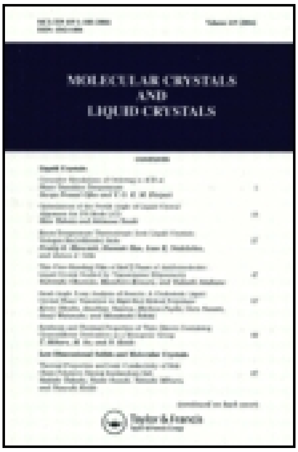

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# Temperature Dependence of Azimuthal Anchoring Strength Measured by Dynamic Light Scattering

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# Temperature Dependence of Azimuthal Anchoring Strength Measured by Dynamic Light Scattering

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Temperature dependence of the azimuthal anchoring energy coefficient of the nematic 5CB on rubbed Nylon is studied using the dynamic light scattering experiment. The method is based on observations of director fluctuations in a planarly aligned nematic liquid crystal cell. The fluctuation relaxation rate depends not only on cell thickness, but also on the surface anchoring strength. Thus, by measuring relaxation times in a wedge cell, the anchoring energy coefficient can be obtained without any external torques acting on the liquid crystal. We measured the anchoring strength in a broad temperature range and found that the anchoring decreases steadily when approaching the nematic to isotropic transition. A comparison with existing theoretical models is made and an excellent agreement with the mean-field model is observed even in the vicinity of the N-I transition.

Keywords: surface anchoring; dynamic light scattering; orientational fluctuations

## INTRODUCTION

Alignment of liquid crystals and the interactions between liquid crystal molecules and aligning substrate have attracted attention in the recent years mainly because of their importance for the liquid crystal display industry. The most important phenomenon in achieving aligned samples is the *surface anchoring* of liquid crystal molecules. The orientation of the bulk liquid crystal in the cell is determined by the substrate-induced orientation of the molecules at the boundaries. A quantitative description of surface anchoring is made by introducing the anchoring energy coefficient $W$[1,2]. It measures the torque required to turn the director away from the direction preferred by the substrate (easy axis) for a certain angle. However, as the interactions between the substrate molecules and the liquid crystal depend on the temperature, so does the anchoring energy coefficient.

Up to now, a variety of aligning substrates have been studied and different temperature behaviour of the anchoring has been observed. The majority of the experiments were performed using an external electric or magnetic field. In several cases the *zenithal anchoring* was found to decrease steadily when approaching the nematic to isotropic transition at $T_{NI}$[3–7]. However, Chung *et al.* reported an increase in the zenithal anchoring strength a few K below the transition for both rubbed polyimide and a photoaligning layer[8]. On the other hand, Kobayashi *et al.* observed a divergence in the extrapolation length $\lambda = K/W$, where $K$ is the Frank elastic constant[4,9].

The *azimuthal anchoring* energy coefficient as a function of temperature has so far been measured mainly on the evaporated SiO layers using strong magnetic fields[10,11] and twisted nematic cells[12]. The former method reveals a divergence in the extrapolation length at $T_{NI}$ as the anchoring strength vanishes when approaching the phase transition, whereas the latter yields a non-zero value of the anchoring at $T_{NI}$.

The significant variations in the temperature behaviour of the anchoring strength may result from different experimental techniques and external fields used in the experiments[2]. In order to resolve these discrepancies, we decided to measure the anchoring energy coefficient using the dynamic light scattering method, where the equilibrium liquid crystal configuration is not distorted during the measurement[13–15]. The method is based on observation of thermal fluctuations in a liquid crystal. In a sufficiently thin sample, the relaxation dynamics is governed by the interaction with the aligning layer. By measuring the fluctation relaxation times as a function of sample thickness, the anchoring energy coefficient can be obtained without any external torques acting on the liquid crystal.

## ORIENTATIONAL FLUCTUATIONS IN A PLANAR CELL

In bulk liquid crystal samples, where the surface effects are negligible, the relaxation time $\tau$ of the collective orientational fluctuations is[16]

$$\tau = \frac{\eta}{K}\frac{1}{q^2}, \tag{1}$$

where $q$ is the fluctuation wave number, $\eta$ is the effective viscosity and $K$ is the Frank elastic constant in the one-constant approximation.

In confined geometry, influence of the boundaries becomes important and the fluctuation dynamics is changed: the spectrum of the orientational fluctuations becomes discrete. The allowed wave vector components $q_z$ for the orientational fluctuations in a planar nematic sample, which is confined only in the $z$ direction, are determined by[17,18]

$$q_z \tan\left(q_z \frac{d}{2}\right) = \frac{W}{K}, \tag{2}$$

where $d$ is the thickness of the slab and $W$ is the anchoring energy coefficient. It is assumed that the anchoring on both sides of the slab is equal and the eigenmodes of the fluctuations are symmetric. Often the extrapolation length $\lambda$ is introduced as the ratio $K/W$. Each solution of Eq. 2 corresponds to a different mode and with properly chosen experimental setup, only the fundamental mode, *i. e.* the first branch of the solutions, can be observed. The upper equation cannot be solved analytically, so often the limiting cases are considered. In the case of *weak anchoring*, series expansion of the secular equation for $q_z d \ll 1$ in conjunction with Eq. 1 yields for the fundamental mode[18]

$$\tau = \frac{\eta}{2W} d. \tag{3}$$

The relaxation time of the fundamental mode depends thus linearly on sample thickness with the slope determined by the rotational viscosity and the anchoring energy coefficient $W$. This gave rise to the idea, that by measuring $\tau$ as a function of sample thickness $d$, the anchoring strength $W$ can be obtained[13,14].

## DYNAMIC LIGHT SCATTERING EXPERIMENT

The relaxation dynamics in a confined liquid crystal is studied by dynamic light scattering[15]. To measure the relaxation time as a function of sample thickness, wedge cells were used. The aligning layer was Nylon that was deposited onto the glass plates by dipping the plates into the solution of Nylon in methanol. The coated glass plates were then rubbed using a velvet cloth and wedge cells were made. Thickness of such cells was ranging from 0.3 $\mu$m to 2 $\mu$m as was very accurately determined by interferometric method using a spectrophotometer. Easy axes on both plates were oriented in the direction of the wedge incline, giving a homogeneous alignment of the liquid crystal. The cells were filled with the liquid crystal 4-n-pentyl-4‘-cyanobiphenyl (5CB) in the nematic phase with the flow direction parallel to the easy axes.

The dynamic light scattering experiment was performed using a standard photon correlation set-up. A He-Ne laser, operating at 632.8 nm, was used and the outgoing beam was linearly polarized in the direction perpendicular to the scattering plane. The beam was then focused and directed onto the sample. In order to observe only the twist fluctuation mode, the director in the liquid crystal cell had to be perpendicular to the laser beam and to the scattering plane. The polarization of the scattered light was chosen to lie in the scattering plane. The scattered light was detected and the autocorrelation function was calculated using the ALV-5000 correlator. During the experiment, the scattering angle was kept constant and was equal to 2° so that the scattering length remained larger than the sample thickness. This enabled us to observe only the fundamental mode of the fluctuations.

An example of the measured autocorrelation function $g^{(2)}(t)$ of the scattered light is shown in Figure 1. The circles are the measured data and the solid line is the fitted mono-exponential decay function. The contribution of dynamically scattered light was fairly low. As the measurements were performed in the heterodyne regime, the characteristic decay time of the autocorrelation function was equal to the fluctuation

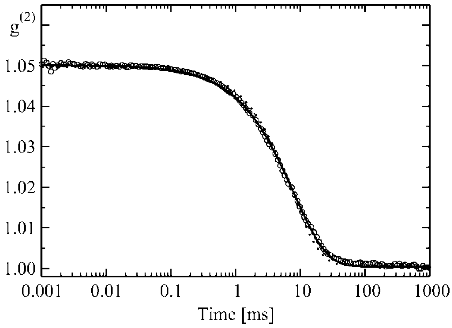

FIGURE 1: Autocorrelation function $g^{(2)}(t)$ of the light scattered by the orientational fluctuation in the nematic 5CB on rubbed Nylon at 32°C. The circles are the experimental data, the solid line represent the exponential fit with the relaxation time $\tau = 7.86 \pm 0.05$ ms.

relaxation time. The relaxation time $\tau$ obtained from the fit shown in Figure 1 is $\tau = 7.86 \pm\ 0.05$ ms.

The autocorrelation functions were then measured at several different sample positions of the wedge cell and the relaxation time was determined as a function of the thickness $d$. The obtained dependence at 32°C is shown in Figure 2. The circles are the measured data and the solid line the linear fit of Eq. 3. Linear dependence of $\tau$ on $d$ indicates the weak anchoring regime. From the slope of the line, the anchoring energy coefficient can be obtained. For the value of the rotational viscosity $\eta = 0.042$ Pa s[19], the anchoring energy coefficient for the measurement shown in Figure 2 is $W_\varphi = (6.1 \pm 0.2) \times 10^{-6}$ J/m$^2$. This corresponds to the extrapolation length of $\lambda = (470 \pm 30)$ nm.

## TEMPERATURE DEPENDENCE OF THE ANCHORING ENERGY COEFFICIENT

The anchoring energy coefficient depends on the aligning substrate, on the way the substrate is treated, on the liquid crystal, and on the temperature.

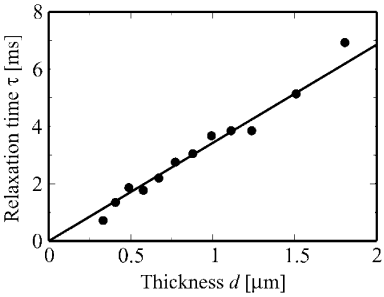

FIGURE 2: The relaxation time of the fundamental twist mode as a function of the sample thickness. The circles are the measured data and the solid line the linear fit. From the slope of the fit, the anchoring energy coefficient is obtained: $W_\varphi = (6.1 \pm 0.2) \times 10^{-6}$ J/m$^2$. The temperature was 32°C.

In our experiment, the temperature dependence of the anchoring energy coefficient was measured using an Instec heating stage. The sample was heated from initial 25°C to approximately 1 K above the nematic to isotropic transition, which occurred at $(35.3 \pm 0.2)$°C. In contrast to some previously reported experiments[20], here no systematic dependence of the transition temperature on the sample thickness was observed. The measured azimuthal anchoring strength $W_\varphi$ as a function of temperature is shown in Figure 3, where the measured data are presented by full circles. The anchoring energy $W_\varphi$ is found to decrease steadily when approaching the nematic to isotropic transition. In the temperature range of 10 K, the coefficient $W_\varphi$ changes from initial $\sim 1 \times 10^{-5}$ J/m$^2$ to approximately $0.3 \times 10^{-5}$ J/m$^2$. No divergence has been observed when approaching the nematic to isotropic transition.

In the following, the experimental data are compared to two significantly different theoretical models. The first one is the phenomenological model of Faetti *et al.*[10]. The authors took into account the spatial variation of the order parameter and, based on the theory of Berreman[21], concluded that the anchoring strength should be proportional to the square of the surface order parameter and vary with temperature as

$$W = \left(a + b(T_{NI} - T)^{1/2}\right)^2 . \quad (4)$$

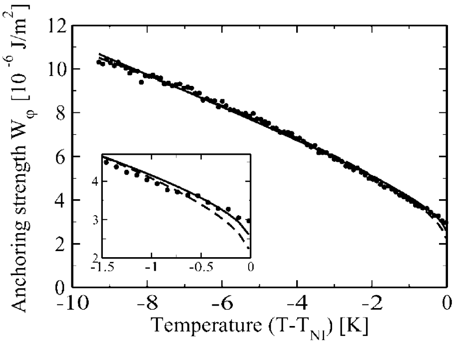

FIGURE 3: The measured anchoring energy coefficient as a function of temperature. The dots are the measured data. The dashed line is the fit of the Faetti model and the solid line is the best fit of the Barbero model.

The temperature $T_{NI}$ is the temperature of the transition into the isotropic phase and the coefficients $a$ and $b$ are determined by the surface coupling constants in the Landau-de Gennes free energy expansion.

The other model has been the recently proposed by Barbero and Zvezdin[22]. This model is based on the molecular mean-field approach and assumes spatially homogeneous scalar order parameter. The calculations were made for the case of weak surface anchoring. They found that the temperature dependence of the surface anchoring strength can be written as

$$W = \alpha S + \gamma S^{10/3}. \tag{5}$$

The two parameters $\alpha$ and $\gamma$ are constants, related to the anisotropy of the aligning surface. The temperature dependence enters through the temperature dependent bulk order parameter $S$. The dependence $S(T)$ is taken from the literature[23] and thus only two adjustible parameters are left to fit the experimental data.

The solid and dashed lines in Figure 3 are the best fits of the theoretical models to the experimental data: the dashed line corresponds to the model of Faetti *et al.*, described by Eq. 4, and the solid line to the model of Barbero and Zvezdin (Eq. 5). In the first case, the values of the fitting parameters are $a = 1.4 \times 10^{-3}$ $\sqrt{\text{J}}$/m and $b = 0.6 \times 10^{-3}$ $\sqrt{\text{J}}/\text{m}\sqrt{\text{K}}$.

When fitting the latter model and using the known $S^{[23]}$, the fitted parameters are $\alpha = 4.5 \times 10^{-6}$ J/m$^2$ and $\gamma = 1.2 \times 10^{-4}$ J/m$^2$.

Both models give excellent agreement in a wide temperature range of almost 10 K. In the vicinity of the N-I transition, however, the phenomenological model begins to deviate from the measured values approximately 0.5 K below the transition. On the other hand, the mean-field approach shows very good agreement up to approximately 0.1 K below the transition although the authors doubted about its validity close to the phase transition.

## CONCLUSIONS

The temperature dependence of the azimuthal anchoring energy coefficient of 5CB on weakly rubbed Nylon was measured using the dynamic light scattering experiment. As the measurements of the anchoring strength are based on the observation of the thermal fluctuations, no external torques act on the liquid crystal. The nonperturbative method thus gives more reliable and more accurate results than the methods where high electric or magnetic fields are needed. We found that the anchoring strength decreases steadily when approaching the transition to the isotropic phase. The results are compared to two theoretical models and a very good agreement is observed in a wide temperature range, with deviations only in the vicinity of the phase transition. With the values of the scalar order parameter taken from the literature, the model of Barbero and Zvezdin describes well the experimental data up to 0.1 K below the transition.

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