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Model for the planar-homeotropic anchoring transition induced by *trans-cis* isomerization

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We present a model to explain the planar-homeotropic anchoring transition of azobenzene induced by UV illumination via *trans-cis* isomerization. We consider bulk and surface as two different phases (separated by an infinitely sharp interface) which are in equilibrium. We obtain a relation for the exposure time after which the transition takes place.

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I. INTRODUCTION

In thermotropic liquid crystals, the phase transitions are induced by temperature. In certain mesogens, the phase transitions between different kinds of order are induced by the changes in molecular structure. These can be induced either by temperature (like in the 4,n-alkyloxybenzoic acids [1] where the structure changes between cycled (closed) dimers, open dimers, and monomers) or by adsorbtion of light {*trans-cis* photoisomerization in 4-hexyloxy-(4′hexyl)azobenzene [2]}.

Although the theoretical model presented in this paper describes the two kinds of experimental results we discuss it only in connection with the *trans-cis* photoisomerization [3–6] that induces a planar-homeotropic anchoring transition. In the experiment [2], a cell of conventional sandwich type consisting of two parallel glass plates was used. In the initial state of the photosensitive material (azobenzene that exhibits a nematic phase in the temperature range 27-68° C), all the molecules are in the *trans* state, and the planar orientation is achieved. With the UV exposure time the concentration of *cis*-isomers increases. The *cis*-isomers having larger polarity are more strongly attracted by the cell surfaces through the polar-polar interactions. As a consequence, the surface density of the *cis*-isomers increases with the exposure time. Since, for steric reasons *cis*-isomers favor homeotropic orientation [2], a planar-homeotropic anchoring transition could be induced by the adsorption phenomenon.

In this paper we present a model that explains these experimental results. In Sec. II we describe the model, while the results obtained are presented in Sec. III. Finally in Sec. IV we make some concluding remarks. In our analysis the adsorption of the *cis*-isomers at the surfaces is described by assuming the mixture of *cis* and *trans*-isomers as a solution of ideal gases.

II. MODEL

We consider that the anchoring free energy of the liquid crystal on the solid surface depends only on the polar angle θ (the angle between the normal and the surface nematic director). Following Rapini and Papoular [7], the anisotropic part of the anchoring free energy f_s per unit surface can be written in the first approximation as

$$f_s=\frac{1}{2}B\cos^2\theta, \tag{1}$$

with

$$B=N_{2s}w_2-N_{1s}w_1, \tag{2}$$

where N_{2s} (N_{1s}) are the numbers of *trans* (*cis*) molecules adsorbed at the surface and w_1 (w_2) are the corresponding surface free energies, per surface particle. Equation (2) holds in the hypothesis of homogeneous adsorption of UV through the sample, as we shall assume in our analysis. Minimizing the surface free energy (1) with respect to θ two solutions are obtained. If $B>0$ the planar orientation ($\theta=\pi/2$) (favored by *trans* molecules) is stable and if $B<0$ the homeotropic orientation ($\theta=0$) (favored by *cis* molecules) is stable. Thus the problem is now to calculate the number of *trans* (N_{2s}) and *cis* (N_{1s}) molecules adsorbed at the surface as a function of time.

In the initial state (at $t=0$) all the molecules of the system $N_2(0)$ are in the *trans* state. We consider that the number of sites N (of possible adsorbed molecules) is constant. This statement constitutes an approximation since the excluded areas of *trans* and *cis* molecules are different. With this approximation, the total number of molecules in the bulk $N_b=N_2(0)-N$ is also a constant. Considering the geometry of the experiment presented in Ref. [2] (a sandwich-type cell consisting of two parallel glass plates) we can roughly estimate the ratio K between the numbers of adsorbed and bulk molecules. The density of azobenzene molecules is of the order of 10^{26} m^{-3}, so that the total number of molecules in the bulk is given by $N_2(0)\approx 10^{26}\times 2\times 10^{-6}\times A=2\times 10^{20}$ A m^{-2} where A is the area of the glass plate and $d=2\times 10^{-6}$ m is the thickness of the cell. Supposing that the adsorbed molecules (with radii of the order of 10^{-10} m) form a uni-molecular layer, the number of these molecules is $N\approx 10^{18}$ A m^{-2}, so that

$$K=\frac{N}{N_b}\approx\frac{N}{N_2(0)}\approx 0.01. \tag{3}$$

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The time evolution of the number of particles of the two constituents is approximated by the relations [8,9]

$$\begin{aligned} N_2(t,x) &= N_2(0)[x+(1-x)\exp(-t/\tau)], \\ N_1(t,x) &= N_2(0)(1-x)[1-\exp(-t/\tau)], \end{aligned} \tag{4}$$

where τ is a characteristic time and x is a parameter that controls the fraction of $trans[N_2(t)]/cis[N_1(t)]$ isomers after the illumination because some kind of recombination has to be considered. Increasing N_1 the nematic properties of the mixture change continuously. As discussed in Ref. [9] there exists a critical concentration of *cis*-isomers such that for concentratrion larger than this critical one the mixture is in the isotropic phase. In what follows we assume to be well below this critical concentration. This hypothesis implies that in Eq. (4) x is rather small with respect to one. With this parametrization at every moment of time t the conservation of number of particles is achieved:

$$N_2(0)=N_1(t)+N_2(t)=N_{1b}(t)+N_{1s}(t)+N_{2b}(t)+N_{2s}(t), \tag{5}$$

where

$$N_b(t)=N_{1b}(t)+N_{2b}(t)=\text{const} \tag{6}$$

represents the total number of molecules in the bulk, and

$$N(t)=N_{1s}(t)+N_{2s}(t)=\text{const} \tag{7}$$

the total number of molecules at the surface.

The concentration c_s of *cis* molecules at the surface is defined by the relation

$$c_s=\frac{N_{1s}}{N}. \tag{8}$$

The concentration C_b of *cis* molecules in the bulk can be expressed with respect to the number of sites by

$$C_b=\frac{N_{1b}}{N_b}. \tag{9}$$

By considering the relations (6) and (7), the time dependence of C_b is given by

$$C_b=\frac{N_1(t)}{N_2(0)}-Kc_s, \tag{10}$$

where K is the ratio defined by Eq. (3). Since $Kc_s \in [0;0.01]$, we can neglect it and obtain

$$C_b=\frac{N_1(t)}{N_2(0)}. \tag{11}$$

The problem is now to obtain the relation between the concentrations of *cis* molecules in the bulk C_b and that of the surface c_s.

We assume that the transfer rate of energy into the system is quite small, so that in every moment the system (bulk and surface) is in a thermodynamic equilibrium state. This assumption implies that the diffusion process is fast enough, as we shall suppose in our analysis. The main idea is the following: we consider an isothermal solution of two different components (*cis* and *trans*) which may exist as two distinct phases, bulk and surface, with an infinitely sharp interface between them.

The bulk free energy density has the following form:

$$f_b(C_b)=C_bf_1+(1-C_b)f_2+\frac{k_BT}{v}[C_b\ln C_b+(1-C_b)\times\ln(1-C_b)], \tag{12}$$

where k_B is the Boltzmann constant and $v=(N_{1b}v_1+N_{2b}v_2)/N_b$ is the molecular volume, which is assumed to be constant (an approximation since N_{1b} and N_{2b} depend on time and $v_1\neq v_2$).

The first two terms in Eq. (12) correspond to the contribution to the free energy density due to the individual free energy densities of the two components and the last term is due to the decrease in energy associated with the mixing of the two components, under our assumption that bulk phase is an ideal solution. A more complex form might include energy of mixing terms proportional to $C_b(1-C_b)$.

We rescale the free energy density by introducing the following dimensionless quantities:

$$\tilde{f}_b=f_b\frac{v}{k_BT};\quad \tilde{f}_i=f_i\frac{v}{k_BT}\quad i=1,2. \tag{13}$$

Omitting the tilde signs, the dimensionless bulk free energy density is given by

$$f_b(C_b)=C_bf_1+(1-C_b)f_2+C_b\ln C_b+(1-C_b)\ln(1-C_b). \tag{14}$$

Minimizing f_b subject to the constraint that number of *cis* molecules is conserved, we obtain [using Eq. (9)]

$$A=\frac{\partial f_b}{\partial C_b}=f_1-f_2+\ln\frac{C_b}{1-C_b}, \tag{15}$$

where A is the corresponding Lagrange multiplier (proportional to the chemical potential).

We take the free energy density corresponding to the surface phase as

$$f_s(c_s)=c_sf_1+(1-c_s)f_2+\frac{k_BT}{v}[c_s\ln c_s+(1-c_s)\times\ln(1-c_s)]+c_s\varepsilon_1+(1-c_s)\varepsilon_2, \tag{16}$$

where $\varepsilon_1(\varepsilon_2)<0$ is the adsorbtion energy of a *cis* (*trans*) molecule. Since the *cis* molecule is more attracted by the surface, $|\varepsilon_1|>|\varepsilon_2|$.

Using the scaling Eq. (13) and $\tilde{\varepsilon}_i=\varepsilon_i v/k_BT$; $(i=1,2)$, and minimizing Eq. (16) with respect to c_s we obtain

$$A=\frac{\partial f_s}{\partial c_s}=f_1-f_2+\ln\frac{c_s}{1-c_s}-\Delta\varepsilon, \tag{17}$$

where $\Delta\varepsilon=\varepsilon_2-\varepsilon_1>0$.

III. RESULTS

In the approximation $f_1 = f_2$, Eqs. (15) and (17) lead to

$$\frac{C_b}{1-C_b} = \frac{c_s}{1-c_s}\exp(-\Delta\varepsilon). \tag{18}$$

Using Eq. (11), the density of *cis* molecules at the surface is given by

$$c_s(t,x) = \left[1 + \frac{N_2(t,x)}{N_1(t,x)}\exp(-\Delta\varepsilon)\right]^{-1}, \tag{19}$$

with $N_1(t,x)$ and $N_2(t,x)$ given by Eqs. (4). This is the central result of our model. We note that if $\varepsilon_1 = \varepsilon_2$, and hence $\Delta\varepsilon = 0$ from Eqs. (18) and (19) one obtains $c_s(t,x) \propto N_1(t,x)$, as expected. In fact, in the case of equal adsorption energies the concentrations of adsorbed molecules are proportional to the bulk concentations.

When $t=0$ one has $c_s(0,x)=0$ (the *cis* molecules do not exist). In the limit of long time exposure, i.e., $t \to \infty$ the concentration of *cis* molecules is controlled by the parameter *x*:

$$c_s(\infty,x) = \left[1 + \frac{x}{1-x}\exp(-\Delta\varepsilon)\right]^{-1}. \tag{20}$$

Using Eq. (2), the planar-homeotropic phase transition takes place after an illumination time $t = t^*$, given by

$$\frac{N_2(t^*,x)}{N_1(t^*,x)} = \frac{w_1}{w_2}\exp(-\Delta\varepsilon). \tag{21}$$

By substituting Eq. (4) into Eq. (21) we obtain

$$t^* = \tau \ln \frac{(1-x)[1-(w_1/w_2)\exp(-\Delta\varepsilon)]}{(1-x)(w_1/w_2)\exp(-\Delta\varepsilon) - x}. \tag{22}$$

Even if the experimental results for τ are available [8], the estimation of t^* is difficult beause the result depends also on *x*, which is a phenomenological parameter connected with the recombination process. To have an order of magnitude of t^* we assume $\tau \sim 10^2$ s [8], $x \sim 0.1$ [2], $w_1 \sim w_2$, and $\Delta\varepsilon \sim 1$. The value assumed for $\Delta\varepsilon$, in $k_B T$ units, is reasonable because, for what concerns the interaction with the surface, the two isomers are very similar. With these values, from Eq. (22) we obtain $t^* \sim 100$ s, in good agreement with the experimental value $t^* \sim 120$ s [2].

IV. CONCLUSIONS

We have presented a theoretical model to explain the planar-homeotropic anchoring transition of azobenzene induced by UV illumination. Experimentally it was found that this transition is a consequence of the *trans-cis* isomerisation and of the fact that *cis* molecules (which tend to induce a homeotropic texture) are more attracted by the surface [2]. The main idea of the present model is to consider bulk and surface as two different phases (separated by an infinitely sharp interface) which are in equilibrium. By minimizing the corresponding free energy densities subject to the constraint that the number of *cis* molecules is conserved, we have obtained the equilibrium condition (19). The increase of concentration of *cis* molecules at the surface is due to the larger (comparing with *trans*) adsorbtion energy. Using this result and a phenomenological dependence of number of particles on time [Eqs. (4)], we have obtained the exposure time after which the transition takes place. Even if the model presented contains some approximations (number of sites at the surface is constant, molecular volume of bulk and, respectively, surface mixture is constant), it explains (at least qualitatively) the experimental results reported in Ref. [2]. This model could be adapted to describe possible similar anchoring phase transitions in nematic mixture [10,11].

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