the ordering of permanent molecular dipoles dominates the order electric contribution in nematic liquid crystals composed of strongly polar molecules. For fluids made from nonpolar or weakly polar molecules, however, this conclusion may no longer hold.

In real nematic liquid crystals the nematic-substrate interface may exhibit extremely complex phenomena. The substrate can adsorb charged impurities from the solvent and these effective surface charges produce a surface electric field [16,17], which then, in turn, can interact with molecular dipoles. The surface electric field can also be present on the boundary between a nematic liquid crystal and the Langmuir-Blodgett film [41]. Whatever its origin, the surface electric field can make a significant contribution to the anchoring strength of the nematic. Its relative importance, however, depends crucially on the nature of the surface and on the concentration of charged impurities, which may strongly vary from one nematic sample to another and thus not be reproducible.

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APPENDIX A: SURFACE FREE ENERGY OF THE POLAR NEMATIC LIQUID CRYSTAL

In the simple model of the polar surface discussed in Sec. III A, the distribution function of the nematic liquid crystal is different in the polar surface layer of thickness ξ and in the bulk, respectively. This distribution function $f_1(\omega,z)$ can be written as

$$f_1(\omega,z) = \Theta(z-\xi)[f_s(\omega) - f_b(\omega)] + f_b(\omega), \qquad \text{(A1)}$$

where $\Theta(x)$ is the Heaviside step function, $\Theta(x)=1$ if $x>0$, and $\Theta(x)=0$ if $x<0$. Here $f_b(\omega)$ and $f_s(\omega)$ are the bulk and surface orientational distribution functions, respectively.

The total free energy is described by Eq. (15). We can distinguish three regions, which are shown schematically in Fig. 1. The regions N and NS contain a liquid crystal, with the region NS, of thickness ξ, containing the surface polar layer. The region S (for substrate) does not contain a liquid crystal. The entropic contribution to the free energy is always local. The energetic contribution, however, is nonlocal and contains (a) terms that couple these regions (in the case of N and NS) and (b) counterterms that compensate for the incomplete interaction between the liquid crystal and the liquid crystal that is not present in the substrate. The counterterms are added to the bulk liquid crystal free energy that continues right up to the interface. Substitution of Eq. (A1) into Eq. (15) yields

$$
\begin{aligned}
F_N={}&F_I+\rho k_BTV\int d\omega\int d\omega f_b(\omega)\ln f_b(\omega)-\rho k_BT\xi\sigma\int d\omega_1[f_{1s}(\omega_1)\ln f_{1s}(\omega_1)-f_{1b}(\omega_1)\ln f_{1b}(\omega_1)]\\
&+\frac{1}{2}\rho^2k_BT\sigma\int_0^\infty dz_1\int_0^\infty dz_2\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})f_b(\omega_1)f_b(\omega_2)\\
&-\frac{1}{2}\rho^2k_BT\sigma\int_0^\xi dz_1\int_0^\xi dz_2\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})[f_s(\omega_1)-f_b(\omega_1)][f_s(\omega_2)-f_b(\omega_2)]\\
&-\rho^2k_BT\sigma\int_0^\infty dz_1\int_0^\xi dz_2\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})f_b(\omega_1)[f_s(\omega_2)-f_b(\omega_2)]. \qquad \text{(A2)}
\end{aligned}
$$

Here the coefficient ξ in the third term of Eq. (A2) comes from the integration of the step function $\Theta(z-\xi)$ over z.

We note that the direct correlation function $C_2(\omega_1,\omega_2,\mathbf{r}_{12})$ depends on the difference z_1-z_2. Thus it is reasonable to change the variables from z_1,z_2 to z_{12},z_1. The integrals over z_1 can be taken explicitly because only the limits of integration in Eq. (A2) depend on z_1 after the change in variables.

Now the fourth term in Eq. (A2) can be split into bulk and surface contributions

$$
\begin{aligned}
&\frac{1}{2}\rho^2k_BT\sigma\int_0^\infty dz_1\int_0^\infty dz_2\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})f_b(\omega_1)f_b(\omega_2)\\
&\quad=\frac{1}{2}\rho^2k_BT\sigma\int_0^\infty dz_1\int_{-\infty}^\infty dz_{12}\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})f_b(\omega_1)f_b(\omega_2)\\
&\quad\quad-\frac{1}{2}\rho^2k_BT\sigma\int_0^\infty dz_{12}\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 z_{12}C_2(\omega_1,\omega_2,\mathbf{r}_{12})f_b(\omega_1)f_b(\omega_2), \qquad \text{(A3)}
\end{aligned}
$$

where we have taken the integral over z_1 in the second term of Eq. (A3). The first term in Eq. (A3) is a contribution to the bulk free energy that is proportional to the thickness of the sample. By contrast, the second term is the surface free energy, which was derived by Sen and Sullivan [3]. This term is the counterterm linking the regions N and NS with S in Fig. 1.

In a similar way one can transform also the last two terms in Eq. (A2). These terms contain the coupling between NS and itself and NS and N. If $\xi>r_c^0$ these terms can be written as

$$
\begin{aligned}
&-\frac{1}{2}\rho^2k_BT\sigma\int_0^\xi dz_1\int_0^\xi dz_2\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})[f_s(\omega_1)-f_b(\omega_1)][f_s(\omega_2)-f_b(\omega_2)]\\
&\quad\approx-\frac{1}{2}\rho^2k_BT\sigma\xi\int_{-\infty}^\infty dz_{12}\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})[f_s(\omega_1)-f_b(\omega_1)][f_s(\omega_2)-f_b(\omega_2)]\\
&\quad\quad+\frac{1}{2}\rho^2k_BT\sigma\int_0^\infty dz_{12}\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 z_{12}C_2(\omega_1,\omega_2,\mathbf{r}_{12})[f_s(\omega_1-f_b(\omega_1)][f_s(\omega_2)-f_b(\omega_2)] \qquad \text{(A4)}
\end{aligned}
$$

and

$$
\begin{aligned}
&-\rho^2k_BT\sigma\int_0^\infty dz_1\int_0^\xi dz_2\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})f_b(\omega_1)[f_s(\omega_2)-f_b(\omega_2)]\\
&\quad\approx-\rho^2k_BT\sigma\xi\int_{-\infty}^\infty dz_{12}\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 C_2(\omega_1,\omega_2,\mathbf{r}_{12})f_b(\omega_1)[f_s(\omega_2)-f_b(\omega_2)]\\
&\quad\quad+\rho^2k_BT\sigma\int_0^\infty dz_{12}\int d^2\mathbf{r}_{12\perp}\int d\omega_1 d\omega_2 z_{12}C_2(\omega_1,\omega_2,\mathbf{r}_{12})[f_b(\omega_1)[f_s(\omega_2)-f_b(\omega_2)]. \qquad \text{(A5)}
\end{aligned}
$$

Finally, combining the surface contributions to the total free energy from Eqs. (A3)–(A5), one obtains the expression for the surface free energy of a polar nematic liquid crystal

$$\begin{aligned}F_s/\sigma={}&\rho k_BT\xi\int d\omega_1[f_{1s}(\omega_1)\ln f_{1s}(\omega_1)-f_{1b}(\omega_1)\ln f_{1b}(\omega_1)]+\frac{1}{2}\rho^2k_BT\int d\omega_1 d\omega_2\widetilde{C}_2(\omega_1,\omega_2,\mathbf{r}_{12})f_{1b}(\omega_1)f_{1b}(\omega_2)\\&+\rho^2k_BT\int d\omega_1 d\omega_2\widetilde{C}_2(\omega_1,\omega_2,\mathbf{r}_{12})[f_{1s}(\omega_1)-f_{1b}(\omega_1)]f_{1b}(\omega_2)-\rho^2k_BT\xi\int d\omega_1 d\omega_2\widetilde{C}_0(\omega_1,\omega_2,\mathbf{r}_{12})\\&\times[f_{1s}(\omega_1)-f_{1b}(\omega_1)]f_{1b}(\omega_2)-\frac{1}{2}\rho^2k_BT\int d\omega_1 d\omega_2\widetilde{C}_2(\omega_1,\omega_2)[f_{1s}(\omega_1)-f_{1b}(\omega_1)][f_{1s}(\omega_2)-f_{1b}(\omega_2)]\\&-\frac{1}{2}\rho^2k_BT\xi\int d\omega_1 d\omega_2\widetilde{C}_0(\omega_1,\omega_2)[f_{1s}(\omega_1)-f_{1b}(\omega_1)][f_{1s}(\omega_2)-f_{1b}(\omega_2)],\end{aligned}\qquad\text{(A6)}$$

with

$$\widetilde{C}_2(\omega_1,\omega_2)=\int d\mathbf{r}_{12}\Omega(\mathbf{r}_{12}\cdot\hat{\mathbf{e}})C_2(\omega_1,\omega_2,\mathbf{r}_{12})\qquad\text{(A7)}$$

and

$$\widetilde{C}_0(\omega_1,\omega_2)=\int d\mathbf{r}_{12}C_2(\omega_1,\omega_2,\mathbf{r}_{12}),\qquad\text{(A8)}$$

where $\xi>r_c^0$ is the thickness of the surface polar layer, with r_c^0 the direct correlation radius.

APPENDIX B: LONG-RANGE PART OF THE ELECTROSTATIC INTERACTION AND THE SURFACE ELECTRIC FIELD

In the molecular field approximation the average interaction between permanent molecular dipoles and quadrupoles can be written as

$$\begin{aligned}U_{\mathrm{el}}={}&\frac{1}{2}\rho^2\int[V_{dd}(1,2)+2V_{dq}(1,2)+V_{qq}(1,2)]\Theta(\xi_{12}-r_{12})\\&\times f_1(1)f_1(2)d(1)d(2),\end{aligned}\qquad\text{(B1)}$$

where $d(1)=d\mathbf{r}_1d\omega_1$ specifies both the position $\mathbf{r}_1$ and the orientation ω_1 of the molecule 1. The step function $\Theta(\xi_{12}-r_{12})$ represents the steric cutoff and ξ_{12} is the minimal distance of approach for two molecules 1 and 2. The function $\Theta(\xi_{12}-r_{12})=0$ when the molecules penetrate each other (i.e., when $r_{12}<\xi_{12}$) and $\Theta(\xi_{12}-r_{12})=1$ otherwise. The dipole-dipole interaction potential $V_{dd}(1,2)$, the dipole-quadrupole potential $V_{dq}(1,2)$ and the quadrupole-quadrupole potential $V_{qq}(1,2)$, are given by the familiar expressions

$$\begin{aligned}V_{dd}(1,2)&=\mu_{1\alpha}T_{\alpha\beta}(\mathbf{r}_{12})\mu_{2\beta},\\V_{dq}(1,2)&=\mu_{1\alpha}T_{\alpha\beta\gamma}(\mathbf{r}_{12})q_{2\beta\gamma},\\V_{qq}(1,2)&=q_{1\alpha\beta}T_{\alpha\beta\gamma\delta}(\mathbf{r}_{12})q_{2\gamma\delta},\end{aligned}\qquad\text{(B2)}$$

with

$$T_{\alpha\beta\cdots\nu}=\nabla_\alpha\nabla_\beta\cdots\nabla_\nu\frac{1}{r_{12}},\qquad\text{(B3)}$$

where $\vec{\mu}_1$ is the permanent dipole of the molecule 1 and $q_{1\alpha\beta}$ is the molecular quadrupole tensor.

At large separation the integral in (B1) diverges for the dipole-dipole potential, while at short distances the effective interaction potential in (B1) vanishes due to the steric cutoff. It is convenient to separate between the short-range and the long-range parts of the effective electrostatic potential. This separation procedure was proposed by Ewald long ago [26] in the dielectric theory of crystal lattices. We have applied the same idea to the description of polar polymer solvents [39], but it is standard in the literature, particularly of charged fluids [25]. The short-range contribution is taken into account in the statistical theory in the usual way, whereas the contribution from the long-range part reduces exactly to the expression for the energy of the average electric field in the volume of the body. This energy gives an additional contribution to the total free energy of a polar sample and is determined by the boundary conditions and sample shape.

In order to separate between the short- and long-range parts of the total electrostatic potential let us add and subtract the same average of the ''pure'' electrostatic interaction potential, without the steric cutoff. Equation (B1) can then be rewritten as

$$U_{\mathrm{el}}=U_{\mathrm{short}}+U_{\mathrm{long}},\qquad\text{(B4)}$$

with

$$\begin{aligned}U_{\mathrm{short}}={}&\frac{1}{2}\rho^2\int[V_{dd}(1,2)+2V_{dq}(1,2)+V_{qq}(1,2)]\\&\times[\Theta(\xi_{12}-r_{12})-1]f_1(1)f_1(2)d1d2,\end{aligned}\qquad\text{(B5)}$$

$$\begin{aligned}U_{\mathrm{long}}={}&\frac{1}{2}\rho^2\int[V_{dd}(1,2)+2V_{dq}(1,2)+V_{qq}(1,2)]\\&\times f_1(1)f_1(2)d1d2.\end{aligned}\qquad\text{(B6)}$$

The quantity U_{short} is now the average of the effective short-range potential $V_{\mathrm{eff}}(1,2)=[V_{dd}(1,2)+2V_{dq}(1,2)+V_{qq}(1,2)][\Theta(\xi_{12}-r_{12})-1]$. This is only nonzero at small intermolecular separations $r_{12}<\xi_{12}<L$, where L is the molecular length.

The long-range part of the initial electrostatic potential is represented by Eq. (B5). This contribution represents the energy of the average electrostatic field in the medium and can be expressed in terms of the average polarization **P**. This is given by

$$P_\alpha(\mathbf{r})=\rho[\langle\mu_\alpha\rangle-\nabla_\beta\langle q_{\alpha\beta}\rangle], \tag{B7}$$

where $\langle d_\alpha\rangle$ and $\langle q_{\alpha\beta}\rangle$ are the average dipole and quadrupole densities, respectively. The average of the long-range part of the electrostatic interaction potential is now

$$\begin{aligned}U_{\text{long}}&=\frac{1}{2}\rho^2\int[V_{dd}(1,2)+2V_{dq}(1,2)+V_{qq}(1,2)]f_1(1)\\&\quad\times f_1(2)d1d2\\&=\frac{1}{2}\int d\mathbf{r}_1d\mathbf{r}_2P_\alpha(\mathbf{r}_1)T_{\alpha\beta}(\mathbf{r}_{12})P_\beta(\mathbf{r}_2).\end{aligned} \tag{B8}$$

This is more conveniently described in the Fourier representation

$$U_{\text{el}}=2\pi\int d\mathbf{k}(\mathbf{P}_{\mathbf{k}}\cdot\mathbf{k})(\mathbf{P}_{-\mathbf{k}}\cdot\mathbf{k})k^{-2}. \tag{B9}$$

In a medium without an external field the average polarization **P** is related to the macroscopic electric field **E** by static Maxwell equations $\boldsymbol{\nabla}\cdot\mathbf{D}=0$ and $\boldsymbol{\nabla}\times\mathbf{E}=\mathbf{0}$, where the induction $\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}$. These equations yield the simple relation between the electric field $\mathbf{E}_{\mathbf{k}}$ and the longitudinal part of the polarization $\mathbf{P}_{\mathbf{k}}$,

$$\mathbf{E}_{\mathbf{k}}=-4\pi\mathbf{k}(\mathbf{k}\cdot\mathbf{P}_{\mathbf{k}})k^{-2}. \tag{B10}$$

Finally, substituting Eq. (B9) into (B8) yields the familiar expression for the energy of the electostatic field

$$U_{\text{el}}=(8\pi)^{-1}\int d\mathbf{k}(\mathbf{E}_{\mathbf{k}}\cdot\mathbf{E}_{-\mathbf{k}}). \tag{B11}$$

Equation (B10) is slightly modified if one takes into consideration not only the electrostatic interaction between permanent multipoles but also the polarizability of the medium [18]. In this case the average electrostatic energy depends on the dielectric tensor $\epsilon_{\alpha\beta}$,

$$U_{\text{el}}=(8\pi)^{-1}\int d\mathbf{k}(\mathbf{E}_{\mathbf{k}}\cdot\boldsymbol{\epsilon}\cdot\mathbf{E}_{-\mathbf{k}}). \tag{B12}$$

Thus we conclude that the free energy of a fluid with long-range electrostatic intermolecular interactions can be calculated using the effective short-range potential $V_{\text{eff}}(1,2)=V_{\text{el}}(1,2)[\Theta(\xi_{12}-r_{12})-1]$. The energy of the average electric field in the medium, which represents the average long-range part of the electrostatic intermolecular interaction, must be added to the free energy at the final stage and must be taken into account in the minimization of the total free energy with respect to the polarization **P**.

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