Surface Energy for Nematic Liquid Crystals: A New Point of View

A. L. Alexe-Ionescu[1], R. Barberi, G. Barbero[2], T. Beica[3], and R. Moldovan[3]

Universitá di Reggio Calabria, Facoltá di Ingegneria, via E. Cuzzocrea 48, 89128 Reggio Calabria, Italy and I.N.F.M., Unitá di Cosenza, Italy

Z. Naturforsch. **47a,** 1235–1240 (1992); received August 19, 1992

The surface energy of nematic liquid crystals is deduced from a phenomenological point of view. The idea of an easy surface tensor order parameter is proposed. An expression similar to a Landau expansion for the free energy of a system characterized by two order parameters is deduced and analysed. An interpretation similar to the one usually accepted for magnetic materials is given. The possibility of surface transitions induced by temperature is discussed.

PACS 61.30 V, 64.70 Md, 61.30 Gd.

1. Introduction

The presence of a surface introduces a surplus of free energy in a nematic liquid crystal [1]. This surplus of energy, usually called surface energy, is partially due to a direct interaction among the molecules of the nematic and the molecules of the substrate and partially to an incomplete interaction among the molecules of the nematic [2]. The first contribution depends on the physical properties of the substrate and of the nematic and, furthermore, on the geometry of the surface. The second contribution depends only on the physical properties of the nematic and on the geometry of the surface. If the surface is flat and isotropic, it is characterised only by its geometrical normal $\bar{\mathbf{N}}$. In the event in which the nematic can be considered as uniaxial, it is characterised by the usual tensor order parameter

$$Q_{ij} = S(n_i n_j - \tfrac{1}{3}\delta_{ij}),$$

where S is the scalar order parameter and $\bar{\mathbf{n}}$ the nematic director [3]. If $\bar{\mathbf{a}}$ is parallel to the long molecular axis of the molecules, supposed rod-like, forming the nematic liquid crystal, S and $\bar{\mathbf{n}}$ are defined by

$$S = \tfrac{3}{2}(\langle \bar{\mathbf{n}} \cdot \bar{\mathbf{a}} \rangle^2 - \tfrac{1}{3}) \quad \text{and} \quad \bar{\mathbf{n}} = \langle \bar{\mathbf{a}} \rangle,$$

where $\langle\;\rangle$ means a statistical average over a macroscopic volume. The surface energy of a nematic phase due to an isotropic and flat substrate is a function of Q_{ij}. This function can be derived by starting from first principles. However, the calculations are very complicated and the number of unknown parameters is so large that the expressions for the surface energy that one can derive from a microscopic point of view, are usually not very useful. In this paper, we propose a phenomenological expression for the surface free energy of the nematic system. Our paper is organised as follows: In Sect. 2 the phenomenological expression for the surface energy is deduced. In Sect. 3 the easy surface tensor order parameter for a planar problem is determined. In Sect. 4 the surface transition of a nematic liquid crystal is analysed and in Sect. 5 the main conclusions of this analysis are stressed.

2. Phenomenological Expression for the Surface Free Energy

It is possible to deduce an expression for the surface energy following a procedure similar to the one used by Landau to study bulk phase transitions [4]. In this procedure, the surface energy $f(Q_{ij})$ is expanded in a power series of Q_{ij} up to some order. The coefficients of this expansion are then deduced by taking into account the symmetry of the problem. In the case considered, the element of symmetry of the surface is represented by the vector, normal to the surface, of components N_i. The element of symmetry characterising the nematic is the tensor Q_{ij}. In the event in which we are interested in the surface properties of a nematic

---

[1] Department of Physics, Polytechnic Institute of Bucharest, Splaiul Independentei 313, 77216 Bucharest, Romania.

[2] Dipartimento di Fisica del Politecnico, Corso Duca degli Abruzzi 24, 10129 Torino, Italy, and I.N.F.M., Unitá di Torino, Italy.

[3] Institute of Physics and Technology of Materials, CP MG7, Bucharest, Romania.

Reprint requests to Dr. R. Barberi, Universitá della Calabria, I.N.F.M. – Dip. Fisica, I-87036 Rende (CS), Italy.

0932-0784 / 92 / 1200-1235 $ 01.30/0. – Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

near to the clearing temperature T_c, where S is small, f may be expanded up to the second order in Q_{ij}. In this case, one obtains

$$f(Q_{ij}) = f(0) + C_{ij}\,Q_{ij} + D_{ijkl}\,Q_{ij}\,Q_{kl} + O(3)\,, \qquad (1)$$

where $f(0)$ is the surface energy of the isotropic phase (the usual surface tension of isotropic liquids), and $O(3)$ means terms of the third order, or larger, in S. The tensors C_{ij} and D_{ijkl} appearing in (1) are supposed to be temperature independent and to take the symmetry of the surface into account [5]. Since $Q_{ij} = Q_{ji}$, in (1) C_{ij} and D_{ijkl} satisfy the following relations of symmetry:

$$\begin{aligned} C_{ij} &= C_{ji}\,, \\ D_{ijkl} &= D_{klij}\,, \qquad (2) \\ D_{ijkl} &= D_{jikl} = D_{ijlk} = D_{jilk}\,. \end{aligned}$$

These tensors can be decomposed by means of Rivlin's rule in term of the unit tensor of the elements δ_{ij} and of the components of the surface normal N_i [6]. Simple calculations give the expression

$$C_{ij} = C_1\,\delta_{ij} + C_2\,N_i\,N_j\,, \qquad (3)$$

and for the tensor D_{ijkl} one obtains

$$\begin{aligned} D_{ijkl} = {} & D_1\,\delta_{ij}\,\delta_{kl} + \tfrac{1}{2}\,D_2(\delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{jk}) \\ & + \tfrac{1}{2}\,D_3(\delta_{ij}\,N_k\,N_l + \delta_{lk}\,N_i\,N_j) \\ & + \tfrac{1}{4}\,D_4(\delta_{ik}\,N_j\,N_l + \delta_{il}\,N_j\,N_k + \delta_{jk}\,N_i\,N_l + \delta_{jl}\,N_i\,N_k) \\ & + D_5\,N_i\,N_j\,N_k\,N_l\,. \qquad (4) \end{aligned}$$

As it follows from the definition of Q_{ij}, its trace is zero: $Q_{ii} = 0$. Consequently, by putting (3) and (4) into (1), one gets for the surface energy

$$\begin{aligned} f(Q_{ij}) = {} & f(0) + \beta_{11}\,N_i\,Q_{ij}\,N_j + \beta_{20}\,Q_{ij}\,Q_{ij} \\ & + \beta_{21}\,N_i\,Q_{ij}\,Q_{jl}\,N_l + \beta_{22}(N_i\,Q_{ij}\,N_j)^2\,, \qquad (5) \end{aligned}$$

where $\beta_{11} = C_2$, $\beta_{20} = D_2$, $\beta_{21} = D_4$, and $\beta_{22} = D_5$. An expression of the kind (5) for f has first been proposed by Sluckin and Poniewierski [7] by following an idea of Goossens [8]. The derivation of (5) could seem unnecessary complicated; in fact, in the simple case of an isotropic substrate it can be directly obtained by writing down the five scalar invariants (up to the second order in S) which can be made up from the tensor of elements Q_{ij} and the vector of components N_i. However, if the surface is not only characterised by its geometrical normal, but also by some symmetry axes (as in the case in which the solid substrate is a crystal), the above presented analysis can be useful. We stress that the term $\beta_{11}\,N_i\,Q_{ij}\,N_j$ is connected to a direct interaction among the nematic molecules and the substrate molecules via, e.g., the Van der Waals interaction [9]. This term is linear in the scalar order parameter and near T_c the most important one. The other terms, bilinear in Q_{ij} have two different origins. The term $\beta_{20}\,Q_{ij}\,Q_{ij}$ is due only to the incomplete nematic-nematic interaction. The other terms are partially due to the incomplete nematic-nematic interaction and partially to the direct interaction of the nematic molecules with the "surface field".

If $\bar{\mathbf{n}}$ is everywhere parallel to a plane, that we call $(x-z)$-plane, it is possible to put $\bar{\mathbf{n}} = (\sin(\vartheta), 0, \cos(\vartheta))$. ϑ is the nematic tilt angle. In terms of S and ϑ the surface energy given by (5) writes

$$\begin{aligned} f(S, \vartheta) = {} & \beta_{11}\,S(x - \tfrac{1}{3}) + \tfrac{2}{3}\,\beta_{20}\,S^2 + \tfrac{1}{3}\,\beta_{21}\,S^2(x + \tfrac{1}{3}) \\ & + \beta_{22}\,S^2(x - \tfrac{1}{3})^2\,, \qquad (6) \end{aligned}$$

where $x = \cos^2\vartheta$ and the isotropic term has been dropped out.

From (6), it is evident that the surface free energy depends on S and ϑ. These quantities play the role of surface order parameters.

It is important to underline that near T_c, where β_{ij} can be considered temperature independent [10], the easy surface scalar order parameter and the easy surface orientation, defined as the values of S and ϑ minimizing f, are temperature independent too.

3. Easy Surface Tensor Order Parameter

The "easy" surface tensor order parameter

$$Q^0_{ij} = S^0\,(n^0_i\,n^0_j - \tfrac{1}{3}\,\delta_{ij})$$

is the one minimizing the surface free energy. In the planar case considered at the end of the previous section, f is given by (6). Consequently the elements of Q^0_{ij}, i.e. the "easy" surface order parameter S^0 and the "easy" direction ϑ^0, are defined as the values of S and ϑ minimizing f given by (6). The values of S and ϑ minimizing f, given by (6), are obtained by putting

$$\partial f/\partial S = 0 \qquad (7)$$

and

$$\partial f/\partial \vartheta = 0\,. \qquad (8)$$

The solutions of the system (7), (8) minimize f if

$$\partial^2 f/\partial S^2 > 0 \qquad (9)$$

and

$$H=\frac{\partial^2 f}{\partial S^2}\frac{\partial^2 f}{\partial \vartheta^2}-\left(\frac{\partial^2 f}{\partial \vartheta\,\partial S}\right)^2>0\,. \qquad (10)$$

By using (6), the system (7), (8) writes

$$\beta_{11}(x-\tfrac{1}{3})+\tfrac{4}{3}\beta_{20}S+\tfrac{2}{3}\beta_{21}S(x+\tfrac{1}{3})+2\beta_{22}S(x-\tfrac{1}{3})^2=0, \qquad (7')$$

$$2\,[\beta_{11}+\tfrac{1}{3}\,\beta_{21}S+2\beta_{22}S(x-\tfrac{1}{3})]\,S\sqrt{x(1-x)}=0\,. \qquad (8')$$

Solutions of system (7′), (8′) are:

$$x_{\mathrm{A}}=1\,,\quad S_{\mathrm{A}}=-\frac{3}{2}\left(\frac{\beta_{11}}{3\beta_{20}+2(\beta_{21}+\beta_{22})}\right), \qquad (11)$$

which corresponds to homeotropic alignment,

$$x_{\mathrm{B}}=0\,,\quad S_{\mathrm{B}}=\frac{3}{2}\left(\frac{\beta_{11}}{6\beta_{20}+(\beta_{21}+\beta_{22})}\right), \qquad (12)$$

which corresponds to planar alignment,

$$x_{\mathrm{C}}=\tfrac{1}{3}\,,\quad S_{\mathrm{C}}=0\,, \qquad (13)$$

which corresponds to the surface isotropic state, and

$$x_{\mathrm{D}}=-\left(1+4\,\frac{\beta_{20}}{\beta_{21}}\right),$$

$$S_{\mathrm{D}}=3\left(\frac{\beta_{11}}{8\beta_{22}\left(1+3\,\dfrac{\beta_{20}}{\beta_{21}}\right)-\beta_{21}}\right), \qquad (14)$$

which corresponds to tilted orientation.

By substituting the solutions (11)–(14) into (9)–(10), simple calculations give

$$\left(\frac{\partial^2 f}{\partial S^2}\right)_{\mathrm{A}}=\tfrac{4}{9}\,[3\beta_{20}+2(\beta_{21}+\beta_{22})]\,, \qquad (15\,\mathrm{a})$$

$$H(A)=2\beta_{11}^2\,\frac{2\beta_{20}+\beta_{21}}{3\beta_{20}+2(\beta_{21}+\beta_{22})}\,, \qquad (15\,\mathrm{b})$$

$$\left(\frac{\partial^2 f}{\partial S^2}\right)_{\mathrm{B}}=\tfrac{2}{9}\,[6\beta_{20}+(\beta_{21}+\beta_{22})]\,, \qquad (16\,\mathrm{a})$$

$$H(B)=\tfrac{2}{3}\,\beta_{11}^2\,\frac{6\beta_{20}+\beta_{21}}{6\beta_{20}+(\beta_{21}+\beta_{22})}\,, \qquad (16\,\mathrm{b})$$

$$\left(\frac{\partial^2 f}{\partial S^2}\right)_{\mathrm{C}}=\tfrac{4}{3}\,[\beta_{20}+\tfrac{1}{3}\,\beta_{21}]\,, \qquad (17\,\mathrm{a})$$

$$H(C)=-\tfrac{8}{9}\,\beta_{11}^2\,. \qquad (17\,\mathrm{b})$$

Similar calculations allow to analyse the stability of the tilted phase. The relations (17) show that the surface isotropic state never corresponds to a stable state, since it yields no extremes for the surface energy *f*. The analysis of (15) shows furthermore that the A-case (homeotropic alignment) is stable if

$$\begin{aligned}&3\beta_{20}+2\,(\beta_{21}+\beta_{22})>0\,,\\&2\beta_{20}+\beta_{21}>0\,,\\&\beta_{11}<0,\quad |\beta_{11}|<\tfrac{2}{3}\,[3\beta_{20}+2\,(\beta_{21}+\beta_{22})]\,,\end{aligned} \qquad (18)$$

following from $(\partial^2 f/\partial S^2)_{\mathrm{A}}>0$, $H(A)>0$, $S_{\mathrm{A}}>0$ and $S_{\mathrm{A}}<1$, respectively. The same analysis shows that the B-case (planar alignment) is stable if

$$\begin{aligned}&6\beta_{20}+(\beta_{21}+\beta_{22})>0\,,\\&6\beta_{20}+\beta_{21}>0\,,\\&\beta_{11}>0,\quad \beta_{11}<\tfrac{2}{3}\,[6\beta_{20}+(\beta_{21}+\beta_{22})]\,,\end{aligned} \qquad (19)$$

following from $(\partial^2 f/\partial S^2)_{\mathrm{B}}>0$, $H(B)>0$, $S_{\mathrm{B}}>0$ and $S_{\mathrm{B}}<1$, respectively.

If $\beta_{20}=0$, i.e. the nematic-nematic interaction is negligible with respect to the nematic-substrate interaction (14) shows that $x_{\mathrm{D}}=-1$ for every β_{ij}. This means that, in this frame, the easy direction is parallel or perpendicular to a solid, flat and isotropic substrate. This result is not surprising and follows directly from the symmetry of the problem. Furthermore, in this case (18) and (19) write

$$\begin{aligned}&\beta_{21}+\beta_{22}>0\,,\\&\beta_{21}>0\,,\\&\beta_{11}<0,\quad |\beta_{11}|<\tfrac{4}{3}\,(\beta_{21}+\beta_{22})\end{aligned} \qquad (18')$$

and

$$\begin{aligned}&\beta_{21}+\beta_{22}>0\,,\\&\beta_{21}>0\,,\\&\beta_{11}>0,\quad \beta_{11}>\tfrac{2}{3}\,(\beta_{21}+\beta_{22})\,.\end{aligned} \qquad (19')$$

Equations (18′) and (19′) show that, according to the sign of β_{11}, if $\beta_{21}+\beta_{22}>0$ and $\beta_{21}>0$, the easy direction is homeotropic ($\beta_{11}<0$) or planar ($\beta_{11}>0$). If $\beta_{21}+\beta_{22}>0$ but $\beta_{21}<0$, the homeotropic or planar alignments correspond to a maximum of the surface energy. Note that, in the cases (18′) and (19′), the fourth inequality is not taken into account in our analysis because it is not connected with the stability of the phase but with the maximum value of the scalar order parameter *S* (which is arbitrarily assumed equal to unity). Finally, if $\beta_{21}/(\beta_{21}+\beta_{22})<0$, f is never extremised for any $\vartheta \in (0, \frac{\pi}{2})$ and $S \in (0, 1)$.

Beside these simple analytical considerations, deduced by the expression of the surface energy f, given by (6), we can conclude that:

i) if $\beta_{20}=0$, the easy direction is homeotropic or planar, according to the values of the phenomenological parameters β_{ij};
ii) if $\beta_{20} \neq 0$, the easy direction can be tilted ($\vartheta \neq 0$ or $\frac{\pi}{2}$), if the β_{ij} coefficients satisfy some conditions;
iii) the isotropic surface state is never stable.

4. Surface Transitions in Nematic Liquid Crystals

All the conclusions obtained in the previous section are independent of the temperature because the expansion coefficients, present in (6), are supposed temperature independent. Recent papers [2, 7], by using a phenomenological expression similar to (6) try to interpret surface transitions experimentally observed in nematic liquid crystals by different groups [11–16]. In the quoted papers the analysis is performed by supposing the surface scalar order parameter equal to the bulk one at the considered temperature. In this frame, the surface energy is considered as a function only of the surface tilt angle. The easy direction is obtained by minimizing the surface energy with respect to the surface tilt angle [2, 7]. By assuming for the surface scalar order parameter a temperature dependence of the kind

$$S(T)=\Delta\sqrt{\frac{T_0-T}{T_0}},$$

where Δ is a constant and T_0 a temperature larger than the clearing temperature T_c by some degrees, it is possible to deduce the temperature behaviour of the surface tilt angle and of the anchoring energy [2]. The theoretical results are in good agreement with the experimental results [2, 7].

In the frame of the present analysis of the surface energy, the approach of [2, 7] has to be considered as a first approximation. In fact, S (as ϑ) on the surface must be considered a free parameter. Of course, by minimizing f given by (6), one obtains the result that the extremising values of S and ϑ on the surface are temperature independent. Consequently no surface transitions could be expected. However, it is necessary to point out that to minimize f in order to find the easy direction is meaningful only if S and ϑ are position independent, i.e. uniform across the sample. If ϑ may be considered constant (since it changes over a distance of the order of the sample thickness), but S is position dependent (since it changes over a distance of the order of the coherence length), the previous analysis has to be modified. In fact, in this case, it is necessary to minimize the total free energy instead of the surface energy alone. The total energy is, in the frame of a Landau-Ginzburg [4] approach

$$\mathscr{F}=\int_0^\infty\left[\frac{1}{2}L\left(\frac{\mathrm{d}S}{\mathrm{d}z}\right)^2+f_\mathrm{b}(S)-f_\mathrm{b}(S_\mathrm{b})\right]\mathrm{d}z+f(\vartheta_0,S_0), \tag{20}$$

where the z-axis is normal to the surface, L is an elastic constant, f_b the bulk free energy density of a uniform nematic, S_b the bulk scalar order parameter depending only on the temperature, and $f(\vartheta_0, S_0)$ the surface energy given by (6), $S_0=S(0)$ and $\vartheta_0=\vartheta(0)$. The first term in (20), as is well known, comes from the non uniformity of S and is a bulk contribution.

By minimizing $\mathscr{F}$ one obtains

$$L\frac{\mathrm{d}^2S}{\mathrm{d}z^2}-\frac{\mathrm{d}f_\mathrm{b}}{\mathrm{d}S}=0 \tag{21}$$

for the bulk and

$$-L\frac{\mathrm{d}S}{\mathrm{d}z}+\frac{\partial f}{\partial S_0}=0, \tag{22}$$

$$\frac{\partial f}{\partial \vartheta_0}=0 \tag{23}$$

for the boundary conditions at $z=0$. By assuming S_0 not very different from S_b at the considered temperature, and hence $|S(z)-S_\mathrm{b}| \ll 1$, trivial calculations give

$$S(z)=S_\mathrm{b}+(S_0-S_\mathrm{b})\,e^{-z/\xi}, \tag{24}$$

where

$$\xi^{-2}=\frac{1}{L}\left(\frac{\mathrm{d}^2f_\mathrm{b}}{\mathrm{d}S^2}\right)_{S=S_\mathrm{b}} \tag{25}$$

is the square of the coherence length in the nematic phase [17]. By substituting (24) into boundary conditions (22) one obtains

$$\frac{\partial f}{\partial S_0}+\frac{L}{\xi}S_0=\frac{L}{\xi}S_\mathrm{b}. \tag{26}$$

Equation (26), with (23) allows to determine S_0 and ϑ_0, i.e. the surface properties of the nematic. We underline that, in the uniform situation in which the scalar order parameter can be considered position independent, instead of (26), one has to use the condition

$\partial f/\partial S = 0$, as shown before. By introducing an effective surface energy, defined by

$$F = f + \frac{1}{2}\,\frac{L}{\xi}\,(S_0 - S_b)^2, \tag{27}$$

the boundary conditions (26) and (23) may be rewritten as

$$\frac{\partial F}{\partial S_0} = \frac{\partial F}{\partial \vartheta_0} = 0, \tag{28}$$

i.e. in the same form in the uniform case. Note that the second term in (27) takes the spatial variation of S into account. It can be deduced by substituting (24) into (20). This term is, actually, a bulk term, even if it plays the role of a surface contribution to the effective surface energy.

By using for f the phenomenological expression (6), F can be rewritten in the form

$$F = \beta_{11} S_0 (x_0 - \tfrac{1}{3}) + \tfrac{2}{3}\beta_{20} S_0^2 + \tfrac{1}{3}\beta_{21} S_0^2 (x_0 + \tfrac{1}{3}) + \beta_{22} S_0^2 (x_0 - \tfrac{1}{3})^2 + \frac{L}{2\xi}(S_0 - S_b)^2, \tag{29}$$

in which the temperature is present through ξ and S_b.

The analysis from now on is standard. From (29), simple calculations give

$$\frac{\partial F}{\partial S_0} = \beta_{11}(x_0 - \tfrac{1}{3}) + \tfrac{4}{3}\beta_{20} S_0 + \tfrac{2}{3}\beta_{21} S_0 (x_0 + \tfrac{1}{3}) + 2\beta_{22} S_0 (x_0 - \tfrac{1}{3})^2 + \frac{L}{\xi}(S_0 - S_b),$$

$$\frac{\partial F}{\partial \vartheta_0} = -\left[\beta_{11} S_0 + \tfrac{1}{3}\beta_{21} S_0^2 + 2\beta_{22} S_0^2 (x_0 - \tfrac{1}{3})\right] \sin(2\vartheta_0).$$

By putting $\dfrac{\partial F}{\partial S_0} = \dfrac{\partial F}{\partial \vartheta_0} = 0$, we obtain that $x = 1$ (homeotropic), $x = 0$ (planar), $x \neq 0, 1$ (tilted) are solutions of the second equation. Let us consider only the homeotropic state. Its scalar order parameter is given by

$$S_{0,\mathrm{A}} = \frac{\dfrac{L}{\xi} S_b - \tfrac{2}{3}\beta_{11}}{\dfrac{L}{\xi} + \tfrac{4}{3}\left[\beta_{20} + \tfrac{2}{3}(\beta_{21} + \beta_{22})\right]}, \tag{30}$$

as follows from the first equation of the system. In the case in which $\beta_{20} < 0$, $\beta_{21} < 0$, $\beta_{22} < 0$ and $\beta_{11} > 0$, straightforward calculations show that the homeotropic phase is stable only if

$$\frac{L}{\xi} > \tfrac{4}{9}\left[3\,|\beta_{20}| + 2(|\beta_{21}| + |\beta_{22}|)\right] \tag{31}$$

and

$$S_{0,\mathrm{A}} > \frac{\beta_{11}}{|\beta_{21}| + 4\,|\beta_{22}|}. \tag{32}$$

Let us suppose, as in a classical Landau theory for the bulk, for $S_b(T)$ and $\xi^{-1}(T)$ the laws

$$S_b(T) = \Delta\sqrt{\frac{T_0 - T}{T_0}}, \quad \frac{1}{\xi(T)} = \frac{1}{\xi_0}\sqrt{\frac{T_0 - T}{T_0}}, \tag{33}$$

where ξ_0 is a bare correlation length. Expressions (33) are written in the hypothesis of a second order phase transition. This is not correct, but the analysis is simpler than the correct one, and the main characteristics do not change. By substituting (33) into (31) and (32), one obtains that the homeotropic phase is stable for $T < \tilde{T}$, where $\tilde{T}$ can be evaluated in terms of the phenomenological parameters β_{ij}. Simple calculations give

$$\tilde{T} = T_0\left\{1 - \left[\frac{2\xi_0}{3L}(2\,|\beta_{20}| + |\beta_{21}| + |\beta_{22}|) - \beta_{11}\right]^2\right\}.$$

For $T > \tilde{T}$, the stable configuration is the tilted or the planar one, according to the values of β_{ij}. In the event in which, for $T > \tilde{T}$, the stable state is the tilted one, it is easy to show that $\vartheta \propto \sqrt{T - \tilde{T}}$, as experimentally detected by Faetti and co-workers [14]. Other information on the surface phase transitions can be deduced by analysing the solutions extremising F given by (29), but they are not important in this context.

5. Conclusions

By using symmetry arguments, a phenomenological expression for the surface energy of a nematic liquid crystal bounded by an isotropic flat medium has been deduced. The analysis of the obtained surface energy allows to introduce the idea of an easy surface tensor order parameter as recently suggested by G. Durand and co-workers [18]. Furthermore the surface order transition, possible in nematic liquid crystals, can be interpreted as a coupling between the bulk and surface scalar order parameter. A simple analysis based on a Landau-Ginzburg expression of the energy has been proposed.

Acknowledgement

Many thanks are due to the referee of Z. Naturforschung, Section A, for useful comments about Equation (5). We wish in particular to thank G. Durand for useful discussions.

[1] J. G. Chan and J. E. Hillard, J. Chem. Phys. **28,** 258 (1958).

[2] G. Barbero, Z. Gabbasova, and M. Osipov, J. de Phys. II, **1,** 691 (1991).

[3] P. G. de Gennes, The Physics of Liquid Crystals, Clarendon, Oxford 1974.

[4] See e.g. L. D. Landau and I. M. Lifchitz, Physique Statistique, MIR, Moscow 1972.

[5] A. J. M. Spencer and R. S. Rivlin, Arch. Ration. Mech. Anal. **11,** 45 (1961).

[6] E. Govers and G. Vertogen, Phys. Rev. A **30,** 1998 (1984).

[7] T. J. Sluckin and A. Poniewierski, Fluid and Interfacial Phenomena (C. A. Croxton, ed.), John Wiley, Chichester 1984.

[8] J. W. Goossens, Mol. Cryst. Liq. Cryst. **124,** 305 (1985).

[9] E. Dubois-Violette and P. G. de Gennes, J. de Phys. Lett. **36,** L255 (1975).

[10] M. Kaganov, JETP **54,** 773 (1980).

[11] M. A. Bouchiat and D. Langevin-Cruchon, Phys. Lett. **34 A,** 331 (1971).

[12] S. Faetti and L. Fronzoni, Solid State Communications **25,** 1087 (1978).

[13] P. Chiarelli, S. Faetti, and L. Fronzoni, J. de Phys. **44,** 1061 (1983).

[14] P. Chiarelli, S. Faetti, and L. Fronzoni, Phys. Lett. **101 A,** 31 (1984).

[15] G. A. Di Lisi, C. Rosenblatt, A. C. Griffin, and Uma Hari, Liq. Cryst. **7,** 359 (1990).

[16] K. Flatischler, L. Komitov, S. T. Lagerwall, B. Stebler, and A. Strigazzi, Mol. Cryst. Liq. Cryst. **189,** 119 (1991).

[17] E. B. Pristley, P. J. Wojtowicz, and Ping Sheng, Introduction to Liquid Crystals, Plenum, New York 1974.

[18] G. Durand, Invited Lecture at the 14th International Liquid Crystal Conference, Pisa, June 21–26, 1992, and M. Nobili, G. Durand, to appear in Phys. Rev. A, 10 October 1992.