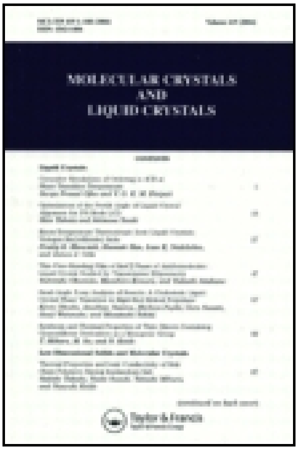

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W. J. A. Goossens [a]

[a] Philips Research Laboratories, Eindhoven, The Netherlands

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Bulk, Interfacial and Anchoring Energies of Liquid Crystals†

W. J. A. GOOSSENS

Philips Research Laboratories, Eindhoven, The Netherlands

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A review is given of the phenomenological description, the experimental determination and the theoretical considerations and calculations of the anchoring energy in liquid crystals. The order of magnitude of the anchoring energy is also compared with the bulk and interfacial energies of liquid crystals.

INTRODUCTION

Liquid crystals are fluids with a long range orientational order. The degree of orientational order is described by the scalar order parameter S, defined as $\frac{1}{2}\langle 3\cos^2\theta - 1\rangle$. The brackets denote a statistical average, where θ is the angle between the long molecular axis and the direction of the average alignment. This direction, which is defined on a macroscopic scale, is called the director **n**.

It is known that the interaction between a LC and a substrate defines the direction of **n** at the interface. This interaction can be described in terms of an interfacial energy that not only depends on **n** but also on S. That part of the interfacial energy that defines **n** is known as the anchoring energy.

Many papers have been published on calculations, descriptions or explanations of the anchoring energy. However, these papers are not very coherent as they mostly deal with only a part of the problem and use a phenomenological, molecular or physico-chemical approach. It has also been suggested that a study of the S-dependence

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of the interfacial energy could help the understanding of the anchoring energy. This point has not been further discussed or elucidated.

In order to gain more insight into what has been done, is understood and what can be done, we would like in this paper to give a coherent description of the problem, discussing the connection between bulk, interfacial and anchoring energies with an emphasis on the relative order of magnitude of these quantities. In section I the problem is defined and discussed in a phenomenological way; the starting point is a general expression for the free energy of the bulk and interface as a function of the tensor order parameter $S_{\alpha\beta} = S(n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta})$ and its spatial derivatives. The experimental methods to measure the anchoring energy and the results obtained are described in section II. In section III the relevant theories and methods used to calculate the strength and the sign of the anchoring energy will be discussed, analysed and modified. Emphasis will be placed on their predicting power.

I. PHENOMENOLOGICAL DESCRIPTION

I.1. *The bulk*

The orientational order of a liquid crystal is described by the tensor order parameter $S_{\alpha\beta}(\mathbf{r}) = S(\mathbf{r})(n_\alpha(\mathbf{r})n_\beta(\mathbf{r}) - \frac{1}{3}\delta_{\alpha\beta})$. Here $S(\mathbf{r})$ is the scalar order parameter and $n_\alpha(\mathbf{r})$ the α-component of the director $\mathbf{n}$, where $\alpha,\beta = x,y,z$ refer to a fixed macroscopic coordinate system. In a phenomenological approach the free energy per unit volume is written as a power series in $S_{\alpha\beta}$.

The expansion can only contain scalar combinations of the tensor order parameter and its spatial derivatives. So one finds with $\mathbf{n}^2 = 1$, references 1, 2:

$$F - F_0 = \tfrac{1}{2}AS^2 - \tfrac{1}{3}BS^3 + \tfrac{1}{4}CS^4 + \tfrac{1}{2}D(\nabla S)^2 + \tfrac{3}{2}DS^2(\nabla\cdot\mathbf{n})^2 - \tfrac{1}{2}N\chi_a^m S(\mathbf{nH})^2. \quad (1)$$

The coefficients a, defined by $A = a(T - T^*), B, C, D$ and the temperature T^* can be considered as empirical parameters. The term $N\chi_a^m S(\mathbf{n}\cdot\mathbf{H})^2$ describes the response of the molecular diamagnetic anisotropy χ_a^m to an applied magnetic field $\mathbf{H}$; N is the number density.

For our purpose it suffices to consider S and $\mathbf{n}$ as depending on one coordinate only, say z; then $(\nabla S)^2 = (\partial S/\partial z)^2 = S_{,z}^2$ and $(\nabla\mathbf{n})^2$

$= (\partial n_\alpha/\partial z)^2 = n^2_{\alpha,z}$. The equilibrium values of $S(z)$ and $n_\alpha(z)$ are such that F is minimum. The corresponding Euler-Lagrange equations read:

$$\frac{\partial F}{\partial S} - \frac{\partial}{\partial z}\frac{\partial F}{\partial S_{,z}} = 0, \tag{2.1}$$

$$\frac{\partial F}{\partial n_\alpha} - \frac{\partial}{\partial z}\frac{\partial F}{\partial n_{\alpha,z}} = \lambda n_\alpha. \tag{2.2}$$

The Lagrange multiplier λ accounts for the constraint that $\mathbf{n}^2 = 1$. These equations for S and n_α are in principle coupled. In practice, however, they can be solved independently. Consider therefore the equations (2.1) and (2.2) for the LC phase not influenced by boundaries; then both S and n_α are constant in space. Neglecting for the moment the diamagnetic energy one finds from equation (1) and equation (2.1)

$$\{a(T - T^*) - BS + CS^2\}S = 0, \tag{3}$$

with the solution $S = 0$ corresponding to the isotropic phase and with the solution

$$S = \frac{B}{2C}\left(1 + \left(\frac{T^+ - T}{T^+ - T^*}\right)^{1/2}\right), \tag{4}$$

corresponding to the anisotropic phase; here

$$T^+ - T^* = \frac{B^2}{4aC}. \tag{5}$$

An elementary analysis of F as a function of $S(T)$ results in the following picture. At $T = T_K$ with $T_K - T^* = 8/9 \cdot (T^+ - T^*)$ there is a first order transition between the isotropic phase with $S(T_K) = 0$ and the ordered phase with $S(T_K) = S_K = 2B/3C$. The latent heat of the transition is $\frac{1}{2}\, aT_K S_K^2$. Above T_K the anisotropic phase can exist as a metastable phase up to T^+, whereas below T_K the isotropic phase can be supercooled down to T^*. The latent heat, the order S_K and the temperature T_K are easily determined. An analysis of light scattering in the isotropic phase, due to short range order fluctuations and proportional to $\xi^2 = (D/a)(T - T^*)^{-1}$ allows one to determine D/a and $T_K - T^*$, reference 3. The experimental data show that $a \simeq 10^6$ erg/cm^3 K, $B \simeq \frac{1}{2}C \simeq 10^7$ erg/cm^3, $D/a \simeq 10^{-12}$ cm^2 K, $D \simeq 10^{-6}$ dyne and $T_K - T^* \simeq 1$ K, see references 1, 2, 3, 4. Well below T_K that part of $F - F_0$ that only depends on S is of the order of 10^7 erg/cm^3. Next we consider the $\mathbf{n}$ dependent part of $F - F_0$. Since the diamagnetic susceptibility $\chi_a = NS\chi_a^m$ is of the order of 10^{-6} c.g.s. units the diamagnetic energy in a field $\mathbf{H} \simeq$ 10 kG is of the order of 10^2 erg/cm^3, reference 1.

Therefore magnetic fields do not interface with the orientational order unless $\mathbf{H} \geqslant 10^3$ kG. However a magnetic field may interface with the elastic energy described by the term $\frac{3}{2}DS^2n^2_{\alpha,z}$.

Considering this term one should keep in mind that the distances R over which the director varies are large, at least greater than 1 μm; therefore $n_{\alpha,z} = n_\alpha/R < 10^3$ cm^{-1}, reference 4 and $DS^2n^2_{\alpha,z} \leqslant 10^2$ erg/cm^3 which should be compared with the term $DS_{,z}^2 \simeq D/\xi^2$ with $\xi \leqslant 10^{-6}$ cm. So one may conclude that in the bulk the director dependent energy is orders of magnitude smaller than the energy dependent on S only. Therefore the equations (2.1) and (2.2) can be considered as independent. From the latter one finds with $n_{\alpha,z} = 0$: $(\mathbf{nH})\mathbf{H} = \lambda\mathbf{n}$ i.e. $\mathbf{n}//\mathbf{H}$. Without fields and boundaries $\mathbf{n}$ is, apart from the constraint $\mathbf{n}^2 = 1$, undetermined. In order to explore the elastic properties, described by the $\mathbf{n}$-dependet part of $F - F_0$, i.e.

$$F_{\mathrm{el}} = \tfrac{1}{2}Kn^2_{\alpha,z} - \tfrac{1}{2}\chi_a(\mathbf{nH})^2, \tag{6}$$

where $K = 3DS^2$, one needs boundaries to fix $\mathbf{n}$.

I.2. *The Interface; dependence on S*

Now we consider the LC phase bounded, say at $z = 0$, by a solid substrate or its own vapour. Experimentally we know that at the interface $z = 0$, $\mathbf{n}$ has a prescribed direction. Then in principle S at the interface is different from the equilibrium value in the bulk, i.e. $S_s = S(z = 0) \neq S(z = \infty) = S_b$. To discuss this point we reconsider equation (2.1) with $S = S(z)$. A first integration yields

$$S_{,z}^2 = \frac{2}{D}\left(f(S(z)) - f(S_b)\right), \tag{7}$$

with $f(S) = \frac{1}{2}AS^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4$. The integration constant $f(S_b)$ ensures that $S_{,z} = 0$ at $z = \infty$ where $S(z) = S_b$. Equation (7) can be solved to give in a first approximation

$$S(z) - S_b = (S_s - S_b)\, e^{-z/\xi}, \tag{8}$$

where S_s is the as yet unknown value of $S(z)$ at $z = 0$. The coherence length $\xi(T)$ is, for $T \leqslant T_K$, given by

$$\xi(T) = \xi_k \cdot \left(\frac{T^+ - T_K}{T^+ - T}\right)^{1/2} \cdot \left(\frac{4}{1 + 3\left(\dfrac{T^+ - T_K}{T^+ - T}\right)^{1/2}}\right)^{1/2} = \xi^+_{(T)}, \tag{9}$$

whereas for $T \geqslant T_K$

$$\xi(T) = \xi_K \cdot \left(\frac{T_K - T^*}{T - T^*}\right)^{1/2} = \xi^*_{(T)}. \tag{10}$$

Here $\xi_K = \xi(T - T_K) = (9CD/2B^2)^{1/2}$.

In order to connect the excess order $S_s - S_b$ at the interface with the properties of that interface we introduce the interfacial energy ω defined as the free energy per unit area of that interface, i.e. $\omega = (\partial F/\partial A)_{z=0}$. The interface acts as a symmetry breaking perturbation; expanding ω as a power series in the tensor order parameter $S_{\alpha\beta}$ we find in the lowest order the scalar combination $S_{\alpha\beta}k_\alpha k_\beta$, where $\mathbf{k}$ is taken as the unit normal to the surface. So we have

$$\omega_s = \omega_0 - \alpha S_s + 0(S_s^2), \tag{11}$$

where the dependence of α on $\mathbf{n}\cdot\mathbf{k}$ is written as

$$\alpha = a + (b - a)(\mathbf{n}\cdot\mathbf{k})^2. \tag{12}$$

Here a and b are introduced as phenomenological coefficients to be discussed later on. The above expansion of ω_s is quite similar to the more familiar expansion of F given in equation (1). The possible extension of the above expansion of ω_s is discussed in appendix A.

The total free energy per unit area of the interface due to the interface and excess order, which extends in the bulk is,

$$\omega = \omega_s + \int_0^\infty dz(F(z) - F(\infty)), \tag{13}$$

where $F(z) - F(\infty) = f(S(z)) - f(S_b) + \frac{D}{2} S_{,z}^2 = DS_{,z}^2$ c.f. equation (7). So one finds

$$\omega = \omega_s + \int_{S_s}^{S_b} \mathrm{d}S \cdot S_{,z}. \tag{14}$$

Minimizing ω with respect to S_s yields

$$(S_{,z})_{z=0} = \frac{1}{D}\frac{\partial\omega_s}{\partial S_s} = -\frac{\alpha}{D}. \tag{15}$$

Combining equation (8) and equation (15) we find

$$S_s - S_b = \frac{\alpha\xi(T)}{D}. \tag{16}$$

With the equations (8), (11) and (16) equation (14) can be evaluated to give:

$$\omega = \omega_0 - \alpha S_b - \frac{\alpha^2\xi}{2D}. \tag{17}$$

These equations show that the excess order and energy at the interface depend on the bulk through ξ and D and on those of the interface through α. Since $\xi/D \lesssim 1$ cm/dyne and $S_s - S_b < 1$, α can be estimated to be approximately equal to or smaller than 1 erg/cm^2. Now the question arises whether we can measure α and its dependence on $\mathbf{n}\cdot\mathbf{k}$? First consider the birefringence due to the ordering. We know that $n_e - n_0 \propto S$. The phase shift δ between the extraordinary and ordinary wave of light passing through a sample of thickness d, which can be measured with great accuracy, can be written as $\delta = \delta_0 \int_0^d \mathrm{d}z \cdot S(z)$ where δ_0 is a known material parameter. From equations (8) and (16) one finds

$$\int_0^d \mathrm{d}z\, S(z) = dS_b + \frac{\alpha\xi^2}{D}. \tag{18}$$

In the ordered phase with $T < T_K$ and $S_b \neq 0$, the contribution of the excess order is not easily detected; $\xi << d$. However, according to equations (11) and (16) excess order may also exist above T_K, where $S_b = 0$ and $S_s = \alpha\xi^*(\mathrm{T})/\mathrm{D}$. An exact calculation shows that for $T \geqslant T_K$

$$\int_0^d \mathrm{d}z\, S(z) = \xi_K S_K \ln\left[\frac{((S_K - S_s)^2 + \tau)^{1/2} - (S_K - S_s)}{(S_K^2 + \tau)^{1/2} - S_K}\right], \tag{19}$$

which for $\tau = 2a(T - T^*)/C \to 0$, i.e. $T \to T^*$ reduces to $\alpha\xi_K^2/D$. A precise analysis of δ as a function of T enables one to determine S_s and α, references 5 and 6. Typically $0 < S_s < 0.4$ and 10^{-1} erg/cm^2 $< \alpha < 1$ erg/cm^2. In these experiments however $\mathbf{n}\cdot\mathbf{k}$ is assumed fixed being zero or one depending on the substrate and the LC. Therefore one measures a or b, c.f. equation (12), but not both together. Therefore no information is obtained concerning the difference (b-a), which as can be seen from equation (12) is the binding energy of the director to the surface, i.e. the anchoring energy.

Secondly we discuss the implications of equation (17). A direct measurement of ω is only possible when the interface at $z = 0$ refers to that between a LC and its own vapour. Then ω is identified as the surface free energy and accordingly denoted as γ. Equation (17) then reads;

$$\gamma = \gamma_0 - \alpha S_b - \frac{\alpha^2\xi^+}{2D}, \qquad T \leqslant T_K, \tag{20.1}$$

$$\gamma = \gamma_0 - \frac{\alpha^2\xi^*}{2D}, \qquad T \geqslant T_K, \tag{20.2}$$

where γ_0 is the surface free energy of the liquid without orientational order. According to these equations the surface free energy is discontinuous at $T = T_k$

$$(\Delta\gamma)_{T=T_K} = \alpha S_K. \tag{21}$$

Moreover the slope $\partial\gamma/\partial T$ is discontinuous at $T = T_K$

$$\frac{\partial\gamma}{\partial T} = \frac{\partial\gamma_0}{\partial T} + \frac{\alpha}{T_K - T^*}\cdot\left(S_K - \frac{5\alpha\xi_K}{4D}\right), \qquad T \leqslant T_K, \tag{22.1}$$

$$\frac{\partial\gamma}{\partial T} = \frac{\partial\gamma_0}{\partial T} + \frac{\alpha}{T_K - T^*}\cdot\frac{\alpha\xi_K}{4D}, \qquad T \geqslant T_K. \tag{22.2}$$

Here $\partial\gamma_0/\partial T$ is negative and small, whereas the second term in both equations is positive and at T_K possibly greater than the leading term. The available experimental data are in agreement with the features described above and consistent with $\alpha \lesssim 1$ dyne/cm.[7,8] However, all the available experimental data refer to situations where $\mathbf{n}\cdot\mathbf{k}$ is fixed; i.e. the measured γ values refer to $\gamma_{\parallel} = \gamma(\mathbf{n}\cdot\mathbf{k} = 0)$ or to $\gamma_{\perp} = \gamma(\mathbf{n}\cdot\mathbf{k} = 1)$, with one exception. Gannon and Faber,[8] who were the first to analyse the surface free energy as a function of temperature in a similar way to that described above, did measure the surface free energy of the LC 5 CB with the Wilhelmy plate method for both homeotropic and planar alignment at the plate. Since the one set of experimental points was adapted to fit with two reference points of the other a possible small difference was not detected. So we conclude that measurements of excess order and (or) excess energy, though very interesting by themselves, do not give information on the anchoring energy.

I.3. *The Interface; dependence on* n

The last point to consider is the explicit dependence of the interfacial energy on **n**; then only the term $(b - a)(\mathbf{n}\cdot\mathbf{k})^2$. S_s in equation (11) becomes important, c.f. equation (12). Consider a LC bounded at $z = 0$, where **n** has a prescribed orientation, say $\mathbf{n}\cdot\mathbf{k} = 1$. Without an external perturbation **n** in the bulk is fixed; $n_z(z) = 1$. Then if we apply a magnetic field perpendicular to **n**, say along the x-axis, the director tends to rotate to the x-axis. Therefore we consider **n** to be $(\sin\theta(z)), 0, \cos\theta(z))$ where $\cos\theta(z = 0) = \mathbf{n}\cdot\mathbf{k}$. From equation (2.2) and (6) we find

$$-n_z\left(K\,\frac{\partial^2 n_x}{\partial z^2} + \chi_a n_x H^2\right) + n_x\left(K\,\frac{\partial^2 n_z}{\partial z^2}\right) = 0, \qquad (23.1)$$

or

$$\frac{\partial^2\theta}{\partial z^2} = \frac{-\chi_a H^2}{K}\cdot\sin\theta\cdot\cos\theta. \qquad (23.2)$$

Equation (23.2) can be integrated to give

$$\theta_{,z}^2 = \frac{\chi_a H^2}{K}\,(\sin^2\theta_m - \sin^2\theta), \qquad (24)$$

where θ_m is the maximum value of θ at some z_m where $\theta_{,z} = 0$. The total free energy per unit area of the interface taking into account the distortion of **n** into the bulk is then, according to equation (13), given by

$$\omega = \omega_s + \int_0^{z_m} \mathrm{d}z \, (F(\theta(z)) - F(\theta_m)), \tag{25}$$

where $F(\theta(z)) - F(\theta_m) = K\theta,_z^2$: c.f. equations (6) (24) and appendix B. Then ω is written as

$$\omega = \omega_s + K \int_{\theta_0}^{\theta_m} \mathrm{d}\theta \, \theta_z, \tag{26}$$

where $\theta_0 = \theta(z = 0)$. Minimizing ω with respect to θ_0 we find with equation (11) for ω_s

$$(\theta,_z)_{r=0} = \frac{1}{K}\frac{\partial\omega_s}{\partial\theta_0} = \frac{2A}{K}\sin\theta_0 \cdot \cos\theta_0, \tag{27}$$

where $A = (a\text{-}b)S_s$ is the anchoring energy. We then substitute equation (24) for θ_z at $z = 0$ into equation (27); so one finds

$$\sin\theta_0 \cdot \cos\theta_0 = \frac{K}{2A}\left(\frac{\chi_a H^2}{K}\right)^{1/2} \cdot (\sin^2\theta_m - \sin^2\theta)^{1/2}, \tag{28}$$

which determines θ_0 as a function of the applied field and the anchoring energy. In order to discuss the implications of this equation we first recall the notion of a threshold field for the distortion of the director field in a finite sample of thickness d. Assume for the moment that $\theta(z)$ can be written as $\theta(z) = \theta_m \sin(\pi z/d)$, where $\theta_m < 1$. Then with $\sin\theta_m = \theta_m$, $\sin\theta = \theta$ equation (24) reads

$$\left(\frac{\pi^2}{d^2} - \frac{\chi_a H^2}{K}\right)\theta_m = 0. \tag{29}$$

For $\chi_a H^2/K < \pi^2/d^2$, θ_m is zero; a non vanishing θ_m requires at least

$$H = \left(\frac{K}{\chi_a}\right)^{1/2} \cdot \frac{\pi}{d}, \tag{30}$$

which defines a threshold field for the distortion of the director field. The assumption $\theta(z) = \theta_m \cdot \sin(\pi z/d)$ implies that $\theta_0 = \theta(z = 0,$

$d) = 0$ whatever the value of H. According to equation (28) however, a finite H implies a non zero θ_0, unless K/A is vanishing small. In order to account for a finite K/A we calculate the threshold field for a non vanishing θ_m taking into account a non vanishing θ_0. Equation (24) is therefore rewritten as:

$$\int_0^{d/2} dz \left(\frac{\chi_a H^2}{K}\right)^{1/2} = \int_{\theta_0}^{\theta_m} d\theta \,(\sin^2\theta_m - \sin^2\theta)^{-1/2}. \tag{31}$$

At threshold $0 < \theta_0 < \theta_m < 1$; therefore with $\sin^2\theta_m = \theta_m^2$, $\sin^2\theta = \theta^2$, equation 31 can be solved to give

$$\frac{d}{2}\left(\frac{\chi_a}{K}\right)^{1/2} \cdot H = \arc\sin \frac{\theta}{\theta_m}\Bigg|_{\theta_0}^{\theta_m} = \frac{\pi}{2} - \frac{\theta_0}{\theta_m}. \tag{32}$$

In the same approximation we find from equation (28) that

$$\theta_0 = \frac{K}{2A}\left(\frac{\chi_a}{K}\right)^{1/2} H\theta_m. \tag{33}$$

Substitution of this equation in equation (32) yields,

$$H = \left(\frac{K}{\chi_a}\right)^{1/2} \frac{\pi}{d + l}, \tag{34}$$

where $l = K/A$ is known as the extra-polation length. A finite l lowers the threshold field which in principle can be measured by plotting H as a function of d. In carrying out such measurements complications may arise when for $H = 0$ $\theta(z = 0)$ is non zero (known as pretilt). To illustrate this point assume $\theta(z)$ to be of the form $\theta(z) = \theta_p + \theta_m \cdot \sin(\pi z/d)$. Then with both θ_m and θ_p small one easily finds

$$\left(\frac{\pi^2}{d^2} - \frac{\chi_a H^2}{K}\right)\theta_m = \frac{\chi_a H^2}{K}\theta_p, \tag{35}$$

which replaces equation (29). In this case there is no precise defined threshold field; θ_m starts growing the moment H is greater than zero.

In order to make these points more quantitative we note that the effects of a finite l and θ_p can easily be combined and exactly formulated. Since $\int_0^\alpha d\theta\,(\sin^2\theta_m - \sin^2\theta)^{-1/2}$ can be written as $\int_0^\beta d\chi \cdot (1 - m^2\sin^2\chi)^{-1/2} = F(\beta/m)$, where $F(\beta/m)$ is the elliptic integral of the first kind with $m = \sin \theta_m$ and $\beta = \arcsin((\sin \alpha)/m)$, equation (31) reads:

$$\frac{d}{2}\left(\frac{\chi_a}{K}\right)^{1/2} \cdot H = F\left(\frac{\pi}{2}\Big/ m\right) - F(\beta_0/m). \qquad (36)$$

Here $\beta_0 = \arcsin((\sin \theta_0)/m)$ where $\theta_0 = \theta(z = 0)$ is determined by equation (28) which is written as

$$\sin(\theta_0 - \theta_p) \cdot \cos(\theta_0 - \theta_p) = \frac{K}{2A}\left(\frac{\chi_a H^2}{K}\right)^{1/2} m \cos \beta_0. \qquad (37)$$

These equations have been derived and evaluated numerically for $l \neq 0$, $\theta_p = 0$ and for $i = 0$, $\theta_p \neq 0$ in reference 9.

II. EXPERIMENTAL DETERMINATION OF THE ANCHORING ENERGY

The first direct experimental determination of the anchoring energy has been described in reference 10. There the magnetic threshold field has been measured as a function of the LC layer thickness; the experimental results clearly show the influence of a finite $l = K/A$, as described in equation (34). The liquid crystal used was MBBA and homeotropic alignment was achieved by the use of various organic surfactants. The values reported for these ranged from 3.5 10^{-3} erg/cm^2 to 1.1 10^{-2} erg/cm^2. As already noted in I.3 an accurate determination of threshold fields can be rather difficult. Moreover the threshold field itself is rather insensitive to changes in the anchoring energy.[11] Therefore the experiments have been extended well above threshold,[11,12] where the director configuration is strongly distorted. Due to the distortion the birefringence of the sample is changed. This field induced birefringence, which can be written as

$$\delta = \frac{2\pi}{\lambda}\int_0^{d/2} dz\, \Delta n(z) = \frac{2\pi}{\lambda}\int_{\theta_0}^{\theta_m} d\theta\, \frac{\Delta n(\theta)}{\theta_{,z}}, \qquad (38)$$

where θ_0 depends on the anchoring energy and applied field, cf. equation (28), and $\theta_{,z}$ is given by equation (24), B9 or B11 as a function of the field, can be measured with great accuracy. Therefore an analysis of the birefringence as a function of the applied field enables one to determine the anchoring energy rather precisely. In ref. 12 the LC used was MBBA and homeotropic alignment was achieved with hexadecylamine. The value obtained for the anchoring energy was $1.17\ 10^{-2}$ erg/cm^2 which is an order of magnitude greater than the value $3.5\ 10^{-3}$ erg/cm^2 reported for the same surfactant and LC.[10] The residual birefringence has been measured[11] as a function of an applied electric field up to saturation for various planar orienting surfaces using both 5 CB and the corresponding cyclohexane compound 5 PCH. The values obtained ranged from $2.5\ 10^{-2}$ erg/cm^2 for 5 CB on SiO$_x$ to 10^{-1} erg/cm^2 for 5 CB and 5 PCH on polyimide.

Another way to determine the anchoring energy is based upon the fact that the threshold field for the unwinding of the helical configuration of the cholesteric phase can be written as:[13]

$$E^2 = \frac{K}{\epsilon_a}\frac{\pi^4}{p^2} \pm \frac{8A}{\epsilon_a d}. \tag{39}$$

The ± sign refer to planar and homeotropic boundary conditions respectively. A plot of $E^2 d$ as a function of d yields a straight line, which intersects the abscissa at $8A/\epsilon_a$. The results obtained[13] were of the order of 10^{-2} erg/cm^2.

A determination of the anchoring energy based upon a distortion of the director field due to different pretilt angles θ_0 and θ_d at the lower and upper boundaries has been described.[14] Assuming that the anchoring energy at the lower boundary is much greater than that at the upper boundary we are only concerned with the boundary condition at the upper plate. From equation (27) one finds to a first approximation,

$$\theta(z=d) - \theta_d = \frac{K}{2A}(\theta_{,z})_{z=d}, \tag{40}$$

whereas equation (23.2) with $H = 0$ can be written as $\theta_{,z} = \text{const} = (\theta_d - \theta_0)/d$. Substitution in equation (40) yields

$$\theta(d) - \theta_d = \frac{K}{2A}\frac{\theta_d - \theta_0}{d}, \tag{41}$$

Measuring the change of $\theta(d)$ as a function of the thickness d enables one to determine A. In the experiment described in reference 14 the one glass plate was covered with an organo-silane for which $\theta_p = 0$

and $A = 1.1\ 10^{-2}$ erg/cm^2, reference 10 and the other was coated with evaporated SiO$_x$ with $\theta_p = 60°$ for which was found $A = 2.10^{-3}$ erg/cm^2; the LC used was 6 CB.

The distortion of the director field in a thin sample with different boundary conditions has been used[15] to determine the anchoring energy at the free surface, i.e. the difference $\Delta\gamma = \gamma_{\parallel} - \gamma_{\perp}$. The method is based upon the observation that in a very thin film of the LC 5 CB on water the director configuration is uniform planar whereas above a critical thickness the director field at the LC/air interfaces changes from planar to homeotropic. The value reported for $\Delta\gamma$ is 4.10^{-3} erg/cm^2. Analogous experiments have been described.[16] A precise analysis can be found in reference 17. Measurements of $\Delta\gamma$ for the LC MBBA have been described.[18,19] These measurements are based upon the distortion of the director configuration at the free surface due to an applied field (similar to the description above for the determination of the anchoring energy). In reference 18 it was found that near T_c, $\Delta\gamma$ could be written as $D.\ (T_c - T)^{\delta}$ with D equal to $5.9\ 10^{-2}$ erg/cm^2 and $\delta \simeq 1$. The value of $\Delta\gamma$ reported in reference 19 is 10^{-5} erg/cm^2, and orders of magnitude smaller. In this context we would like to remark that the scattering in data[10,12] for MBBA as found in $\Delta\gamma$ and the anchoring energy, may be due to differences in purity of the material used. The strong influence of the degree of purity of MBBA on T_c and on the direction of alignment on various substrates has been demonstrated.[20]

Finally we would like to mention the work of Williams and Kleman,[21] which is often quoted in the literature. According to their model there is a balance between the anchoring energy and the elastic deformation energy of defects attached to the boundary, which determines the width of that defect. It is found that:

$$A = \frac{\pi^2 K d}{e^2}, \tag{42}$$

where d is the thickness of the sample and e the width of the defect. Observations of defects allows one to estimate A which ranges from[22,23] 10^{-4} erg/cm^2 up to[21] 10^{-2} erg/cm^2. Though physically appealing this method has for the moment only qualitative significance.

In conclusion the anchoring energies as measured experimentally are rather small—the greatest value reported is 10^{-1} erg/cm^2—and there is a strong scatter in the data depending on the LC's and substrates used. Considering equations (11) and (12) we estimate that $\omega_0 \simeq 10^1-10^2$ erg/cm^2, $a,b \lesssim 1$ erg/cm^2 and $(a\text{-}b)S_s \lesssim 10^{-1}$ erg/cm^2.

III. THEORETICAL

III.1. *Theoretical considerations concerning the anchoring energy*

In section I the interfacial energy ω was introduced as the free energy per unit area of the interface between the solid and the liquid phase in molecular contact; there ω was formally expanded in terms of S and $\mathbf{n} \cdot \mathbf{k}$. Here we express the interfacial energy in terms of other quantities more amenable to direct calculation or experimental determination. According to thermodynamics[24] one has

$$\omega = \gamma_S + \gamma_L - W_a, \tag{43}$$

where γ_S is the surface free energy of the solid with respect to vacuum and γ_L that of the liquid with respect to its saturated vapour phase. W_a is the work of adhesion between the liquid and the solid, i.e. the reversible work to separate a unit area of the L-S interface into two separate areas of each phase. A very useful approximation for W_a is references 24,25,26,

$$W_a = 2\phi(\gamma_L \gamma_S)^{1/2}, \tag{44}$$

where the interaction parameter ϕ can be expressed in terms of the molecular properties of the individual phases; it can also be considered as an empirical parameter. Moreover it can be shown[25] that $1/2\frac{1}{2} \leqslant \phi \leqslant 1$. The work of cohesion W_c of each phase can be defined analogously as the reversible work to create two separate unit areas at an arbitrarily chosen intersection of the bulk phase. Since at such an intersection there is no interfacial energy one has according to equation (43),

$$W_c^L = 2\gamma_L, \; W_c^S = 2\gamma_S, \tag{45}$$

which also follows from equation (2) with $L = S$ or $S = L$ in which case $\phi = 1$.

It is known that a liquid on a solid often does not spread on the solid but remains as a drop having a definite angle of contact between the liquid and the solid phases; this equilibrium is described[24] by,

$$\omega + \gamma_L \cos\theta = \gamma_{SV}, \tag{46}$$

valid for θ nonzero. This equilibrium condition is expressed in terms of the surface free energy γ_{SV} of the solid in contact with the saturated vapour. The difference,

$$\pi_{SV} = \gamma_S - \gamma_{SV}, \tag{47}$$

known as the surface pressure of the absorbed vapour film on the solid surface is in general nonzero, especially in the case where γ_S is large.

Combination of the equations (43), (46) and (47) then yields,

$$W_a = W_a^* + \pi_{SV} = \gamma_L(1 + \cos\theta) + \pi_{SV}, \tag{48}$$

where $W_a^* = \gamma_L(1 + \cos\theta)$ is the work of adhesion between the liquid and the film covered surface. Since γ_L and θ can be determined independently W_a^* can be calculated. From the theoretical point of view W_a is required. Therefore π_{SV} must be determined for example from experimental adsorption isotherms.[24,27] In practice π_{SV} is neglected and W_a identified with W_a^*. It has been argued[25,26] that this should be permissible for γ_S not too great, i.e. $\gamma_S < 100$ erg/cm^2.

For such surfaces it was found experimentally that a plot of cos θ against γ_L for a series of homologous organic liquids often yields a straight line. The intersection of this line with $\cos\theta = 1$ defines a certain value of γ_L which has been called the critical surface tension γ_c of the solid.[24,25] Though its value, in general, depends on the homologous series used it has been a useful concept for comparing wetting properties of solids. However its use as a well defined property of the solid in combination with those of liquid crytals is questionable.

A more general concept for the description of wetting phenomena is the initial spreading coefficient λ_{LS} of the liquid on the solid,[24,26] defined as

$$\lambda_{LS} = \gamma_S - \gamma_L - \omega = W_a - W_c^L, \tag{49}$$

which can also be written as:

$$\lambda_{LS} = \pi_{SV} - \gamma_L(1 \cos\theta). \tag{49.1}$$

When λ_{LS} is greater than zero the free energy of the system decreases when the liquid spreads on the solid and vice-versa. Though the spreading coefficient is a well defined quantity one encounters from the practical point of view the same difficulty as with equation (48), i.e. the occurrence of the surface pressure π_{SV}. Though both γ_c and λ_{LS} are semi empirical quantities we have introduced them because these have been used to describe the alignment of LC's on solid substrates. According to the Creagh-Kmetz rule a LC is aligned perpendicular to the interface, i.e. $\mathbf{n} \cdot \mathbf{k} = 1$ when the critical surface energy γ_c of the solid is smaller than the surface free energy γ_L of the LC and parallel to the interface, i.e. $\mathbf{n} \cdot \mathbf{k} = 0$, when γ_c is greater than γ_L, references 28, 29. This rather intuitive rule has been the subject of considerable controversial debate, references 30–34. Recently it has been stated that the alignment should be related to the sign of the 'spreadability' coefficient,[35] i.e. for $\lambda_{LS} > 0$, $\mathbf{n} \cdot \mathbf{k} = 0$ and for $\lambda_{LS} < 0$, $\mathbf{n} \cdot \mathbf{k} = 1$. This rule has been verified for two different LC's on a variety of low energy surfaces, whereas the Creagh-Kmetz rule was found to be unsatisfactory.[35] However, we would like to show that neither of the two rules can be generally valid. Writing $\Delta\omega = \omega_{\parallel} - \omega_{\perp}$ etc., where $\parallel(\perp)$ refer to $\mathbf{n} \cdot \mathbf{k} = 0$ (1), one finds from equation (43) and (44)

$$\Delta\omega = \Delta\gamma_L - \Delta W_a = (1 - \phi(\gamma_S/\gamma_L)^{1/2})\,\Delta\gamma_L. \tag{50}$$

Here we have made the approximation $\gamma_{\parallel}^{1/2} + \gamma_{\perp}^{1/2} = 2\gamma^{1/2}$, valid as long as $\Delta\gamma_L < \gamma_L$. If one accepts that γ_c is a well defined quantity specific for the solid surface it can be argued[25] that $\phi\gamma_S^{1/2} = \gamma_c^{1/2}$; however, one should keep in mind that in reality γ_c is a relative quantity depending on the test liquids used. A more general substitution can be made by using equation (44) again and putting $\phi(\gamma_S/\gamma_L)^{1/2} = W_a/2\gamma_L$; here W_a refers to the specific system at hand. With these substitutions equation (50) can be written as,

$$\Delta\omega = (\gamma_L{}^{1/2} - \gamma_c{}^{1/2})\Delta\gamma_L/\gamma_L^{1/2}, \tag{51}$$

or alternatively, using equation (49)

$$\Delta\omega = -\lambda_{LS}\Delta\gamma_L/2\gamma_L. \tag{52}$$

These equations show that the sign of $\Delta\omega$ is not only determined by the sign of $\gamma_L^{1/2} - \gamma_c^{1/2}$ or λ_{LS} but also by the sign of $\Delta\lambda_L$ itself. This point has also been mentioned recently in references 33 and 34.

From the above it is clear that equation (52) is based on firmer considerations than equation (51). However, the determination of γ_c from contact angle measurements, with simple test liquids, is much easier carried out than the determination of λ_{LS} for which W_a or π_{SV}

has to be determined. Since the sign of $\Delta\gamma_L$ for most LC's is unknown, it is difficult to check the above equations. However, from the available experimental data, one may conclude that equation (51) does not work at all[33,35] even with due regard to the sign of $\Delta\gamma_L$.

The weak point in the derivation of the above equations is clearly the fact that by using equation (50) the anisotropy of W_a is taken as being solely due to the ansiotropy of γ_L. Specific interactions which could be responsible for the anisotropy of W_a, being a small difference of two rather big quantities, cf. equation (12) in I.2, are not accounted for. This point will be discussed later on.

From the equations (43) and (45) it is clear that the knowledge of W_a and W_c is sufficient to determine ω. In references 36 and 37 these quantities have been calculated using the macroscopic approach, originally due to Lifshitz, in which the different phases are considered as a continuous media. In this approach only dispersion forces are taken into account by defining the interaction energy per unit area in terms of the frequency dependent complex dielectric constant. The solid, a clean flat glass, is considered to be isotropic with ϵ, the dielectric constant a scalar, whereas the anisotropic LC is described by an averaged dielectric constant and the corresponding anisotropy thereof; since this anisotropy is defined with respect to $\mathbf{n}$, it is proportional to S, the order parameter. Then the interaction energies are calculated up to terms linear in $\Delta\epsilon$ for both cases $\mathbf{n}\cdot\mathbf{k} = 0$ and $\mathbf{n}\cdot\mathbf{k} = 1$. Before quoting the results we note that the interaction energy between the two phases i and j (the work of co(ad)hesion is $-U_{ij}$) can schematically be represented by:

$$U_{ij} = A_{ij}\frac{\alpha_i\alpha_j}{d^2} + B_{ij}\frac{\alpha_i\Delta\alpha_j}{d^2}\left(\frac{3}{2}(\mathbf{n}\cdot\mathbf{k})^2 - \frac{1}{2}\right)S. \qquad (53)$$

Here α is some averaged molecular polarisability and $\Delta\alpha$ the corresponding anisotropy thereof; A and B are complicated, well defined functions to be calculated and d is the distance of closest approach between the two phases. Further details concerning the precise formulation and calculations are here of no importance.

The results of the numerical calculations of reference 36 are $\Delta\gamma_L = -6.8$ erg/cm^2 and $\Delta W_a = -7.16$ erg/cm^2. The anisotropy of the interfacial energy is then $\Delta\omega = (-6.8 + 7.16)$ erg/cm^2 $= +0.36$ erg/cm^2. The model calculations of reference 37 give analogous results, $\Delta\gamma_L = -0.18\ \gamma_L$, $\Delta\omega = 0.0065\ \gamma_L$, but are more interesting and illustrative for the following two reasons.

In the first place $\Delta\omega$ was also calculated as a function of the refractive index $n_S = (1 + \alpha)^{1/2}$ of the solid, where n_S is more or less a measure for the surface free energy of the solid. It was found that for $n_S < 1.3$, $\Delta\omega$ was negative, whereas for $n_S > 1.3$, $\Delta\omega$ reversed sign and was positive. Therefore it was concluded that high energy surfaces give a homeotropic alignment, $\mathbf{n} \cdot \mathbf{k} = 1$, and low energy surfaces a planar alignment, $\mathbf{n} \cdot \mathbf{k} = 0$; low and high are here defined with respect to γ_L. Though contradictory to the Creagh-Kmetz rule as to the sign of $\Delta\omega$, $\Delta\gamma_L$ here is negative, it clearly displays the same reversal of the sign of $\Delta\omega$ dependent on the sign of something like $\gamma_L - \gamma_S$.

Secondly it was proposed that d, the distance of closest approach could be a function of the direction of alignment at the interface. If so there is a contribution to $\Delta\gamma_L$ and $\Delta\omega$ proportional to $(d_\perp - d_\parallel)/d_\parallel = \delta/d$, i.e.,

$$\Delta\gamma_L = \left(-0.18 + \frac{2\delta}{d}\right)\gamma_L, \tag{54}$$

and

$$\Delta\omega = \left(0.0065 - \frac{2\delta}{d}\cdot c\right)\gamma_L, \tag{55}$$

with c of the order one.

The most striking feature is the enormous change of the order of magnitude and thereby the possible change of sign of $\Delta\omega$ due to a minor difference between $d_\perp$ and $d_\parallel$, i.e. $\sim 10^{-2}\, d_\parallel$. From theories of orientational order it is well known and generally accepted that the anisotropy of the distance of closest approach i.e. the anisotropy of hard core repulsions can be rather important;[38,39] however its influence shows up only for δ/d of the order one. Apart from the fact that the actual value of d is rather questionable, 10Å in reference 36, 1.38Å in reference 37, the enormous influence of a minor δ/d throws doubt on the reliability of the above procedure for calculating the anisotropy of γ_L and ω (nothing is said, of course, concerning the calculation of γ_L and ω themselves).

Moreover, according to both references quoted, $\Delta\gamma_L$ should be negative for all LCs contrary to experimental observations. In reference 40 the same formalism has been used to describe the interaction between a LC and an anisotropic substrate; the results obtained are similar to those described above.

A microscope approach to the calculation of the surface free energy of LCs has been presented and discussed[41] and extended in greater detail.[42] The problem was simplified in the spirit of a mean field approximation. The results of the rather formal analysis however, do depend somewhat critically on several more or less inaccessible quantities such as the single particle density profile at the interface, the anisotropic radial pair distribution function and the $\mathbf{n} \cdot \mathbf{k}$ dependent single particle orientational distribution, which are both also position dependent. Therefore only qualitative aspects were discussed such as the possible S and T dependences of γ_L.

In order to get more quantitative results drastic approximations have to be made. Therefore it was assumed[43] that the single particle density can be ascribed by a step function, that there is no correlation between position and orientation and that the radial distribution can be taken to be isotropic and position independent. These assumptions are in the spirit of the Fowler-Kirkwood-Buff approximation for simple fluids;[44] the same approximations underly the macroscopic approach discussed before. The results then obtained[43] are:

$$\gamma_{\parallel} = \left(1 - \frac{4}{9}S + \frac{8}{27}S^2\right)\gamma_L, \qquad (56)$$

$$\gamma_{\perp} = \left(1 + \frac{2}{3}S + \frac{1}{6}S^2\right)\gamma_L. \qquad (57)$$

Therefore $\Delta\gamma_L \simeq -S\gamma_L < 0$ and the alignment at the free surface should always be planar. Also the contribution of dipole-dipole interaction to $\Delta\gamma_L$ was calculated for the case of the molecular dipoles directed along the long molecular axis. This contribution results in an enhancement of $\Delta\gamma_L$, which is already remarkably large.

A typical example of such an LC is 5 CB, which is known to orient perpendicularly to the free surface[8,33] with no polar contribution[51] to γ_L. Therefore it was assumed[45] that at the surface polar ordering could exist, to be described with a term proportional to $\mathbf{n} \cdot \mathbf{k}$. Up to now there is no evidence for such order, at least not in nematics. The validity of the above results has also been questioned in references 8, 42, 46, 47.

A quite different, semi empirical approach has been described in a series of papers.[48–51] Considering the fact that polar interactions can be rather important at the interface these interactions are described separately from the dispersive interactions. Following a well known approach[24-26] the interfacial energies are decomposed into a dispersive (d) and polar (p) part, i.e.

$$\gamma = \gamma^d + \gamma^p, \tag{58}$$

$$W_a = W_a^d + W_a^p, \tag{59}$$

whereas instead of equation (44) one now has:[24-26]

$$W_a^d = 2(\gamma_L^d \gamma_S^d)^{1/2}, \tag{60}$$

$$W_a^p = 2(\gamma_L^p \gamma_S^p)^{1/2}, \tag{61}$$

and moreover

$$\gamma_S^d = \gamma_c \tag{62}$$

The dispersive and polar parts of γ_L and γ_S can be obtained from contact angle measurements using, in turn, liquids and solids with known polar and dispersive contributions[24-26] to γ. Then in turn from the experimental W_a, π_{SV}, and from W_a^d, calculated with equation (60), W_a^p can be obtained for the particular situation at hand with $\mathbf{n} \cdot \mathbf{k} = 1$ or 0.

This polar contribution may be approximated by:

$$W_a^p = N_L \mu_L E_S \tag{63}$$

where E_S is the electrostatic surface field of the solid directed along $\mathbf{k}$; μ_L is the effective dipole moment of the LC along $\mathbf{k}$ and N_L the number of LC molecules per unit area. Here both N_L and μ_L depend on $\mathbf{n} \cdot \mathbf{k}$. From the experimental data E_S can be determined, which in turn allows one to calculate W_a^p for the other type of alignment, i.e. for $\mathbf{n} \cdot \mathbf{k} = 0$ or 1. Some typical data for MBBA on humid glass, for which $E_S \simeq 1.5\ 10^5$ esu/cm^2 $\simeq 5.10^7$ v/cm are $W_{a\perp(\parallel)} = 72(78)$ erg/cm^2, $W^p_{a\perp(\parallel)} = 21(27)$ erg/cm^2 with γ_L and γ_L^p 38 and 9 erg/cm^2 respectively. For 5 CB it was found that $W_{a\perp} = 80$ erg/cm^2, $W^p_{a\perp(\parallel)} = 20(0)$ erg/cm^2 with γ_L and γ_L^p 40 and 0 erg/cm^2 respectively.

In the above it was assumed that W_a^d and also γ_L^d were independent of $\mathbf{n} \cdot \mathbf{k}$: then $\Delta\omega = -\Delta W_a^p$, which is quite different from the theoretical results described before. Also the fact that for 5 CB $\gamma^p = 0$ should be noted. In the description of glass covered with poly-soaps, poly(2 methyl/5 vinyl pyridinium)bromide, quaternized by alkyl radicals both W_a^d and W_a^p were considered to be anisotropic.[51] Now first

$W^p_{a\perp(\|)}$ is calculated using a refined version of equation (63) with E_S determined independently from measurements with formamide. From the experimental W_a, the calculated ΔW^p_a and the observed alignment, minimum values for ΔW^d_a are obtained which turn out to be rather large, i.e. up to 50 erg/cm^2; here again γ_L was considered to be isotropic. The main problem with these calculations of $W^p_{a\perp(\|)}$ is the rather poor description of the distribution of molecular and dipole orientations at the surface and the correlation thereof with position. In fact using the formalism of reference 52, which was derived for small dipole molecules oriented by E_S, it was assumed that the orientational order at the interface was perfect, i.e. $S = 1$. One can imagine that in this approximation the calculated ΔW^p_a is strongly exaggerated; the same then applies to ΔW^d_a. The outlined procedure above has been extended both from the experimental and theoretical points of view.[53,54] Here also the different role of the polar and dispersive contributions to the interfacial energy becomes evident. However despite all these quantitative results, which are quite impressive, the discussion remains for the moment qualitative and speculative.

III.2. *Azimuthal anchoring*

Up to now we have only considered whether **n** should be along or perpendicular to **k**. In the latter case **n** is in principle degenerate, all directions in the plane having equal probability. In practice however it is easy to find or to introduce an easy axis (direction) which is defined as that direction of **n**, that minimizes the interfacial free energy. Equation (11) in I.2 for ω then has an additional term βS, where β is proportional to $(\mathbf{n} \cdot \mathbf{l})^2 = \cos^2(\phi - \phi_0)$. Here **l** is a unit vector in the plane of the interface along the easy direction, whereas ϕ_0 and ϕ are the azimuthal angles of **l** and **n** respectively in that plane. Possible easy directions are:

1) a crystallographic axis if the solid substrate is a single crystal,

2) the direction of withdrawal of organic surfactants on a solid substrate, all aliphatic chains being directed along that direction, or the common direction of polymeric chains covering the surface,

3) the direction of flow of the LC entering the cell,

4) the direction of an external field applied when the isotropic phase of the LC is cooled below T_c,

5) the direction of rubbing of the surface,

6) the direction determined by the topographic anisotropy of an evaporated SiO$_x$ film or surface-relief grating.

The existence of an easy axis due to the cases 1) and 2) can easily be understood in terms of anisotropic dispersion forces and steric interactions between the LC molecules and the substrate. The easy axis due to flow alignment can be ascribed to the coupling between **n** and the anisotropy of the viscosity; how this flow alignment becomes coupled to the subtrate is not understood. The azimuthal anchoring strength is sufficiently strong to resist the action of external fields and limiting thermal cycling.[31,55-57] The same applies to 5) where the easy axis, defined by the direction of the applied field, is due to the coupling between **n** and the anisotropy of the magnetic or electric susceptibility.[55-57]

The easy axis along the rubbing direction may be due to the deposition of fatty acids or other long chain organic contaminants on the surface. Another possibility is that the rubbing creates a grooved surface giving rise to a topographic anisotropy. Then the easy axis for both 5) and 6) is determined by that direction of **n** that minimizes the elastic free energy. This point has been considered.[58] The topographic anisotropy of the surface $z = 0$ is described by a sinusoidal wave $z = u \cos(qy)$ with q^{-1} large compared with molecular dimensions. If we take **n** parallel to the local surface we have $\mathbf{n} = (\cos\psi, \sin\psi\cos\phi, \sin\psi\sin\phi)$ with $\phi(z = 0) = -dz/dy = uq \sin qy$; ψ is the arbitrary angle between **n** and the x-axis. Minimizing the elastic free energy yield $\phi = uq \sin qy \cdot \exp(-qz)$ and consequently $F = u^2q^4K/2 \cdot e^{-2qz} \cdot \sin^2\psi$. The surface elastic free energy is then:

$$\omega_{el} = \int dz\, F(z) = \beta \sin^2\psi,\ \beta = \frac{Ku^2q^3}{4}, \tag{64}$$

with $u = 10$ Å, $\lambda = 200$ Å and $K = 10^{-6}$ dyne one has[55] $\omega_{el} = 10^{-2}$ erg/cm^2; with $u = 10^{-1}$ μm and $\lambda = 1$ μm, ω_{el} is of the same order of magnitude. Whether the real surface topology can be described by the simple model presented above is open to discussion. In order to explain the tilted alignment often observed with obliquely evaporated SiO$_x$ films different models have been proposed.[59-61] With **n** locally parallel to the surface there are, dependent on the actual model, three possible overall configurations for **n**, i.e. real planar, tilted planar in a perpendicular direction, and tilted homeotropic. The model calculations, up to now, are not accurate or realistic enough to predict which configuration actually should occur.[61] The interplay between surface-relief gratings and other coupling mechanisms have been studied.[55,57] The experimental results, which are quite instructive, also show how delicate the problem is.

IV. CONCLUSION

In section I, II and III we have reviewed the theoretical and experimental work presented in literature concerning the nature, the strength and the sign of the anchoring energy. Though much has been done and achieved, little progress has been made. The theoretical results obtained do not agree with each other nor with the experimental data. Most theories deal only with a part of the problem. From experiment we know that polar interactions can be rather important at the interface, yet these interactions are not often considered. As far as they are taken into account the approach is too simple to give reliable results. The possible role of steric interactions (anisotropic repulsive forces on a molecular scale) has been suggested by many people. However, these discussions are not quantitative nor conclusive. Although the theory has been rather successful in explaining and describing orientational order in the bulk, coupled or not to translational order, and the corresponding phase transitions, it has great difficulty in calculating thermodynamic quantities with reasonable accuracy.

For this reason it seems senseless to calculate anchoring energies, being a small difference of comparable quantities, along these lines, without knowing or guessing beforehand the really dominant factors. In this respect it seems important to focus attention on the magnitude and sign of $\Delta\gamma_L$ in relation to specific molecular properties such as permanent dipoles and the possible occurrence of smectic order;[8,9,57,62,63] one would also like to know whether $\Delta\gamma_L$ is of the same order of magnitude as ΔW_a or negligible compared to it. In conclusion, despite all the empirical knowledge, concerning the type of anchoring occurring in practice,[64,65] we are not able to calculate its strength or even its sign.

APPENDIX A

The expansion of the interfacial energy described in section I can easily be extended to include higher powers and the gradients of the tensor order parameter. Quite generally one has

$$\begin{aligned}\omega_s &= \omega_0 - \alpha_1(S_{ij}k_ik_j) - \alpha_2(S_{ij}k_ik_j)^2 - \cdots \\ &\quad - \beta_1(\mathbf{k}\cdot\nabla)(S_{ij}k_ik_j) - \beta_2(\nabla\, S_{ij}k_ik_j)^2 - \cdots \\ &= \omega_0 - \alpha_1 S_s(\mathbf{n}\cdot\mathbf{k})^2 - \alpha_2 S_s^2(\mathbf{n}\cdot\mathbf{k})^4 - \cdots \\ &\quad - \beta_1 S_s(\mathbf{k}\cdot\nabla)\cdot(\mathbf{n}\cdot\mathbf{k})^2 - \beta_2 S_s^2(\nabla\cdot(\mathbf{n}\cdot\mathbf{k})^2)^2 - \ldots\end{aligned}$$

As discussed in section I the term $\alpha_2 S_S(\mathbf{n}\cdot\mathbf{k})^2$ and consequently $\alpha_2 S_S(\mathbf{n}\cdot\mathbf{k})^4$ describe the coupling energy of the director at the interface.

These terms make sense because one can make a model, albeit primitive or crude to explain or describe such a coupling. Moreover there is experimental evidence for such coupling; at the surface the director has a prescribed orientation θ_0, imposed on it by the surface.

The terms $\beta_1(\mathbf{k}\cdot\nabla)(S_{ij}k_ik_j)$ and $\beta_2(\nabla\cdot S_{ij}k_ik_j)^2$ describe the surface deformation energy. In order to introduce such terms one must show that the surface itself is the origin or the source of such deformations; cf. reference 66 where these deformations have been described for droplets (curved surfaces). However a geometrical flat surface as introduced in reference 67 can never sustain such deformations on its own. The fact that $(\theta(z)_z)_{z=0} \neq 0$, due to a torque transmitted through the bulk (external fields, different pretilt angles) is quite a different thing; here the deformation is forced upon the surface and vanishes when the bulk torque vanishes. Therefore if one can not show or consider it plausible that the surface itself is the source of a deformation of the director at the surface one is now allowed to take such a deformation into account, i.e., $\beta_1 = \beta_2 = 0$. The results obtained in reference 67 are therefore meaningless.

APPENDIX B

With $\mathbf{n} = (n_x(z), 0, n_z(z)) = (\cos\vartheta(z), 0, \sin\vartheta(z))$ the elastic free energy is [1] [66]:

$$\begin{aligned} F_{el} &= \tfrac{1}{2}(K_{11}(\nabla\mathbf{n})^2 + K_{33}((\mathbf{n}\nabla)\mathbf{n})^2) \\ &= \tfrac{1}{2}K_{11}(1 + k\sin^2\vartheta)\vartheta_{,z}^2,\quad K = \frac{K_{33}-K_{11}}{K_{11}} \end{aligned} \tag{B1}$$

Minimizing the free energy $F = F_{el} + F_f$, where F_f is the dependent part of the free energy due to the applied field, i.e.,

$$\left(\frac{\partial}{\partial z}\frac{\partial}{\partial\vartheta_{,z}} - \frac{\partial}{\partial\vartheta}\right)F_{el} = \frac{\partial}{\partial\vartheta}F_f \tag{B2}$$

yields:

$$K_{11}((1 + k\sin^2\vartheta)\vartheta_{,zz} + k\sin\vartheta\cos\vartheta\,\vartheta_{,z}^2) = \frac{\partial F_f}{\partial\vartheta} \tag{B3}$$

Multiplying both sides with $2\vartheta_{,z}$ gives the result:

$$\frac{d}{dz}\left(\mathrm{K}_{11}\,(1 + k\sin^2\vartheta)\,\vartheta_{,z}^2\right) = \frac{d}{dz}\,(2F_f) \tag{B4}$$

Without any need to specify F_f you find after integration,

$$\begin{aligned} &K_{11}(1 + k\sin^2\vartheta)\vartheta_{,z}^2 = 2(F_f(\vartheta) - F_f(\vartheta_M)),\\ &\vartheta_{,z} = 0 \quad \text{for} \quad \vartheta = \vartheta_M \quad \text{and} \end{aligned} \tag{B5}$$

$$\begin{aligned} F(\vartheta) - F(\vartheta_M) &= \tfrac{1}{2}K_{11}(1 + k\sin^2\vartheta)\vartheta_{,z}^2 + F_f(\vartheta) - F_f(\vartheta_M)\\ &= K_{11}(1 + k\sin^2\vartheta)\vartheta_{,z}^2 = 2(F_f(\vartheta) - F_f(\vartheta_M)) \end{aligned} \tag{B6}$$

With an appropriate choice of $\vartheta(0) = \vartheta(d)$ these equations apply to all configurations. When a magnetic field is applied, say along z, one has

$$F_f = -\tfrac{1}{2}\,\chi_{zz}(\vartheta).H^2,\ \chi_{zz}^{(\vartheta)} = \chi_a\, n_z^2 \tag{B7}$$

because H can usually be considered as the independent variable [69].

When a voltage is applied across the cell, say long z, one usually assumes with [66] or without saying [1] [67] [68] that the electric field can be considered as the independent variable. Then [69],

$$F_f = -\tfrac{1}{2}\,\epsilon(\vartheta).E^2,\ D = \epsilon(\vartheta).E;\ E = \frac{V_{appl.}}{d} \tag{B8}$$

where $\epsilon(\vartheta) = \epsilon_{zz}(\vartheta) = \epsilon_a.n_z^2$. Equation (B5) then reads:

$$K_{11}\,(1 + k\sin^2\vartheta)\,\vartheta_{,z}^2 = (\epsilon(\vartheta_M) - \epsilon(\vartheta))\,E^2 \tag{B9}$$

When taking into account $\nabla\mathbf{D} = 0$ i.e. D_z = constant, one should consider D as the independent variable. Then [69],

$$F_f = +\tfrac{1}{2}\frac{D^2}{\epsilon(\vartheta)},\ E = \frac{D}{\epsilon(\vartheta)};\ D = \frac{V_{appl.}}{\displaystyle\int\frac{dz}{\epsilon}} \tag{B10}$$

and from equation (5):

$$K_{11}\,(1 + k\,\sin^2\vartheta)\vartheta_{,z}^2 = \left(\frac{1}{\epsilon(\vartheta)} - \frac{1}{\epsilon(\vartheta_M)}\right) D^2 \qquad \text{(B11)}$$

In both cases the applied voltage is constant, which however has nothing to do with the thermodynamics of the problem [66].

The derivation of the latter equation, i.e. equation (B11), presented in [67] and [68], using the field energy given by equation (B8), i.e. $F_f = -\frac{1}{2}\epsilon E^2 = -\frac{1}{2} DE$, is incorrect, which can be shown, and inconsistent, which can be seen at once, $\int dz\left(\left(\frac{\partial F_f}{\partial\vartheta}\right)\vartheta_{,z}\right) = F_f$ and not $-F_f$; cf. the equations (B3), (B4) and (B5).

References

1. Priestly, E. B., Wotjowicz, P. J. and Ping Sheng, *Introduction to Liquid Crystals,* (Plenum Press, New York, London), 1975.
2. Legesse Senbetu and Chia-Wei Woo, *Mol. Cryst. Liq. Cryst.,* **84**, 101 (1982).
3. Courtens, E. and Koren, G., *Phys. Rev. Lett.,* **35**, 1711 (1975).
4. Poggi, Y., Filipini, J. C. and Aleonard, R., *Phys. Lett.,* **57A**, 53 (1976).
5. Myano, K., *J. Chem. Phys.,* **71**, 4108 (1979).
6. Sprang, H. A. van, *J. Physique,* **44**, 421 (1983).
7. Krishnaswamy, S. and Shashidar, R., *Mol. Cryst. Liq. Cryst.,* **38**, 353 (1977).
8. Gannon, M. G. J. and Faber, T. E., *Phil. Mag.,* **A37**, 117 (1978).
9. Rapini, A. and Papoular, M. J., *J. Physique, 30* **C4**, 54 (1969).
10. Naemura, S., *Appl. Phys. Lett.,* **33**, 1 (1978).
11. Sprang, H. van, *Proc. of the Tenth International Liquid Crystal Conference,* York, U.K., (1984).
12. Yang, K. H. and Rosenblatt, C., *Appl. Phys. Lett.,* **43**, 62 (1983).
13. Sprang, H. van, to be pubished in *J. Appl. Phys.*
14. Rivière, D. and Lévy, Y. J., *J. Physique,* **40**, L215 (1979).
15. Proust, J. E., Perez, E. and Ter-Minassian-Saraga, L., *Coll. Polym. Sci.,* **254**, 672 (1976), *J. de Physique,* **C3**, 490 (1979).
16. Hochbaum, A. and Labes, M. M., *J. Appl. Phys.,* **53**, 2998 (1982).
17. Barbero, G. and Barberi, R., *J. Physique,* **44**, 609 (1983).
18. Chiarelli, D., Faetti, S. and Fronzoni, L., *Phys. Lett.,* **101A**, 101 (1984).
19. Nersisyan, S. R., Oganesyan, V. O., Pakhalov, V. B., Tabiryan, N. V. and Chilingaryan, Yu.S., *J.E.T.P. Lett.,* **36**, 358 (1982).
20. Ohgawara, M. and Uchida, T., *Jap. J. Appl. Phys.,* **20**, L75 (1981).
21. Williams, C. and Kleman, M., *Phil. Mag.,* **28**, 725 (1973).
22. Ryshenkow, G. and Kleman, M., *J. Chem. Phys.,* **64**, 404 (1976).
23. Porte, G., *J. Physique,* **37**, 1245 (1976).
24. *Advances in Chemistry, Series 43* (American Chemical Society, Washington, D.C., 1964).
25. Good, W. R., *J. Coll. Int. Sci.,* **44**, 63 (1973).
26. Wu, S., *J. Adhesion,* **5**, 39 (1973).
27. Hu, P. and Adamson, A. W., *J. Coll. Int. Sci.,* **59**, 605 (1977).

28. Creagh, L. T. and Kmetz, A. R., *Mol. Cryst. Liq. Cryst.*, **24**, 59 (1973).
29. Kahn, F. J., Taylor, G. N. and Schonhorn, H., *Proc. I.E.E.E.*, **61**, 823 (1973).
30. Haller, I., *Appl. Phys. Lett.*, **24**, 349 (1974).
31. Porte, G., *J. Phys.*, **37**, 1245 (1976).
32. Hiltrop, K. and Stegemeyer, H., *Mol. Cryst. Liq. Cryst.*, **49L**, 61 (1978).
33. Ushida, T., Ishikawa, K. and Wada, M., *Mol. Cryst. Liq. Cryst.*, **60**, 37 (1980).
34. Warenghem, M., *Mol. Cryst. Liq. Cryst.*, **89**, 15 (1982).
35. Datta, P., Kaganowitz, G. and Levine, A. W., *J. Coll. Int. Sci.*, **82**, 167 (1981).
36. Okano, K. and Murakami, J., *J. Phys. Coll.*, **40, C3**-525 (1979).
37. Bernasconi, J., Strässler, S. and Zeller, H. R., *Phys. Rev.*, **A22**, 276 (1980).
38. Baron, B. A. and Gelbart, W. M., *J. Chem. Phys.*, **67**, 5795 (1977).
39. Cotter, M., *J. Chem. Phys.*, **66**, 1098 and **67**, 4268 (1977).
40. Okano, K., Matsuura, N. and Kobayashi, S., *Jap. J. Appl. Phys.*, **21**, L 109 (1982).
41. Croxton, C. A. and Chandresckhar, S., *Proc. Int. Conf. Liq. Cryst.* (Bangladore 1973), **Pramana Suppl. I**, 237 (1975).
42. Croxton, C. A., *Mol. Cryst. Liq. Cryst.*, **59**, 219 (1980).
43. Parsons, J. D., *J. Physique*, **37**, 1187 (1976).
44. Davis, H. T., *J. Chem. Phys.*, **62**, 3412 (1975).
45. Parsons, J. D., *Phys. Rev. Lett.*, **41**, 877 (1978).
46. Faetti, S. and Fronsoni, L., *Sol. State Comm.*, **25**, 1087 (1978).
47. Birecki, H., *Liquid Crystals and Ordered Fluids*, **Vol. 4**, 853 (Eds. A. C. Griffin and J. F. Johnson, Plenum, 1984).
48. Perez, E. and Proust, J. E., *C.R.*, **282 C**, 559 (1976).
49. Proust, J. E. and Ter Minassian-Saraga, L., *J. Phys. Coll.*, **36 C1**-77 (1975).
50. Perez, E., Proust, J. E. and Ter Minassian-Saraga, L., *Mol. Cryst. Liq. Cryst.*, **42**, 167 (1977).
51. Perez, E. and Proust, J. E., *J. Coll. Int. Sci.*, **68**, 48 (1979).
52. Levine, S., Robinson, K., Smith, A. L. and Breit, A. C., *Faraday Disc.*, **59**, 133 (1975).
53. Naemura, S., *J. Appl. Phys.*, **51**, 6149 (1980); *Mol. Cryst. Liq. Cryst.*, **68**, 183 (1981).
54. Mada, H., *J. Chem. Phys.*, **75**, 372 (1981).
55. Cheng, J. and Boyd, G. D., *Appl. Phys. Lett.*, **35**, 444 (1979).
56. Koshida, N. and Kikui, S., *Appl. Phys. Lett.*, **40**, 541 (1982).
57. Känel, H. V., Lister, J. D., Melingailis, J. and Smith, H. I., *Phys. Rev.*, **A24**, 2713 (1981).
58. Berreman, D. W., *Phys. Rev. Lett.*, **28**, 1683 (1972).
59. Guyon, E., Pieransky, P. and Boix, M., *Lett. Appl. Eng. Sc.*, **1**, 19 (1973).
60. Crossland, W. A., Morrisey, J. H., and Needham, B., *J. Phys.* D., **9**, 2001 (1976).
61. Goodman, L. A., McGinn, J. T., Anderson, C. H. and Digeronimo, F., *I.E.E.E. Trans. Electron Devices*, **ED-24**, 795 (1977).
62. Rosenblatt, C. and Ronis, D., *Phys. Rev.*, **A23**, 305 (1981).
63. Als-Nielsen and F. Christensen, *Phys. Rev. Lett.*, **48**, 1107 (1982).
64. Cognard, J., *Mol. Cryst. Liq. Cryst.*, **Supplement I**, 1 (1982).
65. Castellano, J. A., *Mol. Cryst. Liq. Cryst.*, **94**, 33 (1983).
66. Dubois-Violette, E. and Parodi, O., *J. de Physique*, **30 C4**-57 (1969).
67. Mada, H., *Mol. Cryst. Liq. Cryst.*, **51**, 43 (1979).

66 De Gennes, P. G., *The Physics of Liquid Crystals* (Clarendon Press, Oxford) 1974.

67 Deuling, H. J., *Mol. Cryst. Liq. Cryst.* 19 (1972) 123.

68 Blinov, L. M. *Electro-optical and Magneto-optical Properties of Liquid Crystals* (John Wiley & Sons Ltd.) 1983.

69 Landau, L. D. and Lifshitz, E. M., *Electrodynamics of Continuous Media*, (Pergamon Press, Oxford London New York Paris) 1960.