Temperature dependence of the nematic anchoring energy: 
mean field analysis

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Abstract

In the mean field approximation, we evaluate the temperature dependence 
of the anchoring energy strength of a nematic liquid crystal in contact with a 
solid substrate due to thermal fluctuations. Our study is limited to the weak 
anchoring case, where the microscopic surface energy is small with respect 
to the mean field energy due to the nematic phase. We assume furthermore 
that the physical properties of the substrate can be considered temperature 
independent in the range of the nematic phase. According to the thermo-
dynamical perturbative approach, the macroscopic surface energy is deduced 
by averaging the microscopic one, with a density matrix containing only the 
nematic mean field. We show that the thermal renormalization of the an-
choring energy coefficients is proportional to the generalized nematic order 
parameters. Our analysis shows also that the thermal renormalization of the 
anchoring energy coefficients predicted by means of Landau-like theories is a
first and rather rough approximation in the whole nematic temperature range.

61.30.-v, 61.30.Cz, 68.10.Cr
One of the least-understood areas of physics and chemistry of liquid crystals concern the anchoring phenomenon and the temperature surface transitions at the interface liquid crystal-solid or soft substrate. These phenomena are important also from a practical point of view, since they play fundamental role in the realization of displays. In this Letter we analyse these phenomena in nematic liquid crystal media.

Nematic liquid crystals are anisotropic fluids made by anisometric molecules having quadrupolar symmetry. Their intermolecular interaction, \( V_N \), is such to orient the molecular axes, \( \mathbf{u} \), along a common direction \( \mathbf{n} \), called director [1]. It coincides with the optical axis of the medium. When a nematic liquid crystal is in contact with a substrate, the orientation of \( \mathbf{n} \) at the surface results from a balance of the anisotropic interactions with the bulk and with the substrate. In the absence of bulk distortions, the surface orientation of the nematic director coincides with the “easy axis”, \( \mathbf{n}_0 \) [2]. It is such to minimize the anisotropic part of the surface energy characterizing the interface between the nematic and the substrate. Long ago Bouchiat and Langevin-Cruchon [3] found a strong temperature dependence of the easy axis. The measurements of Ref. [3] have been repeated by other groups with similar results [4–9]. Several models have been proposed to interpret this phenomenon. According to Parson [10] the easy axis results from the competition between dipolar and quadrupolar interactions, which depend on the temperature in different manner. In special situations a surface nematic orientation temperature dependent can be observed. The idea of Parson has been generalized by Sluckin and Poniewierski [11–13] and by Sen and Sullivan [14]. In all the models, the temperature surface transitions are due to a temperature dependence of the anisotropic part of the anchoring energy, which depends on the symmetry of the substrate and on the symmetry of the nematic phase.

The aim of our paper is to analyze the temperature dependence of the anisotropic part of the surface energy. We assume that the nematic liquid crystal is not polar. From the molecular point of view it has a quadrupolar symmetry, whose principal axis coincides with \( \mathbf{u} \). The elements of the relevant tensor are \( q_{ij} = (3/2)[u_i u_j - (1/3)\delta_{ij}] \). In our analysis, we expand the surface energy in 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 which contains contributions of different orders.

We analyze the temperature dependence of the anchoring energy using an approach based on the 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 mean field due to the other nematic molecules, whose corresponding energy is $V_N$, and to the interaction with the substrate, $V_S$. In this framework, the total energy, $V$, of a given 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, and it is not interesting for us here. The interesting case is the one in which $V_N \gg V_S$, corresponding to a situation where $b \gg a$. This case 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 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 to be a small quantity.

$V_N$ describes the tendency of $u$, which defines the molecular orientation, to be oriented along the nematic director $n$. Usually, it is approximated by means of the Maier-Saupe’s mean field $[15]$, $V_N^M$, according to which $V_N^M \propto n_i q_{ij} n_j = P_2(n \cdot u)$, where $P_2$ is the second order Legendre Polynomial. In this framework $V_N^M = -vP_2(n \cdot u)S$, where $v$ is a molecular constant and $S = \langle P_2(n \cdot u) \rangle$ the nematic scalar parameter. A generalization of the Maier-Saupe theory has been proposed by Humphries et al. $[17]$. According to this generalized mean field theory the nematic mean field is given by
\[ V_N(\mathbf{n} \cdot \mathbf{u}) = - \sum_l v_{2l} P_{2l}(\mathbf{n} \cdot \mathbf{u}) S_{2l}, \]

where \( v_{2l} \) are molecular parameters, and \( S_{2l} = \langle P_{2l}(\mathbf{n} \cdot \mathbf{u}) \rangle \) the nematic order parameters, given by the self-consistent equations

\[ S_{2l} = \frac{\int_0^1 P_{2l}(\mathbf{n} \cdot \mathbf{u}) \exp[-\beta V_N(\mathbf{n} \cdot \mathbf{u})] d(\mathbf{n} \cdot \mathbf{u})}{\int_0^1 \exp[-\beta V_N(\mathbf{n} \cdot \mathbf{u})] d(\mathbf{n} \cdot \mathbf{u})}. \]

The Maier-Saupe potential, \( V_N^M \), is obtained from \( V_N \) putting \( v_{2k} = v \delta_{1,k} \).

The interaction connected to \( V_S \) has to describe the tendency of the surface to orient the surface nematic molecules along the “easy direction”, \( \mathbf{n}_0 \). This direction depends on the symmetry of the surface and on the molecular properties of the mesophase. Since we limit our analysis to non-polar media, \( V_S \) has to be an even function of \( \mathbf{u} \). It follows that \( V_S \) is, actually, a function of the tensor \( \vec{q} \) and can be written, in general, as

\[ V_S(\mathbf{u}) = V_S(\vec{q}) = \sum_k w_k(0) L_k(\vec{q}), \]

where \( L_k(\vec{q}) \) indicate the scalar quantities we can build with the molecular tensor of elements

\[ q_{ij} = (3/2)[u_i u_j - (1/3)\delta_{ij}] \]

and the elements of symmetry characterizing the surface. Each term of the expansion of \( V_S(\vec{q}) \) represents a given interaction, like induced dipole-induced dipole or quadrupole-quadrupole and so on \([18]\); the “intrinsic” anchoring coefficients \( w_k(0) \) are physical parameters connected with the type of interaction described by \( L_k(\vec{q}) \). \( w_k(0) \) refer to specific fundamental interactions, and are assumed to be temperature independent.

In this case thermal effects arise only from the temperature dependence of the degree of alignment of the nematic molecules. This conclusion is valid only if in the temperature range of the nematic phase the physical properties of the substrate can be considered constant. In the opposite case \( w_k(0) \) depend also on the temperature, via the substrate. Since we assume that \( w_k(0) \) are temperature independent, our theory works well when the substrate is a solid crystal. Deviations from our prediction are expected for nematic samples oriented by means of surfactants.

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. Let \( \Theta, \Phi \) and \( \theta, \phi \) be the polar and azimuthal angles defining \( u \) and \( n \), respectively. Consequently

\[
V_S(q) = V_S(\Theta, \Phi) = \sum_k w_k(0) L_k(\Theta, \Phi). \tag{3}
\]

By decomposing the functions \( L_k(\Theta, \Phi) \) in series of spherical harmonics functions \( Y^m_l(\Theta, \Phi) \) we obtain \( L_k(\Theta, \Phi) = \sum_m a^m_l Y^m_l(\Theta, \Phi) \). Since \( L_k = L_k(q) \) and hence \( L_k(\Theta, \Phi) = L_k(\pi - \Theta, \pi + \Phi) \) for all \( k \), we deduce that \( k = 2l \). It follows that for non-polar nematic liquid crystals \( L^2_l(\Theta, \Phi) = \sum_m a^m_{2l} Y^m_{2l}(\Theta, \Phi) \), and the microscopic surface energy can be written as

\[
V_S(\Theta, \Phi) = \sum_l w_{2l}(0) \sum_m a^m_{2l} Y^m_{2l}(\Theta, \Phi). \tag{4}
\]

The macroscopic anchoring energy \( W(n) = W(\theta, \phi) \) is obtained by averaging \( V_S \) over the molecular orientations \( u \), or over \( \Theta \) and \( \Phi \). 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 \[19\] we have \( W(\theta, \phi) = \langle V_S(\Theta, \Phi) \rangle \), and hence, as it follows from Eq.(4),

\[
W(\theta, \phi) = \sum_l w_{2l}(0) \sum_m a^m_{2l} \langle Y^m_{2l}(\Theta, \Phi) \rangle, \tag{5}
\]

where \( \langle A \rangle = Tr(\rho A)/Tr(\rho) \), 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 coordinates system based on the director \( n \) as polar axis. The cartesian reference frame has to be rotated in such a way that \( z' = n \). We will indicate with \( \vartheta, \varphi \) the polar angles of \( u \) with respect to the rotated coordinate system. In this case \[20\]

\[
Y^m_l(\Theta, \Phi) = \sum_{m'} D^l_{m,m'}(\theta, \phi) Y^m_{l'}(\vartheta, \varphi), \tag{6}
\]

where \( D^l_{m,m'}(\theta, \phi) \) are the elements of Wigner’s matrix. Since \( \langle Y^m_{l'}(\vartheta, \varphi) \rangle = \langle Y^0_{l'}(\vartheta) \rangle \delta_{m',0} \) we obtain from Eq.(3) \( \langle Y^m_l(\Theta, \Phi) \rangle = D^l_{m,0}(\theta, \phi) \langle Y^0_{l}(\vartheta) \rangle \). By taking into account that \( D^l_{m,0}(\theta, \phi) = Y^m_l(\theta, \phi) \), we have finally, as it follows from Eqs.(3,4,5),

\[
W(\theta, \phi) = \sum_l w_{2l}(0) S_{2l} L_{2l}(\theta, \phi), \tag{7}
\]
where we have taken into account that \( Y_{2l}^0(\vartheta, \varphi) = P_{2l}(\cos \vartheta) \). Eq. (7) is a consequence of the fact that we regard all anisotropic effects as perturbation, so that they do not need to be included in the computation of the averages values. There is axial symmetry about the direction of \( \mathbf{n} \) in the imperturbed system and only the member \( m = 0 \) of the \( Y_{l}^{m} \) is different from zero. By comparing Eq.(7) with Eq.(3) we deduce that the temperature dependence of the parameters describing the anisotropic part of the surface energy is given by

\[
 w_{2l}(T) = w_{2l}(0)S_{2l}.
\]

This means that 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.(7), the thermal renormalization of the anchoring coefficients is given by Eq.(8). From these results it follows that the anchoring coefficients of the same order in the expansion have the same temperature dependence. Consequently, in the frame of our model, temperature surface transitions are possible only in nematic samples whose anchoring energy contains contributions from different order in the spherical harmonic functions expansion.

The ratios \( S_{2l}/S \) vs. \( S \), for \( l = 2, 3 \) and \( 4 \), in the Maier-Saupe approximation, can be easily evaluated in the nematic phase, where \( 0.4 \leq S \leq 0.8 \). A direct calculation shows that \( S_{2l}/S \leq 0.2 \), for \( l = 3, 4 \), as it is shown in Fig.1. This explains why, usually, the anisotropic part of the surface anchoring energy given by Eq.(7) is well approximated by few terms \([21]\).

In the low temperature region, where \(-\beta V_N \gg 1\), the fluctuations of \( \mathbf{u} \) with respect to \( \mathbf{n} \) are small. In this region \( \mathbf{n} \cdot \mathbf{u} = \cos \vartheta \sim 1 - (1/2)\vartheta^2 + \mathcal{O}(4) \), i.e. \( \vartheta \ll 1 \), and \( P_{2l}(\cos \vartheta) = 1 - [l(2l + 1)/2] \vartheta^2 + \mathcal{O}(4) \). Consequently, from Eq.(4), the order parameter \( S_{2l} \) is found to be

\[
 S_{2l} \sim 1 - \frac{l(2l + 1)}{B} \sim \exp \left\{ - \frac{l(2l + 1)}{B} \right\},
\]

where \( B = \beta \sum_k k(2k + 1)v_{2k}S_{2k} \). The main nematic scalar order parameter \( S = \langle P_{2}(\mathbf{n} \cdot \mathbf{u}) \rangle \) is given by \( S = \exp(3/B) \), as it follows from Eq.(3). The other order parameters can be
determined in terms of $S$ by $S_{2l} = S^{(2l+1)/3}$. In the low temperature region, the thermal renormalization of the anchoring coefficient is then given by

$$w_{2l}(T) = w_{2l}(0) S^{(2l+1)/3}.$$  \hfill (10)

In particular, in this range of temperature, $w_2(T)/w_2(0) = S$ and $w_4(T)/w_4(0) = S^{10/3}$. The temperature dependence given by Eq.(10) reminds the Akulov-Zener law for magnetic anisotropy, well known in ferromagnetism theory \[22,23\].

As an example, we consider now a nematic liquid crystal limited by an isotropic substrate. In this case only the polar angle $\theta$ enters in the description. The analysis of the temperature surface transitions in a system of this kind is usually performed by means of a Landau’s expansion of the anisotropic part of the surface energy \[11,24\]. According to this approach $W(\mathbf{n})$ is expanded in power series of the invariants made with the elements of symmetry characterizing the nematic phase (which is the nematic tensor order parameter of elements $Q_{ij} = (3/2)S[n_i n_j - (1/3)\delta_{ij}]$, and the substrate (which is the geometrical normal $\mathbf{z}$). In the Landau-like approaches the quantity playing the role of expansion parameter is $S$. However, since the nematic-isotropic phase transition is first order, $S$ is never very small (at the transition point it is of the order of 0.3 \[16\]). At the second order in $S$, $W^L(\theta) = w_2^L P_2(\cos \theta) + w_4^L P_4(\cos \theta) + O(3)$, where $w_2^L = a_1 S + a_2 S^2$ and $w_4^L = a_3 S^2$, in which $a_1, a_2$ and $a_3$ are constant parameters, temperature independent \[11,14,24\].

Now we want to compare the prediction of a Landau’s expansion up to the second order in $S$ with the result of our mean field analysis. In the case under consideration the angular functions $L_{2l}(\theta, \phi)$ reduce to $L_{2l}(\theta) = P_{2l}(\cos \theta)$, and

$$W(\theta) = \sum_l w_{2l}(T) P_{2l}(\cos \theta).$$  \hfill (11)

From Eq.(8) we obtain $w_2(T)/w_2(0) = S$. This means that at the first order in $S$ the temperature dependence of the anchoring energy deduced by means of symmetry considerations, $w_2^L$, and by means of the mean field agree. 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
$w_4(T)/w_4(0) = S_4 \neq S^2$, whereas the Landau’s approach predicts the temperature dependencies $w_2^l(T) = a_1 S + a_2 S^2$ and $w_4^l(T) = a_3 S^2$. 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, $S_4 \propto S^2$. However, in the case of large $S$ the discrepancy between the two approaches can be large. In the low temperature region, where it is possible to use the approximate expressions given by Eq. (10) for the thermal renormalization of the anchoring coefficients, our mean field approach predicts $w_2(T) \propto S$ and $w_4(T) \propto S^{10/3}$. In Fig.2 we show $S^2$, predicted by Landau-like models, and $S^{10/3}$, predicted by our mean field theory in the low temperature region, vs. $S$. As it is evident from this figure, our theory represents an improvement with respect to the Landau-like approaches in the whole temperature range.

To conclude we stress the main results reported in the paper. We have shown that the renormalization due to the thermal fluctuations of the anchoring coefficients $w_2^l$ is of the kind $w_2^l(T)/w_2^l(0) = S_2^l$ where $S_2^l$ is the $2l$-th scalar order parameter. In the particular case in which the nematic phase is described by the Maier-Saupe theory, $w_2^l(T)/w_2^l(0)$ coincides with the average value of the $2l$-th Legendre polynomial. We have also shown that only 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. This is a consequence of the hypothesis of small $S$, over which is based the validity of the Landau-like expansions of $W(n)$ in power of $S$. We have proposed also approximate expressions for the thermal renormalization of the anchoring coefficients, valid in the low temperature region, where the fluctuations of the molecular directions with respect to the nematic director are small.

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FIGURES

FIG. 1. $S_{2l}/S$ vs. $S$ according to Maier-Saupe theory. In the usual nematic range, where $0.4 \leq S \leq 0.8$, $S_6/S$, $S_8/S \leq 0.2$. This explains why, usually, two terms are enough to approximate the macroscopic surface energy. The contribution from higher harmonics disappears as a result of the thermal fluctuations of the nematic molecules with respect to the director.

FIG. 2. $S^2$ and $S^{10/3}$ vs. $S$. According to Landau-like models at the second order in $S$, the thermal renormalization of the surface energy in $P_4(\cos \theta)$ is proportional to $S^2$. According to our mean field theory, it is proportional to $S_4$. In the low temperature region, where the fluctuations of the molecular orientation with respect to the nematic director are small, $S_4 \sim S^{10/3}$. The figure shows that our approximate expression for $S_4$ represents an improvement with respect to the Landau-like analyses.
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