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Thermal renormalization of the anchoring energy of nematic liquid crystals

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The temperature dependence of the anchoring energy of a nematic liquid crystal on thermal fluctuations is studied. We consider the weak anchoring case, where the interaction of a nematic molecule on the surface with the substrate is small with respect to the mean field energy due to the other nematic molecules. The analysis is performed by means of a perturbation method in which the expansion parameter is the surface interaction. The presented model is valid for any value of the scalar order parameter. We show that the renormalization of the anchoring coefficients due to thermal fluctuations is proportional to the generalized scalar order parameters. We show also that, at the lowest order in the scalar order parameter, Landau-like theories agree with our mean field approach. An expression for the thermal renormalization of the anchoring coefficients valid in the low temperature region, where the fluctuations are small, is derived. The agreement between our theoretical predictions and the experimental data obtained by other groups is fairly good over a large temperature range.

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I. INTRODUCTION

Nematic liquid crystals have the long range orientational order of anisotropic molecules [1]. In uniaxial nematic liquid crystals with macroscopic cylindrical symmetry, the director **n**, which is a unit vector along the average direction of orientation of the rodlike molecules, is apolar in nature. They are characterized by a tensor order parameter $\overleftrightarrow{Q}$, of elements $Q_{ij}=(3/2)S[n_in_j-(1/3)\delta_{ij}]$. S is the nematic scalar order parameter given by $S=\langle n_iq_{ij}n_j\rangle$, where $\langle\rangle$ means the statistical average, and $q_{ij}=(3/2)[u_iu_j-(1/3)\delta_{ij}]$ are the elements of a molecular tensor defined by means of the molecular orientation **u** (parallel to the long molecular axis). The tensor $\overleftrightarrow{q}$ is defined in such a way as to take into account the quadrupolar symmetry of the nematic molecules. For these media, the bulk macroscopic properties and their temperature dependencies are well understood and interpreted by means of existing theories [2–7]. In contrast, the contrary, the influence of a solid substrate on the macroscopic properties of a nematic liquid crystal is far from being understood in all aspects. There exists experimental evidence that a solid substrate is able to orient **n** in a well defined direction, called the ''easy axis'' and indicated by $\mathbf{n}_0$. This results from a direct interaction between the nematic medium and the substrate. It is such as to minimize the anisotropic part of the surface energy of the two media in contact [8]. In some situations a temperature dependence of $\mathbf{n}_0$ has been observed [9–19]. This is a consequence of the temperature dependence of the anisotropic part of the surface energy. A theoretical description of this phenomenon has been given with Landau-like models based on symmetry, similar to the ones used for the bulk [20–24], or with microscopic models based on the Onsager's theory [25–29]. However, the applicability of Landau-like approaches is questionable, as will be discussed in Sec. II, and the microscopic models contain a large number of unknown parameters so that their physical predictions are not immediate. For these reasons, in our paper we propose an analysis of the anisotropic part of the surface energy based on the mean field. It is valid for all values of the nematic scalar order parameter, and allows a simple understanding of the effect of the temperature on the anchoring coefficients.

In our analysis, we expand the surface energy in a series of spherical harmonic functions. The coefficients of the expansion are the experimentally detectable anchoring coefficients. According to our model, all the anchoring coefficients of the same order depend on the temperature in the same manner. From this result it follows that in nematic liquid crystals the alignment transitions driven by the surface (the so called temperature surface transitions) are due to a surface anchoring energy that contains contributions of different orders.

Our paper is organized as follows. In Sec. II the usual Landau-like description of the surface energy characterizing the nematic-substrate interface is recalled, and the temperature dependence of the anisotropic part of the surface energy briefly discussed. According to this approach, based on the symmetry of the nematic phase and of the substrate, the anisotropic part of the surface energy is expanded in a power series of the surface scalar order parameter, which is considered a small parameter. However, since the nematic-isotropic phase transition is of first order, with a jump of the scalar order parameter at the transition temperature of ~ 0.3, this parameter is not really very small, and to use it as the expansion parameter could be questionable. In Sec. III a model based on a perturbation method is developed, in the framework of mean field theory, valid for all values of the scalar order parameter. According to this model, the surface energy is expanded in a power series of the surface interaction, which is very small with respect to the nematic mean field energy in the weak anchoring situation. In Sec. III this model is applied to the simple case of a nematic liquid crystal limited by a flat isotropic surface and by a surface having monoclinic symmetry. In Sec. IV a comparison with the Akulov-Zener law is discussed, and approximate expressions for the thermal renormalization valid in the low temperature range are deduced. In Sec. V we reobtain the results of Sec. III and Sec. IV using the procedure of averaging with a continuous Hamiltonian. Section VI is devoted to a comparison of the theoretical predictions of our model relevant to the temperature dependence of the anchoring energy strength with the experimental data obtained by other groups. The main results of our paper are discussed in Sec. VII.

II. SURFACE ANCHORING ENERGY: CONSIDERATIONS BASED ON THE SYMMETRY

We suppose that the nematic liquid crystal occupies the semi-infinite space $z \geqslant 0$, bounded by a flat and homogeneous substrate at $z=0$. In our analysis we consider only uniform liquid crystals. In this framework the presence of the surface does not introduce any biaxiality, and from the crystallographic point of view the nematic is characterized by the uniaxial tensor order parameter $\overleftrightarrow{Q}$.

Let us consider the anisotropic part of the surface energy W characterizing the nematic-substrate interface. When an undistorted nematic liquid crystal is in contact with a solid substrate or limited by another medium, the nematic director is oriented along the easy axis $\mathbf{n}_0$. For deviations of the actual surface director $\mathbf{n}_S$ from the easy direction $\mathbf{n}_0$, $W = W(\mathbf{n}_0,\mathbf{n}_S)$. $W(\mathbf{n}_0,\mathbf{n}_0)$ corresponds to the minimum value of W, whereas $W(\mathbf{n}_0,\mathbf{n}_S) \geqslant W(\mathbf{n}_0,\mathbf{n}_0)$ is the surplus of surface energy due to the surface distortion $\delta\mathbf{n}=\mathbf{n}_S-\mathbf{n}_0$. For small deviations of $\mathbf{n}_S$ from $\mathbf{n}_0$, $W(\mathbf{n}_S,\mathbf{n}_0)=W_2P_2(\mathbf{n}_S\cdot\mathbf{n}_0)$, where $W_2<0$ is the macroscopic anchoring strength and $P_2(\mathbf{n}_S\cdot\mathbf{n}_0)=(3/2)[(\mathbf{n}_S\cdot\mathbf{n}_0)^2-(1/3)]$ the second order Legendre polynomial [30]. This simple expression does not hold true when the deviation of $\mathbf{n}_S$ from $\mathbf{n}_0$ is large. In this case $W(\mathbf{n}_S,\mathbf{n}_0)$ is usually approximated by an expansion in terms of Legendre polynomials [31] of the kind $W(\mathbf{n}_S,\mathbf{n}_0) = \Sigma_l W_{2l}P_{2l}(\mathbf{n}_S\cdot\mathbf{n}_0)$.

As stated above, the easy direction $\mathbf{n}_0$ is defined as the surface orientation of the nematic director for which $W(\mathbf{n}_S,\mathbf{n}_0)$ has a minimum. In the case of homogeneous substrates, $\mathbf{n}_0$ depends on the physical properties of the substrate and of the nematic liquid crystal. Several interactions contribute to the surface energy characterizing the nematic-substrate interface. To find $\mathbf{n}_0$ in practice it is necessary to write down the surface energy W in terms of the elements of symmetry of the surface and of the nematic liquid crystal, and to look for its minimum with respect to the nematic director. Experimental data show that $\mathbf{n}_0$ can be temperature dependent. This phenomenon has been termed the ‘‘temperature surface transition’’ and discussed by several authors [14–18,25,32–34].

In the past the temperature dependence of $\mathbf{n}_0$ has been analyzed by following a procedure similar to the one used for the elastic description in the bulk [7], i.e., by decomposing the surface energy in terms of the elements of symmetry of the surface and of the nematic liquid crystal, and using as expansion parameter the scalar order parameter S. In the case of a flat isotropic surface, characterized by the geometrical normal $\mathbf{k}$, the surface energy is written as [20–22]

$$W=A_0+A_1k_iQ_{ij}k_j+A_2Q_{ij}Q_{ji}+A_3(k_iQ_{ij}k_j)^2 +A_4k_iQ_{il}Q_{lj}k_j+O(S^3), \tag{1}$$

at second order in the surface order parameter. Strictly speaking expansion (1) is valid only for small S. However, since the nematic-isotropic phase transition is of first order, with a finite jump of S at the critical temperature ($\Delta S \sim 0.3$ [4]), it is not clear when Eq. (1) works well. In Eq. (1) the quantities A_i are temperature independent phenomenological parameters. As discussed in Refs. [20,22] the coefficients A_2, A_3, and A_4 of the quadratic terms in S in Eq. (1) arise from modification of the mean field potential between two nematic molecules near the substrate. In contrast, the coefficient A_1 has contributions both from that effect and from the direct wall-molecule interaction [35]. Using for Q_{ij} the expression $Q_{ij}=(3/2)S[n_in_j-(1/3)\delta_{ij}]$, where $\mathbf{n}=\mathbf{n}_S$, Eq. (1) can be rewritten in terms of the angle $\theta=\cos^{-1}(\mathbf{n}_S\cdot\mathbf{k})$ formed by $\mathbf{n}_S$ with $\mathbf{k}$ as

$$W=W_0+W_2P_2(\cos\theta)+W_4P_4(\cos\theta), \tag{2}$$

where the coefficients $W_i=W_i(S)$, $i=0,2,4$, are given by

$$W_0=A_0+\frac{15A_2+2A_3+5A_4}{10}S^2,$$
$$W_2=A_1S+\frac{8A_3+7A_4}{28}S^2, \quad W_4=\frac{18}{35}A_3S^2. \tag{3}$$

By assuming for the surface value of S the temperature dependence obtained in the bulk, by means of the phenomenological expansion given by Eq. (2) it is possible to study the surface transitions induced by the temperature [20,21]. This model can also be refined by taking into account that the surface scalar order parameter is different from the bulk one by means of a Landau-Ginzburg approach [22,36–38].

Sen and Sullivan [22] discuss how one can derive Eq. (1) from a molecular mean field theory. They assume that the free energy F of the system under consideration is a functional of the single-particle probability density, and that spatial variations occur only in the z direction [39]. F is written as the sum of three bulk contributions. The first describes the interaction between the nematic and the substrate, characterized by a potential $\mathcal{U}[\mathbf{u}(z),z]$. The second describes the nematic-nematic interaction, characterized by a potential $\mathcal{V}[\mathbf{u}(z_1),\mathbf{u}(z_2);|z_1-z_2|]$, where the subscripts 1 and 2 are relevant to the two nematic interacting molecules. The third term is a functional of the orientational distribution. To reduce the nonlocal two-body term to a local one, they make a formal gradient expansion of the single-particle probability density. Then, the effective surface energy generating Eq. (1) is defined by comparing the gradient expansion of the free energy with the full starting expression for F, according to a standard recipe [40]. In this way the surface energy receives contributions only from the direct interactions of the nematic molecules with the substrate, via $\mathcal{U}(\mathbf{u},z)$ evaluated at the surface, and from the incomplete nematic-nematic interaction. Following this scheme it is possible to obtain the correct number of terms of the surface energy. However, as underlined above, the main limit of Eq. (1) is that it is an expansion in power series of the scalar order parameter S, and this quantity is never very small.

III. SURFACE ANCHORING ENERGY: MEAN FIELD APPROACH

In this section we reanalyze the temperature dependence of the anchoring energy using an approach based on mean field theory. In our analysis we neglect all the inhomogeneities. We assume, furthermore that the surface potential is short range.

Let us consider a surface molecule of the nematic liquid crystal. It is submitted to the interaction with the other nematic molecules and to the interaction with the substrate. The relevant interaction energies will be indicated by V_N and V_S, respectively. The separation of the total energy of a surface molecule into a bulk part and a surface part is not well defined, because the nematic symmetry is broken near the surface, as discussed in Appendix A. In our analysis we assume that V_N, due to the nematic-nematic interaction, can be evaluated in a mean field theory. It is supposed position independent. All variations of V_N due to the broken symmetry connected with the presence of the bounding surface are considered as surface contributions, and enter in the effective surface energy V_S.

The total energy V of a surface molecule is $V=V_N+V_S$. If $V_N\sim V_S$ the extrapolation length $b=K/W\sim aV_N/V_S$, where K is an average elastic constant and a a molecular dimension, is of the order of a molecular dimension [1]. In this case, in the continuum limit, it is possible to put $b=0$ and assume that the surface nematic orientation is fixed by the surface interaction. This situation is known as the strong anchoring case. The interesting case is the one in which $V_N\gg V_S$, where $b\gg a$. It corresponds to the weak anchoring situation, to which we will limit our investigation. In our analysis the small parameter used to expand the surface energy in a power series is $V_S/V_N\ll 1$, in the weak anchoring situation. On the contrary the surface scalar order parameter S is not supposed a small quantity.

V_N describes the tendency of the nematic molecules, characterized by the molecular orientation **u**, to be oriented along the nematic director **n**. In the following it will be approximated by means of the Maier-Saupe mean field [3], V_N^M according to which $V_N^M\propto n_i q_{ij} n_j=P_2(\mathbf{n}\cdot\mathbf{u})$. In this framework $V_N^M=-vP_2(\mathbf{n}\cdot\mathbf{u})S$, where v is a molecular constant and $S=\langle P_2(\mathbf{n}\cdot\mathbf{u})\rangle$ the nematic scalar parameter [4]. We will consider also a generalization of the Maier-Saupe theory proposed by Humphries *et al.* [41]. According to this generalized mean field theory the nematic mean field, which now we indicate by V_N^H, is given by $V_N^H=-\Sigma_l v_{2l}P_{2l}(\mathbf{n}\cdot\mathbf{u})S_{2l}$, where $S_{2l}=\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle$ are the nematic order parameters.

Let us now consider V_S. It is clear that this interaction has to describe the tendency of the surface to orient the surface nematic molecules along a given direction, which we have termed above the easy direction and indicated by $\mathbf{n}_0$. This direction depends on the symmetry of the surface and on the molecular properties of the mesophase. Taking into account that we limit our analysis to nonpolar media, V_S has to be an even function of **u**. It follows that V_S is actually a function of the tensor $\overleftrightarrow{q}$ and can be written, in general, as $V_S(\mathbf{u})=V_S(\overleftrightarrow{q})=\Sigma_k w_k(0)L_k(\overleftrightarrow{q})$, where $L_k(\overleftrightarrow{q})$ indicate the scalar quantities we can build with the molecular tensor of elements $q_{ij}=(3/2)[u_iu_j-(1/3)\delta_{ij}]$ and the elements of symmetry characterizing the surface. Each term of the expansion of $V_S(\overleftrightarrow{q})$ represents a given interaction, like the induced dipole–induced dipole or quadrupole-quadrupole interaction and so on [42]; the ‘‘intrinsic’’ anchoring coefficients $w_k(0)$ are physical parameters connected to the type of interaction described by $L_k(\overleftrightarrow{q})$. In our analysis we assume that the physical properties of the substrate can be considered constants in the temperature range of the nematic phase. In this framework, since $w_k(0)$ refer to specific fundamental interactions, they are temperature independent. So thermal effects arise only from the temperature dependence of the degree of alignment of the nematic molecules. For our previous hypothesis of the temperature independence of the physical properties of the substrate, our theory correctly describes nematic liquid crystals in contact with solid substrates. However, deviations from our predictions are expected for nematic samples oriented by means of surfactants, because their thermal behavior is similar to that of the liquid crystal materials.

For our future considerations it is useful to describe the molecular direction and the nematic director in terms of the polar angles with respect to a Cartesian reference frame having the z axis parallel to the geometrical normal to the flat surface and the x axis along the possible surface anisotropy. We indicate with Θ,Φ and θ,ϕ the polar angles defining **u** and **n**, respectively. In this framework $V_S(\overleftrightarrow{q})$ can be rewritten as $V_S(\Theta,\Phi)=\Sigma_k w_k(0)L_k(\Theta,\Phi)$. By decomposing the functions $L_k(\Theta,\Phi)$ in a series of spherical harmonic functions $Y_k^m(\Theta,\Phi)$ we obtain $L_k(\Theta,\Phi)=\Sigma_m a_k^m Y_k^m(\Theta,\Phi)$. Since $L_k=L_k(\overleftrightarrow{q})$ and hence $L_k(\Theta,\Phi)=L_k(\pi-\Theta,\pi+\Phi)$ for all k, we deduce that $k=2l$, i.e., L_k for odd k are absent in the expansion of $V_S(\Theta,\Phi)$. It follows that for nonpolar nematic liquid crystals $L_{2l}(\Theta,\Phi)=\Sigma_m a_{2l}^m Y_{2l}^m(\Theta,\Phi)$, and the microscopic surface energy can be written as

$$V_S(\Theta,\Phi)=\sum_l w_{2l}(0)L_{2l}(\Theta,\Phi), \tag{4}$$

or, as follows from the discussion reported above, in the form

$$V_S(\Theta,\Phi)=\sum_l w_{2l}(0)\sum_m a_{2l}^m Y_{2l}^m(\Theta,\Phi). \tag{5}$$

The macroscopic anchoring energy $W(\mathbf{n})=W(\theta,\phi)$ is obtained by averaging V_S over the molecular orientations **u**, or over Θ and Φ. Since in the problem under consideration $V_S\ll V_N$, V_S can be treated as a perturbation. According to the thermodynamic perturbation theory [43] we have $W(\theta,\phi)=\langle V_S(\Theta,\Phi)\rangle$, and hence

$$W(\theta,\phi)=\sum_l w_{2l}(0)\sum_m a_{2l}^m\langle Y_{2l}^m(\Theta,\Phi)\rangle, \tag{6}$$

where $\langle A\rangle=\mathrm{Tr}(\rho A)/\mathrm{Tr}(\rho)$, and $\rho=\exp(-\beta V_N)$ is the density matrix. In order to derive the macroscopic surface energy $W(\theta,\phi)$ we have first to express $V_S(\Theta,\Phi)$ in terms of a polar coordinate system based on the director **n** as polar axis. The Cartesian reference frame has to be rotated in such a way that $\mathbf{z}'=\mathbf{n}=\langle\mathbf{u}\rangle$. We will indicate by ϑ,φ the polar angles of $\mathbf{u}$ with respect to the rotated coordinate system. In this case [44]

$$Y_l^m(\Theta,\Phi)=\sum_{m'} D^l_{m,m'}(\theta,\phi)Y_l^{m'}(\vartheta,\varphi), \tag{7}$$

where $D^l_{m,m'}(\theta,\phi)$ are the elements of the Wigner matrix. Since there is axial symmetry about the direction of $\mathbf{n}$ in the unperturbed system, only the member $m=0$ of the Y_l^m is different from zero. Consequently $\langle Y_l^{m'}(\vartheta,\varphi)\rangle=\langle Y_l^0(\vartheta)\rangle\delta_{m',0}$ and from Eq. (7) we obtain that $\langle Y_l^m(\Theta,\Phi)\rangle=D^l_{m,0}(\theta,\phi)\langle Y_l^0(\vartheta)\rangle$. By taking into account that [44] $D^l_{m,0}(\theta,\phi)=Y_l^m(\theta,\phi)$, we have finally, as follows from Eqs. (4) and (6),

$$W(\theta,\phi)=\sum_l w_{2l}(0)\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle L_{2l}(\theta,\phi), \tag{8}$$

where we have taken into account that $Y^0_{2l}(\vartheta,\varphi)=P_{2l}(\cos\vartheta)$. Equation (8) is a consequence of the fact that we regard all anisotropic effects as perturbations, so that they do not need to be included in the computation of the average values. By comparing Eq. (8) with Eq. (4) we deduce that the temperature dependence of the parameters describing the anisotropic part of the surface energy is given by

$$w_{2l}(T)=w_{2l}(0)\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle. \tag{9}$$

Let us calculate $\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle$ in the mean field approximation. By assuming $V_N=V_N^M$, Eq. (9) gives

$$\frac{w_{2l}(T)}{w_{2l}(0)}=\frac{\int_0^1 P_{2l}(\mathbf{n}\cdot\mathbf{u})\exp[\beta v P_2(\mathbf{n}\cdot\mathbf{u})S]d(\mathbf{n}\cdot\mathbf{u})}{\int_0^1 \exp[\beta v P_2(\mathbf{n}\cdot\mathbf{u})S]d(\mathbf{n}\cdot\mathbf{u})}. \tag{10}$$

The integrals can easily be calculated and give the temperature dependence we are looking for. By assuming $V_N=V_N^H$, Eq. (9) gives simply

$$\frac{w_{2l}(T)}{w_{2l}(0)}=S_{2l}. \tag{11}$$

This means that in the framework of a generalized mean field theory of the kind represented by V_N^H the temperature dependence of $w_{2l}(T)/w_{2l}(0)$ coincides with the temperature dependence of the $(2l)$th scalar order parameter.

According to the analysis presented above, where the macroscopic anchoring energy is given by the series expansion in spherical harmonic functions shown in Eq. (8), the thermal renormalization of the anchoring coefficients is given by Eq. (10) or by Eq. (11). From these results it follows that anchoring coefficients of the same order in the expansion have the same temperature dependence. Consequently, in the framework of our model, temperature surface transitions are possible only in nematic samples whose anchoring energy contains contributions from different orders in the spherical harmonic function expansion.

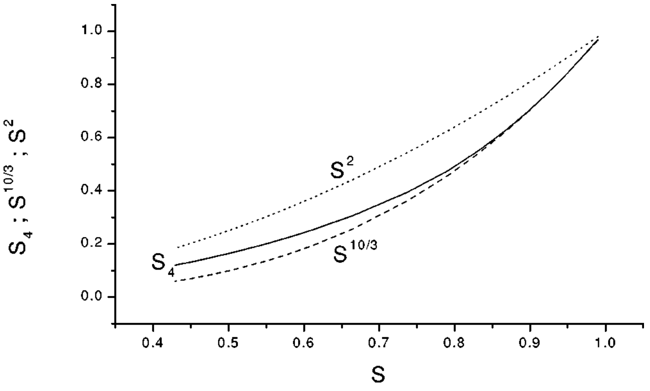

FIG. 1. Dependence of $\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle=S_4$ vs S. The S dependence of S^2, which is the next term in the surface energy expansion predicted by Landau-like analyses, and of $S^{10/3}$, predicted by our mean field approach in the large range of S, are also shown. As is evident from the figure, the Akulov-Zener law works well when the fluctuations of $\mathbf{u}$ with respect to $\mathbf{n}$ are small (large S).

The ratios $\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle/S$ vs S, for $l=2$,3, and 4, in the Maier-Saupe approximation can be easily evaluated in the nematic phase, where $0.4\leqslant S\leqslant 0.7$. A direct calculation shows that $\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle/S\leqslant 0.1$, for $l=3,4$. This explains why usually the anisotropic part of the surface anchoring energy given by Eq. (8) is well approximated by few terms [45].

Let us consider, as an example, a nematic liquid crystal limited by an isotropic substrate, using the simple Maier-Saupe mean field theory. In this case only the polar angle θ enters into the description, and $L_{2l}(\theta)=P_{2l}(\cos\theta)$. From Eq. (10) we obtain $w_2(T)/w_2(0)=S$. This means that at the lowest order in S the temperature dependence of the anchoring energy deduced by means of symmetry considerations, as in Eq. (2), and by means of the mean field agree. In fact, according to the recipe based on symmetry one has $W_2(T)=A_1S$ and according to the mean field $w_2(T)=w_2(0)S$. However, for $l=2$ there is a discrepancy between the two approaches. In fact, according to the mean field we have $w_2(T)/w_2(0)=S$, and $w_4(T)/w_4(0)=\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle\neq S^2$, whereas the approach based on symmetry predicts the temperature dependencies given by Eq. (3). More precisely, it predicts a renormalization of the coefficient of $P_2(\cos\theta)$, by means of a S^2 contribution, and a temperature dependence of the coefficient of $P_4(\cos\theta)$ like S^2. Of course, in the limit of small S the two predictions agree. In fact, if $S\ll 1$ the renormalization of $P_2(\cos\theta)$ in S^2 can be neglected with respect to the linear term in S. Furthermore, in this approximation, $\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle\propto S^2$. However, in the case of large S the discrepancy between the two approaches can be large. In Fig. 1 we show $\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle$ and S^2 vs S. From this figure it follows that in the nematic range $(0.4\leqslant S\leqslant 1)$ the difference between S^2 and $\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle$ is always rather large.

Let us consider now a nematic sample bounded by a surface having monoclinic symmetry, such as the one obtained by means of the SiO oblique evaporation technique [18]. The (y,z) plane is the evaporation plane, the normal to the substrate is parallel to the z axis, and the direction of the grooves coincides with the x direction. In this framework, at second order in the spherical harmonic expansion we have

$$L_2(\Theta,\Phi)=\sum_{m=-2}^{2} a_2^m Y_2^m(\Theta,\Phi). \tag{12}$$

Since [46]

$$Y_2^{\pm 2}(\Theta,\Phi)=\sqrt{15/(32\pi)}\sin^2\Theta\ \exp(\pm 2i\Phi),$$

$$Y_2^{\pm 1}(\Theta,\Phi)=\mp\sqrt{15/(8\pi)}\sin\Theta\ \cos\Theta\ \exp(\pm i\Phi), \tag{13}$$

$$Y_2^{0}(\Theta,\Phi)=\sqrt{5/(16\pi)}(3\cos^2\Theta-1),$$

from Eq. (8) we obtain

$$W(\theta,\phi)=w_2(T)[C_1\cos(2\theta)+C_2\sin^2\theta\cos(2\phi)+C_3\sin(2\theta)\cos\phi], \tag{14}$$

where C_i are numerical factors [47]. This equation shows clearly that, at second order in the spherical harmonic function expansion of $W(\theta,\phi)$, the nematic orientation is expected to be temperature independent. The temperature surface transitions, in which the nematic orientation variations are driven by the surface, can be interpreted, in the framework of our model, only by taking into account also terms in $Y_4^m(\Theta,\Phi)$ in the microscopic surface energy $V_S(\Theta,\Phi)$.

IV. COMPARISON WITH AKULOV-ZENER LAW

At low temperature, when the fluctuations are small, i.e., $-\beta V_N \gg 1$, it is possible to rewrite Eq. (10) in an interesting manner, well known in other fields of solid state physics as the Akulov-Zener law [48,49]. In order to obtain this expression, we have to take into account that in the low temperature region, where $S\sim 1$ and hence the fluctuations of $\mathbf{u}$ with respect to $\mathbf{n}$ are very small, $\mathbf{n}\cdot\mathbf{u}=\cos\vartheta\sim 1-(1/2)\vartheta^2+O(4)$, i.e., $\vartheta \ll 1$. In this framework $P_2(\mathbf{n}\cdot\mathbf{u})\sim 1-(3/2)\vartheta^2+O(4)$, and $P_4(\mathbf{n}\cdot\mathbf{u})\sim 1-5\vartheta^2+O(4)$. Consequently, by taking into account that $w_2(T)/w_2(0)=\langle P_2(\mathbf{n}\cdot\mathbf{u})\rangle$ and $w_4(T)/w_4(0)=\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle$, we obtain [50], by assuming $V_N=V_N^M$,

$$\frac{w_2(T)}{w_2(0)}=\frac{\int_0^\pi\left(1-\frac{3}{2}\vartheta^2\right)\exp\left[\beta v S\left(1-\frac{3}{2}\vartheta^2\right)\right]\vartheta d\vartheta}{\int_0^\pi \exp\left[\beta v S\left(1-\frac{3}{2}\vartheta^2\right)\right]\vartheta d\vartheta}$$
$$\sim 1-\frac{1}{\beta v S}$$
$$\sim \exp\left(-\frac{1}{\beta v S}\right) \tag{15}$$

and

$$\frac{w_4(T)}{w_4(0)}=\frac{\int_0^\pi(1-5\vartheta^2)\exp\left[\beta S\left(1-\frac{3}{2}\vartheta^2\right)\right]\vartheta d\vartheta}{\int_0^\pi \exp\left[\beta v S\left(1-\frac{3}{2}\vartheta^2\right)\right]\vartheta d\vartheta}$$
$$\sim 1-\frac{10}{3\beta v S}$$
$$\sim \exp\left(-\frac{10}{3\beta v S}\right). \tag{16}$$

Since according to the Maier-Saupe theory $S=\langle P_2(\mathbf{n}\cdot\mathbf{u})\rangle$, from Eqs. (15) and (16) we have $w_2(T)/w_2(0)=S$ and $w_4(T)/w_4(0)=S^{10/3}$. In Fig. 1 we show $\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle$ and $S^{10/3}$ vs S in the nematic phase $(0.4\leqslant S\leqslant 1)$. As follows from this figure, for large values of S $\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle\sim S^{10/3}$. In the same figure we also show S^2, which is the term predicted by Landau-like models at second order in S.

The calculations reported above for $l=1$ and $l=2$ can be generalized for all l. The final result is that in the low temperature region the thermal renormalization of the anchoring coefficient is

$$\frac{w_{2l}(T)}{w_{2l}(0)}=\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle=S^{l(2l+1)/3}. \tag{17}$$

Equation (17) has been obtained by assuming $V_N=V_N^M$. However, as is shown in Appendix B, it holds true also in the case where $V_N=V_N^H$.

Expression (17) can be compared with the Akulov-Zener law for ferromagnetic materials well known in solid state physics [51,52],

$$\frac{\mathcal{L}_n(T)}{\mathcal{L}_n(0)}=\left(\frac{M_S(T)}{M_S(0)}\right)^{n(n+1)/2}, \tag{18}$$

where $M_S(T)$ is the magnetization and $\mathcal{L}_n(T)$ is the n-order coefficient of the magnetic crystallographic anisotropy, magnetostriction, etc.

It is not difficult to show that expression (17) follows immediately from the Akulov-Zener law. Indeed, in the low temperature range where $S\sim 1$ and hence $\vartheta\ll 1$, $P_1(\mathbf{n}\cdot\mathbf{u})=\mathbf{n}\cdot\mathbf{u}\sim 1-(1/2)\vartheta^2$, $P_2(\mathbf{n}\cdot\mathbf{u})\sim 1-(3/2)\vartheta^2\sim P_1^3(\mathbf{n}\cdot\mathbf{u})$. Consequently, $S(T)=\langle P_2(\mathbf{n}\cdot\mathbf{u})\rangle\sim\langle P_1(\mathbf{n}\cdot\mathbf{u})\rangle^3=q^3$. Since $M_S(T)/M_S(0)=\langle P_1(\mathbf{n}\cdot\mathbf{u})\rangle=q$, Eq. (17) yields

$$\frac{w_{2l}(T)}{w_{2l}(0)}=q^{l(2l+1)}, \tag{19}$$

which is just the Akulov-Zener formula for $w_{2l}(T)$.

Although the proof of Eqs. (15) and (16) is rigorously valid only for small perturbations and low temperatures, an exact calculation performed for magnetic materials [53] shows that the power law is fairly accurate even for relatively large perturbations, and is roughly followed almost up to the critical temperature.

At arbitrary temperatures we have

$$\frac{w_{2l}(T)}{w_{2l}(0)}=\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle=\mathcal{L}_{2l}(\mathcal{Z}^{-1}(S(T))), \tag{20}$$

where

$$\mathcal{L}_n=\frac{\int_0^1 P_n(\mathbf{n}\cdot\mathbf{u})\exp[P_2(\mathbf{n}\cdot\mathbf{u})/\tau]d(\mathbf{n}\cdot\mathbf{u})}{\int_0^1 \exp[P_2(\mathbf{n}\cdot\mathbf{u})/\tau]d(\mathbf{n}\cdot\mathbf{u})}, \tag{21}$$

$$\mathcal{Z}=\frac{\int_0^1 P_2(\mathbf{n}\cdot\mathbf{u})\exp[P_2(\mathbf{n}\cdot\mathbf{u})/\tau]d(\mathbf{n}\cdot\mathbf{u})}{\int_0^1 \exp[P_2(\mathbf{n}\cdot\mathbf{u})/\tau]d(\mathbf{n}\cdot\mathbf{u})}=S, \tag{22}$$

and

$$\tau=\frac{1}{\beta v S(T)}=\frac{k_B T}{v S(T)} \tag{23}$$

is a reduced temperature. This parametric representation allows one to deduce $\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle$ as a function of S, without knowing the interaction parameter v.

V. PROCEDURE OF AVERAGING WITH A CONTINUOUS HAMILTONIAN

The aim of this section is to reobtain the results of Sec. III and Sec. IV using the procedure of averaging with a continuous Hamiltonian (elastic energy density). According to Eq. (8) the macroscopic anchoring energy can be expanded in a series of $L_{2l}(\theta,\phi)$. The expansion coefficients are the anchoring coefficients $w_{2l}(T)=w_{2l}(0)\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle$ thermally renormalized by the presence of $\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle$. Using the local reference frame, in which $\mathbf{n}\cdot\mathbf{u}=\cos\vartheta$, where $\vartheta=\vartheta(\mathbf{r}_S)$ and $\mathbf{r}_S$ is the position vector of a surface nematic molecule, $P_{2l}(\mathbf{n}\cdot\mathbf{u})$ can be decomposed as

$$P_{2l}(\mathbf{n}\cdot\mathbf{u})=P_{2l}(\cos\vartheta)=\sum_{m=0}^{l} b_{2m}^{2l}\cos(2m\vartheta), \tag{24}$$

where b_{2m}^{2l} are numerical factors [46]. From Eq. (24) it is possible to obtain the thermal average of $P_{2l}(\mathbf{n}\cdot\mathbf{u})$ using the procedure of averaging with a continuous Hamiltonian. We indicate with the subscript loc the thermal average obtained in this framework. We have

$$\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle=\sum_{m=0}^{l} b_{2m}^{2l}\langle\cos(2m\vartheta)\rangle_{loc}. \tag{25}$$

In the local reference frame, where $\mathbf{n}\|\mathbf{z}'$, the elastic energy density is $f_0=(1/2)K(\nabla\vartheta)^2$, as shown in Appendix C, where K is the Frank elastic constant, of the order of $K\sim V_N/a$ [1]. This expression for f_0 is valid in the harmonic approximation. Hence it holds true only for $\vartheta\ll 1$. By decomposing ϑ in a Fourier series we have $\vartheta=\Sigma_{\mathbf{q}}[A(\mathbf{q})\cos(\mathbf{q}\cdot\mathbf{r})+B(\mathbf{q})\sin(\mathbf{q}\cdot\mathbf{r})]$. The elastic energy $H_0=\int_V f_0 d\mathbf{r}$, where V is the volume of the nematic sample, using Fourier's expansion of ϑ, is given by $H_0=(VK/2)\Sigma_{\mathbf{q}}q^2[A^2(\mathbf{q})+B^2(\mathbf{q})]$. The thermal average of $\cos(n\vartheta)$ is

$$\langle\cos(n\vartheta)\rangle_{loc}=\frac{\int\mathcal{D}(\vartheta)\cos(n\vartheta)\exp(-\beta H_0)}{\int\mathcal{D}(\vartheta)\exp(-\beta H_0)}. \tag{26}$$

By writing $\cos(n\vartheta)$ in the exponential form, and taking into account the expression for H_0 written above, we obtain

$$\langle\cos(n\vartheta)\rangle_{loc}=\mathrm{Re}\frac{\prod_{\mathbf{q}}\int dA(\mathbf{q})dB(\mathbf{q})e^{-\gamma_q}}{\prod_{\mathbf{q}}\int dA(\mathbf{q})dB(\mathbf{q})e^{-\nu_q}}. \tag{27}$$

In Eq. (27) $\gamma_q=\gamma_q^A+\gamma_q^B$, where

$$\gamma_q^A=\frac{1}{2}\beta VKq^2\left[A(\mathbf{q})-i\frac{n}{\beta VK}\frac{\cos(\mathbf{q}\cdot\mathbf{r})}{q^2}\right]^2+\frac{n^2}{2\beta VK}\frac{\cos^2(\mathbf{q}\cdot\mathbf{r})}{q^2}, \tag{28}$$

$$\gamma_q^B=\frac{1}{2}\beta VKq^2\left[B(\mathbf{q})-i\frac{n}{\beta VK}\frac{\sin(\mathbf{q}\cdot\mathbf{r})}{q^2}\right]^2+\frac{n^2}{2\beta VK}\frac{\sin^2(\mathbf{q}\cdot\mathbf{r})}{q^2}, \tag{29}$$

and

$$\nu_q=\frac{1}{2}\beta VKq^2[A^2(\mathbf{q})+B^2(\mathbf{q})]. \tag{30}$$

Taking into account that $\int_0^\infty dx\exp(-\lambda x^2)=\sqrt{\pi/\lambda}$, we have for the thermal averages we are looking for

$$\langle\cos(n\vartheta)\rangle_{loc}=\exp\left(-\frac{n^2}{2\beta VK}\sum_{\mathbf{q}}\frac{1}{q^2}\right). \tag{31}$$

Since

$$\frac{1}{V}\sum_{q=q_{min}\sim 0}^{q_{max}=2\pi/a}\frac{1}{q^2}=\frac{1}{8\pi a}, \tag{32}$$

we obtain, finally, $\langle\cos(n\vartheta)\rangle_{loc}=\exp[-(1/2)n^2t]$, where $t=1/(4\pi\beta Ka)$. It follows that $\langle\cos(2m\vartheta)\rangle_{loc}=\exp[-2m^2t]$, and consequently, using Eq. (25),

$$\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle=\sum_{m=0}^{l} b_{2m}^{2l}\exp[-2m^2t], \tag{33}$$

which represents a generalization of the result reported in Ref. [45].

The expression used above for f_0 is valid only in the quadratic approximation for the elastic energy. It follows that the thermal fluctuations of $\mathbf{u}$ with respect to $\mathbf{n}$ have to be small. This implies that $\vartheta\ll 1$, and hence, as follows from the expression for $\langle \cos(n\vartheta)\rangle_{loc}$ written above, $t \ll 1$. In this approximation $\exp[-2m^2 t] \sim \cos(2m\sqrt{t})$. By substituting this result into Eq. (33) we obtain

$$\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle = \sum_{m=0}^{l} b_{2m}^{2l} \cos(2m\sqrt{t}). \tag{34}$$

It is useful, for further considerations, to put $\sqrt{t} = \langle\vartheta\rangle$. In this manner Eq. (34) reads

$$\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle = \sum_{m=0}^{l} b_{2m}^{2l} \cos(2m\langle\vartheta\rangle) = P_{2l}(\cos\langle\vartheta\rangle), \tag{35}$$

if Eq. (24) is taken into account. The macroscopic anchoring energy can be rewritten, as follows from Eq. (8) and Eq. (35), as

$$w(\theta,\phi) = \sum_{l=0}^{\infty} w_{2l}(0) P_{2l}(\cos\langle\vartheta\rangle) L_{2l}(\theta,\phi). \tag{36}$$

By taking into account that $\langle\vartheta\rangle \ll 1$ we have that

$$\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle \sim \exp\left\{-\frac{l(2l+1)}{2}\langle\vartheta\rangle^2\right\} \tag{37}$$

and

$$\langle P_2(\mathbf{n}\cdot\mathbf{u})\rangle = S \sim \exp\left\{-\frac{3}{2}\langle\vartheta\rangle^2\right\}. \tag{38}$$

From Eq. (38) the thermal average of ϑ is connected to S by $\langle\vartheta\rangle^2 = -(2/3)\ln S$. Substituting this result into Eq. (37) we have finally $\langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle = S^{l(2l+1)/3}$, which coincides with the Akulov-Zener law reported above in the low temperature region.

VI. THEORETICAL PREDICTIONS AND EXPERIMENTAL DATA

The temperature dependence of the anchoring energy strength has been measured by several groups with different techniques [13,19,36,37,54–57]. In this section we shall compare our theoretical predictions with the experimental data.

The simplest case to consider is the one relevant to isotropic substrates treated with a surfactant to give homeotropic orientation. In this experimental arrangement the anchoring energy strength is usually measured by means of a Freedericksz-type experiment [13,54]. The anisotropic part of the surface energy relevant to this situation is given by

$$W(\theta) = \sum_{l} w_{2l}(T) P_{2l}(\cos\theta) \tag{39}$$

as discussed at the end of Sec. III. The anchoring energy strength is experimentally deduced by measuring the threshold field for the Freedericksz transition [1,30]. In this way one measures the quantity [13,54]

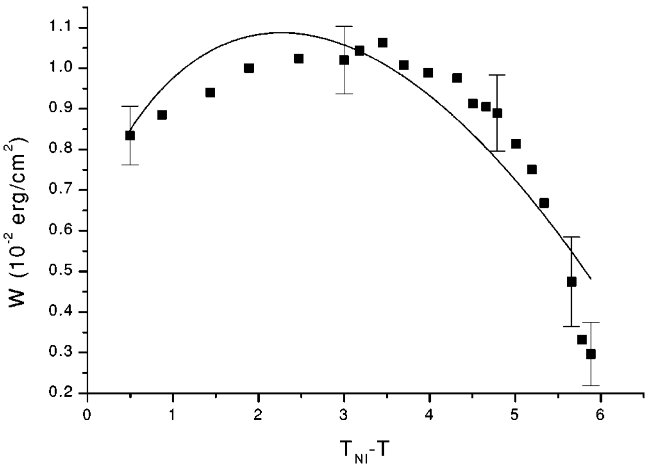

FIG. 2. Behavior of the anchoring energy strength near a temperature surface transition at the nematic substrate interface according to Di Lisi *et al.* [13]. Points: experimental data; solid line: our best fit.

$$w = \left\{\frac{d^2 W(\theta)}{d\theta^2}\right\}_{\theta=0} = -\sum_{l} l(2l+1) w_{2l}(T). \tag{40}$$

$w > 0$ because the homeotropic orientation is stable in the absence of the magnetic field. As discussed above, two terms of the expansion Eq. (39) are enough to approximate $W(\theta)$. By assuming $W(\theta) = w_2(T)P_2(\cos\theta) + w_4(T)P_4(\cos\theta)$, Eq. (40) reads

$$w = -[3w_2(0)\langle P_2(\mathbf{n}\cdot\mathbf{u})\rangle + 10 w_4(0)\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle], \tag{41}$$

if Eq. (9) is taken into account. In the following Eq. (41) will be written as

$$w = \alpha S + \gamma\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle, \tag{42}$$

where $S = \langle P_2(\mathbf{n}\cdot\mathbf{u})\rangle$, $\alpha = -3w_2(0)$, and $\gamma = -10w_4(0)$. In the low temperature region, where $\langle P_4(\mathbf{n}\cdot\mathbf{u})\rangle = S^{10/3}$, Eq. (42) is equivalent to

$$w = \alpha S + \gamma S^{10/3}. \tag{43}$$

In Ref. [13] the experimental data refer to the nematic liquid crystal dialkoxyphenilbenzoate (5OO5) sandwiched between two glass slides coated with diacetylenic phospholipid surfactant. This sample is shown to exhibit a surface structural transition several degrees below the nematic-isotropic phase transition temperature (T_{NI}), at $T = T_S$. For $T_S \leq T \leq T_{NI}$ the sample is uniformly oriented in the homeotropic orientation, whereas for $T < T_S$ the sample is tilted. The measurement of w has been done in the temperature range $T_S \leq T \leq T_{NI}$. In Fig. 2 we report the experimental data from [13] and our theoretical best fit, obtained by means of Eq. (43). For $S(T)$ we assume

$$S(T) = S(T_{NI})\left(\frac{T_c - T}{T_c - T_{NI}}\right)^{1/2}, \tag{44}$$

with $S(T_{NI}) \sim 0.32$ and $T_c - T_{NI} \sim 0.5$K [58]. The parameters of the best fit are $\alpha \sim 2.04 \times 10^{-2}$ erg/cm^2 and $\gamma \sim -1.17 \times 10^{-2}$ erg/cm^2. The agreement of our theory with the experimental data is reasonably good.

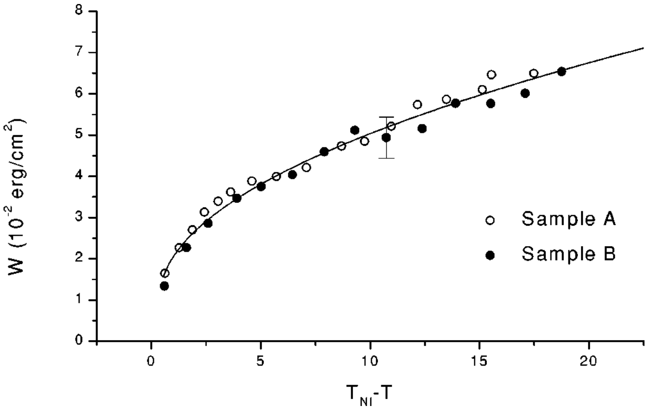

FIG. 3. Temperature dependence of the anchoring energy strength at the nematic liquid crystal–wall interface according to Rosenblatt [54]. Points: experimental data; solid line: our best fit.

In Ref. [54] the experimental data refer to the nematic liquid crystal N-(P-methoxy benzilidene)-P-butylaniline (UBBA) in a cell with glasses treated with dodecyl-trimethyl–ammonium chloride (DTAC). In Fig. 3 we report the experimental data from [54] and our theoretical best fit obtained by means of Eq. (42). Since the temperature range is of the order of 20 K, it is no longer correct to use for $S(T)$ its expression given by Landau's theory, of the kind of Eq. (44), and the Akulov-Zener approximation for $\langle P_4\rangle$. For the fit we use for $S(T)$ and for $\langle P_4\rangle(T)$ the experimental data obtained by measurements of resonance Raman scattering [58]. The parameters of the best fit are $\alpha\sim 3.54\times 10^{-2}$ erg/cm^2 and $\gamma\sim 25.10\times 10^{-2}$ erg/cm^2. In Fig. 3 the open and closed circles refer to two different samples of the same liquid crystal, indicated with the names "sample A" and "sample B," analyzed in [54]. In this case also the agreement between our theoretical predictions and the experimental data is reasonably good over the whole temperature range.

A comment concerning the parameters α and γ of our best fits is necessary because γ is of the same order as or larger than α. The contribution of w linear in S could be connected with the interaction of the nematic molecules with a surface field $\mathbf{E}(z)$, static [59] or fluctuating, due to the substrate. For homogeneous substrates, limited by a flat surface, this field is parallel to the surface geometrical normal. The relevant contribution to the surface energy is proportional to $q_{ij}E_iE_j$ or to $q_{ij}\partial E_i/\partial x_j$. The first term is due to the molecular dielectric anisotropy, the second to the molecular quadrupolar momentum. These terms, after thermodynamic averaging, are proportional to S. They are present even in the case in which the substrate is isotropic. However, the experimental data analyzed in our paper refer to nematic samples, homeotropically oriented by means of surfactants. In this case the surfactant deposited on the glass plate gives rise to a smectic-A-like layer, characterized by anisotropic dielectric properties, in particular by anisotropic polarizability. It follows that the electrostatic interaction between the nematic medium and this smectic-A-like layer gives a contribution to the anisotropic surface energy. It is mainly due to the interactions between (i) the fluctuating dipole in the nematic molecules $\mathbf{p}(t)=p(t)\mathbf{u}$ and the dipolar momentum induced in the surfactant, and (ii) the electrical quadrupolar momentum of the nematic molecules $\overleftrightarrow{D}=e_0\overleftrightarrow{q}$, where e_0 is the molecular quadrupolar momentum modulus, and the dipolar momentum induced in the surfactant.

The first contribution to the surface energy is proportional to $\mathcal{A}\langle p^2(t)\rangle$, where $\mathcal{A}$ is a molecular property and $\langle\rangle$ means a time average. After thermodynamic averaging, the macroscopic surface energy connected to this term is found to be $\mathcal{A}\langle p^2(t)\rangle S$. Hence, $\alpha=\mathcal{A}\langle p^2(t)\rangle$.

The second contribution to the surface energy is proportional to $\mathcal{G}e_0^2$, where $\mathcal{G}$ is another molecular property. The relevant contribution to the macroscopic surface energy is $\mathcal{G}e_0^2\langle P_4\rangle$. Consequently $\gamma=\mathcal{G}e_0^2$.

Hence, the surfactant plays two different roles. First, it strongly reduces the effect of the surface field due to the substrate, because it introduces a screening between the substrate and the liquid crystal. Second, it is responsible for the interaction between the nematic molecular fluctuating dipole and the static quadrupole and the induced dipole in the surfactant. The first contribution is proportional to the square of the fluctuating dipole, whereas the second contribution is proportional to the static quadrupolar momentum. For this reason the $\langle P_4\rangle$ contribution to w is expected to be not negligible with respect to the S contribution.

The classification of the contributions to w from fundamental interactions reported above is supported by the experimental data of Ref. [57], where the anchoring energy of a monomer and its dimer at a polymer-coated interface is measured. The liquid crystal investigated is 5OO5 and its dimer. These liquid crystals have rather low conductivity. Hence, in a first approximation, we can neglect the contribution to the anisotropic part of the surface energy connected with selective ion absorption, giving rise to a static surface field.

The samples were in planar alignment, obtained by rubbing glass substrates coated with polymide. The anchoring energy was obtained by measuring the Freedericksz magnetic threshold field in the splay geometry. The experimental data show that for both monomer and dimer the anchoring energy increases with decreasing temperature. The anchoring energy for the dimer, however, was found to be an order of magnitude larger than that for the monomer, at comparable reduced temperature. According to the authors of Ref. [57] this monomer-dimer pair represents a nearly ideal system for study: one species is simply two monomers attached almost rigidly end to end. From this observation, it follows that the fluctuating dipole, along the major axis, of the dimer is twice that of the monomer. Furthermore, the electrical quadrupolar moment of the dimer is also expected to be twice that of the monomer. The surface energy is proportional to the number of interacting atoms forming the nematic molecules, which for the dimer is twice that for the monomer. Consequently $\mathcal{A}(\mathrm{dim})=2\mathcal{A}(\mathrm{mon})$ and $\mathcal{G}(\mathrm{dim})=2\mathcal{G}(\mathrm{mon})$. Hence, we expect that the anchoring energy for the nematic liquid crystal formed by dimer will be eight times that of the liquid crystal formed by the monomer. Our prediction about the increase of the anchoring energy for the dimer is a little smaller than that detected experimentally. However, we are aware that other interactions contribute to the effective anchoring energy, and our prediction has to be considered just as a very rough estimate.

In Fig. 4 and Fig. 5 we present the experimental data from [57] relevant to monomer and dimer, respectively, and our best fits. Since we do not know the true $S(T)$ and $\langle P_4\rangle(T)$

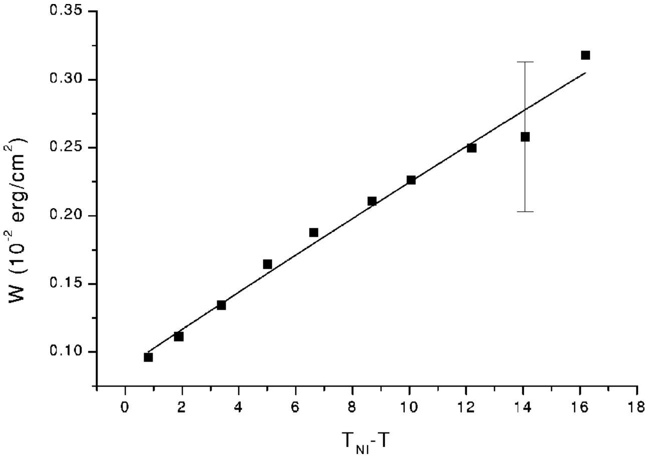

FIG. 4. Temperature dependence of the anchoring energy strength for the monomer 5O05 planar orientation according to [57]. Points: experimental data; solid line: our best fit.

functions, we evaluate them by assuming $V_N = V_N^M$. The parameters of the best fits are $\alpha(\text{mon}) \sim -1.14 \times 10^{-2}$ erg/cm^2, $\gamma(\text{mon}) \sim 4.81 \times 10^{-2}$ erg/cm^2, and $\alpha(\text{dim}) \sim -9.81 \times 10^{-2}$ erg/cm^2, $\gamma(\text{dim}) \sim 43.75 \times 10^{-2}$ erg/cm^2. The results of the best fits confirm the model proposed. In fact, according to the discussion reported above,

$$\frac{\alpha}{\gamma} = \frac{\mathcal{A}\langle p^2(t)\rangle}{\mathcal{G}e_0^2}, \tag{45}$$

and

$$\begin{aligned} p(t,\text{dim}) &\sim 2p(t,\text{mon}), \quad e_0(\text{dim}) \sim 2e_0(\text{mon}), \\ \mathcal{A}(\text{dim}) &\sim 2\mathcal{A}(\text{mon}), \quad \mathcal{G}(\text{dim}) \sim 2\mathcal{G}(\text{mon}). \end{aligned} \tag{46}$$

Consequently

$$\frac{\alpha(\text{dim})}{\gamma(\text{dim})} \sim \frac{\alpha(\text{mon})}{\gamma(\text{mon})}, \tag{47}$$

in agreement with the results of our best fits.

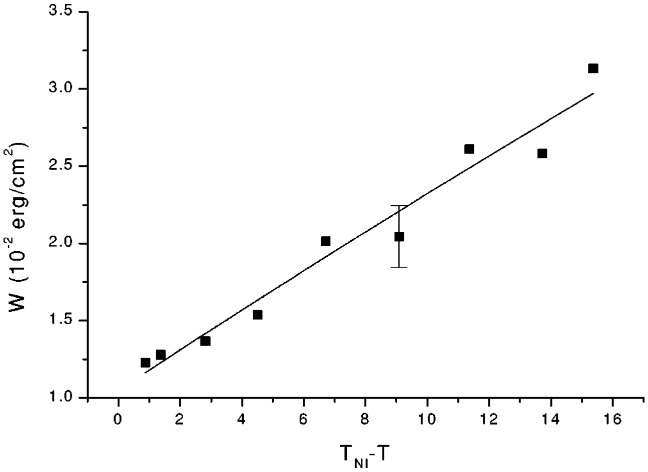

FIG. 5. Temperature dependence of the anchoring energy strength of the dimer of 5O05 with orientation according to [57]. Points: experimental data; solid line: our best fit.

VII. CONCLUSION

We have evaluated the thermal renormalization of the anchoring energy for the whole angular range of the surface director. It has been shown that the renormalization due to the thermal fluctuations of the anchoring coefficients w_{2l} is of the kind $w_{2l}(T)/w_{2l}(0) = \langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle$. If the nematic phase is described by means of a generalized mean field theory one simply obtains $w_{2l}(T)/w_{2l}(0) = S_{2l}$, where S_{2l} is the $(2l)$th scalar order parameter. In the particular case in which the nematic phase is described by the Maier-Saupe theory, $w_{2l}(T)/w_{2l}(0)$ coincides with the average value of the $(2l)$th Legendre polynomial. We have also shown that at the lowest order in the scalar order parameter the simple approach based just on the symmetry of the problem agrees with our mean field approach.

ACKNOWLEDGMENTS

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APPENDIX A

In the bulk the mean field energy due to the interaction of a nematic molecule with other nematic molecules is of the kind $V_N = V_N(\mathbf{n}\cdot\mathbf{u})$, i.e., it depends only on the relative orientation of $\mathbf{u}$ with respect to $\mathbf{n}$. The symmetry of the interaction is SO3. Near the surface this symmetry is broken, and V_N is, in general, of the type

$$V_N = V_N(\mathbf{r},\mathbf{u},\mathbf{n}) = V_N(z,\mathbf{u}\cdot\mathbf{r},\mathbf{u}\cdot\mathbf{n}), \tag{A1}$$

where $\mathbf{r}$ is the position of a given nematic molecule, and z its distance from the surface. As discussed elsewhere [60], the functional dependence of V_N on $\mathbf{u}\cdot\mathbf{r}$ can be responsible for subsurface deformations. Near the surface it is possible to rewrite Eq. (A1) as

$$V_N = V_N(\mathbf{n}\cdot\mathbf{u}) + \delta V_N(z,\mathbf{u}\cdot\mathbf{r},\mathbf{u}\cdot\mathbf{n}), \tag{A2}$$

where

$$\delta V_N(z,\mathbf{u}\cdot\mathbf{r},\mathbf{u}\cdot\mathbf{n}) = V_N(z,\mathbf{u}\cdot\mathbf{r},\mathbf{u}\cdot\mathbf{n}) - V_N(\mathbf{n}\cdot\mathbf{u}) \tag{A3}$$

represents the deviation of the actual mean field energy V_N from the SO3 symmetry. The function $\delta V_N(z,\mathbf{u}\cdot\mathbf{r},\mathbf{u}\cdot\mathbf{n}) \neq 0$ in a surface layer whose thickness is of the order of the range of the molecular forces responsible for the nematic phase. From this observation it follows that $\delta V_N(z,\mathbf{u}\cdot\mathbf{r},\mathbf{u}\cdot\mathbf{n})$ can be considered as an ''intrinsic'' surface energy. The effective surface energy is then obtained by adding to the surface energy due to the direct interaction between the nematic molecules and the substrate the intrinsic surface energy. In our analysis V_S has the meaning of the effective surface energy, and V_N means $V_N(\mathbf{n}\cdot\mathbf{u})$.

APPENDIX B

Let us assume $V_N = V_N^H = -\Sigma v_{2l} S_{2l} P_{2l}(\cos\vartheta)$. In the low temperature region, where the fluctuations of $\mathbf{u}$ with respect to $\mathbf{n}$ are small, $\vartheta \ll 1$. In this case

$$P_{2l}(\cos\vartheta) = 1 - \frac{1}{2} l(2l+1)\vartheta^2 + O(4). \tag{B1}$$

Consequently,

$$V_N^H(\cos\vartheta) = -[N - M\vartheta^2] + O(4), \tag{B2}$$

where

$$N = \sum_l v_{2l} S_{2l} \quad \text{and} \quad M = \frac{1}{2}\sum_l l(2l+1) v_{2l} S_{2l}. \tag{B3}$$

It follows that

$$S_{2l} = \langle P_{2l}(\mathbf{n}\cdot\mathbf{u})\rangle = 1 - \frac{1}{2} l(2l+1) \frac{\int_0^\infty \vartheta^3 e^{-M\vartheta^2} d\vartheta}{\int_0^\infty \vartheta e^{-M\vartheta^2} d\vartheta}, \tag{B4}$$

from which one obtains

$$S_{2l} = 1 - \frac{l(2l+1)}{2M} \sim \exp\left\{-\frac{l(2l+1)}{2M}\right\}. \tag{B5}$$

In particular, the main nematic order parameter is found to be

$$S = \langle P_2(\mathbf{n}\cdot\mathbf{u})\rangle = \exp\left(-\frac{3}{2M}\right). \tag{B6}$$

By substituting Eq. (B6) into Eq. (B5) we have, finally,

$$S_{2l} = S^{l(2l+1)/3}, \tag{B7}$$

which coincides with Eq. (17).

APPENDIX C

The aim of this Appendix is to show that in the local reference frame the elastic energy density can be written as $f_0 = (1/2)K[\boldsymbol{\nabla}\vartheta(\mathbf{r})]^2$. The elastic energy of a nematic liquid crystal is given by

$$H_0 = \tfrac{1}{2}\int_V [K_1(\operatorname{div}\mathbf{n})^2 + K_2(\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2 + K_3(\mathbf{n}\times\operatorname{rot}\mathbf{n})^2] d\mathbf{r}, \tag{C1}$$

where K_1, K_2 and K_3 are the Frank elastic constants [1]. In the one-constant approximation, where $K_1 = K_2 = K_3 = K$, Eq. (C1) becomes

$$H_0 = \frac{1}{2}K\int_V [(\operatorname{div}\mathbf{n})^2 + (\operatorname{rot}\mathbf{n})^2]\, d\mathbf{r}. \tag{C2}$$

In the local reference frame in which $\mathbf{n}$ coincides with the polar axis (z axis), the fluctuations of $\mathbf{u}(\mathbf{r})$ at any point $\mathbf{r}$ are described by small nonzero components $u_x(\mathbf{r})$ and $u_y(\mathbf{r})$. At the second order in $u_x(\mathbf{r})$ and $u_y(\mathbf{r})$ Eq. (C2) reads

$$\begin{aligned} H_0 = \frac{1}{2}K\int_V \{ & [u_{x,x}(\mathbf{r}) + u_{y,y}(\mathbf{r})]^2 + [u_{x,y}(\mathbf{r}) - u_{y,x}(\mathbf{r})]^2 \\ & + [u_{x,z}(\mathbf{r})]^2 + [u_{y,z}(\mathbf{r})]^2\} d\mathbf{r}, \end{aligned} \tag{C3}$$

where $u_{i,j}(\mathbf{r}) = \partial u_i(\mathbf{r})/\partial x_j$. Let us expand $u_i(\mathbf{r})$ in an exponential Fourier series as

$$u_i(\mathbf{r}) = \sum_{\mathbf{q}} u_i(\mathbf{q}) \exp(i\mathbf{q}\cdot\mathbf{r}), \tag{C4}$$

where $u^*(\mathbf{q}) = u_i(-\mathbf{q})$ because $u_i(\mathbf{r})$ are real quantities. By substituting Eq. (C4) into Eq. (C3) we obtain

$$H_0 = \frac{KV}{2}\sum_{\mathbf{q}} [|u_x(\mathbf{q})|^2 + |u_y(\mathbf{q})|^2]. \tag{C5}$$

In the limit of small fluctuations $u_z(\mathbf{r}) = 1 - (1/2)[u_x^2(\mathbf{r}) + u_y^2(\mathbf{r})]$ and also $u_z(\mathbf{r}) = \cos\vartheta(\mathbf{r}) = 1 - (1/2)\vartheta^2(\mathbf{r})$. Consequently $\vartheta^2(\mathbf{r}) = u_x^2(\mathbf{r}) + u_y^2(\mathbf{r})$. A simple calculation shows that $|\vartheta(\mathbf{q})|^2 = |u_x(\mathbf{q})|^2 + |u_y(\mathbf{q})|^2$, where $\vartheta(\mathbf{q})$ are the coefficients of the exponential Fourier expansion of $\vartheta(\mathbf{r})$. From this observation we derive that Eq. (C5) is equivalent to

$$H_0 = \frac{KV}{2}\sum_{\mathbf{q}} q^2 |\vartheta(\mathbf{q})|^2. \tag{C6}$$

It can be rewritten as

$$\frac{KV}{2}\sum_{\mathbf{q}} q^2 [A^2(\mathbf{q}) + B^2(\mathbf{q})], \tag{C7}$$

where $A(\mathbf{q})$ and $B(\mathbf{q})$ are the Fourier coefficients of the expansion of $\vartheta(\mathbf{r})$ in terms of $\cos(\mathbf{q}\cdot\mathbf{r})$ and $\sin(\mathbf{q}\cdot\mathbf{r})$, which we have used in the text. A direct calculation shows that Eq. (C6) can be obtained by assuming $f_0 = (1/2)K[\boldsymbol{\nabla}\vartheta(\mathbf{r})]^2$ and decomposing $\vartheta(\mathbf{r})$ in a Fourier series.

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