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Structure of a nematic liquid crystal between aligning walls

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The structure of a model nematic liquid crystal confined between two symmetric aligning walls has been investigated using density-functional theory. In the case where wall-particle and particle-particle potentials favor different orientations at the surface, their relative ranges are found to play a crucial role in determining the equilibrium director configuration. If the surface interaction is the longer ranged, it will align the nematic fairly uniformly throughout the whole sample, along a direction close to that which we would obtain if the wall were the sole source of anchoring. If, on the other hand, the ranges of the two interactions are comparable, anchoring at the surfaces will still be dominated by the wall potential but the director will rotate (in general, incompletely) towards the orientation favored by the intermolecular potential, over a distance of the order of the molecular diameter, thereby producing a strong subsurface deformation. In this context I will critically discuss some related theoretical work. [S1063-651X(97)05202-1]

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Practical as well as fundamental considerations have conspired to produce a lasting interest in the surface behavior of liquid crystals (LCs). The basic problem is to understand how a given surface modifies the properties of a given LC, and, in particular, how it induces a given alignment, or anchoring, thereof, for given values of experimentally controllable parameters, such as temperature and applied fields [1]. Whereas technologists aim at making better devices, which at present rely mostly on finely tuned anchoring [2], theorists pursue a description of the phenomenon in the framework of the statistical mechanics of nonuniform fluids [3,4]. Of particular relevance to the latter is the detailed structure of the interface, which very often differs quite radically from the bulk.

The most popular formalism, the elastic theory of Frank and Oseen [5–7], circumvents the problem by replacing the true surface by a structureless wall endowed with a boundary condition [8]. This approach was, however, dealt a blow by Oldano and Barbero's discovery that the existence of a nonzero K_{13} elastic constant should lead to formally infinite subsurface deformations [9,10]. Since, on the one hand, consistency seems to require that the K_{13} term be included in the standard free energy [11] and, on the other hand, there is no fundamental reason why K_{13} should vanish in general [12–15], we are faced with a paradox—the so-called ''K_{13} problem.'' Several solutions have been proposed [16–22], and I shall not discuss them here; suffice it to say that one of them still leaves open the possibility of strong (but finite) deformations in a surface layer of microscopic thickness [16]. The price to pay for this is the introduction of a new, higher-order, elastic constant.

In my view, it is doubtful that the question of whether strong subsurface deformations are real, or a mere artifact, will ever be resolved satisfactorily within elastic theory: this is, strictly speaking, not valid near a surface, where its underlying assumptions of uniaxiality, uniformity of the order parameter, and the very existence of a nematic director, break down (more on this last point below). An elastic description of surfaces can thus have, at best, a heuristic value (see in this connection the very illuminating discussion in [22]). However, surface-induced reorientation of the director over distances of the order of molecular dimensions has been found in simulations [23], hence some microscopic insight into the problem is clearly desirable.

Recently, Barbero and co-workers have reported several microscopic calculations of the structure of a nematic confined between two aligning plates [24–26]. These revealed the occurrence of strong subsurface deformations if the intermolecular potential contains terms which couple orientational and translational degrees of freedom. Such deformations are a consequence of the competition between the different aligning tendencies of fluid-fluid and wall-fluid interactions. The authors assumed, however, that the director orientation at the surface is fixed, which corresponds to taking an infinitely strong surface potential of zero range. How this direct transplantation from elastic theory may affect results, is the point we wish to address here.

The role of different interaction ranges was first studied by Dubois-Violette and de Gennes [27,28], who used a mixed elastic-microscopic treatment. They found that a combination of strong short-ranged and weaker long-ranged anchoring potentials, could give rise to large tilt angle distortions near the surface [28]. This work has recently been extended by Alexe-Ionescu and collaborators [29], who investigated the stability of uniform and nonuniform tilt angle profiles for different strengths of the short-ranged surface potential. In this paper we present what is, to our knowledge, the first density-functional calculation of the structure of a nematic film between aligning walls, using the theory of Telo da Gama [30–32]. This is just briefly sketched here, and we refer the reader to the original references for details. The grand potential free energy Ω of a nonuniform, one component fluid confined between two plates is the minimum of the functional

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$$\frac{\Omega[\rho(z,\omega)]}{S}=\frac{\mathcal{F}[\rho(z,\omega)]}{S}+\int_{-d/2}^{d/2}dz\ d\omega\ \rho(z,\omega)\times\left[V_{ext}\left(z+\frac{d}{2},\omega\right)+V_{ext}\left(\frac{d}{2}-z,\omega\right)\right]-\mu\int_{-d/2}^{d/2}dz\ d\omega\ \rho(z,\omega), \tag{1}$$

where S is the area of the interface, $\rho(z,\omega)$ is the density-orientational profile in the presence of the external potential $V_{ext}(z,\omega)$ and μ is the chemical potential. z is the position coordinate along the normal to the plates, located at $z=-d/2$ and $z=d/2$, and $\omega=(\phi,\theta,\chi)$ is the set of orientation coordinates (Euler angles) of a molecule [33]. (In the present model molecules have rodlike symmetry, and ϕ and θ are then just the azimuthal and polar angles, respectively.) $\mathcal{F}[\rho(z,\omega)]$ is a unique functional of the density which is independent of the external potentials and represents the intrinsic Helmholtz free energy of the inhomogeneous fluid. The mean-field approximation for a fluid characterized by a pairwise intermolecular potential, $\phi(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2)$, yields [34]

$$\mathcal{F}[\rho(z,\omega)]=\mathcal{F}_{ref}[\rho(z,\omega)]+\frac{1}{2}\int_{-d/2}^{d/2}dz_1dz_2\int dx_1dy_1dx_2dy_2\times\int d\omega_1d\omega_2\ \rho(\mathbf{r}_1,\omega_1)\phi_p(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2)\times\rho(\mathbf{r}_2,\omega_2), \tag{2}$$

where $\mathbf{r}_i=(x_i,y_i,z_i)$, and we have defined a ‘‘perturbative’’ interaction

$$\phi_p(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2)=\phi(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2)-\phi_{ref}(\mathbf{r}_1,\mathbf{r}_2). \tag{3}$$

In Eq. (2), $\mathcal{F}_{ref}[\rho(z,\omega)]$ corresponds to a reference system in which the particles interact via a pairwise potential $\phi_{ref}(\mathbf{r}_1,\mathbf{r}_2)$ and the density is constrained to be $\rho(z,\omega)$. This is treated in a local-density approximation

$$\mathcal{F}_{ref}[\rho(z,\omega)]=\int dz\ d\omega\ f_{ref}(\rho(z,\omega)). \tag{4}$$

In what follows we shall consider the simple generalized Maier-Saupe model characterized by the potential [32]

$$\phi_{ref}(r)=\begin{cases}+\infty, & r\leqslant\sigma\\ 0, & r>\sigma\end{cases} \tag{5}$$

$$\phi_p(r,\omega_1,\omega_2)=\begin{cases}0, & r\leqslant\sigma\\ -A\left(\frac{\sigma}{r}\right)^6-B\left(\frac{\sigma}{r}\right)^6P_2[\cos(\omega_1,\omega_2)] & \\ +C\left(\frac{\sigma}{r}\right)^6\{P_2[\cos(\omega_1,\omega_{12})]+P_2[\cos(\omega_2,\omega_{12})]\}, & r>\sigma\end{cases} \tag{6}$$

where σ is the hard-sphere diameter, ω_{12} is the direction of the intermolecular vector, and $P_2(x)$ is the second Legendre polynomial. A and B are the strengths of the isotropic and Maier-Saupe parts of the potential, respectively. C is the strength of the coupling between the spatial and orientational dependences of the pair potential: $C>0$ corresponds to prolate molecules, and $C<0$ to oblate molecules [32]. In addition, we choose a wall potential which favors anchoring at $\pi/4$ rad (45°) to the normal [31]

$$V_{ext}(z,\omega)=V_{iso}(z)-C_V\ e^{-z/\lambda}\sin2\theta\cos\phi, \tag{7}$$

where C_V is the strength of the anisotropic part of the potential, λ is a range parameter, and we leave the isotropic part $V_{iso}(z)$ unspecified, for reasons discussed below. Finally, the free energy density of the reference system is approximated by

$$f_{ref}(\rho(z,\omega))=f_{hs}(\rho(z))+\rho(z)k_{\mathrm{B}}T\langle\ln[4\pi\hat{f}(z,\omega)]\rangle, \tag{8}$$

where $\hat{f}(z,\omega)$ is the orientational distribution function defined through $\rho(z,\omega)=\rho(z)\hat{f}(z,\omega)$, $\langle\mathcal{A}\rangle=\int\mathcal{A}\hat{f}(z,\omega)d\omega$ and $f_{hs}(\rho(z))$ is the free energy density of a hard-sphere system, which is given, for consistency with previous work, by the Percus-Yevick compressibility approximation [30]

$$f_{hs}(T,\rho)=\frac{\rho}{\beta}\left[\ln(\Lambda^3\rho)-1-\ln(1-\xi)+\frac{6\xi-9\xi^2+3\xi^3}{2(1-\xi)^3}\right], \tag{9}$$

where Λ is the de Broglie thermal wavelength and $\xi=\pi/6\rho\sigma^3$ is the packing fraction.

We assume that the director is always in the xz plane, i.e., that there are no twist distortions. Substitution of Eqs. (5), (6), and (8) into Eq. (2), and of the resulting expression into Eq. (1), then yields, via standard manipulations [32]

$$
\begin{aligned}
\frac{\Omega[\rho(z),\hat{f}(z,\omega)]}{S} ={}& \int_{-d/2}^{d/2} dz\, d\omega\, f_{ref}(\rho(z,\omega)) + k_{\mathrm{B}}T \int_{-d/2}^{d/2} dz\, \rho(z)\langle \ln[4\pi \hat{f}(z,\omega)]\rangle - \mu \int_{-d/2}^{d/2} dz\, \rho(z) \\
&- \frac{1}{2}A \int_{-d/2}^{d/2} dz_1 dz_2\, \Phi(|z_1-z_2|)\rho(z_1)\rho(z_2) - \frac{1}{2}B \int_{-d/2}^{d/2} dz_1 dz_2\, \Phi(|z_1-z_2|)\rho(z_1)\rho(z_2)\,\eta(z_1)\,\eta(z_2) \\
&- \frac{3}{8}B \int_{-d/2}^{d/2} dz_1 dz_2\, \Phi(|z_1-z_2|)\rho(z_1)\rho(z_2)[\nu(z_1)\nu(z_2)+\tau(z_1)\tau(z_2)] \\
&+ \frac{1}{2}C \int_{-d/2}^{d/2} dz_1 dz_2\, \Phi(|z_1-z_2|)\Phi'(|z_1-z_2|)\rho(z_1)\rho(z_2)[\eta(z_1)+\eta(z_2)] + \int_{-d/2}^{d/2} dz\, \rho(z) \\
&\times\left[V_{iso}\left(z+\frac{d}{2}\right)+V_{iso}\left(\frac{d}{2}-z\right)\right] - C_V \int_{-d/2}^{d/2} dz\, \rho(z)\nu(z)[e^{-(z+d/2)/\lambda}+e^{-(d/2-z)/\lambda}], \qquad (10)
\end{aligned}
$$

where the xy-averaged potentials are

$$
\Phi(z)=\begin{cases} \dfrac{\pi\sigma^2}{2}, & |z|\leqslant\sigma \\ \dfrac{\pi\sigma^6}{2z^4}, & |z|>\sigma \end{cases} \qquad (11)
$$

$$
\Phi'(z)=\begin{cases} \dfrac{z^2}{\sigma^2}-\dfrac{1}{2}, & |z|\leqslant\sigma \\ \dfrac{1}{2}, & |z|>\sigma \end{cases} \qquad (12)
$$

and the three orientational order parameters in the laboratory-fixed frame with the z axis perpendicular to the bounding surfaces, are defined as ([32] note the slightly different notation)

$$\eta(z)=\langle P_2(\cos\theta)\rangle, \qquad (13)$$

$$\nu(z)=\langle \sin 2\theta\cos\phi\rangle, \qquad (14)$$

$$\tau(z)=\langle \sin^2\theta\cos 2\phi\rangle. \qquad (15)$$

In this first approach, and to make closer contact with earlier work, we assume the density to be constant throughout the film (i.e., take the density profile to be steplike). This avoids all complications associated with wetting and adsorption phenomena (for a review see, e.g., [35]), which, while certainly interesting in their own right, would likely obscure the main points of the present study. Some additional justification can be derived from the result that it is always possible to choose an isotropic surface potential $V_{iso}(z)$ as will create a step-function density profile [36].

Minimizing Eq. (10) with respect to $\hat{f}(z,\omega)$ [30,32], we obtain

$$
\begin{aligned}
\hat{f}(z,\omega) = Z^{-1}\exp[&\alpha_1(z)P_2(\cos\theta)+\alpha_2(z)\sin 2\theta\cos\phi \\
&+\alpha_3(z)\sin^2\theta\cos 2\phi], \qquad (16)
\end{aligned}
$$

$$
\begin{aligned}
Z = \int d\omega\, \exp[&\alpha_1(z)P_2(\cos\theta)+\alpha_2(z)\sin 2\theta\cos\phi \\
&+\alpha_3(z)\sin^2\theta\cos 2\phi], \qquad (17)
\end{aligned}
$$

where

$$
\begin{aligned}
\alpha_1(z) ={}& \frac{B}{k_{\mathrm{B}}T}\rho \int_{-d/2}^{d/2} dz\, \Phi(|z-z'|)\,\eta(z') \\
&- \frac{C}{k_{\mathrm{B}}T}\rho \int_{-d/2}^{d/2} dz\, \Phi(|z-z'|)\Phi'(|z-z'|), \qquad (18)
\end{aligned}
$$

$$
\begin{aligned}
\alpha_2(z) ={}& \frac{3}{4}\frac{B}{k_{\mathrm{B}}T}\rho \int_{-d/2}^{d/2} dz\, \Phi(|z-z'|)\,\nu(z') \\
&+ \frac{C_V}{k_{\mathrm{B}}T}[e^{-(z+d/2)/\lambda}+e^{-(d/2-z)/\lambda}], \qquad (19)
\end{aligned}
$$

$$
\alpha_3(z) = \frac{3}{4}\frac{B}{k_{\mathrm{B}}T}\rho \int_{-d/2}^{d/2} dz\, \Phi(|z-z'|)\,\tau(z'). \qquad (20)
$$

The consistency equations for the order parameters, Eqs. (13)–(15), have been solved iteratively for $A/k_{\mathrm{B}}=2000$ K, $B/k_{\mathrm{B}}=C/k_{\mathrm{B}}=600$ K, $\rho\sigma^3=0.9$, T=436 K; these are chosen so as to position us in the nematic region of the LC phase diagram [30]. Moreover, $C>0$ favors homeotropic anchoring at the nematic free surface [32] (or, what is equivalent in this type of theory, at an inert wall). The film thickness was taken to be $d=40\sigma$. The angular integrations were performed by 24 point Gauss-Legendre quadrature [37], and the spatial integrals in Eqs. (18)–(20) by the method described in [38,39], with mesh size $\Delta z=0.1\sigma$. The tilt angle and order parameters in the director frame are found by inverting Eqs. (2.16) in [40]

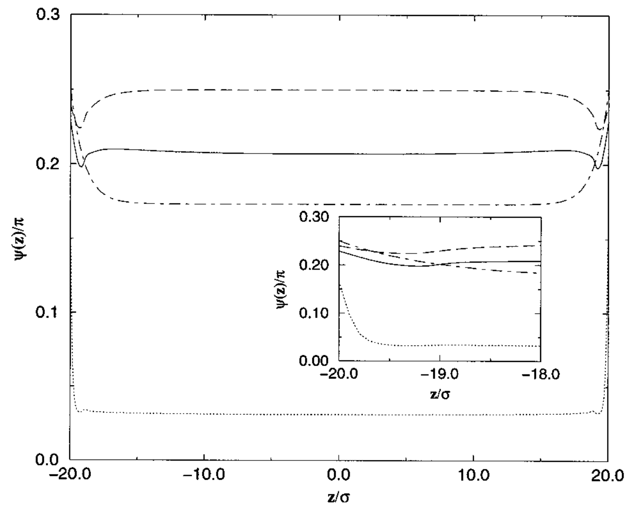

FIG. 1. Tilt angle vs z for $C_V/k_B=600$ K and $\delta_{WN}=4.6\sigma$ (solid line); $\delta_{WN}=46\sigma$ (dashed line); and $\delta_{WN}=0.46\sigma$ (dotted line). Note the dips at $\sim\sigma$ from the walls, corresponding to the range of the intermolecular potential. The dotted-dashed curve is the second-order elastic theory prediction [16]. Inset: detail of the structure near the left wall. In contrast to Fig. 3, the surface tilt angle from microscopic theory is always $\lesssim\pi/4$; it is smaller the shorter ranged the surface potential.

$$\psi(z)=\frac{1}{2}\tan^{-1}\frac{2\nu(z)}{2\eta(z)-\tau(z)}, \tag{21}$$

$$S(z)=\frac{1}{4}\left\{\eta(z)+\frac{3}{2}\tau(z)+3\sqrt{[\eta(z)-(1/2)\tau(z)]^2+\nu(z)^2}\right\}, \tag{22}$$

$$\mu(z)=\sqrt{\frac{3}{4}}\left\{\eta(z)+\frac{3}{2}\tau(z)-\sqrt{[\eta(z)-(1/2)\tau(z)]^2+\nu(z)^2}\right\}, \tag{23}$$

where S is the usual uniaxial nematic order paramter, and μ the biaxiality.

Given our choice of potentials, Eqs. (5) and (6), we need to define what is meant by the range of an inverse power law; following [41], we take the range of the intermolecular potential to be the distance over which it decays to 1% of its value at contact (i.e., at $r=\sigma$). This gives $\delta_{NN}\simeq1.1\sigma$. Likewise, the range of the wall potential is $\delta_{WN}=2\lambda\ln10\simeq4.6\lambda$. Results for different surface potential ranges and strengths are shown in Figs. 1–4. For completeness we have also included the second-order elastic theory prediction ([16], Eq. (15)) where, consistently with the above, we have taken $b=\sigma$, and $R=K_{13}/K$ is given by Eq. (58) in [15]. If $\delta_{WN}\gg\delta_{NN}$, the wall will win over the LC's intrinsic tendency to order homeotropically and produce $\psi\sim\pi/4$ rad (45°) throughout the whole film, the more effectively the stronger and longer ranged the surface potential (compare Figs. 1 and 3). If, however, $\delta_{WN}\lesssim\delta_{NN}$, then the surface potential will already be very weak where the intermolecular potential is still strong and "sees" the interface, hence ψ rotates by $\sim0.1\pi$ rad ($\sim20°$) in two surface layers of thickness $\sim\sigma$. The tilt angle is thus considerably smaller in the "bulk" than "at" the surfaces. We emphasize that this is *not* a K_{13} effect (as witness the disagreement between our results and the second-order elastic theory prediction) or anything intrinsic to the LC alone, which would be present independently of δ_{WN}. Nor is it related to surface-induced "melting" into the isotropic phase of the LC, which remains nematic right up to the walls, since $S(\pm d/2)$ never drops below ~0.4 (see Figs. 2 and 4).

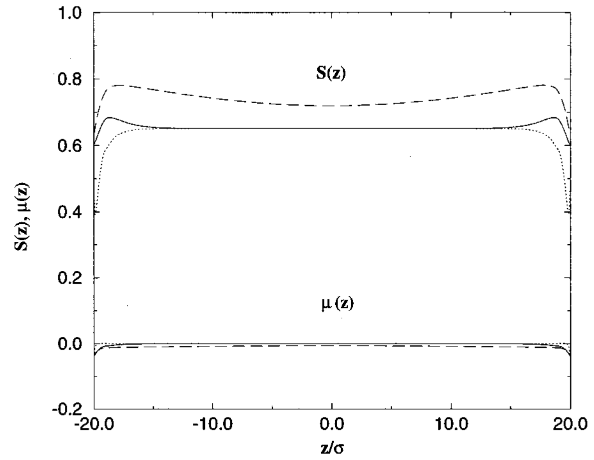

FIG. 2. Uniaxial S and biaxial μ order parameters vs z for the systems in Fig. 1 (same symbols). Note the enhanced nematic order at the surface with increasing range of the wall potential, and the smallness of the biaxiality, whose modulus never exceeds ~0.03.

It is interesting to compare our results with those of Tjipto-Margo and Sullivan, who derived a Landau-de Gennes free energy from a microscopic Helmholtz free energy functional [42]. In a previous paper we generalized this approach to the case of a LC in contact with a solid substrate [43], where the anchoring energy contains an additional contribution due to the surface potential. In the spirit of Tjipto-

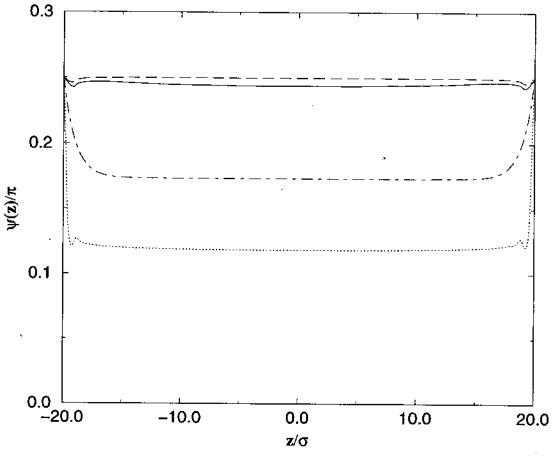

FIG. 3. Same as Fig. 1, but for $C_V/k_B=6000$ K. Now $\psi(z)\approx\pi/4$ for both $\delta_{WN}=4.6\sigma$ and $\delta_{WN}=46\sigma$. Moreover, $\psi(\pm d/2)\approx\pi/4$ in all cases, and the curve for $\delta_{WN}=0.46\sigma$ has shifted upwards considerably in consequence.

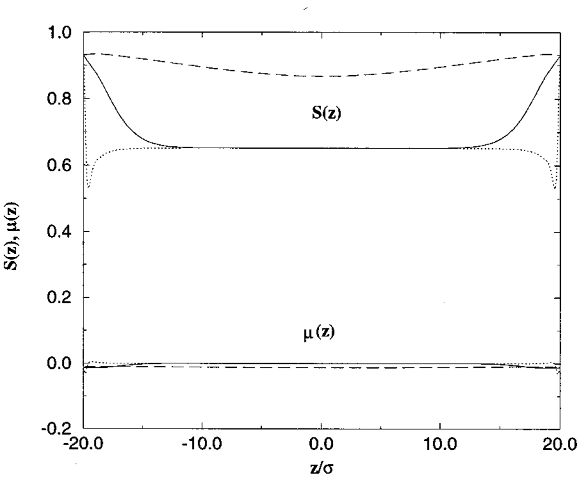

FIG. 4. Uniaxial S and biaxial μ order parameters vs z, but now for the systems in Fig. 3 (same symbols). The longest-ranged wall potential enhances order thoughout the whole film.

Margo and Sullivan's theory, we approximate this contribution [the last term in Eq. (10)] as

$$-C_V\rho\nu\left(\pm\frac{d}{2}\right)\int_{-d/2}^{d/2}dz[e^{-(z+d/2)/\lambda}+e^{-(d/2-z)/\lambda}]$$
$$=-2C_V\rho\nu\left(\pm\frac{d}{2}\right)\lambda(1-e^{-d/\lambda})$$
$$=-2C_V\rho\nu\left(\pm\frac{d}{2}\right)\overline{\lambda}$$
$$=-C_V\rho S_W\overline{\lambda}\sin 2\psi_W, \qquad (24)$$

where $\psi_W=\psi(\pm d/2)$ and $S_W=S(\pm d/2)$ is the surface nematic order parameter measured relative to the director [42]. (Here we have neglected biaxiality, as it is generally small.) The (tilt-angle-dependent part of the) surface term in the free energy is then, for our choice of intermolecular interactions, Eqs. (5) and (6) (we consider only one solid surface for simplicity),

$$f_W=\mathcal{W}\sin 2\psi_W+w_2P_2(\cos\psi_W), \qquad (25)$$

with [43]

$$\mathcal{W}=-\tfrac{1}{2}C_V\rho S_W\overline{\lambda}, \qquad (26)$$

$$w_2=-\frac{\pi}{8}C\rho^2S_W\sigma^4. \qquad (27)$$

The equilibrium tilt angle is then found by minimizing Eq. (25), whence

$$\psi_W^{eq}=\frac{1}{2}\tan^{-1}\frac{16C_V\lambda^*}{3\pi C\rho^*}, \qquad (28)$$

where $\lambda^*=\overline{\lambda}/\sigma$. Note that ψ_W^{eq} does not depend on S_W, which would have to be found self-consistently. Numerical values of ψ_W^{eq} for the same ranges and strengths of the surface potential as in Figs. 1 and 2, are given in Table I. We see that Tjipto-Margo and Sullivan's theory predicts the "bulk" tilt angle fairly accurately, but completely misses any strong subsurface deformations. This is a consequence of the fact that by treating the surface contribution to the free energy as in Eq. (24), one is basically averaging over any surface inhomogeneities. Changing the range of the wall potential is then equivalent to renormalizing its strength.

TABLE I. "Bulk" tilt angle from our microscopic calculation [$\psi(0)$] and "surface" tilt angle from Tjipto-Margo and Sullivan's theory [42] (ψ_W^{eq}), for all cases shown in Figs. 1 and 2.

C_V/k_B (K)	δ_{WN}/σ	$\psi(0)/\pi$	ψ_W^{eq}/π
600	0.46	0.031	0.030
600	4.6	0.207	0.172
600	46	0.250	0.241
6000	0.46	0.118	0.172
6000	4.6	0.244	0.242
6000	46	0.250	0.249

I conclude with some reflections on our results and the "K_{13} problem." In microscopic theory there is no natural lower bound on the length scale over which distortions can occur, i.e., over which the order parameter profiles can be inhomogeneous. One can always *formally* define a nematic director [via Eq. (21) or equivalent], but it is by no means clear whether this has any physical significance (i.e., whether one is still dealing with a nematic in the usual sense). Recall that, in elastic theory, the director is defined as the average molecular orientation inside a mesoscopic volume element whose actual size is always left unspecified, but which is assumed to contain "enough" molecules. Finally, by its very essence, K_{13} is a bulklike quantity (but see [44] for a dissenting view, subsequently elaborated in [22]): indeed, it arises as a coefficient in the expansion of the *bulk* free energy density of deformation in the Frank-Oseen theory. It is only by virtue of Gauss' theorem that the corresponding term in the free energy acquires a "surfacelike" form (i.e., it is transformed into a surface integral) [45]. As already noted by Barbero, Evangelista, and Ponti [25], a nonzero K_{13} is merely an indication that the intermolecular potential contains terms which favor a specific alignment at a surface. My major conclusion is that one should be extremely cautious about using the results of microscopic theories in which near-surface deformations exist, in order to draw conclusions about the effect or otherwise of the K_{13} surfacelike term (indeed, Yokoyama [22] has recently claimed that K_{13} is an artifact of the phenomenological free energy expansion, which vanishes if the same is properly derived from density-functional theory).

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