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Thickness dependence of the anchoring strength in dye-doped nematic liquid crystal cells

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Anchoring properties of polymer coated glass surfaces in nematic liquid crystal cells should not depend on the thickness of the cell. Nevertheless, in the case of cells filled with dye-doped nematic liquid crystals the anchoring energy decreases when the cell thickness increases. This experimental fact was explained by considering that adsorption of dye molecules onto the polymer coatings plays the role of defects on the aligning surfaces. A theoretical model, in terms of free energy formalism, was suggested that explains well the experimental results.

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1. Introduction

Nematic liquid crystals (NLC) present, in a certain temperature range, a characteristic uniaxial (rarely biaxial) mesophase uniform within the infinite bulk and described by the non zero average orientation of molecular long axes. The average orientation defines the unit vector, $\mathbf{n}$, the director, and the dispersion of the individual molecules' long axes about $\mathbf{n}$ is described by the order parameter $S\,(0 \le S \le 1)$. The value of S is a thermodynamic characteristic of the mesophase, depending strongly on temperature. The direction of $\mathbf{n}$ is quite arbitrary (i.e. degenerate) in the infinite bulk. In practice, the liquid crystal is always confined within planar capillary cells, the surfaces of which remove the degeneracy and impose a certain surface orientation. Depending on the orientation imposed by the surfaces, the bulk director orientation has a well defined characteristic expressed in terms of the director field $\mathbf{n}(\mathbf{r})$. For a semi-infinite bulk crystal, which is in contact only to one surface, the surface orientation extends freely into the bulk, thus being defined the *easy axis*. The anchoring properties of a surface, i.e. to impose an easy axis, is characterized by a certain *anchoring energy*, minimum when the director field about the surface is uniformly oriented along the easy axis, but larger the more distorted from it the director field is. In the case of the capillary planar cell the director field results from a compromise of the two (usually different) easy axes of the surfaces and the (usually different) anchoring energies, also taking into account the elastic properties of the bulk.

For standard applications, like liquid crystal displays, the chemical and physical nature of liquid crystals used are well known. A very important research programme is now undertaken just in connection to anchoring properties of aligning surfaces [1-4]. Both experimental and theoretical studies have been performed in the last 20 years. A rather good understanding has been got in the case of standard surfaces coated with polymers [5]. Yet, new substances, procedures and set-ups appear, revealing new behaviours and effects.

In the last time, interesting phenomena have been observed when using plasma polymerized polyaniline, polypyrrhole, or poly-o-anisidine. Under special conditions a very short relaxation time has been observed (of less than $300\,\mu s$) making the devices very attractive to display builders. Certainly, there is some more work to do until deeply reproducible and economically rewarding LCDs enter the market [6-8].

In the same trend, the influence of azo-dyes dissolved in NLCs (mainly 5CB type) on the anchoring properties of polyvinyl alcohol (PVA) has been observed [9]. Experiments concerning the influence of azo-dyes on plasma or chemically polymerized polypyrrhole and polyaniline are in progress.

One of the striking results of the experiments reported in [9] consists in a dependence of the anchoring strength on the thickness of the cell. The anchoring strength, first introduced in Rapini and Papoular model [10], is the physical measurable quantity that characterizes the anchoring energy [11-12]. Being, the later, an interfacial property, it should not depend on the thickness of a cell, unless some features in the bulk alter the surface properties. In the recent paper [9], an evident decrease of the unified anchoring energy with the increase of cell thicknesses has been observed for mixtures of 5CB liquid crystal doped with a small percentage ($1 \div 2$ %) of azo-dyes (Methyl Red (MR), Disperse Red (DR13), Disperse Orange (DO25)) ([9] and tables 1,2,3 therein). For instance, for $1.5\cdot 10^{-2}$ wt MR in 5CB.

Table 1. Anchoring strength vs. cell thickness.

Cell thickness (μm)	Anchoring strength ($10^{-5} J/m^2$)
8	6.16
19	3.52
23	3.17

This dependence is not reported for pure NLC cells [9].

The logical explanation was that the adsorption of the dye molecules on the two limiting surfaces is responsible for the anchoring energy dependence on the cell thickness. The anchoring energy decreases because the dye molecules are adsorbed on the polymeric orienting surfaces. The presence of the dye molecules acts like defects on the aligning substrate. The larger is the concentration of dissolved dye molecules in the bulk the larger is the adsorption on the surfaces and therefore the smaller is the anchoring energy, compared to that observed for pure 5CB.

2. Model

In the adsorption process, the molecules go to surface substrate and remain attached to it. In general, the adsorption phenomenon happens due to the electro-chemical interaction between the particles of the system and the surface. Since the process is generated in a macroscopic system, at constant temperature, it can be described using thermodynamic models.

In the following, the free-energy formalism for the particle adsorption, first introduced by Adelman and co-workers (for a review see [13]) to describe the kinetic adsorption of surfactants and generalized for non dilute regime by Gosslin and Mohrbach [14], is used.

As in [14] we consider *N* neutral particles in a slab of thickness *d* delimited by two surfaces of area *S*. We divide the slab into discrete cells of size a^3 (the size of the particle's perturbing sphere), and each cell is limited to a single-particle occupation. Let N_b the number of sites in the bulk and N_s the number of surface adsorption sites. In thermodynamic equilibrium we define n_b and n_s the number of particles in the bulk and at the surface, respectively. The volume fraction is then $\sigma_b = \frac{n_b}{N_b}$, and the surface density $\sigma_s = \frac{n_s}{N_s}$. The conservation of the total number of particles is

$$N = n_b + n_s \tag{1}$$

and the (number) density is

$$\Sigma = \frac{n_b + n_s}{N_b + N_s}. \tag{2}$$

Taking into consideration the geometry of the slab, one gets

$$\Sigma = 2\sigma_s \frac{a}{d} + \sigma_b \left(1 - \frac{2a}{d}\right), \tag{3}$$

remembering that the slab has two delimiting surfaces, and assuming σ_b is constant in the bulk. If not,

$$\Sigma = 2\sigma_s \frac{a}{d} + \frac{1}{d} \int_{-(d-2a)/2}^{(d-2a)/2} \sigma_b(x) dx , \tag{4}$$

the two surfaces being in positions $x = -\frac{d}{2}$ and $x = \frac{d}{2}$, respectively.

Following [13] we write the total free energy as a function of the volume fraction in the bulk

$$\frac{F(\sigma)}{S} = 2 f_s(\sigma_s) + \int_{-(d-2a)/2}^{(d-2a)/2} f_b(\sigma_b(x)) dx \tag{5}$$

where the bulk free energy is written as

$$f_b(\sigma_b) = \frac{kT}{a^3}\left\{\left[\sigma_b(x)\ln\sigma_b(x) + (1-\sigma_b(x))\ln(1-\sigma_b(x))\right] - \mu\sigma_b(x)\right\} \tag{6}$$

and the surface free energy density is equal to

$$f_s(\sigma_s) = \frac{kT}{a^2}\left\{\left[\sigma_s \ln\sigma_s + (1-\sigma_s)\ln(1-\sigma_s)\right] - \mu\sigma_s(x) - \varepsilon\sigma_s\right\} \tag{7}$$

The quantity μ represents the chemical potential of the system (in *kT* units), and ε is the energy of adsorption of one molecule on the surface. Of course, $\sigma_b \ln\sigma_b$ or $(1-\sigma_b)\ln(1-\sigma_b)$ terms represent the entropy of the system. At thermodynamic equilibrium the competition between the system energy (characterized by μ and ε) and the thermal agitation (characterized by the entropy) leads to a minimum of the free energy, determining the equilibrium σ_b. This may be obtained by varying *F* with respect to $\sigma_b(x)$, that is,

$$\frac{\delta F}{\delta\sigma_b(x)} = 0 \tag{8}$$

that yields

$$\sigma_b(x) = \sigma_b = \frac{1}{1+e^{-\mu}} , \tag{9}$$

and the condition

$$\frac{\delta F}{\delta \sigma_s} = 0 \tag{10}$$

yields

$$\sigma_s = \frac{1}{1 + e^{-\mu-\varepsilon}} . \tag{11}$$

Relation (3) allows to determine the chemical potential μ in terms of adsorption energy ε, the total density (number concentration) Σ, and the ratio $\frac{2a}{d}$.

Several particular cases can be analysed:

1) Case $1 > \Sigma >> \frac{2a}{d}$.

In this approximation, the chemical potential is obtained from $e^{-\mu} = \frac{1-\Sigma}{\Sigma}$ and the volume density is $\sigma_b = \Sigma$. Therefore, after the adsorption process takes place, a negligible variation of the bulk density appears. The surface density (surface coverage)

$$\sigma_s = \frac{\Sigma}{1 + (1-\Sigma) e^{-\varepsilon}}$$

is independent of the thickness of the cell. This approximation corresponds to a large concentration of dye, that is not our case.

2) The opposite case $\Sigma << \frac{2a}{d}$ corresponds to the dilute case, a situation that might be encountered in our system. The chemical potential, in this case, is

$$e^{-\mu} = \frac{1 + \frac{2a}{d}\left(e^{\varepsilon} - 1\right)}{\Sigma} \tag{12}$$

and, respectively the bulk densities and the surface densities are

$$\sigma_b \approx \frac{\Sigma}{1 + \frac{2a}{d}\left(e^{\varepsilon} - 1\right)} , \tag{13}$$

and

$$\sigma_s \approx \frac{\Sigma}{\frac{2a}{d} + e^{-\varepsilon}\left(1 - \frac{2a}{d}\right)} . \tag{14}$$

If $d << 2ae^{\varepsilon}$, σ_b is negligible and, from (3),

$$\sigma_s \approx \Sigma \frac{d}{2a} . \tag{15}$$

The last equation tells that the surface covered with adsorbed particles increases linearly with the thickness of the sample. In other words, a large number of the dye molecules adsorb on the surface, their bulk concentration being negligible. Of course, this happens in the case when $\varepsilon \approx \ln\left(\frac{d}{2a}\right)$, i.e. a rather large number, greater than 8 (in kT units) when the actual geometric parameters of the cell are considered. In this case almost all dye molecules stick on the surface, their bulk concentration being extremely small.

The experimental results mentioned previously [9] show that the decrease of the anchoring strength does not correspond to a linear trend. The dye concentration was about $1.5 \cdot 10^{-2}$ (wt.), corresponding for Σ to the same $1.5 \cdot 10^{-2}$ value, as the molecular masses of both dye and liquid crystal molecules are similar.

Let $a \sim 50\,nm$ and $d \approx 8\,\mu m$ in one case, or $d \approx 19\,\mu m$, $d \approx 23\,\mu m$ in another cases, one can see easily that the condition 2) is not fulfilled.

Even in this case, provided ε is conveniently large; a dependence on thickness d of the slab may appear, though not linear as in (15). It has been mentioned that the chemical potential can be determined by using (3) and, consequently correct expressions for σ_b and σ_s are possible from (9) and (11). Although analytic solutions for σ_b and σ_s are not easy to get, for various values of ε, numerical calculations can be performed.

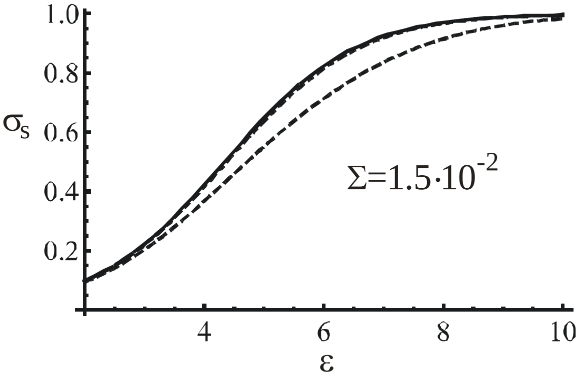

Fig.1. The surface coverage σ_s *as function of* ε *for* $d = 8\mu m$ *(dashed line), d = 19 μm (dot-dashed line), and* $d = 23\mu m$ *(solid line).*

In Fig. 1 we have plotted the surface coverage σ_s as a function of ε for values of Σ and $\frac{d}{2a}$ appropriate to our measurements. It is evident from the plot that differences between σ_s values appear only for a small domain of ε. For instance, considering $\varepsilon = 6$ there is an adsorption energy of 0.15eV at room temperature. Such a value is completely plausible. The precise dependence of anchoring energy on the surface coverage of the polymer is not well known, unfortunately. Nevertheless, a crude approximation is a proportionality to the surface not obscured (or perturbed) by the adsorbed dye $\left(1-\sigma_s\right)$. In Figure 2 we have represented the function $g\left(d\right)=a_1\left(1-\sigma_s\right)$ where a_1 is a proportionality factor and $\sigma_s=\sigma_s\left(d\right)$ calculated for $\varepsilon=6$. The experimental values are indicated by dots and error bars.

A best fit indicates $a_1=2\cdot 10^{-4}J/m^2$. In the same figure we have plotted another function $f\left(d\right)=a_2\exp\left[\alpha\left(1-\sigma_s\right)\right]$, where $a_1=10^{-5}J/m^2$ (practically a scale factor) and $\alpha=6.43$.

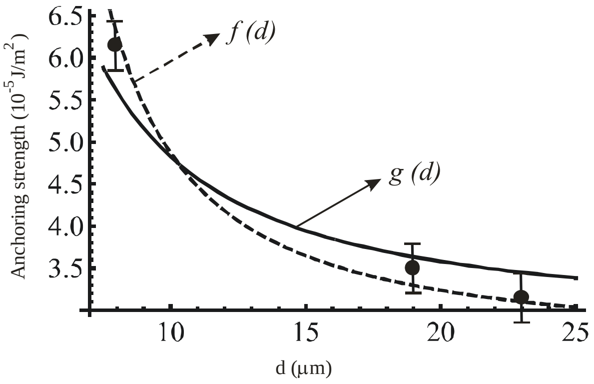

Fig. 2. Anchoring energy vs. cell thickness d.

This function gives a better fit than the previous one, at least within the range of *d* shown in figure. Comparing the two functions we may say that a series expansion of the exponential, apart from higher powers in $\left(1-\sigma_s\right)$, also gives a linear term (similar to *g(d)*) and a constant. For values of σ_s approaching *1* (for large *d*), $g\left(d\right)\rightarrow 0$, that is an almost complete covering of the polymer destroys the anchoring, a rather unrealistic fact. Probably, we better consider that even dye covered parts of the polymer anchor the liquid crystal, yet with a smaller strength. Instead, the function *f(d)* gives a correct answer to this fact. On the other hand, a drawback of the function *f(d)* is that for $d\rightarrow 0$ (and $\sigma_s\rightarrow 0$, as well) the anchoring strength becomes very large. Of course, either $d\rightarrow 0$ is an unrealistic fact.

Both functions (that we may consider as two limiting cases, because any polynomial in $\left(1-\sigma_s\right)$ is a truncated exponential) give the general trend of decreasing with a higher slope for small values of *d* and going to a low value for large *d*, exactly as the experimental results show.

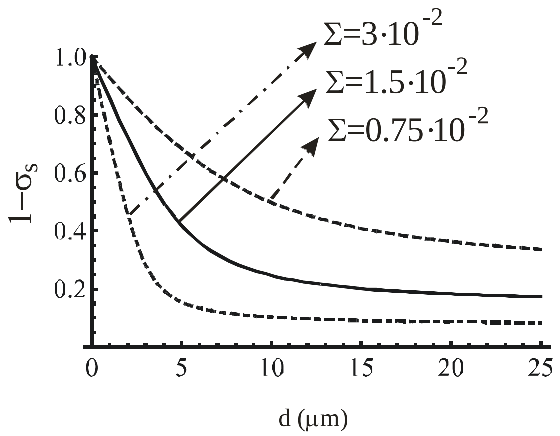

Fig. 3. The uncovered surface $\left(1-\sigma_s\right)$ vs. d for three values of Σ.

In Fig. 3, there are three plots of $\left(1-\sigma_s\right)$ for three different values of dye concentrations Σ. One can see a larger range for a linear dependence of $\left(1-\sigma_s\right)$ on *d* appears for a smaller dye concentration (for instance, less than 10^{-4}), but such values are no longer interesting for applications (e.g. laser excitation azimuthal reorientation of the easy axis, etc.).

3. Conclusions

The anomalous dependence of the anchoring strength of polymeric coatings when the cell is filled with nematic liquid crystals doped with azo-dyes has been explained by considering the adsorbed dye molecules on the aligning surfaces as defects altering the anchoring phenomena. Statistical mechanics considerations prove that, within a certain concentration range, the experimentally observed decrease of anchoring strength with the increase of cell thickness can be conveniently modelled. A linear decrease of the anchoring strength with the thickness of the cell is expected in the limit of small concentrations. Last but not the least, a practical conclusion may be drawn that for effective liquid crystal displays using dye doped mesophases, it would be advantageous to have dyes that are selectively non-adsorbed by the alignment layer.

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