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Anchoring energy for the nematic liquid crystal–Langmuir Blodgett film interface†

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We analyse the effect of a Langmuir–Blodgett (LB) multilayer on the surface properties of a nematic liquid crystal (NLC). We show that the easy axis of the LB–NLC interface coincides with that of the LB–solid surface interface. On the contrary, the effective anchoring energy of the LB–NLC interface is lower than that associated with the LB–solid substrate interface. We show in a first approximation that the anchoring energy characterizing the NLC may be separated into three contributions: one connected with the interaction between the LB film and the solid substrate, one due to the direct LB–NLC interaction and the other one having an elastic origin. Nevertheless, to be more precise, one has to consider also the term associated with the interaction energy between the NLC and the substrate, which is screened by the LB film. The elastic contribution is of the order of the elastic constant of the LB film over the thickness of the multilayer. This quantity is estimated to be of the order of 10^{-2}–10^{-1} erg cm^{-2}, as experimentally observed. Possible extensions of our model are also discussed.

1. Introduction

Nematic liquid crystals (NLC) present a quadrupolar order around the 'director' **n** ($\mathbf{n}\cdot\mathbf{n}=1$). The director is defined by the statistical average of the molecular major axis direction **a**. From the crystallographic point of view, NLCs behave like uniaxial crystals, whose optical axis coincides with **n** [1,2]. The orientation of **n** in a NLC sample depends on the applied external field and on the surface treatment [3]. In this paper, we are mainly interested in the NLC orientation induced by a solid substrate covered by a multilayer Langmuir–Blodgett (LB) film. In previous papers we have analysed different aspects of this problem. In [4], we have shown that a spatial variation of the elastic constant is equivalent to an 'intrinsic' anchoring energy. The extrapolation length connected to this intrinsic anchoring energy is of the order of the thickness over which the spatial variation of the elastic constant takes place. In [5], we have evaluated the profiles of the elastic constants and the associated surface energy by means of a simple molecular model for the intermolecular interaction energy among the molecules forming the NLC. The analysis reported in [4,5] concerns a NLC in contact with a vacuum. Hence only the intrinsic part of the anchoring energy is considered. The effect of a monolayer of LB film on the NLC orientation has been analysed in [6], by using the model proposed by Hiltrop and Stegemeyer [7]. In [6], by supposing that the steric interaction of LB–NLC is very strong and neglecting the elastic deformations, we have shown that the NLC orientation depends on the surface molecular density of the LB film.

The analysis of [6] has been generalized in [8], where, besides the steric interaction LB–NLC, the dispersion interaction between the NLC and the LB film and between the NLC and the solid substrate have also been considered. In this framework, it is possible to obtain interesting phase diagrams of the NLC orientation versus the LB surface density. This is discussed in detail in [8]. In a recent paper, the model proposed in [8] has been applied to analyse the influence of an amorphous polymer on the NLC orientation [9].

In the present paper we want to consider the effect of a multilayer LB film on the NLC orientation. This has been partially done in [6] where the LB and NLC

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orientations are considered as position independent. This hypothesis works well only when the number of LB layers, n, is very small (~ 1–3). For $n \sim 5$, the LB multilayer has to be considered as a smectic liquid crystal characterized by a well-defined splay elastic constant. In this situation, the system LB–NLC is equivalent to a junction of two different liquid crystals. This system may be analysed by means of the formalism developed in [4]. In particular, it will be possible to connect the effective anchoring energy with the number of LB layers.

Our paper is organized as follows. In § 2, the physical system LB–NLC is described and the basic hypotheses are presented. The mathematical problem is discussed in § 3 and § 4. The actual physical system LB–NLC is analysed in § 5. Finally the most important results of our paper are discussed in § 6.

2. Physical system and basic hypotheses

We assume that the system LB–NLC may be considered as a junction of two different NLC, called in the following NLC1 (LB), NLC2 (NLC). In the one constant approximation, the elastic constant changes with z, the coordinate normal to the solid substrate (at $z=0$), as shown in figure 1. In that figure l is the thickness of the LB multilayer and d the thickness of the NLC sample. Consequently $K_1 = K(0 \leqslant z \leqslant l)$ is the splay elastic constant of the LB multilayer and $K_2 = K(l \leqslant z \leqslant d)$ is the usual elastic constant of the NLC. The easy direction on the surface at $z=0$ is assumed to be homeotropic, whereas the one at $z=d$ is supposed to be at an angle Φ with respect to the z axis. The NLC and LB deformations are supposed to be in the plane defined by the z axis and the *easy axis* on the surface at $z=d$. The tilt angle made by the NLC director or the LB molecular orientation with the z axis is indicated by $\phi_1(z) = \phi$ $(0 \leqslant z \leqslant l)$ and by $\phi_2(z) = \phi(l \leqslant z \leqslant d)$. The anchoring

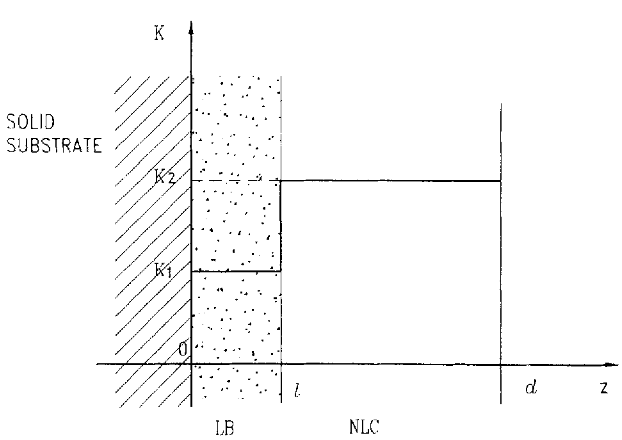

Figure 1 The system LB multilayer–NLC. K_1 and K_2 are the splay elastic constants for the LB and NLC, respectively; l is the thickness of the LB multilayer.

energy on the surface at $z=d$ is assumed to be strong. For what concerns the surface at $z=0$, the cases of strong and weak anchoring are considered separately. In this framework the total energy per unit surface is given by

$$F = \int_0^l f_1(\phi_1, \phi_1')\,dz + \int_l^d f_2(\phi_2, \phi_2')\,dz + g[\phi_1(0)] + H[\phi_1(l), \phi_2(l)], \tag{1}$$

where $X' = dX/dz$. In (1) f_i $(i=1,2)$ are the bulk elastic energy densities in NLC1 and NLC2, $g[\phi_1(0)]$ takes into account the direct interaction between the LB film and the substrate and $H(\phi_1(l), \phi_2(l))$ represents the LB–NLC interaction at the interface at $z=l$. This contribution is expected depending only on the relative LB–NLC orientation. Hence, it is of the kind

$$H(\phi_1(l), \phi_2(l)) = H(\phi_1(l) - \phi_2(l)) \tag{2}$$

In the hypothesis in which the molecules are nematic-like and the LB–NLC interaction tends to orient the NLC molecules parallel to the LB film, as we will suppose in the following, H reaches its minimal value for $\phi_1(l) = \phi_2(l)$.

For the sake of simplicity in equation (1), we have neglected the elastic contributions connected to the splay–bend elastic constants [3]. In the one-constant approximation and for a small variation from the homeotropic orientation on the surface at $z=0$, we have

$$f_1 = \tfrac{1}{2}K_1\phi_1'^2, \qquad f_2 = \tfrac{1}{2}K_2\phi_2'^2, \tag{3}$$

for the bulk elastic energies, and

$$g = \tfrac{1}{2}W\phi_1^2(0), \qquad H = \tfrac{1}{2}\beta[\phi_2(l) - \phi_1(l)]^2, \tag{4}$$

for the surface energy densities. In equation (4), W is the anchoring energy and $\beta > 0$ the LB–NLC interface energy. Note that for $H \to \infty$, or $\beta \to \infty$, $\phi_1(l) = \phi_2(l)$ as in the model of Hiltrop and Stegemeyer [7]. By substituting equation (3) and (4) into equation (1), one obtains for F the expression

$$F = \int_0^l \tfrac{1}{2}K_1\phi_1'^2\,dz + \int_l^d \tfrac{1}{2}K_2\phi_2'^2\,dz + \tfrac{1}{2}W\phi_1^2(0) + \tfrac{1}{2}\beta[\phi_2(l) - \phi_1(l)]^2. \tag{5}$$

Equations (1) and (5) hold in the hypotheses in which there are no other contributions to F. This means that the effect of the interface LB–NLC is described by means of a spatial variation of the elastic constant and of an interface energy $H(\phi_1(l), \phi_2(l))$.

3. Mathematical model and variational problem

The LB and NLC tilt angle profiles are the ones minimizing equation (1). Simple calculations give for the first variation of F, given by (1), the expression

$$\delta F=\int_0^l\left[\frac{\partial f_1}{\partial\phi_1}-\frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial f_1}{\partial\phi_1'}\right]\delta\phi_1\,\mathrm{d}z+\int_l^d\left[\frac{\partial f_2}{\partial\phi_2}-\frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial f_2}{\partial\phi_2'}\right]\delta\phi_2\,\mathrm{d}z+\left[-\frac{\partial f_1}{\partial\phi_1'}+\frac{\partial g}{\partial\phi_1}\right]_{z=0}\delta\phi_1(0)+\left[\frac{\partial f_2}{\partial\phi_2'}\right]_{z=d}\delta\phi_2(d)+\left[\left(\frac{\partial f_1}{\partial\phi_1'}+\frac{\partial H}{\partial\phi_1}\right)\delta\phi_1+\left(-\frac{\partial f_2}{\partial\phi_2'}+\frac{\partial H}{\partial\phi_2}\right)\delta\phi_2\right]_{z=l},\qquad(6)$$

where $\delta\phi_1$ and $\delta\phi_2$ are an arbitrary function of the C_1 class. Since for $z=d$ the anchoring is supposedly strong, $\delta\phi_2(d)=0$. By taking into account the strong anchoring condition at $z=d$, from equation (6) we obtain

$$\delta F=\int_0^l\left[\frac{\partial f_1}{\partial\phi_1}-\frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial f_1}{\partial\phi_1'}\right]\delta\phi_1\,\mathrm{d}z+\int_l^d\left[\frac{\partial f_2}{\partial\phi_2}-\frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial f_2}{\partial\phi_2'}\right]\delta\phi_2\,\mathrm{d}z+\left[-\frac{\partial f_1}{\partial\phi_1'}+\frac{\partial g}{\partial\phi_1}\right]_{z=0}\delta\phi_1(0)+\left[\left(\frac{\partial f_1}{\partial\phi_1'}+\frac{\partial H}{\partial\phi_1}\right)\delta\phi_1\right]_{z=l}+\left[\left(-\frac{\partial f_2}{\partial\phi_2'}+\frac{\partial H}{\partial\phi_2}\right)\delta\phi_2\right]_{z=l}.\qquad(7)$$

Since the actual $\phi(z)$ profile has to minimize F, $\delta F=0\ \forall\,\delta\phi_i(z)\in C_1$, $i=1,2$. It follows that $\phi_1(z)$ and $\phi_2(z)$ are solutions of the differential equations

$$\frac{\partial f_1}{\partial\phi_1}-\frac{\mathrm{d}}{\mathrm{d}z}\left[\frac{\partial f_1}{\partial\phi_1'}\right]=0,\qquad 0\leqslant z\leqslant l,\qquad(8)$$

$$\frac{\partial f_2}{\partial\phi_2}-\frac{\mathrm{d}}{\mathrm{d}z}\left[\frac{\partial f_2}{\partial\phi_2'}\right]=0,\qquad l\leqslant z\leqslant d,\qquad(9)$$

and satisfy the boundary conditions

$$-\frac{\partial f_1}{\partial\phi_1'}+\frac{\partial g}{\partial\phi_1}=0,\qquad z=0,\qquad(10)$$

$$\frac{\partial f_1}{\partial\phi_1'}+\frac{\partial H}{\partial\phi_1}=0,\qquad z=l,\qquad(11)$$

$$-\frac{\partial f_2}{\partial\phi_2'}+\frac{\partial H}{\partial\phi_2}=0,\qquad z=l,\qquad(12)$$

$$\phi_2(d)=\Phi,\qquad z=d.\qquad(13)$$

As underlined before, $H(\phi_1(l),\phi_2(l))=H(\phi_1(l)-\phi_2(l))$. Consequently

$$\frac{\partial H}{\partial\phi_1(l)}=-\frac{\partial H}{\partial\phi_2(l)}.$$

Hence, from equations (10) and (11) it follows that

$$\frac{\partial f_1}{\partial\phi_1'}-\frac{\partial f_2}{\partial\phi_2'}=0,\qquad z=l.$$

This equation states that the torque density is continuous at the LB–NLC interface. This conclusion holds even in the case in which $\phi(z)$ presents a discontinuity point for $z=l$. In the event in which equations (3) and (4) hold, the previous equations (8) and (9) and the boundary conditions (10)–(13) become

$$\phi_1''=0,\qquad 0\leqslant z\leqslant l,\qquad(14)$$

$$\phi_2''=0,\qquad l\leqslant z\leqslant d,\qquad(15)$$

and

$$K_1\phi_1'=W\phi_1,\qquad z=0,\qquad(16)$$

$$K_1\phi_1'(l)+\beta(\phi_1(l)-\phi_2(l))=0,\qquad z=l,\qquad(17)$$

$$-K_2\phi_2'(l)+\beta(\phi_2(l)-\phi_1(l))=0,\qquad z=l,\qquad(18)$$

$$\phi_1(d)=\Phi,\qquad z=d.\qquad(19)$$

All the results reported above have been deduced by assuming F is given by equation (1). Of course, a direct interaction between the NLC and the solid substrate may also exist. However, in the case in which the multilayer is thick enough ($n\geqslant 5$), this contribution is usually negligible.

4. Solution of the variational problem

In the simple case in which equations (14) and (15) and equations (16)–(19) hold, the tilt angle profiles are given by

$$\phi_1(z)=\phi_1(0)+\frac{\phi_1(l)-\phi_1(0)}{l}z,\qquad(20)$$

$$\phi_2(z)=\phi_2(l)+\frac{\Phi-\phi_2(l)}{d-l}(z-l),\qquad(21)$$

where $\phi_1(0)$ is the surface tilt angle at the LB–solid substrate interface, $\phi_1(l)$ and $\phi_2(l)$ are the tilt angles at the LB–NLC interface, see figure 2. As follows from (16)–(19), these quantities are given by

$$\phi_1(0)=\frac{\Phi}{1+W[l/K_1+(d-l)/K_2]+(W/\beta)},\qquad(22)$$

$$\phi_1(l)=\frac{1+W(l/K_1)}{1+W[l/K_1+(d-l)/K_2]+(W/\beta)}\Phi,\qquad(23)$$

$$\phi_2(l)=\frac{\phi_1(l)}{1+K_2/[\beta(d-l)]}+\frac{\Phi}{1+[\beta(d-l)]/K_2}.\qquad(24)$$

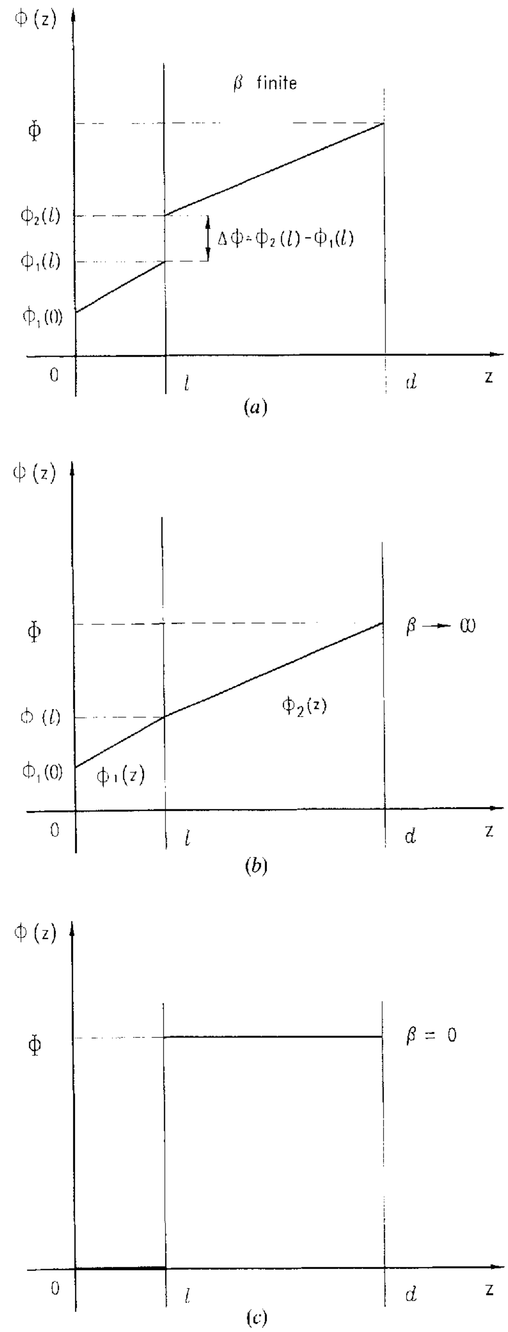

Figure 2 Tilt angle profile in the LB multilayer–NLC system. It is supposed that the LB–solid substrate interface is characterized by an easy axis normal to the solid substrate (homeotropic) and by weak anchoring. The interface at $z=d$ is supposed to be characterized by a tilted easy axis and strong anchoring. (*a*) weak LB–NLC interaction ($\beta \sim W$); (*b*) strong LB–NLC interaction ($\beta \gg W$). (*c*) negligible LB–NLC interaction ($\beta \sim 0$). Note that for all β-values the torque is continuous for $z=l$: $K_1\phi_1'(l)=K_2\phi_2'(l)$.

From equations (23) and (24) we deduce that the $\phi(z)$ profile minimizing the total energy per unit area, given by equation (1) or (5), presents a discontinuity point at $z=l$. The discontinuity of $\phi(z)$ for $z=l$ is given by

$$\Delta\phi=\phi_2(l)-\phi_1(l)=\frac{\Phi-\phi_1(l)}{1+(\beta/K_2)(d-l)}. \tag{25}$$

It is interesting to consider the two limiting cases in which $\beta\to\infty$ and $\beta\to 0$. The first situation corresponds to the Hiltrop–Stegemeyer model, where the LB–NLC interaction is supposed to be very strong. The second one is connected to the case in which the LB–NLC interaction is negligible. Let us consider first the case $\beta\to\infty$. In this event equations (22)–(25) write

$$\phi_1(0)=\frac{\Phi}{1+W[l/K_1+(d-l)/K_2]}, \tag{26}$$

$$\phi_1(l)=\phi_2(l)=\frac{1+W(l/K_1)}{1+W[l/K_1+(d-l)/K_2]}\,\Phi, \tag{27}$$

and hence

$$\Delta\phi(l)=0. \tag{28}$$

This means that in this approximation, $\phi(z)$ is a continuous function of z (see figure 2(*b*)). As follows from equations (22)–(25), this works well when $\beta\gg K_2/(d-l)$. Since usually $W\gg K_2/d$, the Hiltrop–Stegemeyer approximation holds for $\beta\gg W$. In the other case in which $\beta\to 0$, equations(22)–(25) become

$$\phi_1(0)=0, \qquad \phi_1(l)=0, \qquad \phi_2(l)=\Phi, \tag{29}$$

and hence

$$\Delta\phi=\Phi. \tag{30}$$

As is easy to understand, in this situation the sample is undistorted for $0\leqslant z\leqslant l$ and for $l\leqslant z\leqslant d$. The tilt angle has a discontinuity equal to Φ for $z=l$ (see figure 2(*c*)). From the above reported discussion it follows that $\phi_2(l)$ plays the role of the surface tilt angle ϕ_s of the NLC at the interface LB–NLC (see figure 3). By supposing that the LB–NLC interface is characterized by an easy axis normal to the interface, it is possible to define an equivalent anchoring energy W_e. To do this we have just to consider the case in which the NLC total energy is given by

$$F=\int_l^d \tfrac{1}{2}K_2\phi_2'^2\,dz+\tfrac{1}{2}W_e\phi_s^2, \tag{31}$$

where W_e is the 'equivalent' anchoring energy we are looking for.

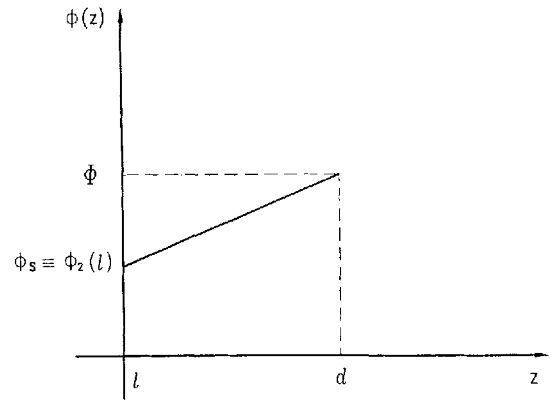

Figure 3 The equivalent NLC tilt angle profile to deduce the anchoring energy for the LB–NLC interface.

By minimizing equation (31), we find that $\phi_2(z)$ is given by

$$\phi_2(z) = \phi_s + \frac{\Phi - \phi_s}{d - l} z, \tag{32}$$

where the 'surface' tilt angle ϕ_s is found to be

$$\phi_s = \frac{K_2/(d-l)}{W_e + K_2/(d-l)} \Phi. \tag{33}$$

By identifying $\phi_2(l)$ with ϕ_s we derive W_e as

$$\frac{1}{W_e} = \frac{1}{W} + \frac{1}{K_1} + \frac{1}{\beta}. \tag{34}$$

Equation (34) generalizes a well-known formula [4]. This expression shows that besides the 'true' anchoring energy W relevant to the LB–solid substrate interface, it is necessary to take into account also the direct LB–NLC surface energy and another anchoring energy having an elastic origin and given by

$$W_i = \frac{K_1}{l}. \tag{35}$$

A simple inspection of equation (34) shows that if

$$W \to \infty, \qquad \frac{1}{W_e} = \frac{1}{\beta} + \frac{l}{K_1}, \tag{36}$$

and if

$$W \to 0, \qquad W_e = W. \tag{37}$$

This means that W_e is always finite.

5. Equivalent anchoring energy

In the previous section we have evaluated the equivalent anchoring energy for the LB–NLC junction. Equation (34) for W_e has been obtained by supposing that:

(i) the LB–solid substrate interaction is characterized by an easy axis normal to the geometrical surface (homeotropic alignment);
(ii) there is no direct NLC–solid substrate interaction.

In this framework, we have shown that the effective easy axis (for the NLC–LB interface) is still homeotropic and that the effective anchoring energy is given by equation (34). Of course it is possible to drop out the simplifying hypothesis (ii), as discussed recently [9]. However, since in this paper we want to consider thick LB multilayers, the direct NLC–solid substrate interaction may be neglected. In fact the direct interaction is strongly screened by the LB multilayer, since the interaction law between NLC and substrate decreases as the inverse cubic power of the distance. As follows from equation (34)

$$W_e < W. \tag{38}$$

This means that the direct LB–NLC interaction and the LB elastic deformation destabilize the homeotropic interaction. By supposing the anchoring energy to be infinite (strong homeotropic orientation at the LB–solid substrate interface) and a strong LB–NLC interaction, we have

$$W_e = \frac{K_1}{l}. \tag{39}$$

The K_1 elastic constant for smectic A liquid crystals, and in particular for the LB film, is very small with respect to that of a NLC [10]. To obtain the order of magnitude of W_e, we assume $K_1 \approx 10^{-7}$ cgs [1,2] and $l \approx 200$ Å, corresponding to a penta-layer of stearic acid [11]. With these values for K_1 and l, we obtain $W_e \sim 5 \times 10^{-2}\,\mathrm{erg\,cm^{-2}}$. This is of the same order of magnitude of the anchoring energy detected using different techniques by several groups [12]. Hence, it is possible to imagine that the anchoring energy for a NLC oriented by a LB multilayer has an elastic origin. Of course, in the event in which the number of layers is very small ($n \sim 1$–3), our model does not work any longer, because the direct NLC–solid substrate interaction may play an important role.

A few words about the manner in which the effective anchoring energy has been introduced may clarify our point of view. In a recent paper devoted to the elastic origin of the NLC anchoring energy [4], we have considered as the 'surface' tilt angle the extrapolated value of the bulk tilt. This means that ϕ_s was identified with $\phi_2(0) = \phi_{ex}$. As follows from equation (21) and equations (23) and (24), ϕ_{ex} is given by

$$\phi_{ex} = \phi_2(0) = \frac{1 + Wl[1/K_1 - 1/K_2] + W/\beta}{1 + W[l/K_1 + (d-l)/K_2] + W/\beta} \Phi. \tag{40}$$

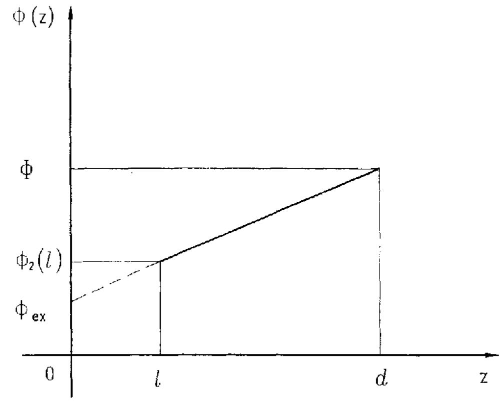

Figure 4 An alternative manner in which to define the anchoring energy.

Since $l \ll d$, the physical properties of the NLC sample are practically coincident with those in which the LB layer is absent and the director profile is of the kind shown in figure (4). Following this point of view, we have to consider the 'extrapolated' anchoring energy in the case in which the total energy per unit surface of the NLC sample is given by

$$F_{ex} = \int_0^d \tfrac{1}{2} K_2 \phi'^2 \, dz + \tfrac{1}{2} W_{ex} \phi_{ex}^2. \qquad (41)$$

By operating as in §4 we have now

$$\phi_{ex} = \frac{\Phi}{1 + W_e(d/K_2)}. \qquad (42)$$

By comparing equation (40) and equation (42), W_{ex} is found to be

$$\frac{1}{W_{ex}} = \frac{1}{W} + \frac{1}{\beta} + l \frac{K_2 - K_1}{K_2 K_1}. \qquad (43)$$

For the system considered by us in which $K_2 \gg K_1$, equation (43) is practically coincident with equation (34). However, since the physical properties of the LB film may be evaluated in a separate manner, according to this point of view, the correct result is the one given by equation (34).

6. Conclusions

The orienting effect of a LB multilayer on a NLC has been considered. We have shown that the experimentally detectable NLC anchoring energy may be separated into three contributions. The first coincides with the LB–solid substrate anchoring. The second has an elastic origin and is of the order of K_1/l, where K_1 is the LB splay elastic constant and l the total thickness of the LB multilayer. The third term arises from the LB–NLC direct interaction. We remember that there is also another term which is due to the interaction energy between the NLC and the substrate, screened by the LB film. We stress that, in this paper, we have not taken into account this last term. By assuming for K_1 and l reasonable values found in literature, the elastic contribution to the NLC anchoring energy is estimated to be of the order of 10^{-2}–10^{-1} erg cm^{-2}, agreeing with the order of magnitude of this parameter detected experimentally.

Our model can also be used to analyse the influence of a smectic layer, present at the NLC–vacuum interface. To do this, it is necessary to write in our main formula the smectic coherence length in the nematic phase instead of l.

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