

## Photo-orientation at liquid crystal–polymer interfaces

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**Abstract.** It is suggested that liquid crystal–polymer interfaces are coupled systems, in which the components mutually influence the orientational state of each other. The photo-orientation process at liquid crystal–polymer interfaces provides a striking example of such a coupling. Experiments show that the anisotropic structure generated by polarised light at a polymer surface is strongly affected by the phase of the liquid crystal covering the polymer. Photo-orientation is significantly more efficient when the liquid crystal is in the isotropic phase than when it exhibits orientational order. The observations are interpreted by assuming that in the smectic and nematic phases the liquid crystal stabilises to a large extent polymer chain-segments aligned parallel to the director, while it blocks the photo-induced formation of chain-segments in the perpendicular direction. Other situations, in which the coupling between the liquid crystal and the polymer can be important, are also discussed briefly.

**Keywords.** Photo-anisotropy; photo-alignment; liquid crystal–polymer interaction.

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### 1. Introduction

The interaction between polymer surfaces and liquid crystals plays an essential role in the operation of many liquid crystal-based devices. This interaction determines the alignment properties of a liquid crystal at its interface with a polymer layer. For example, in conventional displays the substrates are coated with polyimide layers and rubbed unidirectionally in order to induce anisotropy in the surface structure of the polymer. As a result, at the interface the liquid crystal director becomes parallel to the rubbing direction.

In the procedure outlined above, the liquid crystal apparently plays a purely passive role, its orientation is fully determined by the previous treatment of the polymer. There are, however, other cases, in which the influence of the liquid crystal on the surface structure of the polymer is also important. The aim of the present paper is to discuss such situations. We suggest that, in general, a polymer–liquid crystal interface should be regarded as a coupled system, where the two components – the polymer and the liquid crystal – mutually affect each other's structure.

In this paper, we demonstrate the importance of the coupling with a specific example, namely the influence of the presence of a liquid crystal on the so-called photo-orientation technique in dye-doped polymers. In this technique – as it will be described in detail in §2 – mechanical rubbing is replaced by the illumination of the polymer with polarised light,

which generates an anisotropic structure in the polymer network. Experiments with azo dye-doped polymers show that the alignment of a liquid crystal at the interface is significantly modified when the polymer is in contact with the liquid crystal during illumination. In §3, we present results of light-induced director reorientation at the photosensitive interface. We demonstrate that the effectiveness of the reorientation depends markedly on the phase of the liquid-crystalline material in which the irradiation was carried out. The reorientation is strongest for irradiation in the isotropic phase, very weak for the smectic phase and intermediate for the nematic phase.

The observations can be explained by assuming that the liquid-crystalline order affects the light-induced rearrangement of the polymer network in the vicinity of the interface. More specifically, we assert that rearrangement processes, which result in the decrease of the interaction energy between the polymer and the liquid crystal, are favoured against ones, which lead to the increase of this energy. This selectivity has no influence on the process in isotropic phase, while in smectic or nematic phase it has a stabilising effect on the actual director orientation. In §4, we present a simple model based on this idea, which reproduces the main characteristics of the experimental curves. In §5, we discuss some other situations, where the mutual interaction between the polymer and the liquid crystal can be important.

## 2. Photo-orientation of liquid crystals

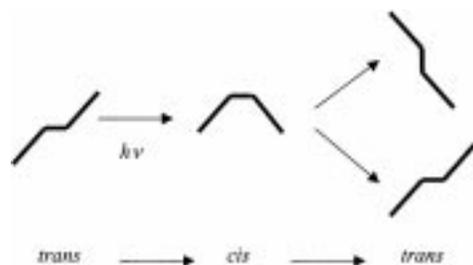
In this section we first review the mechanism leading to light-induced anisotropy in solids, then we discuss the application of this process to the orientation of liquid crystals on polymer films.

### 2.1 Photo-induced anisotropy in solids

The first observation of photo-induced anisotropy in solid state goes back to 1919, when Weigert found that silver chloride films become dichroic and birefringent under the influence of polarised light [1]. Since then, similar effects have been detected in other photosensitive materials, like chalcogenide glasses [2] or dye-doped polymers [3]. Photo-induced changes of the optical properties usually have an irreversible part (occurring only during the first illumination of the sample), as well as a reversible one. Regarding photo-induced anisotropy, reversibility means that the symmetry axis of the anisotropic structure can be switched between different orientations by changing the polarisation direction of the irradiating light.

Reversible photo-induced changes can be attributed to the presence of bistable atomic configurations localised in the solid. The concept of bistable configurations [4] was first introduced in connection with the specific heat anomaly observed in glasses at low temperatures. The extension of this model to photo-induced phenomena was proposed by Tanaka [5]. In this paper, we illustrate the main idea of the model, applying it to polymers doped with azo dyes.

We consider a polymer containing dye molecules, either attached chemically to the main chains or simply mixed with the polymer. We discuss azo dyes specifically, which exhibit *trans*–*cis* isomerisation. In the absence of illumination, the position and orientation of the dye molecules cannot change and the *trans* configuration is stable. Excitation by a photon



**Figure 1.** Schematic representation of the bistable configuration model. As a result of a *trans*–*cis*–*trans* cycle, the dye molecule can rotate away from its original position.

can transform the molecule to the *cis* state (figure 1). The *trans* state is eventually restored by a further absorption process or through thermal relaxation. As indicated in figure 1, a *trans*–*cis*–*trans* cycle can result, with a certain probability, in the rotation of the dye molecule relative to the host matrix. It is assumed that the new orientation is stable, but a next *trans*–*cis*–*trans* cycle might rotate back the molecule to its original orientation. In the bistable configuration model it is supposed that only two stable orientations exist for a given dye (although the model could be easily generalised to take into account more than two configurations).

The development of light-induced anisotropy is related to the difference in the excitation probabilities for the two orientations. If, as a result of rotation from the first orientation to the second one, the angle between the transition dipole moment and the light polarisation increases, the excitation probability decreases. As a consequence, under continuous illumination, the dye molecule can be found with higher probability at the second orientation than at the first one. Considering all dye molecules and orientations, one finds that the population of the dye molecules is maximum for the orientation where the transition dipole moment and the light polarisation are perpendicular, and minimum (in principle zero) where they are parallel to each other. The anisotropic angular distribution of the dye is the origin of the observed dichroism. We note that due to the interaction between the dye molecules and the polymer network, the polymer chains also become oriented to a certain extent. The birefringence can originate both from the dye molecules and the distorted polymer structure.

The bistable configuration model accounts for the basic observations, like development of anisotropy in initially isotropic films, reversible reorientation of the symmetry axis and the possibility to erase anisotropy (in the plane perpendicular to light propagation) by using circularly polarised or unpolarised radiation. A quantitative treatment of the model will be presented in §4.

## 2.2 Alignment of liquid crystals on polymers

As discussed in §1, photo-induced anisotropy of polymers can be used to control the alignment of liquid crystals. For display applications, irreversible processes are used. The polymer is irradiated with polarised UV light, which creates cross-links between the chains [6,7] or, in other systems, breaks the polymer chains [8]. Both processes are polarisation sensitive, i.e., the probability to break a chain or to establish a cross-link is the highest

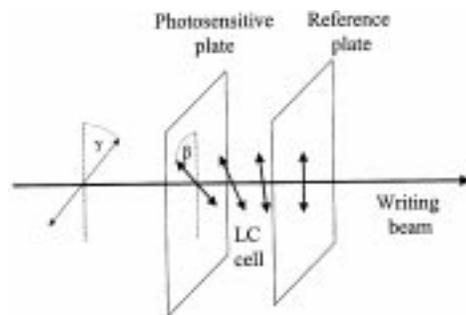
when the chain segment or the link is oriented parallel to the light polarisation and gradually decreases as the angle between the orientation and the polarisation increases. The resulting anisotropic polymer structure orients the liquid crystal usually perpendicular to the polarisation direction.

Reversible processes in dye-doped polymers, discussed in §2.1, can also be used to align liquid crystals [9]. The orientation of a nematic liquid crystal at the interface corresponds to the main direction of the dye orientation. This effect can be applied to write high resolution grey-scale images into the liquid crystal cell [10]. To create the image, each pixel of the image is illuminated with an appropriately polarised, focused laser beam. Because of reversibility, the pixels can be reconfigured several times by changing the polarisation direction of the laser beam. In the latter application the structural changes in the polymer must be induced in the presence of the liquid crystal. As mentioned in §1, this has a strong influence on the director orientation process. The details, based on an earlier investigation [11], are given in the following sections.

### 3. Experiment

Photo-alignment was studied in sandwich-type cells (figure 2). One plate was treated conventionally, i.e., it was coated with a polyimide layer (Du Pont PI 2555) and rubbed unidirectionally to assure planar anchoring. The photosensitive plate was coated with a filtered and saturated solution of the azo dye Disperse Orange 3 (Aldrich Chemicals) in a polyamic acid solution and subsequently heat treated for 2 h to complete imidization. The cells were filled in the isotropic phase and cooled to the smectic phase in the presence of a strong magnetic field, parallel to the rubbing direction. This procedure ensured a good initial planar alignment. Photo-alignment was induced with an unfocused argon laser beam at 488 nm, at power levels 70 mW. The polarisation direction of the pump beam was at  $45^\circ$  from the rubbing direction. The cells were illuminated from the photosensitive side.

In the experiments the liquid crystals 4-cyano-4'-*n*-octylbiphenyl (8CB) and 4-cyano-4'-*n*-octyloxybiphenyl (8OCB) were studied. Both compounds have smectic A and nematic phases. The smectic A–nematic phase transitions occur at  $32^\circ\text{C}$  and at  $67^\circ\text{C}$ , the clearing points are at  $39^\circ\text{C}$  and  $80^\circ\text{C}$  respectively for the two compounds.

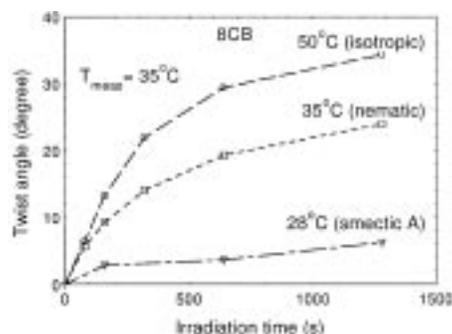


**Figure 2.** Experimental set-up for the investigation of photo-orientation.  $\gamma$ : angle between the light polarisation and the rubbing direction.  $\beta$ : angle between the director on the photosensitive plate and the rubbing direction (twist angle).

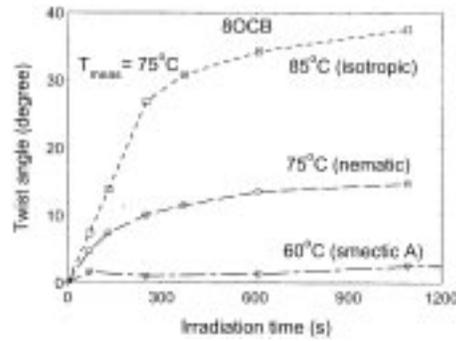
To investigate the influence of the liquid crystal on the photo-orientation process, we irradiated the sample at different temperatures, corresponding to various phases (smectic A, nematic and isotropic). When irradiation was carried out in the nematic phase, photo-alignment was seen immediately. The director on the photosensitive plate turned towards the direction perpendicular to the light polarisation, creating a twist deformation in the cell (figure 2). The twist angle could be readily measured in a polarising microscope or with the help of a probe beam. On the other hand, the effect of irradiation completed in the isotropic or smectic A phase, could be investigated only indirectly. In the isotropic phase, because of the lack of liquid-crystalline order, a ‘latent’ orientation is generated, which becomes apparent only when the sample is cooled down to the nematic range. Regarding the smectic A phase, twist deformation is incompatible with the layered structure of the phase. Therefore, photo-induced director realignment on the photosensitive plate is blocked. To make the effect of irradiation evident, the sample has to be heated up to the nematic range, where twist deformation can take place. In view of the above considerations, in the experiments light-induced twist angles were measured always in the nematic phase, at the same temperature, irrespective of the temperature of irradiation.

In figures 3 and 4, results of irradiation at different phases are shown. For the two liquid crystals, we plotted the photo-induced twist angle as a function of the irradiation time. The experimental curves clearly show the significance of the liquid crystalline order in the kinetics of the surface reorientation. In spite of the temperature differences, the curves for the isotropic, nematic and smectic phases are qualitatively similar for the two materials. When irradiation is carried out in the smectic phase, the twist angle saturates at few degrees. For the isotropic phase, the twist angle approaches the possible highest value,  $\pi/4$ . In the nematic phase, one obtains substantially higher twist angles compared to the smectic phase, but the increase in the deformation is much more gradual than in the isotropic phase.

From the curves, it is evident that the observed differences are due to the changes in the liquid-crystalline phase and not due to the differences in the irradiation temperature. As a striking example, one may compare the curve for the isotropic phase of 8CB at 50°C, with the one for the smectic phase of 8OCB at 60°C. Although the photosensitive layer was the same in both cases and the temperature was even lower in the former case, the irradiation was much more effective when the polymer was in contact with the isotropic 8CB rather than the smectic 8OCB.



**Figure 3.** Twist angle as a function of irradiation time at different temperatures for 8CB.  $\gamma = -\pi/4$ .



**Figure 4.** Twist angle as a function of irradiation time at different temperatures for 8OCB.  $\gamma = -\pi/4$ .

#### 4. Model

In this section we discuss a simplified model of photo-alignment, which nevertheless retains the essential features of the phenomenon.

##### 4.1 Calculation of the dye distribution

In order to calculate the orientational distribution of the dye molecules in the presence of illumination, we use the bistable configuration model, outlined in §2.1. To keep mathematics simple, we deal with a two-dimensional model, i.e., we take into account only dye molecules aligned within the plane of the sample. The orientation of such molecules can be characterised through the azimuthal angle  $\xi$  between their transition dipole moment (in the *trans* state) and a reference direction, which we choose to be parallel to the rubbing direction. The probability per unit time that during a *trans-cis-trans* cycle a dye molecule rotates from a first orientation to a second one (1→2 transition) can be written as

$$p_{12} = \sigma I \Lambda_{12} \cos^2(\xi_1 - \gamma), \quad (1a)$$

where  $I$  is the light intensity,  $\sigma$  the absorption cross-section,  $\xi_1$  the direction of the transition dipole at the initial orientation,  $\gamma$  the angle between the polarisation direction and the rubbing direction. Finally,  $\Lambda_{12}$  denotes the quantum efficiency, i.e., the probability that the excitation is followed by a change of orientation during the cycle. The probability of an inverse process (2→1 transition) is, similarly

$$p_{21} = \sigma I \Lambda_{21} \cos^2(\xi_2 - \gamma). \quad (1b)$$

As a further simplification, it is assumed that in the bulk of the polymer all configurations are identical with each other, except orientation, and the angle between the two possible orientations of a dye is a fixed value. This assumption implies that the quantum efficiencies are the same for all dye molecules and they are equal for direct and inverse transitions, i.e.,  $\Lambda_{12} = \Lambda_{21}$ . The same holds near the interface, provided the liquid crystal is in the isotropic phase. For the nematic and smectic phases, however, the interaction between the liquid

crystal and the dye molecules, located in the vicinity of the interface, breaks the symmetry of the two orientations. It is plausible to assume that transitions, leading to a decrease of the liquid crystal–polymer interfacial energy, are biased with respect to inverse transitions.

In analogy to the guest–host effect in the bulk of nematic or smectic phases, we write the interfacial energy, associated with a dye molecule oriented along  $\xi$ , in the form

$$U(\xi) = -U_0 \cos^2(\xi - \beta). \quad (2)$$

Here  $\beta$  is the azimuthal angle of the director at the photosensitive plate.  $U_0$  is of the same order of magnitude as that of the liquid crystal mean-field potential, i.e., it is few times  $kT$ . The liquid crystal potential cannot induce transitions in itself, but it can, however, influence the light-induced transitions. Obviously, rotations of a dye molecule towards the director are more probable than a rotation away from it. We include this fact into the model by multiplying the quantum efficiencies with a Boltzmann factor:

$$\begin{aligned} \Lambda_{12} &= \Lambda_0 \exp \left\{ -\frac{U_0}{2kT} \cos^2(\xi_1 - \beta) \right\}, \\ \Lambda_{21} &= \Lambda_0 \exp \left\{ -\frac{U_0}{2kT} \cos^2(\xi_2 - \beta) \right\}. \end{aligned} \quad (3)$$

In order to calculate the dye distribution function, one has to first distinguish between the ‘1st’ and ‘2nd’ configurations of a given dye molecule. We label by number 1 the initial configuration, in which the dye could be found before starting the illumination. As initially the polymer is isotropic, the dye orientational function,  $f(\xi)$ , at the start of irradiation ( $t = 0$ ) is

$$f(\xi, t = 0) = N/2\pi, \quad (4)$$

where  $N$  is the number of dyes/unit interfacial area.

To find the orientational density of molecules during irradiation, one should consider that to an initial orientation  $\xi_1$  there belongs two possible  $\xi_2$  values, corresponding respectively to clockwise and anticlockwise rotation during the configurational transition. In order to avoid minor complications, we consider here the case, when  $\xi$  and  $-\xi$  are equivalent directions (no polar character) and the rotation angle during a  $1 \rightarrow 2$  or  $2 \rightarrow 1$  transition is  $\pi/2$ . In this case clockwise and anticlockwise rotations are physically the same, and the rate equation can be written in the form

$$df(\xi)/dt = -p_{12}(\xi)f(\xi) + p_{21}(\hat{\xi})f(\hat{\xi}), \quad (5a)$$

$$df(\hat{\xi})/dt = -p_{21}(\hat{\xi})f(\hat{\xi}) + p_{12}(\xi)f(\xi), \quad (5b)$$

with the notation  $\hat{\xi} = \xi + \pi/2$ . From eq. (5) and the initial condition it follows that

$$f(\xi) + f(\hat{\xi}) = \text{const.} = N/\pi.$$

Applying this relation, the rate equation can be rewritten in the form

$$df(\xi)/dt = (f_s - f(\xi))/\tau,$$

with

$$f_S = N p_{21}(\hat{\xi}) \tau / \pi \quad \text{and} \quad 1/\tau = p_{12}(\xi) + p_{21}(\hat{\xi}). \quad (6)$$

With the help of eq. (6) and the initial condition (eq. (4)), the dye distribution can be calculated, provided all parameters are specified, and the director angle  $\beta$  on the photosensitive plate is known.

#### 4.2 Determination of the twist angle

We first consider the question of the initial orientation of the director on the photosensitive plate. As described in the experimental section, we filled the cell in isotropic phase and cooled it to the liquid crystalline phase in the presence of a strong magnetic field, applied parallel to the rubbing direction. This procedure leads to stable planar orientation. There are two possible mechanisms, which can stabilise the planar alignment. Firstly, this orientation corresponds to the minimum bulk energy of the nematic phase, as there is no director distortion in the cell. Secondly, the formation of a liquid-crystalline order can induce irreversible changes in the polymer surface structure, leading to the so-called surface memory effect [12]. As a result of such changes, finite azimuthal anchoring energy can develop at the interface, stabilising the initial orientation. The relative importance of the two mechanisms can be separated, by investigating the thickness dependence of light-induced surface reorientation. As shown in an earlier publication [13], in our cells the dominant contribution comes from the anchoring energy due to the initial interaction of the polymer and the liquid crystal; the elastic energy can be neglected even if the cell thickness is only a few microns. One can write the contribution of this initial anchoring to the interfacial energy in the form

$$W_{\text{pol}} = -W_0 \cos^2 \beta. \quad (7)$$

The interfacial energy due to the dye–liquid crystal interaction can be given as

$$W_{\text{dye}} = \int_0^{2\pi} f(\xi) U(\beta) d\xi = - \int_0^{2\pi} f(\xi) U_0 \cos^2(\beta - \xi) d\xi, \quad (8)$$

where the potential  $U$  is taken from eq. (2). The measured twist angle,  $\beta$ , corresponds to the minimum of the total interfacial energy. As a simple calculation shows, the minimisation of the sum of  $W_{\text{dye}}$  and  $W_{\text{pol}}$  leads to

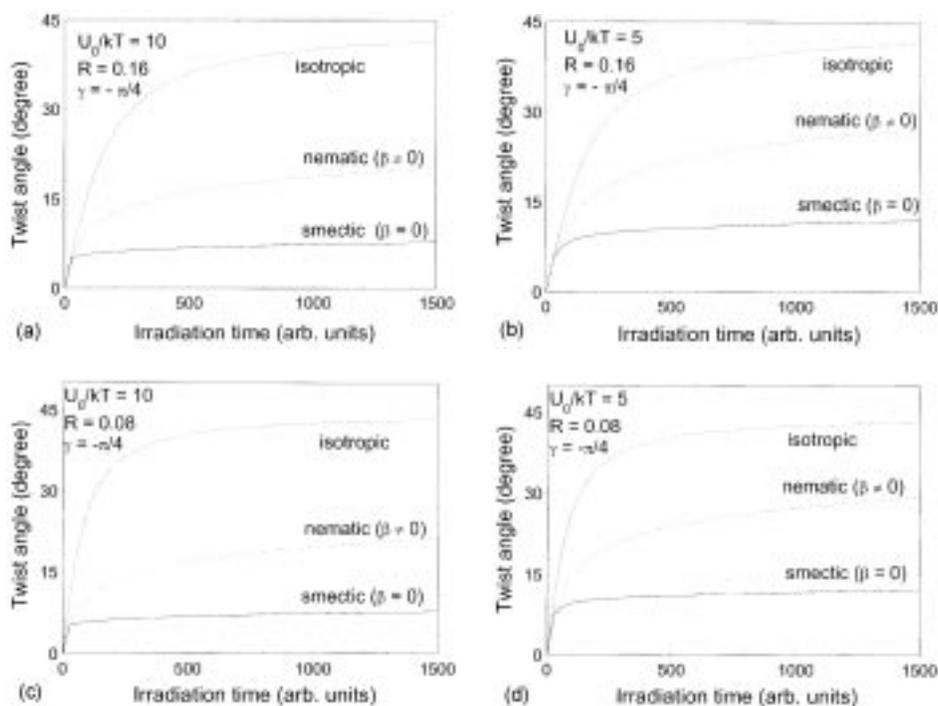
$$\beta = \frac{1}{2} \arctan \frac{S}{C + R} \quad (9)$$

with

$$S = \frac{1}{N} \int_0^{2\pi} f(\xi) \sin 2\xi d\xi, \quad C = \frac{1}{N} \int_0^{2\pi} f(\xi) \cos 2\xi d\xi \quad \text{and} \quad R = \frac{W_0}{\pi N U_0}.$$

$R$  is a dimensionless parameter and it gives the ratio of the initial anchoring strength to the anchoring strength one would obtain, if the dye molecules were perfectly oriented.

In figure 5, examples of calculated kinetic curves are shown. For the isotropic phase,  $U_0$  was set to zero. In the case of the smectic phase, twist deformation is not allowed, hence we assumed  $\beta = 0$  during the entire irradiation time. To a large extent the presence of the



**Figure 5.** (a)–(d) Calculated kinetics curves for irradiation in different phases, for different  $U_0$  and  $R$  parameters.

liquid crystal potential blocks the light-induced rearrangement of the dye molecules at the polymer surface. As a result, the twist angle induced by irradiation in the smectic phase (and measured in the nematic phase), is only a fraction of the twist angle obtained after a corresponding irradiation in the isotropic phase.

For the nematic phase, the same mean-field potential was assumed than for the smectic phase. In the nematic phase, however, twist deformation can occur during irradiation. To calculate the reorientation, one has to solve the coupled equations, eqs (6) and (9), which give respectively the dye distribution and the director orientation on the photosensitive plate. As can be seen from the curves, the progress of the twist deformation in nematics is slowed down in comparison to the process in the isotropic phase, but the twist angle saturates at a significantly higher value than in the smectic phase.

The qualitative similarity between the measured and calculated kinetic curves, shown in the figures, is apparent. In view of the simplifications made in our model, we did not try to fit quantitatively the theoretical plots to the experimental data. We note, however, that the main features of the calculated curves are retained for a large range of reasonable values of the parameters  $U_0$  and  $R$ , thus supporting the ideas presented in the paper.

### 5. Other possible effects

The influence of the liquid crystal on the surface structure of the polymer can play a role in numerous other situations. In the discussion of photo-induced phenomena, we neglected

the possibility that the liquid-crystalline order can itself induce structural changes in the polymer. The development of the initial anchoring (§4.2), however, can be due to such rearrangements. In terms of the model used in this paper, one can assume that there are bistable configurations (not necessarily associated with dye molecules), where the two states are separated by a barrier with a height which is few times  $kT$ . In a liquid-crystalline potential these configurations become asymmetric and transitions can occur between them. The transitions always take place in that direction, which decreases the interfacial energy. As a consequence, the process tends to stabilise the actual alignment of the liquid crystal.

A similar mechanism can govern the so-called director-gliding effect [14,15]. It is found that in certain polymers, strong magnetic or electric fields can realign to some extent the surface nematic director in the plane of the interface. To interpret this effect, one has to take into account the finite anchoring strength of the interfacial director orientation. When the field is switched on, the director at the interface rotates by a small amount, until the sum of the interfacial and field energy becomes minimal. The new director orientation induces structural changes in the polymer, bringing closer the minimum of the interfacial energy to the actual director orientation. This change, however, allows the director to rotate further towards the field and the process continues until equilibrium is reached.

An analogous process can take place in the case of zenithal anchoring. There are evidences that when a strong electric field is applied normal to the interface, the pre-tilt angle at a polymer–liquid crystal interface can change permanently (or at least for a much longer time than predicted from bulk relaxation of the director). This effect can play a role in image sticking, observed in nematic displays [16]. It may also be one of the sources of the difficulties encountered when the anchoring energy on polymer surfaces is measured [17]. According to our picture, the change of the pre-tilt is due to the rearrangement of the polymer chains under the influence of the nematic potential.

In conclusion, we have shown that liquid crystals can create anisotropy, or can modify existing anisotropic structures at polymer surfaces. This effect can have a significant role in various phenomena, where director reorientation takes place.

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