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Surface energy of biaxial nematics

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In this paper, a form of surface energy for biaxial nematics is derived. The methods follow those for deriving Landau elastic energy Frank elastic energy for bulk nematics. The surface energy can also be derived in rotation matrix expansion. The result shows that in the first order approximation, there are four independent coefficients in the surface energy. When each of the three orthogonal directors of biaxial nematics coincides with its corresponding easy axis, the surface energy is linearly proportional to the order parameters. An application of this surface energy is discussed and possible experimental measurements of three linear combinations of the four coefficients are explored.

1. Introduction

The surface energy of a nematic liquid crystal has been used in all problems involving weak anchoring boundary conditions. The interaction between the liquid crystal and a confining surface gives rise to a surface energy in a form first suggested by Rapini–Papoular [1]. For homeotropic alignment, it was proposed that the surface energy has the form $W \sin^2 \theta/2$, where W is the polar anchoring strength in units of energy density, and θ is the polar angle the director $\mathbf{n}$ makes with the easy axis $\mathbf{n}^0$. For homogeneous alignment, de Gennes [2] used a similar expression, i.e. $F_s = 1/2\, W\theta^2$ where W is the azimuthal anchoring strength, and θ is the angle the director in the surface plane makes with the easy axis. In the computer simulation of finger-print texture of cholesteric liquid crystal induced by an external field, Shiyanovskii and Lavrentovich [3] used a surface energy in a generalized Rapini form, $F_s = -1/2\, W_{ij} n_i n_j$, to describe a pretilt angle as well as different polar and azimuthal anchoring. Here the repeated index means summation.

Apart from the forms that describe the deviation of the director from the easy axis in uniaxial nematics, other forms of surface energy related to the order parameter have been suggested. Sheng [4] and other authors [5] used the expression $-GS$ for surface energy, where G is a constant denoting the strength of the potential felt by each molecule and $S = \langle P_2(\cos\theta)\rangle$. When $G > 0$ (or $G < 0$) the long molecular rods tend to align parallel (or perpendicular) to the director. In this type of expression, the director is assumed to be along the easy axis.

Because both the deviation of directors from easy axes and the degree of molecular orientation along the directors contribute to the surface energy, it is necessary to find a general form of surface energy for biaxial nematics in terms of order parameters and relative orientation of directors with respect to easy axes. In the following sections, we will first use a similar approach to that used in Landau theory [6] to form a rotational invariance for the surface energy where the anchoring strengths depend on the order parameters. Then a similar method to that used in Frank elastic theory [7] will be employed in deriving another form of surface energy. The validity of these forms is further checked by a rotation matrix series expansion. These two forms of surface energy will be compared and possible experimental measurements for the anchoring strengths will be explored.

2. Theory

Consider a triad of orthogonal director fields of a biaxial nematic liquid crystal **a**, **b** and **c**. In the boundary surface, suppose three orthogonal easy axes are denoted by $\mathbf{a}^0$, $\mathbf{b}^0$ and $\mathbf{c}^0$ respectively. In weak anchoring conditions, the relative orientations of directors **a**, **b** and **c** with respect to $\mathbf{a}^0$, $\mathbf{b}^0$ and $\mathbf{c}^0$ can be realized by three rotations in the following order:

(1) rotation of angle ϕ_a around $\mathbf{a}^0$ axis ($0 \leqslant \phi_a < 2\pi$);
(2) rotation of angle ϕ_b around $\mathbf{b}^0$ axis ($0 \leqslant \phi_b < \pi$);
(3) rotation of angle ϕ_c around $\mathbf{c}^0$ axis ($0 \leqslant \phi_c < 2\pi$).

Note the angles ϕ_a, ϕ_b and ϕ_c are not Euler angles. The benefit of using this system of rotations is that when the

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directors' deformation involves only one of the rotations, the result can be expressed in a single angle, while in Euler angles two may be involved.

In the $\mathbf{a}^0, \mathbf{b}^0, \mathbf{c}^0$ system, in terms of ϕ_a, ϕ_b, and ϕ_c, directors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ can be expressed as

$$\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix}=\begin{pmatrix}\cos\phi_c\cos\phi_b & \sin\phi_c\cos\phi_b & -\sin\phi_b\\ \cos\phi_c\sin\phi_b\sin\phi_a-\sin\phi_c\cos\phi_a & \sin\phi_c\sin\phi_b\sin\phi_a+\cos\phi_c\cos\phi_a & \cos\phi_b\sin\phi_a\\ \cos\phi_c\sin\phi_b\cos\phi_a+\sin\phi_c\sin\phi_a & \sin\phi_c\sin\phi_b\cos\phi_a-\cos\phi_c\sin\phi_a & \cos\phi_b\cos\phi_a\end{pmatrix}\begin{pmatrix}\mathbf{a}^0\\ \mathbf{b}^0\\ \mathbf{c}^0\end{pmatrix}$$

$$=U(\phi_a,\phi_b,\phi_c)\begin{pmatrix}\mathbf{a}^0\\ \mathbf{b}^0\\ \mathbf{c}^0\end{pmatrix}. \qquad (1)$$

While in terms of Euler angles (α, β, γ)

$$\begin{pmatrix}\mathbf{a}\\ \mathbf{b}\\ \mathbf{c}\end{pmatrix}=\begin{pmatrix}\cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma & -\sin\beta\cos\gamma\\ -\cos\alpha\cos\beta\sin\gamma-\sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma+\cos\alpha\cos\gamma & \sin\beta\sin\gamma\\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta\end{pmatrix}\begin{pmatrix}\mathbf{a}^0\\ \mathbf{b}^0\\ \mathbf{c}^0\end{pmatrix}$$

$$\equiv U(\alpha,\beta,\gamma)\begin{pmatrix}\mathbf{a}^0\\ \mathbf{b}^0\\ \mathbf{c}^0\end{pmatrix}. \qquad (2)$$

The surface energy must satisfy the following requirements: (1) the energy must be rotational invariant; (2) the states of molecular orientation near the surface are indistinguishable for $\mathbf{a}$ and $-\mathbf{a}$, or $\mathbf{b}$ and $-\mathbf{b}$, or $\mathbf{c}$ and $-\mathbf{c}$. Therefore the surface energy must be invariant under each of the following six operations: (1) $\mathbf{a}\rightarrow-\mathbf{a}$, (2) $\mathbf{b}\rightarrow-\mathbf{b}$, (3) $\mathbf{c}\rightarrow-\mathbf{c}$, (4) $\mathbf{a}^0\rightarrow-\mathbf{a}^0$, (5) $\mathbf{b}^0\rightarrow-\mathbf{b}^0$, and (6) $\mathbf{c}^0\rightarrow-\mathbf{c}^0$. Consequently, there will be no linear terms and cross terms such as $\mathbf{a}$, $\mathbf{a}\cdot\mathbf{b}$ etc. The terms like $(\mathbf{a}\cdot\mathbf{b})\mathbf{c}$ satisfy this requirement since $(\mathbf{a}\cdot\mathbf{b})\mathbf{c}=(\mathbf{a}\cdot\mathbf{b})(\mathbf{a}\times\mathbf{b})$, yet it is not a rotational invariant and therefore should be disregarded. This requirement is the same one used in deriving Frank elastic energy for the bulk uniaxial nematics [2]. The same symmetry property in Saupe's elastic energy for biaxial nematics is also assumed [8] (see equation (30) for the form of elastic energy of biaxial nematics). The surface energy, $F_s=-1/2\,W_{ij}n_in_j$ used in [5] also satisfied this requirement.

When $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ coincide with $\mathbf{a}^0$, $\mathbf{b}^0$, and $\mathbf{c}^0$ respectively, neglecting the higher order terms, the surface energy is linearly proportional to the order parameters. The proof is as follows. For a rod-like molecule, suppose the long axis of molecule in the $\mathbf{a}^0, \mathbf{b}^0, \mathbf{c}^0$ system is oriented with polar and azimuthal angles θ and ϕ, respectively. The microscopic surface energy F_s^m in general is a function of θ and ϕ. Expanding F_s^m in a series of spherical harmonics $Y_{lm}(\theta,\phi)$, we have

$$F_s^m(\theta,\phi)=\sum_{l=0}\sum_{m=-l}^{l}a_{lm}Y_{lm}(\theta,\phi). \qquad (3)$$

Neglecting higher order terms of $l\geqslant 3$ and considering the fact that F_s^m is real, we have $a_{22}=a_{2-2}$, $a_{11}=-a_{1-1}$. Suppose the unit vector along the long axis of rod-like molecule is $\mathbf{n}$ (it is not the director of uniaxial nematics). For the macroscopic surface energy $F_s=\langle F_s^m(\theta,\phi)\rangle$ where $\langle\,\rangle$ represents the thermal average, it must be invariant under the reversion of $n_x\rightarrow-n_x$ (i.e. $\phi\rightarrow\pi-\phi$). Therefore it gives $a_{11}=0$ and

$$\begin{aligned}F_s&=a_{20}\left(\frac{5}{4\pi}\right)^{1/2}\langle P_2(\cos\theta)\rangle\\&\quad+a_{22}\left(\frac{15}{32\pi}\right)^{1/2}\left\langle\frac{3}{2}\sin^2\theta\cos 2\phi\right\rangle\\&\equiv a_{20}\left(\frac{5}{4\pi}\right)^{1/2}S+a_{22}\left(\frac{15}{32\pi}\right)^{1/2}P\end{aligned} \qquad (4)$$

where

$$S=\langle P_2(\cos\theta)\rangle,\quad P=\left\langle\frac{3}{2}\sin^2\theta\cos 2\phi\right\rangle.$$

Generally, for a rigid molecule of arbitrary shape, three orthogonal unit vectors $\mathbf{l}$, $\mathbf{m}$, $\mathbf{n}$ are linked to the molecules. In Euler angles, $\mathbf{l}$, $\mathbf{m}$, $\mathbf{n}$ can be expressed as

$$\begin{pmatrix}\mathbf{l}\\ \mathbf{m}\\ \mathbf{n}\end{pmatrix}=U(\alpha,\beta,\gamma)\begin{pmatrix}\mathbf{a}^0\\ \mathbf{b}^0\\ \mathbf{c}^0\end{pmatrix} \qquad (5)$$

where $U(\alpha,\beta,\gamma)$ is given by equation (2). Since the microscopic surface energy is a function of Euler angles, it can be expanded into a series of rotation matrices, i.e.

$$\begin{aligned}F_s^m(\alpha,\beta,\gamma)&=\sum_{j=0}\sum_{m'=-j}^{j}\sum_{m=-j}^{j}A^j_{m'm}D^{(j)}_{m'm}(\alpha,\beta,\gamma)\\&=\sum_{j=0}\sum_{m'=-j}^{j}\sum_{m=-j}^{j}A^j_{m'm}\exp(-\mathrm{i}m'\alpha)\\&\quad\times d^j_{m'm}(\beta)\exp(-\mathrm{i}m\gamma)\end{aligned} \qquad (6)$$

where

$$d^j_{m'm}(\beta) = [(j+m)!(j-m)!(j+m')!(j-m')!]^{1/2} \times \sum_{\kappa} \frac{(-1)^{\kappa}}{(j-m'-\kappa)!(j+m-\kappa)!(\kappa+m'-m)!\kappa!} \times \left(\cos\frac{\beta}{2}\right)^{2j+m-m'-2\kappa}\left(-\sin\frac{\beta}{2}\right)^{m'-m+2\kappa}. \qquad (7)$$

The macroscopic surface energy is the thermal average of $F^{\mathrm{m}}_{\mathrm{s}}(\alpha, \beta, \gamma)$. Neglecting higher order terms of $j \geqslant 3$, we have

$$F_{\mathrm{s}} = \left\langle \sum_{j=0,1,2} \sum_{m'=-j}^{j} \sum_{m=-j}^{j} A^j_{m'm} \times \exp(-\mathrm{i}m'\alpha) d^j_{m'm}(\beta) \exp(-\mathrm{i}m\gamma) \right\rangle. \qquad (8)$$

Under the operation of $\mathbf{a}_0 \to -\mathbf{a}_0$, $\mathbf{b}_0 \to -\mathbf{b}_0$ (i.e. $\alpha \to \alpha + \pi$) and $\mathbf{l} \to -\mathbf{l}$, $\mathbf{m} \to -\mathbf{m}$ (i.e. $\gamma \to \gamma + \pi$), the surface energy should be invariant. Therefore we have all the coefficients of $j = odd$, $m' = odd$, $m = odd$ equal to zero. Since F_{s} is real and invariant under the operation of $\mathbf{l} \to -\mathbf{l}$, $\mathbf{n} \to -\mathbf{n}$ (i.e. $\beta \to \pi - \beta$, $\alpha \to \alpha + \pi$, $\gamma \to \pi - \gamma$), we have

$$A^2_{-20} = A^2_{20}, \quad A^2_{0-2} = A^2_{02}, \quad A^2_{-2-2} = A^2_{22} = A^2_{-22} = A^2_{2-2}. \qquad (9)$$

Therefore F_{s} can be simplified as

$$\begin{aligned} F_{\mathrm{s}} &= A^2_{00}\langle P_2(\cos\beta)\rangle + \frac{\sqrt{6}}{2}A^2_{02}\langle \cos 2\alpha \sin^2\beta\rangle \\ &\quad + \frac{\sqrt{6}}{2}A^2_{20}\langle \cos 2\gamma \sin^2\beta\rangle \\ &\quad + A^2_{22}\langle (\cos^2\beta + 1)\cos 2\alpha \cos 2\gamma \\ &\quad - 2\cos\beta \sin 2\alpha \sin 2\gamma\rangle \\ &= A^2_{00}S + \frac{\sqrt{6}}{3}A^2_{02}P + \frac{\sqrt{6}}{3}A^2_{20}D + \frac{2}{3}A^2_{22}C \qquad (10\,a) \end{aligned}$$

where

$$S = \frac{1}{2}\langle 3n_z^2 - 1\rangle, \quad P = \frac{3}{2}\langle n_x^2 - n_y^2\rangle$$

$$D = \frac{3}{2}\langle l_z^2 - m_z^2\rangle, \quad C = \frac{3}{2}\langle l_x^2 - l_y^2 - m_x^2 + m_y^2\rangle. \qquad (10\,b)$$

The order parameter matrix elements are

$$\begin{aligned} Q^{(\mathrm{d})}_{\alpha\beta} &= A_{ll}\frac{1}{2}\langle 3l_\alpha l_\beta - \delta_{\alpha\beta}\rangle + A_{mm}\frac{1}{2}\langle 3m_\alpha m_\beta - \delta_{\alpha\beta}\rangle \\ &\quad + A_{nn}\frac{1}{2}\langle 3n_\alpha n_\beta - \delta_{\alpha\beta}\rangle \\ &= \frac{3}{2}(A_{nn} - \bar{A})Q^{(0\mathrm{d})}_{\alpha\beta} + \frac{1}{2}(A_{ll} - A_{mm})T^{(\mathrm{d})}_{\alpha\beta} \qquad (11) \end{aligned}$$

where $A_{ii}(i = l, m, n)$ are three diagonal polarizability elements in the $\mathbf{l}$, $\mathbf{m}$, $\mathbf{n}$ system, $\bar{A} = (A_{ll} + A_{mm} + A_{nn})/3$ is its average, $Q^{(0\mathrm{d})}$ and $T^{(\mathrm{d})}$ are the diagonalized matrices where $Q^{(0\mathrm{d})}_{11} = -(S-P)/2$, $Q^{(0\mathrm{d})}_{22} = -(S+P)/2$, $Q^{(0\mathrm{d})}_{33} = S$, $T^{(\mathrm{d})}_{11} = (D-C)/2$, $T^{(\mathrm{d})}_{22} = -(D+C)/2$, $T^{(\mathrm{d})}_{33} = D$; S, P, D, and C are given by equation (10 *b*). Comparing equations (10 *a*) and (11), we have a surface energy as a linear combination of order parameters S, P, D, and C for the arbitrary shaped molecule. When $A_{ll} = A_{mm}$, the order parameter matrix $Q^{(\mathrm{d})} = Q^{(0\mathrm{d})}$ and the system have only two order parameters S and P. When $A_{ll} \neq A_{mm}$, we have two independent order parameter matrices $Q^{(0\mathrm{d})}$ and $T^{(\mathrm{d})}$.

When **a**, **b**, and **c** are rotated away from $\mathbf{a}_0$, $\mathbf{b}_0$, and $\mathbf{c}_0$, in the $\mathbf{a}_0$, $\mathbf{b}_0$, $\mathbf{c}_0$ system, the order parameter matrices become

$$Q^0_{ij} = U_{i\alpha}U_{j\beta}Q^{(0\mathrm{d})}_{\alpha\beta}, \quad T_{ij} = U_{i\alpha}U_{j\beta}T^{(\mathrm{d})}_{\alpha\beta} \qquad (12)$$

where $U_{i\alpha} = \mathbf{e}_i \cdot \mathbf{e}'_\alpha$ are given by equations (1) and (2). Here $\mathbf{e}_1 = \mathbf{a}$, $\mathbf{e}_2 = \mathbf{b}$, $\mathbf{e}_3 = \mathbf{c}$, $\mathbf{e}'_1 = \mathbf{a}_0$, $\mathbf{e}'_2 = \mathbf{b}_0$, $\mathbf{e}'_3 = \mathbf{c}_0$.

Generally, since the surface energy is a function of $Q^{(0)}$ and T, it can be expanded into Taylor series of $Q^0_{\alpha\beta}$ and $T_{\alpha\beta}$. Keeping only the linear terms, and considering the requirement (1), we have

$$F_{\mathrm{s}} = V_{ji}Q^0_{ij} + W_{ji}T_{ij} \qquad (13)$$

where V and W are the second rank tensor coefficients.

Rewriting V as

$$V_{ij} = \frac{1}{2}(V_{ij} + V_{ji}) + \frac{1}{2}(V_{ij} - V_{ji}) \equiv V^{(\mathrm{S})}_{ij} + V^{(\mathrm{A})}_{ij} \qquad (14)$$

where $V^{(\mathrm{S})}$ is a symmetric matrix, $V^{(\mathrm{A})}$ is anti-symmetric matrix. Similarly, we can write $W = W^{(\mathrm{S})} + W^{(\mathrm{A})}$. Substituting V and W into equation (12), we have

$$F_{\mathrm{s}} = V^{(\mathrm{S})}_{ji}Q^{(0)}_{ij} + V^{(\mathrm{A})}_{ji}Q^{(0)}_{ij} + W^{(\mathrm{S})}_{ji}T_{ij} + W^{(\mathrm{A})}_{ji}T_{ij}. \qquad (15)$$

Since $V^{(\mathrm{A})}_{ji}Q^0_{ij} = -V^{(\mathrm{A})}_{ij}Q^0_{ij} = -V^{(\mathrm{A})}_{ij}Q^0_{ji}$, we have $V^{(\mathrm{A})}_{ji}Q^0_{ij} = 0$. Similarly $W^{(\mathrm{A})}_{ji}T_{ij} = 0$. Therefore F_{s} can be written as

$$F_{\mathrm{s}} = V^{(\mathrm{S})}_{ji}Q^0_{ij} + W^{(\mathrm{S})}_{ji}T_{ij}. \qquad (16)$$

That means we can always choose two symmetric matrices as coefficient matrices. Dropping the superscripts and bearing in mind that V and W are symmetric, we can simply write $F_s = V_{ji}Q^0_{ij} + W_{ji}T_{ij}$.

Subtracting

$$(V_{11} + V_{22} + V_{33})\delta_{ij}Q^0_{ij}/3 + (W_{11} + W_{22} + W_{33})\delta_{ij}T_{ij}/3 = 0$$

from equation (16), we have

$$\begin{aligned} F_s &= \left(V_{ij} - \frac{1}{3}\sum_k V_{kk}\delta_{ij}\right)Q^0_{ij} + \left(W_{ij} - \frac{1}{3}\sum_k W_k\delta_{ij}\right)T_{ji} \\ &\equiv v_{ij}Q^0_{ij} + w_{ij}T_{ji} \end{aligned} \tag{17}$$

where v and w are traceless tensors. Therefore there are only five independent coefficients for each matrix.

Substituting equation (12) into (17) we have

$$F_s = v_{ij}U_{i\alpha}U_{j\beta}Q^{(0d)}_{\alpha\beta} + w_{ij}U_{i\alpha}U_{j\beta}T^{(d)}_{\alpha\beta}. \tag{18}$$

Since F_s is a function of α, β, γ and is invariant under the operation of $\gamma \to \gamma + \pi$ (i.e. $\mathbf{a} \to -\mathbf{a}$ and $\mathbf{b} \to -\mathbf{b}$), $\beta \to \pi - \beta$, $\alpha \to \alpha + \pi$, $\gamma \to \pi - \gamma$ (i.e. $\mathbf{a} \to -\mathbf{a}$, $\mathbf{c} \to -\mathbf{c}$), we have the off-diagonal elements of v and w equal to zero. Therefore there will be only two independent elements for v and two for w.

Note that when **a**, **b**, and **c** coincide with $\mathbf{a}_0$, $\mathbf{b}_0$, and $\mathbf{c}_0$, respectively, the surface energy is linearly proportional to the order parameters S, P, D, and C, as shown in equation (10 *a*); we found that $\mathbf{a}_0$, $\mathbf{b}_0$, and $\mathbf{c}_0$ are the three eigenvectors in which the symmetric matrices v and w are diagonalized.

3. The second form of surface energy

If we do not consider the influence of order parameters, we can form four independent rotational invariants:

$$b_{0i}b_{0j}b_ib_j, \quad b_{0i}b_{0j}c_ic_j, \quad c_{0i}c_{0j}b_ib_j, \quad c_{0i}c_{0j}c_ic_j. \tag{19}$$

Using $a_ia_j = \delta_{ij} - b_ib_j - c_ic_j$, $a_{0i}a_{0j} = \delta_{ij} - b_{0i}b_{0j} - c_{0i}c_{0j}$, other rotational invariants such as $a_{0i}a_{0j}a_ia_j$, $a_{0i}a_{0j}b_ib_j$, $a_{0i}a_{0j}c_ic_j$, $b_{0i}b_{0j}a_ia_j$, $c_{0i}c_{0j}a_ia_j$ can all be expressed as the linear combination of the four independent invariants listed in expression (19). Obviously, cross terms such as $b_{0i}c_{0j}b_ic_j$ do not satisfy the requirement (2) and therefore should be disregarded.

$$F^{(2)}_s = g_1(\mathbf{b}\cdot\mathbf{b}_0)^2 + g_2(\mathbf{c}\cdot\mathbf{b}_0)^2 + g_3(\mathbf{b}\cdot\mathbf{c}_0)^2 + g_4(\mathbf{c}\cdot\mathbf{c}_0)^2 \tag{20}$$

In order to compare this form of surface energy with that in § 2, we write F_s as

$$\begin{aligned} F^{(1)}_s = {} & 3(v_{11}Q^0_{11} + w_{11}T_{11}) + [(v_{22} - v_{11})(Q^0_{22} - Q^0_{11}) \\ & + (w_{22} - w_{11})(T_{22} - T_{11})](\mathbf{b}\cdot\mathbf{b}_0)^2 \\ & + [(v_{22} - v_{11})(Q^0_{33} - Q^0_{11}) \\ & + (w_{22} - w_{11})(T_{33} - T_{11})](\mathbf{c}\cdot\mathbf{b}_0)^2 \\ & + [(v_{33} - v_{11})(Q^0_{22} - Q^0_{11}) \\ & + (w_{33} - w_{11})(T_{22} - T_{11})](\mathbf{b}\cdot\mathbf{c}_0)^2 \\ & + [(v_{33} - v_{11})(Q^0_{33} - Q^0_{11}) \\ & + (w_{33} - w_{11})(T_{33} - T_{11})](\mathbf{c}\cdot\mathbf{c}_0)^2. \end{aligned} \tag{21}$$

Here the superscript d in the Q^0 and T matrix is dropped. Comparing equations (20) and (21), we find that if

$$\begin{aligned} g_1 &= (v_{22} - v_{11})(Q^0_{22} - Q^0_{11}) + (w_{22} - w_{11})(T_{22} - T_{11}) \\ g_2 &= (v_{22} - v_{11})(Q^0_{33} - Q^0_{11}) + (w_{22} - w_{11})(T_{33} - T_{11}) \\ g_3 &= (v_{33} - v_{11})(Q^0_{22} - Q^0_{11}) + (w_{33} - w_{11})(T_{22} - T_{11}) \\ g_4 &= (v_{33} - v_{11})(Q^0_{33} - Q^0_{11}) + (w_{33} - w_{11})(T_{33} - T_{11}) \end{aligned} \tag{22}$$

$F^{(1)}_s$ and $F^{(2)}_s$ will differ only by a constant. Notice that in both $F^{(1)}_s$ and $F^{(2)}_s$, there are four independent coefficients.

The surface energy can also be derived by expanding it into a series of rotation matrices $D^j_{m'm}(\alpha\beta\gamma)$ given by equations (6) and (7)

$$F_s = \sum_{j=0}\sum_{m'=-j}^{j}\sum_{m=-j}^{j} B^j_{m'm}D^j_{m'm}(\alpha\beta\gamma). \tag{23}$$

Neglecting all the higher terms of $j \geqslant 3$, we have the expansion

$$\begin{aligned} F_s = {} & \sum_{j=0,1,2}\sum_{m'=-j}^{j}\sum_{m=-j}^{j} B^j_{m'm} \\ & \times \exp(-\mathrm{i}m'\gamma)d^j_{m'm}(\beta)\exp(-\mathrm{i}m\alpha). \end{aligned} \tag{24}$$

Under the operation of $\alpha \to \alpha + \pi$ (i.e. $\mathbf{a} \to -\mathbf{a}$, $\mathbf{b} \to -\mathbf{b}$) and $\gamma \to \gamma + \pi$, (i.e. $\mathbf{a}_0 \to -\mathbf{a}_0$, $\mathbf{b}_0 \to -\mathbf{b}_0$), the surface energy should be invariant. Therefore we have all the coffficents of $j = odd$, $m' = odd$, $m = odd$ equal to zero.

Since F_s is real and invariant under operation of $\beta \to \pi - \beta$, $\alpha \to \alpha + \pi$, $\gamma \to \pi - \gamma$, (i.e. $\mathbf{a}_0 \to -\mathbf{a}_0$, $\mathbf{c}_0 \to -\mathbf{c}_0$), we have

$$\begin{aligned} & B^2_{-20} = B^2_{20}, \quad B^2_{0-2} = B^2_{02}, \\ & B^2_{-2-2} = B^2_{22} = B^2_{-22} = B^2_{2-2}. \end{aligned} \tag{25}$$

Therefore F_s is simplified as

$$
\begin{aligned}
F_s = {} & B_{00}^2 P_2(\cos\beta) + \frac{\sqrt{6}}{2} B_{02}^2 \cos 2\alpha \sin^2\beta \\
& + \frac{\sqrt{6}}{2} B_{20}^2 \cos 2\gamma \sin^2\beta \\
& + B_{22}^2 [(\cos^2\beta + 1)\cos 2\alpha \cos 2\gamma \\
& - 2\cos\beta \sin 2\alpha \sin 2\gamma]. \qquad (26)
\end{aligned}
$$

Meanwhile, according to equations (2) and (18), the surface energy in terms of Euler angles is

$$
\begin{aligned}
F_s = {} & \sum_{i,j} (v_{ii} U_{ij}^2 Q_{jj}^{(0d)} + w_{ii} U_{ij}^2 T_{jj}^{(d)}) \\
= {} & \frac{3}{2}(v_{33} S + w_{33} D) P_2(\cos\beta) \\
& + \frac{3}{4}[S(v_{11} - v_{22}) + D(w_{11} - w_{22})] \cos 2\gamma \sin^2\beta \\
& - \frac{3}{4}(P v_{33} + C w_{33}) \sin^2\beta \cos 2\alpha \\
& + \frac{1}{4}[P(v_{11} - v_{22}) + C(w_{11} - w_{22})][(\cos^2\beta + 1) \\
& \times \cos 2\alpha \cos 2\gamma - 2\cos\beta \sin 2\alpha \sin 2\gamma]. \qquad (27)
\end{aligned}
$$

Comparing equation (26) with (27), we have

$$
\begin{aligned}
B_{00}^2 &= \frac{3}{2}(v_{33} S + w_{33} D), \\
B_{02}^2 &= \frac{\sqrt{6}}{4}[S(v_{11} - v_{22}) + D(w_{11} - w_{22})] \\
B_{20}^2 &= -\frac{\sqrt{6}}{4}(P v_{33} + C w_{33}), \qquad (28) \\
B_{22}^2 &= \frac{1}{4}[P(v_{11} - v_{22}) + C(w_{11} - w_{22})].
\end{aligned}
$$

When $\mathbf{a} = \mathbf{a}^0$, $\mathbf{b} = \mathbf{b}^0$, $\mathbf{c} = \mathbf{c}^0$ and for rod-like molecules, equation (27) gives

$$
F_s = \frac{3}{2} v_{33} S + \frac{1}{2}(v_{11} - v_{22}) P. \qquad (29)
$$

If $v_{11} = v_{22}$, $F_s = 3 v_{33} S/2$. It has been suggested that, for an unrubbed polymer coated substrate with no preferred direction in the plane of the surface, the molecules of the nematic liquid crystal may lie perpendicular to the substrate normal, resulting in a uniaxial surface layer with negative orientation order at temperatures above the bulk nematic–isotropic phase transition [5]. This corresponds to the situation where $v_{33} > 0$. This type of ordering leads to the possibility of phase transition from uniaxial to biaxial nematics near the surface as the temperature decreases. If $v_{22} - v_{11} \neq 0$, the surface provides not only a mean field to align molecules perpendicular to the surface normal, but also a biaxial field to produce biaxiality.

Consider a liquid crystal confined between two parallel plates where the upper and lower plates are at $z = 0, d$. Suppose the easy axis of $\mathbf{c}^0$ is along the film normal and $\mathbf{a}^0$, $\mathbf{b}^0$ are in the plane of the film. When the film thickness approaches infinity, the mid-plane directors will not be influenced by the boundary conditions. Minimizing the bulk elastic free energy in Landau–de Gennes form and the surface energy given by equation (29), we get the Euler–Lagrange equations for the order parameters $S(z)$ and $P(z)$ where z is the coordinate normal to the plane of the film. Since the equations do not have analytic solutions, we use trial functions $S(z; \xi, \eta)$, $P(z; \xi, \eta)$ to obtain the minimum free energy where ξ, η are the parameters to be optimized. The result shows that the order parameter at the surface $P(0)$ approaches $-3S(0)(S(0) < 0)$ for $v_{11} - v_{22} < 0$ and $v_{33} > 0$, when either temperature decrease or the biaxial part of the surface energy coefficient $|v_{11} - v_{22}|$ increase. For details of discussion and calculation see [9].

4. Possible experimental measurements of anchoring strengths

When the rotation angles $\phi_a \ll 1$, $\phi_b \ll 1$, $\phi_c \ll 1$, we have

$$
\begin{aligned}
F_s^{(1)} = {} & v_{11} Q_{11}^0 + v_{22} Q_{22}^0 + v_{33} Q_{33}^0 + w_{11} T_{11} + w_{22} T_{22} \\
& + w_{33} T_{33} - [(v_{22} - v_{33})(Q_{22}^0 - Q_{33}^0) \\
& + (w_{22} - w_{33})(T_{22} - T_{33})]\phi_a^2 \\
& - [(v_{33} - v_{11})(Q_{33}^0 - Q_{11}^0) \\
& + (w_{33} - w_{11})(T_{33} - T_{11})]\phi_b^2 \\
& - [(v_{11} - v_{22})(Q_{11}^0 - Q_{22}^0) \\
& + (w_{11} - w_{22})(T_{11} - T_{22})]\phi_c^2. \qquad (30)
\end{aligned}
$$

In the small angle approximation, neglecting a constant, equation (30) can be derived in the following simple way. Suppose the rotation torque is linearly proportional to the angular displacement vector, i.e. $\mathbf{L} = W_a \phi_a \mathbf{a}^0 + W_b \phi_b \mathbf{b}^0 + W_c \phi_c \mathbf{c}^0$: the energy stored in the final configuration of ϕ_a, ϕ_b and ϕ_c is

$$F = \int \mathbf{L} \cdot (\mathrm{d}\phi_a \mathbf{a}_0 + \mathrm{d}\phi_b \mathbf{b}_0 + \mathrm{d}\phi_c \mathbf{c}_0)$$

$$= \frac{1}{2} W_a \phi_a^2 + \frac{1}{2} W_b \phi_b^2 + \frac{1}{2} W_c \phi_c^2. \quad (31)$$

This form is similar to that of Rapini–Papoula and therefore we call W_a, W_b and W_c the biaxial anchoring strengths. The relation between W_a, W_b, W_c and v_{ii}, w_{ii}, Q_{ii}^0, T_{ii} ($i = 1, 2, 3$) can be easily obtained by comparing equations (30) and (31).

Consider a biaxial nematic confined between two parallel plates at $z = \pm d$. At the upper and lower boundaries, assume the easy axes $\mathbf{a}_0 = \mathbf{x}$, $\mathbf{b}_0 = \mathbf{y}$, $\mathbf{c}_0 = \mathbf{z}$. When a magnetic field $\mathbf{H} = H\mathbf{x}$ is applied and exceeds a certain threshold value, there will be a Fréedericksz transition. According to Saupe [8], the elastic energy density of biaxial nematics is

$$F_{\mathrm{e}} = \frac{1}{2} \sum_a \{K_{aa}[\mathbf{c} \cdot (\mathbf{a} \cdot \nabla \mathbf{b})]^2 + K_{ab}[\mathbf{b} \cdot (\mathbf{a} \cdot \nabla \mathbf{a})]^2$$

$$+ K_{ac}[\mathbf{c} \cdot (\mathbf{a} \cdot \nabla \mathbf{a})]^2 + 2C_{ab}(\mathbf{a} \times \nabla \times \mathbf{a}) \cdot (\mathbf{b} \times \nabla \times \mathbf{b})$$

$$+ 2K_{0a} \nabla \cdot (\mathbf{a} \cdot \nabla \mathbf{a} - \mathbf{a} \nabla \cdot \mathbf{a})\} \quad (32)$$

where the summation over a has three terms corresponding to the cyclic permutation of a, b, and c. For example, $\Sigma_a f(a, b, c) = f(a, b, c) + f(b, c, a) + f(c, a, b)$. K_{aa}, K_{bb}, K_{cc} terms describe the directors **b** and **c**, **c** and **a**, **a** and **b** rotating around **a**, **b** and **c** respectively. K_{ab}, K_{ac}, K_{bc}, K_{ba}, K_{ca} and K_{cb} terms describe six simple distortion patterns of bend and splay. C_{ab}, C_{bc}, C_{ca} are the coupling terms with K_{0a}, K_{0b}, K_{0c} contribute to the surface energy.

The external field energy density is

$$F_{\mathrm{ex}} = -\frac{1}{2} \sum_a \chi_{aa} (\mathbf{H} \cdot \mathbf{a})^2 \quad (33)$$

where χ_{aa}, χ_{bb}, χ_{cc} are the three diagonal element of magnetic susceptibility. For the sake of definiteness, we assume $\chi_{cc} > \chi_{bb} > \chi_{aa}$. The surface energy density at small angle approximation is given by equation (31). Therefore the total energy is

$$F = \int (F_{\mathrm{e}} + F_{\mathrm{ex}}) \mathrm{d}r + \int F_{\mathrm{s}} \mathrm{d}S. \quad (34)$$

At the vicinity of the lowest threshold field of Fréedericksz transition, the Euler–Lagrange equation is linearized as

$$\begin{aligned} K_{bc}\phi_{azz} + \Delta\chi_{cb} H^2 \phi_a &= 0 \\ K_{bb}\phi_{bzz} &= 0 \\ K_{ba}\phi_{czz} - \Delta\chi_{ba} H^2 \phi_c &= 0 \\ (\pm K_{bc}\phi_{az} + W_a \phi_a)_{z=\pm d} &= 0 \\ (\pm K_{bb}\phi_{bz} + W_b \phi_b)_{z=\pm d} &= 0 \\ (\pm K_{ba}\phi_{cz} + W_c \phi_c)_{z=\pm d} &= 0. \end{aligned} \quad (35)$$

Solving the equations, we obtain a transcendental equation from which the threshold field for the Fréedericksz transition can be found:

$$h \tan h = \frac{W_a d}{K_{bc}} \quad (36)$$

where $h = (\Delta\chi_{cb}/K_{bc})^{1/2} Hd$, $\Delta\chi_{cb} \equiv \chi_{cc} - \chi_{bb}$. If the elastic constant K_{bc} can be measured (for the possible experimental measurements of fifteen elastic constants of biaxial nematics, see [10]), the value of W_a can be determined if h_{F}, the threshold field for Fréedericksz transition is measured.

Similarly, consider the geometry where $\mathbf{a}_0 = -\mathbf{y}$, $\mathbf{b}_0 = -\mathbf{z}$, $\mathbf{c}_0 = -\mathbf{x}$, $\mathbf{H} = H\mathbf{y}$. Then the differential equations and boundary conditions are

$$\begin{aligned} K_{ba}\phi_{czz} + \Delta\chi_{ba} H^2 \phi_c &= 0 \\ K_{bb}\phi_{bzz} + \Delta\chi_{ca} H^2 \phi_b &= 0 \\ (\pm K_{ba}\phi_{cz} + W_c \phi_z)_{z=\pm d} &= 0 \\ (\pm K_{bb}\phi_{bz} + W_b \phi_b)_{z=\pm d} &= 0. \end{aligned} \quad (37)$$

The transcendental equations are

$$h_1 \tan h_1 = \frac{W_c d}{K_{ba}}, \quad h_2 \tan h_2 = \frac{W_b d}{K_{bb}} \quad (38)$$

where $h_1 = (\Delta\chi_{ba}/K_{ba})^{1/2} Hd$, $h_2 = (\Delta\chi_{ca}/K_{bb})^{1/2} Hd$, $\Delta\chi_{ba} \equiv \chi_{bb} - \chi_{aa}$, $\Delta\chi_{ca} = \chi_{cc} - \chi_{aa}$. If K_{ba}, K_{bb}, $\Delta\chi_{ba}$ and $\Delta\chi_{ca}$ are known, then by measuring the threshold field of the Fréedericksz transition, we can determine either W_b or W_c, depending on which threshold field is lower.

5. Summary

In the present paper, we derive a form of surface energy for biaxial nematics. The method is similar to those used in deriving Landau elastic energy for bulk nematics and Frank elastic energy. The same surface energy can also be derived by rotation matrix expansion. The result shows that there are four independent coefficients in the surface energy. One application of surface energy when each of the three directors is along its corresponding easy axis is briefly mentioned, and possible experimental measurements of three linear combinations of four coefficients, i.e. the anchoring strengths in small angle approximation, is explored.

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