

## Liquid crystal-surface interactions studied by light scattering

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### Abstract

*Anchoring energy of liquid crystals on solid substrates is a key parameter in liquid crystal technology. A nonperturbative method of its measurement by dynamic light scattering on thermal orientational fluctuations is presented. The ratio of the zenithal and azimuthal anchoring coefficients is shown to be equal to the ratio of the orientational elastic constants.*

### 1. Introduction

Liquid crystals (LC) are standardly aligned by a suitably treated substrate, usually rubbed or photosensitive polymer. The direction of the surface induced orientation of the LC molecules is called the easy axis of the surface. The energy of the deviation of the LC director from the easy axis can be assumed to have the Rapini- Popoular form

$$W_{surf} = \frac{1}{2}W_{\phi} \sin^2 \phi + \frac{1}{2}W_{\theta} \sin^2 \theta \quad (1)$$

where  $\phi$  and  $\theta$  are the azimuthal (in-plane) and zenithal (out-of-plane) angles of the director deviation from the easy axis and  $W_{\phi}$  and  $W_{\theta}$  are the corresponding anchoring coefficients.

The usual technique to measure the anchoring coefficients is to apply some external torque on the LC sample by external fields or by twisting of the bounding plates. This introduces large distortions of the LC and often complex behavior like easy axis creep that make the interpretation of the experiments difficult. Also, both anchoring coefficients can not be measured by the same method. So the reported values are very different and often

inconsistent. In particular, different measurements give very different values of the ratio  $W_{\phi} / W_{\theta}$ , with  $W_{\theta}$  which is more difficult to measure, often considerably larger than  $W_{\phi}$ .

We have developed a method to measure both anchoring coefficients in an equilibrium situation by observing the relaxation rate of the thermally excited orientational fluctuations as a function of the thickness of the sample [1-3]. In a thick sample the relaxation rate is governed by the ratio of the bulk orientational elastic constants  $K_1$ ,  $K_2$ , and  $K_3$  to an effective viscosity. In samples thin in comparison with the scattering length we observe only the fundamental orientational fluctuation mode with the effective wave vector  $q$  determined by the solution of the transcendental equation:

$$q \tan \left( q \frac{d}{2} \right) = \frac{W_i}{K_i} \quad (2)$$

where  $i$  designates the relevant anchoring coefficient and elastic constant. The relaxation rate of the fluctuation mode is given by

$$\frac{1}{\tau} = \frac{K_i}{\eta_{eff}} q^2 \quad (3)$$

where  $\eta_{eff}$  is an effective rotational viscosity. The solution of the above two equations gives the measured relaxation rate which depends also on the anchoring coefficient.

The parameter  $\lambda = K / W$  is known as the extrapolation length. When  $d < \lambda$ , the transcendental equation for  $q$  can be expanded in power series of  $d/\lambda$ . Then the

relaxation rate of the fundamental fluctuation mode can be approximately written

$$\tau = \frac{\eta}{2W}d + \frac{\eta}{12K}d^2 \quad (4)$$

This expression can be intuitively understood. For thin samples most of the deformation of the fluctuations on which the light is scattered is at the sample surface and the relaxation rate is governed by the surface anchoring energy. The bulk viscosity makes the relaxation rate linear in  $d$ . The quadratic term in  $d$  is just the contribution of the bulk orientational deformation. As the elastic constants  $K_i$  and viscosity are known from the experiments in the bulk, light scattering measurements of the relaxation rate allow us to determine the anchoring coefficients  $W_i$ . The transcendental equation (2) can also be approximately solved for  $d \gg \lambda$ . In that case we obtain

$$\tau = \frac{\eta}{\pi^2 K}d^2 + \frac{4\eta}{\pi^2 W}d \quad (5)$$

Again the term containing  $W$  is linear in  $d$ , but now the leading term is the bulk one and the surface term is a small correction. So for reliable measurements of  $W$  it is necessary that the sample is sufficiently thin.

By choosing the proper polarization of the scattered light and orientation of the director azimuthal or zenithal deformation of the LC at the surface can be observed. For the observation of the azimuthal deformations the director and one polarization must be perpendicular to the scattering plane and one polarization must be in the scattering plane. For zenithal fluctuations the director and both polarizations must lie in the scattering plane. In this way both  $W_\theta$  and  $W_\phi$  can be determined.

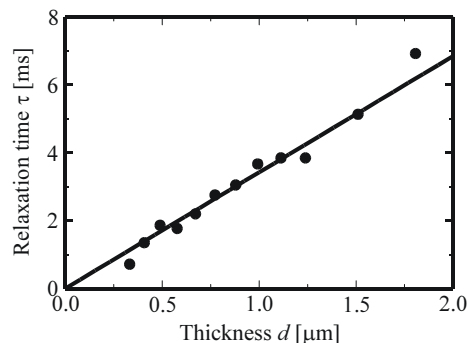
In some cases the dependence of the relaxation rate of the fundamental mode on sample thickness does not extrapolate to zero at  $d = 0$ . This effect can be interpreted as an additional dissipation process that is

localized to a thin surface layer. It is possible to introduce a surface viscosity  $\zeta$  as the proportionality coefficient between the rate of change of the director at the surface and an additional dissipative surface torque. One can then also introduce a length parameter  $h = \zeta / \eta$  which is a measure of the effective thickness of the dissipative surface layer.

## 2. Results

The most convenient way to perform the experiments is to use wedge-like LC samples. In our experiment rubbed polyimide as aligning layer ensured stable homogeneous alignment of nematic pentyl-cyanobiphenyl (5CB) in the cell. The easy axes on both sides of the cell were parallel to the gradient of the sample thickness. Thickness of such wedge cells was ranging from  $\sim 0.3 \mu\text{m}$  to  $2 \mu\text{m}$  as determined by interferometric method using a spectrophotometer. The cell was filled with liquid crystal with flow direction parallel to the easy axes.

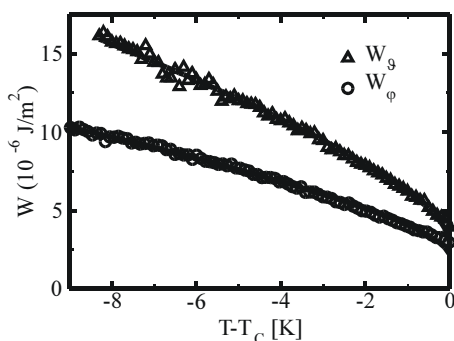
Figure 1 shows the relaxation rate of the fundamental director fluctuation mode as a function of sample thickness. As expected, for sufficiently thin sample the relation is linear, allowing us to determine the anchoring coefficient from equation 4.



**Figure 1. The dependence of the relaxation rate on sample thickness for 5Cb on rubbed polyimide**

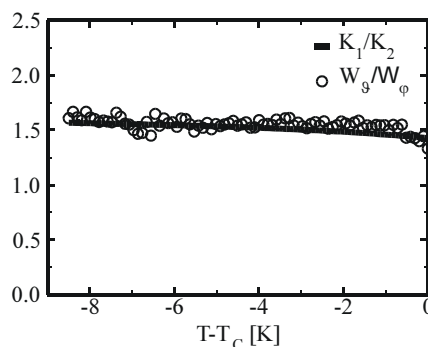
The temperature dependence of the azimuthal and zenithal anchoring

coefficients is shown in Figure 2. The absolute magnitude of the anchoring strength depends on the amount of rubbing. The azimuthal anchoring coefficient ranges from  $6.2 \cdot 10^{-6} \text{ J/m}^2$  for weak (single stroke) rubbing to  $5.6 \cdot 10^{-6} \text{ J/m}^2$  for strong rubbing. The form of the temperature dependence and the relative magnitudes of the two coefficients, however, does not depend on the amount of rubbing. On approaching the transition temperature both anchoring coefficients go to a small value. Also, the value of the zenithal anchoring is only 1.5 times larger than that of the azimuthal one. This is



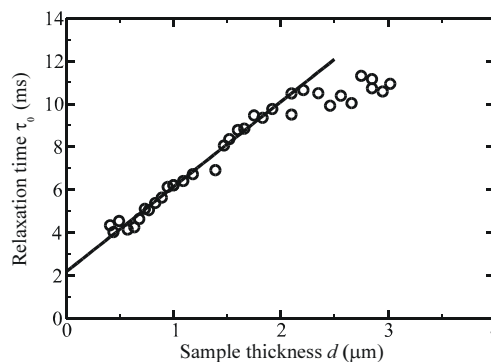
**Figure 2. Azimuthal and zenithal anchoring coefficients for 5CB on rubbed polyimide as functions of temperature**

different from most of the reported measurements till now, which usually show that the value of the zenithal anchoring is substantially larger than the azimuthal one. The ratio  $W_\theta / W_\phi$  is nearly temperature independent and is nearly equal to the ratio of the twist and splay elastic constant, as shown in Fig. 3. In our opinion this shows that the effective anchoring on oriented polymer surfaces is the result of weakly ordered microdomains of the adsorbed molecular layer. This order is then elastically transmitted to the liquid crystal bulk through nematic elastic interactions.



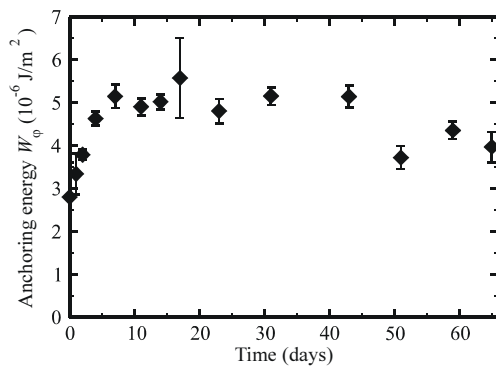
**Figure 3. The ratio of the azimuthal and zenithal anchoring coefficient and splay and twist elastic constants for 5CB on rubbed polyimide as functions of temperature**

We have also measured the anchoring energy on a polarized UV light aligned polyvinyl-cinnamate [1]. The dependence of the relaxation rate on sample thickness in this case does not extrapolate to zero at zero thickness, indicating an additional surface dissipation process.



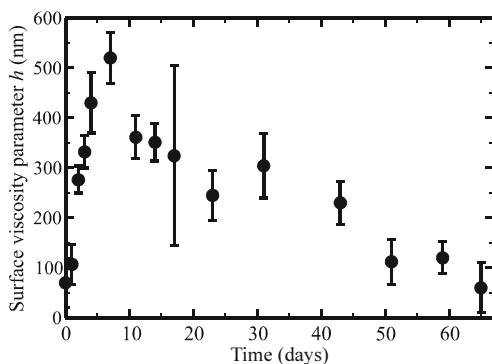
**Figure 4. The dependence of the relaxation rate on sample thickness for 5CB on photoaligned polyvinyl-cinnamate**

The value for the azimuthal anchoring coefficient was relatively small and ranged from  $3$  to  $5 \cdot 10^{-6} \text{ J/m}^2$ . We also observed that on a timescale of days after the irradiation of the alignment surface and formation of the sample the anchoring strength changes. It substantially increases in around 10 days after UV irradiation.



**Figure 5. Curing of the anchoring coefficient of 5CB on polyvinyl-cinnamate as a function of time after photo-irradiation.**

The existence of a surface dissipation process can be attributed to a thin layer of LC close to the surface that is contaminated by the polymer and exhibits considerably higher viscosity than pure LC. The surface viscosity length  $h$ , which we can determine from our measurements, is shown in Figure 6 as a function of time after UV irradiation. This length is according to our modeling approximately the thickness of the contaminated layer and also shows curing behavior on the same time-scale as the anchoring strength



**Figure 6. The surface viscosity parameter for 5CB on polyvinyl-cinnamate as a function of time after UV irradiation**

### 3. Conclusions

Using light scattering to determine the anchoring coefficients has several advantages over the traditional methods. Our method does not disturb the equilibrium and does not introduce large deformations, so it measures true small amplitude anchoring energy. It is also quite precise and is capable of measuring a large range of values provided that one can make a sufficiently thin wedge type sample. The thinnest end must be of the order of the extrapolation length, i.e. a few tenths of  $1 \mu\text{m}$ . Our results show that the anchoring coefficients are closely connected with the bulk elastic constants. Up till now it was believed that the zenithal anchoring is considerably larger. This can be explained by assuming that at the surface the LC forms microdomains which are only weakly ordered and it is the bulk elasticity that then transmits the orientation to the bulk through a layer of the order of the nematic coherence length.

### 4. References

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