

## Aging of surface anchoring and surface viscosity of a nematic liquid crystal on photoaligning poly-(vinyl-cinnamate)

Mojca Vilfan,<sup>1</sup> I. Drevenšek Olenik,<sup>1,2</sup> A. Mertelj,<sup>1</sup> and M. Čopič<sup>1,2</sup>

<sup>1</sup>*J. Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

<sup>2</sup>*Department of Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia*

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Dynamic light scattering was used to measure the azimuthal anchoring energy coefficient  $W_\varphi$  of nematic liquid crystal (5CB) on photoaligning poly-(vinyl-cinnamate) layer. Measurements were repeated several times within two months. The results show that  $W_\varphi$  increases in the first few days after filling the cell with liquid crystal. Then it remains approximately constant at  $W_\varphi = 5 \times 10^{-6} \text{ J/m}^2$  for at least two months. Also, presence of very large effective surface viscosity is observed. This phenomenon is of transient nature and attributed to swelling and dissolving of photosensitive polymer into the liquid crystal, which gives rise to an inhomogeneity of viscoelastic properties. Numerical modeling of the fluctuation spectrum shows that an inhomogeneous surface layer can account for the observed effective surface viscosity.

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### I. INTRODUCTION

Surface induced alignment of liquid crystals on polymeric layers is of great importance for operation of liquid crystal (LC) display devices. Standard method of preparation of aligning layers is based on mechanical rubbing of the substrate (usually polyamide or polyimide). In 1991, Gibbons *et al.* proposed a novel way of aligning by introducing photosensitive layers [1]. Illumination of such layers with linearly polarized light induces surface anisotropy that is needed for successful alignment. As recent developments show, this noncontact method seems to be very promising for applications in the display industry [2].

One of the photopolymers that give good alignment of nematic liquid crystals is poly-(vinyl-cinnamate) (PVCi) [3,4]. Although many experiments were made, the origin of the aligning ability of PVCi is not yet fully understood [2,3,5–8]. It was also found that the alignment was unstable on longer time scales [5]. In order to find the origin of this instability we studied aging properties of the PVCi-LC interface.

The main parameter describing the orientational interaction between a substrate and a liquid crystal is the anchoring energy coefficient [9,10]. Its magnitude is determined by the torque needed to turn the average molecular orientation (director) at the surface away from the direction of the substrate easy axes. Two separate cases can be considered: the deviation can be either in the plane of the substrate (azimuthal anchoring) or perpendicular to it (polar anchoring); the polar anchoring is usually considerably stronger [9,11].

The azimuthal anchoring coefficient  $W_\varphi$  can be measured by different methods that usually apply an external torque to the liquid crystal. The torque can be either mechanic [11–13], electric [14–16], or magnetic [17,18]. A major drawback of these methods is that the corresponding distortion can affect the intrinsic alignment of the liquid crystal. To avoid this possibility and to observe a liquid crystal in undistorted configuration we performed the measurements with a method based on dynamic light scattering (DLS) [19–21]

in which we analyze thermally excited orientational fluctuations in a thin liquid crystal slab and hence no external fields are needed. It is thus particularly appropriate to test the hypothesis indicated recently by Stoenescu *et al.* [22] that the unwinding of twisted nematic cells is a consequence of gliding of the easy axes due to an external mechanical torque and not of reduced anchoring. In this paper, we present a proof that the anchoring energy coefficient indeed remains approximately constant for over two months.

### II. ORIENTATIONAL FLUCTUATIONS IN CONFINED PLANAR GEOMETRY

To obtain the anchoring energy coefficient from the DLS measurements we first analyze the orientational fluctuations  $\delta\vec{n}$  of the director in a nematic liquid crystal slab. In bulk samples, where thermal excitations of director orientation are overdamped plane waves, the spectrum of the fluctuations is continuous. The relaxation time  $\tau$  is related to the fluctuation wave number  $q$  by the well-known equation [23]

$$\tau = \frac{\eta}{K} \frac{1}{q^2}, \quad (1)$$

where  $K$  stands for the Frank elastic constant in one constant approximation, and  $\eta$  for effective orientational viscosity.

In confined planar geometry, the sample is limited in the direction perpendicular to the glass plates ( $z$  direction) and the fluctuation eigenmodes are overdamped sinusoidal standing waves given by the diffusion equation

$$K\nabla^2 \delta\vec{n} = \eta \frac{\partial}{\partial t} \delta\vec{n}. \quad (2)$$

Fluctuations with wave vector parallel to the plates remain undistorted. The boundary conditions for Eq. (2) are determined as the balance of the torque from the bulk elastic deformations and the surface torque acting on the liquid crystal at the boundaries,

$$K \frac{\partial}{\partial z} \delta \vec{n} \pm W_\varphi \delta \vec{n} \Big|_{z=0,d} = \vec{0}, \quad (3)$$

where  $d$  is the sample thickness. The wave numbers  $q_z$  of fluctuations in confined planar geometry are then solutions of the secular equation [24]

$$q_z \tan\left(q_z \frac{d}{2}\right) = \frac{W_\varphi}{K}, \quad (4)$$

giving a discrete set of allowed values. The ratio of the elastic constant  $K$  and anchoring energy coefficient  $W_\varphi$  is the extrapolation length  $\lambda = K/W_\varphi$ . In the case of extremely strong (infinite) anchoring,  $\lambda$  is zero and the eigenvalues are simple functions of the sample thickness,

$$q_{zn} = \frac{(n+1)\pi}{d}, \quad n=0,1,2,3,\dots \quad (5)$$

In the case of finite anchoring, Eq. (4) can be expanded in terms of small deviations from  $q_{zn}$ . If the anchoring is weak, i.e., the extrapolation length is larger or comparable to the sample thickness, series expansion of the secular equation for the relaxation time of the fundamental mode ( $n=0$ ), taking into account Eq. (1), yields

$$\tau_0 \approx \frac{\eta}{2W_\varphi} d, \quad (6)$$

thus giving linear dependence of  $\tau_0$  as a function of  $d$ . By measuring  $\tau_0$  at different thicknesses  $d$ , and by knowing the orientational viscosity  $\eta$ , the anchoring energy coefficient  $W_\varphi$  can be obtained.

So far, the dissipation processes at the boundaries have been neglected. To take into account these effects, an additional term has to be added to the boundary conditions [25],

$$-K \frac{\partial \delta \varphi}{\partial z} + W_\varphi \delta \varphi \Big|_{z=0,d} = -\zeta \frac{\partial \delta \varphi}{\partial t}, \quad (7)$$

where  $\delta \varphi$  is the in-plane component of the director fluctuation, i.e.,

$$\delta \varphi = \delta \vec{n} \cdot \hat{e}_{xy}. \quad (8)$$

The parameter  $\zeta$  represents the surface viscosity, which is defined as the ratio of the torque needed to change the orientation of the director at the surface for a certain angle and the corresponding relaxation velocity [26,27]. In this case the secular equation, Eq. (4), transforms into

$$q_z \tan\left(q_z \frac{d}{2}\right) = \frac{W_\varphi}{K} - \frac{\zeta}{K} \frac{1}{\tau}. \quad (9)$$

For weak anchoring, series expansion of Eq. (9) in conjunction with Eq. (1) results in the following relation for the relaxation time  $\tau_0$  of the fundamental mode:

$$\tau_0 \approx \frac{\zeta}{W_\varphi} + \frac{\eta}{2W_\varphi} d. \quad (10)$$

The linear relation between the sample thickness and relaxation time is conserved and the anchoring energy coefficient can still be determined regardless of the surface viscosity. The surface viscosity only contributes a term independent of sample thickness. A similar effect can, however, be obtained also by a different phenomenon, as will be shown in Sec. IV.

### III. EXPERIMENT

The aligning substrate used in our experiment was photoactive PVCi that changes configuration if illuminated with UV light. Most probably both photoinduced effects, photoisomerization and photocycloaddition are responsible for liquid crystal alignment [5]. Alignment of the liquid crystal is planar and the molecules are on average oriented in the direction perpendicular to the polarization of UV light.

To attach the aligning substrate to glass plates, PVCi was dissolved in chloroform at a concentration of 0.05 wt%. Cleaned glass plates were dipped into the solution, dried and put for 1 h in a low pressure chamber at 50 °C in order to evaporate the rest of the solvent. The plates were then illuminated with linearly polarized UV light for 50 min using Hg lamp (Osram Ultra-Vitalux 300 W). PVCi coated glass plates were used to make wedge cells as the DLS measurements have to be performed at different cell thicknesses. Thicknesses of wedge cells were ranging from approximately 400 nm to 6  $\mu$ m and was very accurately determined by interferometric method using a Hewlett-Packard 8453 UV-Vis spectrophotometer. Easy axes on both plates were chosen parallel, giving a homogeneous alignment of the liquid crystal.

The liquid crystal used in our experiment was 4-*n*-pentyl-4'-cyanobiphenyl (5CB) from Sigma-Aldrich, which was used as received. The cells were filled in the nematic phase with flow direction parallel to substrate easy axes. The experiment was performed at constant temperature, equal to 32 °C.

The dynamic light scattering experiment was performed with a standard photon correlation setup using a Uniphase He-Ne laser operating at 632.8 nm. The normalized intensity autocorrelation function, defined as

$$g^{(2)}(t) = \frac{\langle I(t')I(t'+t) \rangle}{\langle I(t') \rangle \langle I(t'+t) \rangle} \quad (11)$$

was measured using an ALV-5000 correlator, which enables observation of dynamical processes in the range of  $10^{-8}$  s to  $10^3$  s. During the experiment, the scattering angle was constant and equal to 3° so that the scattering length was always larger than the sample thickness. For thicknesses up to approximately 2  $\mu$ m we therefore observe only the fundamental mode of the orientational fluctuations. For larger thickness the influence of higher modes becomes dominant and will not be discussed here. The polarization of the incoming light was parallel to the liquid crystal director and the outgoing polarization was orthogonal, as shown in Fig. 1. In such a scattering geometry (*e-o* geometry) only the twist modes of the director fluctuations are observed and they are determined by the in-plane anchoring.

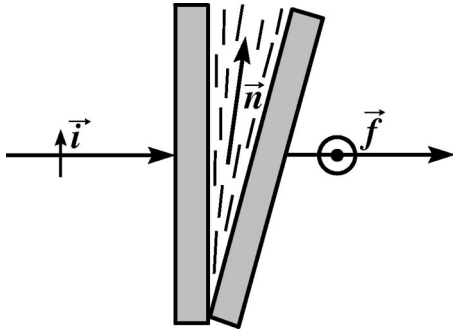


FIG. 1. Schematic illustration of the experiment. Substrate’s easy axes are parallel to the director  $\vec{n}$  and to the polarization of the incoming light  $\vec{i}$ , while the polarization of the outgoing beam  $\vec{f}$  is orthogonal.

An example of measured  $g^{(2)}$  is shown in Fig. 2, where dots represent measured data. The data can be fitted with a single exponent decay function and because the measurements were performed in a heterodyne regime, the characteristic decay time is equal to the fluctuation relaxation time  $\tau_0$ . The best single exponent fit is plotted as a solid line in Fig. 2. By translating the sample in the direction perpendicular to the laser beam and not changing any other parameters, the autocorrelation function and the relaxation time was measured as a function of sample thickness.

IV. RESULTS AND DISCUSSION

Figure 3 shows a characteristic dependence of the relaxation time  $\tau_0$  on the sample thickness  $d$ . In the region below approximately  $2\mu\text{m}$  the data can be fitted with a straight line in accordance with Eq. (10) and the slope of the line yields  $\eta/2W_\varphi$ . The value for  $\eta=0.03\text{ Pa}\cdot\text{s}$  for 5CB was taken from the literature [28]. The anchoring energy coefficient associated with the data shown in Fig. 3 is  $W_\varphi=3.34(1\pm 0.11)\times 10^{-6}\text{ J/m}^2$ . The observed nonzero value of  $\tau_0$  for  $d=0$  indicates the presence of a surface viscosity  $\zeta$ . It is convenient to present the viscosity ratio  $h=\zeta/\eta$ , having the dimension of length. The measurement shown in Fig. 3 gives  $h=(107\pm 38)\text{ nm}$ .

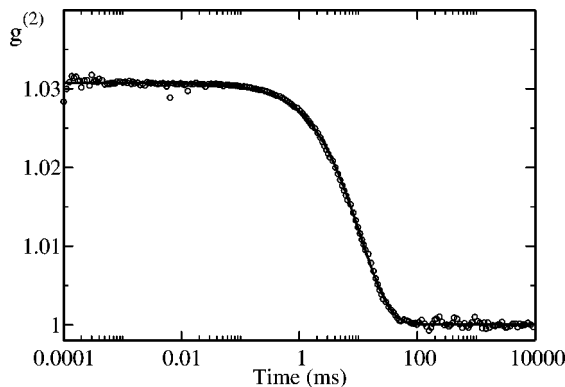


FIG. 2. Measured autocorrelation function of dynamically scattered light on nematic 5CB. The dots represent experimental data, the solid line is the single-exponent decay fit to the data.

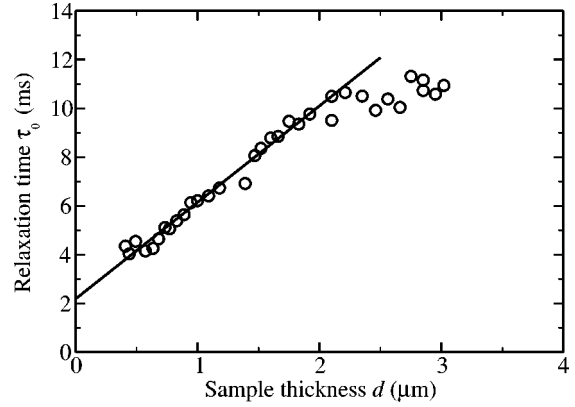


FIG. 3. Fluctuation relaxation time  $\tau_0$  plotted as a function of sample thickness. Circles represent the experimental data obtained on the second day after filling the cell with the liquid crystal, the solid line is linear fit. Anchoring energy coefficient is determined from the slope of the line and the obtained value for this measurement is  $W_\varphi=3.34(1\pm 0.11)\times 10^{-6}\text{ J/m}^2$ . The effective surface viscosity is  $h=(107\pm 38)\text{ nm}$ .

The DLS experiment was repeated several times during a 2-month period and the corresponding time dependence of the anchoring energy coefficient is shown in Fig. 4. In the first few days the anchoring energy coefficient increases. This increase is probably due to induced ordering of the polymer by the liquid crystal. PVCi is fairly soft and the strong liquid crystal order can additionally orient the polymer side chains [29,30]. This process is saturated after one week, when  $W_\varphi$  attains a value of approximately  $W_\varphi=5\times 10^{-6}\text{ J/m}^2$ . The anchoring energy coefficient then remains almost constant for another 60 days. The whole measurement was repeated with two different cells and in both cases the anchoring energy showed similar behavior.

With these measurements we support the idea that the unwinding observed in twisted nematic cells [22] is a consequence of easy axes gliding and that the anchoring energy coefficient  $W_\varphi$  does not change significantly on longer time scales [31].

The effective viscosity ratio  $h$  shows much stronger time variation than  $W_\varphi$  as can be seen in Fig. 5. A very strong

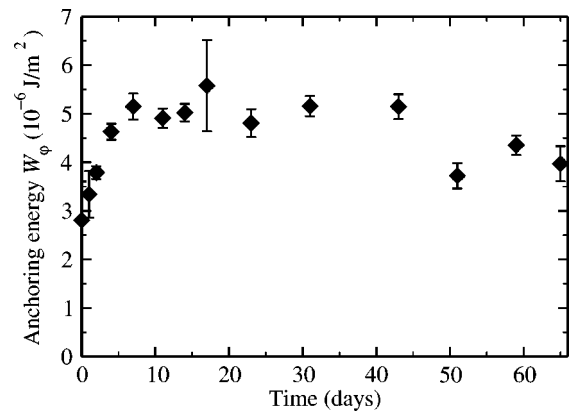


FIG. 4. Anchoring energy coefficient  $W_\varphi$  for 5CB on photoactive PVCi as a function of time.

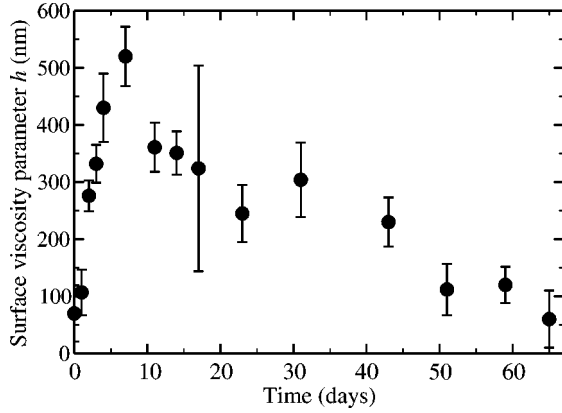


FIG. 5. Surface viscosity parameter  $h$  for 5CB on photoactive PVCi as a function of time.

increase is observed within the first week, when the measured value changes from initial  $h = 70 \text{ nm} \pm 45 \text{ nm}$  to over  $500 \text{ nm} \pm 60 \text{ nm}$ . The effective viscosity then decreases slowly until it reaches its initial value after approximately 2 months. Very similar behavior was again observed when the whole set of measurements was repeated with another cell. The measured values for surface viscosity are surprisingly large. If the observed effects were indeed a consequence of pure dissipation processes on the surface, the expected value of  $h$  would be of the order of molecular length. As seen in Fig. 5, this is not the case. Studying aging of surface viscosity, we see that apparently two processes contribute to the behavior shown in Fig. 5. We suggest that the increase in the first week is due to swelling of the photopolymer, and the slow relaxation process observed in the following 2 months is a consequence of slow diffusion of polymer molecules into the liquid crystal. When equilibrium is finally established, the sample structure is again homogeneous and the apparent surface viscosity vanishes. This is consistent with the observations of Perny *et al.* [5], who also proposed swelling as a possible explanation for alignment instability.

To prove the presented model, we use numerical calculations to describe how severely the swelling affects the fluctuation modes of the nematic sample. Since the process of swelling blurs the LC-PVCi interface, it changes the viscoelastic properties of the liquid crystal at the boundaries. First, the dissolved polymer significantly modifies the orientational viscosity of the liquid crystal [32,33]. It also reduces the liquid crystal order parameter in the vicinity of the substrate, which results in reduced Frank elastic constant at the boundary [23]. Due to these effects, the viscoelastic parameters of the liquid crystal become spatially inhomogeneous. Taking into account the spatial variation in  $z$  direction, the diffusion equation in one dimension is transformed as

$$K(z) \frac{\partial^2 \delta \vec{n}}{\partial z^2} + \frac{\partial K}{\partial z} \frac{\partial \delta \vec{n}}{\partial z} = \eta(z) \frac{\partial}{\partial t} \delta \vec{n} \quad (12)$$

while the boundary conditions, Eq. (3), remain unchanged. In our calculation the spatial dependencies of orientational viscosity and Frank elastic constant were taken as

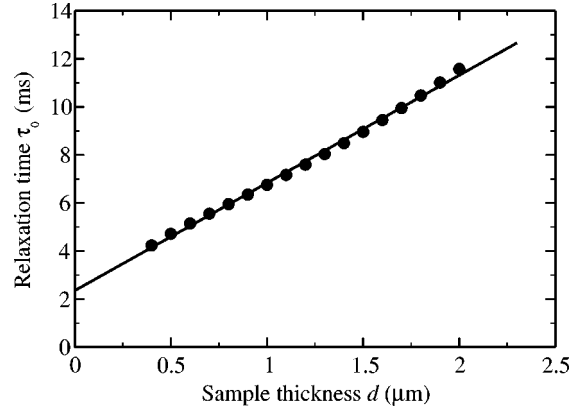


FIG. 6. Numerical calculations of the fundamental mode relaxation time as a function of sample thickness. The nonzero value at  $d=0$  is obtained by spatial variation of the orientational viscosity. At the boundaries, the viscosity is taken to have five times the bulk value, and the thickness of the contaminated layer  $d_1$  is 150 nm. The dots are numerically obtained relaxation times and the solid line is linear fit to the data.

$$K(z) = K_0(1 - K_1 e^{-z/d_0}), \quad (13)$$

$$\eta(z) = \eta_0(1 + \eta_1 e^{-z/d_1}), \quad (14)$$

where  $K_0$  and  $\eta_0$  are the bulk values and  $K_1$  and  $\eta_1$  are the amplitudes of the spatial variations. The thicknesses up to which the contamination effects have a significant influence on the constants are denoted as  $d_0$  and  $d_1$ , whereas the parameter  $z$  runs from the PVCi-LC interface towards the middle of the cell symmetrically from both plates. The differential equation, Eq. (12), was then solved numerically and the eigenvalue of the fundamental mode was calculated as a function of the cell thickness. Since the elastic constant can not be expected to vary more than a factor of 2 even at large polymer concentrations [32], it only slightly affects the calculated values for  $\tau_0$ . It was thus for simplicity considered as spatially independent, i.e.,  $K_1$  was taken to be zero.

The calculations show that for  $d=0$  a nonzero relaxation time can be obtained only by increased orientational viscosity at the boundaries. An example of calculated dependence is presented in Fig. 6. Bulk parameters  $\eta$  and  $K$  for 5CB for this calculation were taken from the literature [28]. An intermediate surface layer with  $d_1 = 150 \text{ nm}$  was assumed and orientational viscosity at the boundaries was chosen to be five times the bulk value accordingly to previously reported observations [32]. The calculated relaxation time  $\tau_0$  shown in Fig. 6 is obviously in good qualitative as well as quantitative agreement with the measured values (Fig. 3).

The observed aging phenomenon of the apparent surface viscosity can also be explained with our model. The increase of orientational viscosity at the boundaries in the first days after the filling of the cell, which results in the increase of the relaxation time at  $d=0$ , is induced by swelling of the substrate. This is a fairly fast process compared to the slow decrease of the relaxation time at  $d=0$  in the following weeks. This decrease is modeled by an increase of the thickness  $d_1$  of the contaminated layer, which might be a conse-



quence of the slow diffusion of the polymer molecules into the liquid crystal. If  $\eta_1$  is decreased because of finite amount of dissolved polymer, the constant term in relaxation time is reduced. When the sample is homogeneous, the term disappears, which is consistent with the experiments. Our results thus support the hypothesis that the observed large surface viscosity is not a consequence of the surface dissipation process but can be attributed to the spatial variation of the liquid crystal viscoelastic parameters.

## V. CONCLUSIONS

Dynamic light scattering was used to study aging of azimuthal anchoring energy of a nematic liquid crystal on pho-

toaligning poly-(vinyl-cinnamate). The anchoring energy coefficient is found to increase in the first few days after filling the cell with liquid crystal due to reverse influence of large orientational order of the liquid crystal on the polymer. The anchoring energy then saturates and remains almost constant for another 2 months. This proves that the observed unwinding in twisted nematic cells appears because of gliding of polymer easy axes and not because of reduced anchoring. Our measurements show also a large effective surface viscosity. This effect may result from spatial variation of liquid crystal viscoelastic parameters and not from specific surface dissipation processes. Hence, the influence of polymer swelling has to be considered in analysis of fluctuations in nematic cells.

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