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Contribution of the smectic-nematic interface to the surface energy

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The contribution of the smectic-nematic interface to the surface energy of a nematic liquid crystal sample is analyzed. By means of a simple model it is shown that the surface energy depends on the thickness of the region over which the transition smectic-nematic takes place. For perfectly flat substrates this thickness is of the order of the correlation length entering in the transition. An estimate of this contribution shows that it is greater than the one arising from the nematic-substrate interaction. Moreover, it is also shown that the surface energy determined in this way presents a nonmonotonic behavior with the temperature. [S1063-651X(97)50802-6]

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The nematic liquid crystalline phase consists of long molecules that present a shape anisotropy. In the nematic mesophase, these molecules tend to align parallel one to the other, thus presenting an orientational order. The average molecular orientation is described by the unit vector $\hat{n}$, called the director [1]. When this system is limited by a flat surface, the translational invariance of the phase is broken. The presence of a surface is responsible for an excess of free energy, usually called surface energy, which has an anisotropic part resulting from the orientational order characteristic of the nematic phase [2]. This quantity has been measured by different techniques [2–5] and its origin is usually connected to the nematic-substrate interaction and to the incomplete intermolecular interaction.

However, the presence of a substrate can also induce a positional order in the molecules in the vicinity of the surface. In fact, near to the surface the center of mass of the molecules tend to form layers parallel to the surface as indicated by several experiments [3]. Since these molecules are oriented perpendicular or tilted with respect to the layers, they form smectic layers near the boundaries. As pointed out by Cognard, the energy confined in these layers is higher than can be added to the LC film by other actions, such as mechanical, thermal, or electrical ones [2]. Therefore, it seems very important to analyze the contribution to the surface energy coming from the smectic-nematic interface.

The aim of this paper is then to show that the main contribution to the surface energy of the system can be connected to the interaction between the smectic and the nematic layers. The nematic-smectic interface is supposed to have a thickness ε along which the system passes from one phase to the other. On the other hand, the system can be treated as a simple junction [6], where we explicitly evaluate the surface energy in the transition zone by introducing the smectic coherence length in the nematic phase. In this manner also the temperature dependence of the interfacial energy can be analyzed, as is done for the nematic liquid crystal wall-interface [7].

Let us consider a nematic slab of thickness d. The Cartesian reference frame has the x,y plane coinciding with the surfaces of the slab. The problem is supposed to be one-dimensional with all the quantities depending only on the z coordinate. The director is everywhere parallel to the x,z plane and $\phi(z)=\arccos(\hat{n}\cdot\hat{z})$ is the tilt angle formed by $\hat{n}$ and the z axis. The tilt angle assumes the value $\phi_1(z)$ in the smectic layer, $\phi_2(z)$ in the nematic phase and $\phi_3(z)$ in the smectic-nematic transition region. By considering that the transition occurs in a layer of thickness ε the total elastic energy per unit surface can be written as

$$F=\int_0^b \frac{1}{2}K_1\phi_1'^2dz+\int_b^{b+\varepsilon}\frac{1}{2}K(z)\phi_3'^2dz+\int_{b+\varepsilon}^d\frac{1}{2}K_2\phi_2'^2dz, \qquad (1)$$

where b is the thickness of the smectic region, K_1 and K_2 are the elastic constants of the smectic and nematic phases respectively, and $\phi'=d\phi/dz$. Equation (1) holds in the hypothesis that the smectic layer is present only at the interface close to the surface at $z=0$. A smectic layer can also be formed at $z=d$ interface. However, in order to estimate the contribution of a smectic-nematic interface to the surface energy, it is sufficient to consider only the $z=0$ interface. The second addendum in Eq. (1) represents the contribution to the total elastic energy coming from the smectic-nematic interface. In this region $K(z)$ can be written, in a first approximation, as

$$K(z)=K_1+\frac{K_2-K_1}{\varepsilon}(z-b). \qquad (2)$$

In the strong anchoring hypothesis the boundary conditions at the surface are $\phi(0)=0$ and $\phi(d)=\Phi$. Note that the strong homeotropic anchoring at $z=0$ is equivalent to impose the existence of a perfect smectic layer at this border. To obtain the solutions of the Euler-Lagrange equations resulting from the minimization of the functional (1), we have to consider the continuity of $\phi(z)$ and of the mechanical torque [6] at $z=b$ and $z=b+\epsilon$. The solutions for each region are

$$\phi_1(z)=\frac{C}{K_1}z, \quad 0\leqslant z\leqslant b,$$

$$\phi_3(z)=\frac{C\varepsilon}{K_2-K_1}\ln K(z)+C\left[\frac{b}{K_1}-\frac{\varepsilon}{K_2-K_1}\ln K_1\right],$$
$$b\leqslant z\leqslant b+\varepsilon,$$

$$\phi_2(z)=\Phi+\frac{C}{K_2}(z-d),\quad b+\varepsilon\leqslant z\leqslant d, \tag{3}$$

where

$$C=\left[\frac{\varepsilon}{K_2-K_1}\ln\left(\frac{K_2}{K_1}\right)+\frac{d-b-\varepsilon}{K_2}+\frac{b}{K_1}\right]^{-1}\Phi. \tag{4}$$

From Eqs. (3) and (4) one obtains for an arbitrary point $z=\tilde{b}$

$$\phi_2(\tilde{b})=\Phi+\frac{C}{K_2}(\tilde{b}-d). \tag{5}$$

On the other hand, as already indicated, it is possible to treat the problem as a smectic-nematic junction where the total elastic energy per unit surface takes the form

$$\tilde{F}=\int_0^{\tilde{b}}\frac{1}{2}K_1\tilde{\phi}_1'^2dz+\int_{\tilde{b}}^{d}\frac{1}{2}K_2\tilde{\phi}_2'^2dz+\frac{1}{2}\beta[\tilde{\phi}_1(\tilde{b})-\tilde{\phi}_2(\tilde{b})]^2. \tag{6}$$

In Eq. (6) the last term represents the contribution connected to the smectic-nematic junction to the total elastic energy, and β is the surface energy. Again, by minimizing Eq. (6) subjected to the boundary conditions $\tilde{\phi}(0)=0$ and $\tilde{\phi}(d)=\Phi$ one obtains

$$\tilde{\phi}_1(z)=\frac{\tilde{C}}{K_1}z,\quad 0\leqslant z\leqslant\tilde{b},$$

$$\tilde{\phi}_2(z)=\Phi+\frac{\tilde{C}}{K_2}(z-d),\quad \tilde{b}\leqslant z\leqslant d, \tag{7}$$

where

$$\tilde{C}=\left[\frac{1}{\beta}+\frac{d-\tilde{b}}{K_2}+\frac{\tilde{b}}{K_1}\right]^{-1}\Phi. \tag{8}$$

From Eq. (7) we obtain

$$\tilde{\phi}_2(\tilde{b})=\Phi+\frac{\tilde{C}}{K_2}(\tilde{b}-d). \tag{9}$$

The main measurements performed on a real nematic sample concern the bulk properties, such as , for instance, the optical path difference. Since $d\gg b$ and $d\gg\varepsilon$, the physical situations described by F and $\tilde{F}$ must be the same in the bulk. Consequently, we will assume that $\phi_2(z)=\tilde{\phi}_2(z)$ and that the border of the nematic phase is localized in $z=b+\varepsilon$. From Eqs. (4), (5), (8), and (9), with $\tilde{b}=b+\varepsilon$, we obtain for the surface energy

$$\beta=\left[\frac{1}{K_2-K_1}\ln\left(\frac{K_2}{K_1}\right)-\frac{1}{K_1}\right]^{-1}\frac{1}{\varepsilon}. \tag{10}$$

Moreover, if we consider $K_1=\alpha K_2$ then

$$\beta=\lambda\frac{K_2}{\varepsilon}, \tag{11}$$

where

$$\lambda=\frac{\alpha(\alpha-1)}{\alpha\ln\alpha-\alpha+1}. \tag{12}$$

It is important to stress that $\phi_2(z)=\tilde{\phi}_2(z)$ implies in the equality of the total energies F and $\tilde{F}$.

In order to estimate β we remember that ε is essentially of the order of the correlation length ξ, characterizing the region where the smectic-nematic transition occurs at a temperature T^*. Thus, ξ refers to the coherence length of the smectic-nematic transition. Moreover, ξ is expected to be of the order of several molecular lengths. It is also expected that ξ increases near the transition temperature. From these considerations a reasonable estimate is $\varepsilon\approx 1000$ Å. For a typical nematic such as the PAA, $K_2\approx 7\times 10^{-7}$ dyn [1]. Moreover, it is expected that the elastic constant of the smectic phase K_1 is greater than the elastic constant of the nematic phase K_2. If we assume that $\alpha\approx 3$, we obtain for the surface energy $\beta\approx 0.3$ erg/cm^2. The surface energy measured on real samples is of the order of 10^{-1} and 10^{-2} erg/cm^2 [4]. Therefore, our results indicate that the surface energy is mainly connected to the smectic-nematic interface, in the hypothesis that ε is not too large.

If we consider that $\tilde{b}<b+\varepsilon$, then, in general, β is a negative quantity for $K_1>K_2$. This situation is not physically meaningful. It happens only because in this case we are extending the nematic phase to a region where the phase is not purely nematic.

On the other hand, several recent measurements that were performed on lyotropic nematic samples [8] indicate an agreement with the present estimate. In these experiments with discotic nematic liquid crystals, the surfaces of the substrates are with and without treatment. The measured values of the optical path difference are the same for both situations. This fact indicates that the lamellar phase that is formed between the glass plates and the nematic liquid crystals is responsible for a strong attenuation of the effect of the glass on the nematic phase.

Another point that deserves mention is the dependence of the surface energy stored on the interface with the temperature. In this sense we have used a mean field approximation for the determination of the correlation length, namely, $\xi\approx(T-T^*)^{-1/2}$, where T^* is a temperature for the structural phase transition in the smectic-nematic interface. From this observation and by considering that $\varepsilon\approx\xi$ and $\beta\approx K_2/\varepsilon$, we can conclude that near T^*, $\beta\approx K_2(T-T^*)^{1/2}$, where K_2 is assumed to be temperature independent. This hypothesis is not valid near the nematic-isotropic temperature transition (T_{NI}), because in this case $K_2\propto T_{\mathrm{NI}}-T$. Since we are close to the smectic-nematic transition, the temperature dependence of K_2 can be neglected. This result indicates that as the transition temperature is approximated, the surface energy of the interface becomes negligible. It also indicates that β has a nonmonotonic behavior with the temperature, which agrees with the results obtained by Di Lisi *et al.* [9] for a structural transition at a nematic-substrate interface.

Let us briefly discuss the main consequences of our model. In dealing with the problem of the surface energy in nematics, it is convenient to divide the contributions to the anisotropic part of the surface energy into two parts: the extrinsic part, which comes directly from the nematic-substrate interaction, and the intrinsic one. The intrinsic contribution comes, obviously, from the NLC itself. In a pseudomolecular basis, it is usually connected to the incomplete interaction among the liquid crystal molecules near the substrate, where the symmetry is reduced. This introduces a spatial dependence on the elastic constants in the vicinity of the surface. As suggested by Yokoyama *et al.* [10] and reconsidered by many authors [5,11–13], the spatial variation of the elastic constant can be considered as equivalent to a surface energy. In a simple elastic model, based on the Maier-Saupe approximation, the elastic contributions to the surface energy are connected to the the spatial variation of the elastic constant and to the spatial variation of the scalar order parameter [14]. This latter contribution is, in general, the dominant one, because the extrapolation length connected to it is found to be of the order of the coherence length in the NLC phase, and then it is in the experimentally detectable range.

Recently, an analysis of the anchoring competition between short-range and long-range nematic-substrate interactions has been considered [15]. In this approach, the alignment of a nematic sample results from the competition between an external, position dependent field, localized in a microscopic layer or a local surface field, and the nematic-substrate interaction. It is possible to show that the phenomenon presents a threshold behavior like the Freédericksz transition. The analysis shows that according to the anchoring strength the final orientation of the whole sample can be planar, distorted or, for large values of the anchoring strenght, homeotropic.

In our approach the competition effect is not considered because the boundary conditions impose a perfect smectic layer near the substrate and a nematic order in the bulk. Moreover, the long-range parts of the surface energy are not considered [16–18]. The emphasis is then on the effects along the interface where the orientation changes. Our model shows that, if this effect is present in a real nematic sample, then the contribution of this interface to the surface energy has to be taken into account. This is reinforced by the fact that the order of magnitude of this energy is comparable with the one experimentally measured [4]. In fact, this order of magnitude of the contribution to the surface energy depends on the thickness of the coherence length in a crucial manner. As stressed before, for reasonable estimates of this quantity it seems that this contribution is the dominant one. On the other hand it is well known that the existence of geometrical nonuniformities can affect the surface energy that is experimentally detected [19,20]. In fact, this kind of nonuniformity can be responsible for a surface energy that is of geometrical origin and of elastic nature. In some cases of surface treatment or surface shape, the experimental situation can lead one to detect an apparent extrapolation length (i.e., an apparent anchoring energy) when the expected situation is that of strong anchoring (infinite anchoring strength) [21]. Actually, a surface energy that is localized in the vicinity of the interface and whose origin is connected with the geometrical properties of the surfaces is a true surface energy. It is difficult to distinguish between this contribution and the one which arises from the interaction of the NLC molecules and the substrate, i.e., the extrinsic contribution.

Then, the above conclusions regarding our model for the contribution of the smectic-nematic interface can be valid at least in the case in which perfectly flat substrates are supposed to form the slab.

Consequently, among all the contributions to the surface energy, the contribution arising from the smectic-nematic interface cannot be neglected. It has an order of magnitude that can be comparable with the one arising from the spatial variation of the scalar order parameter and with those connected to the geometrical effects.

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