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Azimuthal and zenithal anchoring of nematic liquid crystals

Mojca Vilfan[1] and Martin Čopič[1,2]
[1]*Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*
[2]*Department of Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia*

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Temperature dependence of azimuthal and zenithal anchoring energy coefficients of the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl on rubbed nylon is measured using dynamic light scattering. The method is based on observations of director fluctuations in a planarly aligned wedge cell, where the anchoring energy coefficients can be obtained without any external torques acting on the liquid crystal during the measurement. We found that both anchoring coefficients decrease steadily on approaching the nematic-isotropic transition. Moreover, in the whole temperature range of the nematic phase, the ratio between the zenithal and the azimuthal anchoring coefficients is almost equal to the ratio between the splay and the twist Frank elastic constants. The same result is obtained also for the nematic phase of 4-*n*-octyl-4′-cyanobiphenyl. This indicates that the aligning nylon layer directly affects only the monomolecular layer at the surface whereas the observed anchoring is governed by the elastic properties of the alkyl-cyanobiphenyl.

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I. INTRODUCTION

Liquid crystal (LC) alignment has been extensively studied in the past few years mainly due to its great importance in the liquid crystal display industry. The standard and most widely used method for achieving planar LC alignment is by depositing liquid crystals onto a treated substrate, usually a rubbed polymer [1]. In recent years, several alternative methods of alignment have been proposed, for example, photoalignment [2,3], self-assembled monolayers [4], atomic force microscope treated surfaces [5], or alignment with atomic beams [6]. In all these cases, a certain anisotropy of the alignment layer is required to induce an orientation of the LC molecules, i.e., to orient the LC sample. The surface induced orientation of the director at the boundary is called the easy axis and when no external stress is imposed on the LC, the director field in the sample is determined by the easy axes of the confining surfaces. The orientation of the liquid crystal director due to the presence of a surface is called surface anchoring [7].

The anchoring energy coefficient or anchoring strength W is defined by the increase in the free energy density of the system, F_s, if the director at the surface deviates from the easy axis for a small angle Φ [8]:

$$F_s=\frac{1}{2}W\sin^2\Phi. \qquad (1)$$

The anchoring energy coefficient of a substrate thus gives a quantitative characterization of the aligning substrate and usually two different coefficients are introduced: the azimuthal anchoring coefficient W_φ related to director deviations in the LC-substrate plane and zenithal (or polar) anchoring coefficient W_ϑ related to the director deviations in the direction perpendicular to the LC-substrate boundary.

So far, several experimental techniques have been developed to measure the anchoring energy coefficients. Usually, some external torque is applied to the LC and the response of the sample to the imposed distortion is observed. The external field was either electric [9–12], magnetic [13–15], or mechanical [16–18]. Although extensive measurements have been performed on different substrates, there are still some open problems concerning the anchoring behavior: in some cases the zenithal anchoring coefficient was found to decrease on approaching the nematic-isotropic transition [19,20], whereas Chung *et al.* reported an increase of a few kelvins below the transition for both rubbed polyimide and a photoaligning layer [21]. Also the azimuthal anchoring measured on evaporated SiO was found both vanishing [22] as well as having a finite value close to the transition [23].

The inconsistencies in the observed temperature behavior of the anchoring strengths may result from different experimental techniques used in these studies as different external fields applied to the liquid crystal influence the measurement in different ways [7]. Besides, strong applied fields may result in melting of the LC rather than in a strong elastic deformation [24], meaning that the obtained measured values of anchoring energy coefficients can depend on the strength of the imposed field.

In previous papers we introduced measurement of the anchoring energy coefficients using dynamic light scattering on a wedge cell with planar alignment [25–27]. The method [25,28] is based on observations of thermal fluctuations spectrum in thin LC samples and thus avoids applying external fields to the LC during the measurement. Moreover, the same cell can be used to determine both zenithal and azimuthal anchoring energy coefficients [27]. In order to solve the discrepancies related to the temperature dependence of anchoring energies found in the literature, we decided to measure the anchoring strengths on the same cell over a broad temperature range using this nonperturbative optical method. The results presented in this paper show a steady decrease in the anchoring strengths of alkyl-cyanobiphenyl liquid crystals with increasing temperature and a finite value at the transition into the isotropic phase. The comparison with the corresponding elastic constants in the same temperature range suggests that the LC-nylon interaction directly affects only the first adsorbed LC monolayer, whereas elastic forces are responsible for the macroscopic effect of anchoring.

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II. EXPERIMENT

In a sufficiently thin LC cell, the relaxation dynamics of thermally excited fluctuations is strongly influenced by the presence of the boundaries [29]: the fluctuation spectrum is discrete and the relaxation time τ of the fundamental fluctuation mode depends on both the sample thickness d and the anchoring energy coefficients. This means that if τ is measured as a function of d, anchoring coefficients can be obtained. The fluctuation relaxation time is measured using dynamic light scattering experiment, where thin LC sample is illuminated with laser light. The light is scattered on thermally excited fluctuations and the autocorrelation function $g^{(2)}$ of the scattered light is obtained. It can be shown that the characteristic decay time of $g^{(2)}$ equals the relaxation time of the chosen overdamped fluctuation mode τ [30,31] from which anchoring strength can be determined.

The most convenient way to perform these experiments is to use wedgelike LC samples. In our experiment rubbed nylon as aligning layer ensured stable homogeneous alignment of nematic alkyl-cyanobiphenyls [4-*n*-pentyl-4′-cyanobiphenyl and 4-*n*-octyl-4′-cyanobiphenyl (5CB and 8CB)] 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 ≈0.3 μm to 2 μm as determined by interferometric method using a spectrophotometer. The cell was filled with liquid crystal with flow direction parallel to the easy axes.

The setup used in our experiment was a standard photon correlation setup using a He-Ne laser as a light source and ALV-5000 correlator to obtain the autocorrelation function of the scattered light. The polarizations of the incoming and outgoing light beams and orientation of the sample were chosen with respect to the anchoring energy coefficient that was measured (a detailed description is found in Ref. [27]). The two anchoring coefficients can thus be determined using the same LC cell as the only change in the setup is the change of polarizations and orientation of the cell. In the case of azimuthal anchoring strength, the incident light was polarized and the LC director oriented in the direction perpendicular to the scattering plane whereas the polarization of the scattered light was in the scattering plane. The scattering angle was only a few degrees so that for sample thickness below ≈2 μm only the fundamental twist mode contributed to scattering. In the case of zenithal anchoring strength measurements, both polarizations of incident and outgoing beams as well as the LC director lay in the scattering plane. With the described scattering geometry and small scattering angle, an almost pure fundamental splay mode was observed.

The fluctuation relaxation times τ of the two modes obtained from the measurement is directly related to the anchoring energy coefficients. For weak anchoring the dependence of τ on the sample thickness d is given by the simple expressions [27]

$$\tau_{\text{twist}}=\frac{\eta}{2W_{\varphi}}d \quad \text{and} \quad \tau_{\text{splay}}=\frac{\eta}{2W_{\vartheta}}d \tag{2}$$

with η being the effective rotational viscosity. Taking into account the Leslie viscosity coefficients from the literature [32], it can be shown that the difference between the viscosities for two different scattering geometries is less than 2% and can be neglected in further analysis.

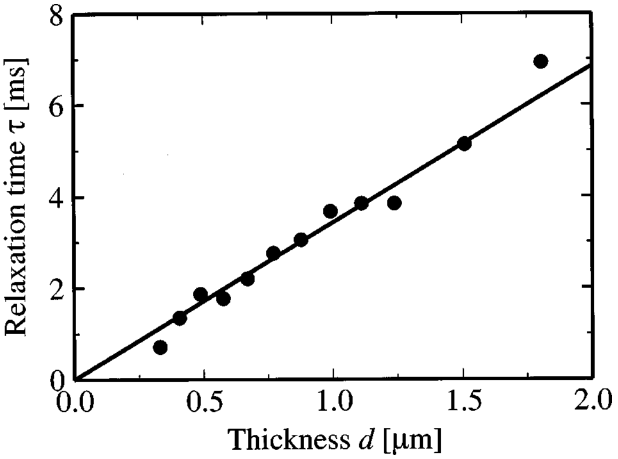

FIG. 1. Relaxation time τ of the fundamental twist mode for nematic 5CB as a function of sample thickness d. The circles are the measured data and the solid line the linear fit of Eq. (2). From the slope of the fit, the anchoring energy coefficient is obtained: $W_{\varphi}=(6.1\pm0.2)\times10^{-6}$ J/m^2 at 32 °C.

The measurements of the anchoring coefficients were performed in a broad temperature range. For this purpose, an Instec heating stage was used and during the experiment, the sample containing 5CB was heated from initial 25 °C to approximately 1 K above the nematic-isotropic transition, which occurred at (35.3±0.2) °C. Using a different liquid crystal 8CB the measurements of the azimuthal anchoring coefficients were performed in the whole range of the nematic phase from ≈34 °C to (40.5±0.3) °C. In this case, due to a very weak signal, the zenithal anchoring could be determined only in the vicinity of the transition into the isotropic phase. The heating rate was 0.1 K/min when measuring W_{φ}, and 0.012 K/min for determination of W_{ϑ}.

III. RESULTS AND DISCUSSION

A typical measured $\tau(d)$ dependence for the twist fluctuation mode for 5CB at 32 °C is shown in Fig. 1, where the circles are the measured data and the solid line the linear fit of Eq. (2). From the slope of the line and taking into account the value of rotational viscosity found in the literature $\eta=0.042$ Pa s [33], the anchoring energy coefficient at this temperature is $W_{\varphi}=(6.1\pm0.2)\times10^{-6}$ J/m^2. A very similar behavior is observed when splay fluctuations are detected and the zenithal anchoring at 32 °C for the same sample is $W_{\vartheta}=(10\pm1)\times10^{-6}$ J/m^2.

Often the extrapolation lengths λ are introduced, defined as the ratio between the corresponding Frank elastic constant and the anchoring strength [34]:

$$\lambda_{\varphi}=\frac{K_2}{W_{\varphi}} \quad \text{and} \quad \lambda_{\vartheta}=\frac{K_1}{W_{\vartheta}}. \tag{3}$$

For the presented measurements this yields $\lambda_{\varphi}=(470\pm30)$ nm and $\lambda_{\vartheta}=(440\pm60)$ nm.

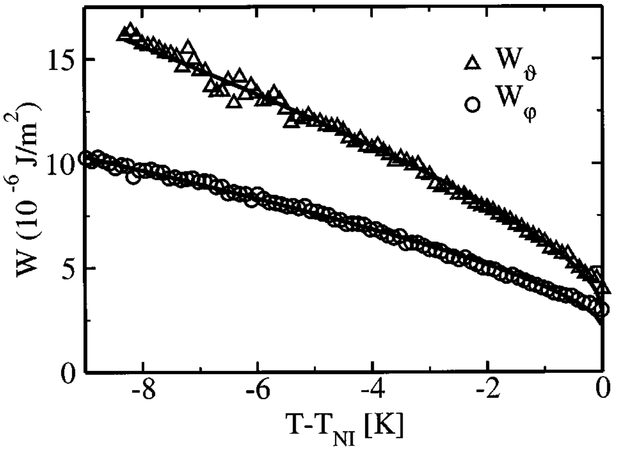

FIG. 2. Azimuthal and zenithal anchoring energy coefficients W_φ and W_ϑ measured by dynamic light scattering for nematic 5CB on rubbed nylon plotted as a function of temperature. A steady decrease on approaching the nematic-isotropic phase transition is observed. The solid lines are best fits of Eq. (4) to the experimental data.

The measured temperature dependence of the two anchoring coefficients for 5CB on rubbed nylon is shown in Fig. 2, where the circles and triangles represent azimuthal and zenithal anchoring energy coefficients, respectively. A steady decrease on approaching the isotropic phase is observed in both cases. In the interval of 9 K, the coefficients W_φ and W_ϑ decrease to approximately one-third of the initial (deep nematic phase) value, leaving nonvanishing values at the nematic-isotropic (N-I) transition.

The observed temperature dependence of the anchoring energy coefficients can be well described by a phenomenological model of Faetti *et al.* [22]. In their model, the authors assumed a spatial variation of the order parameter and, based on the theory of Berreman [35], concluded that the anchoring strength should be proportional to the square of the surface order parameter and vary with temperature as

$$W=[a+b(T_{NI}-T)^{1/2}]^2. \tag{4}$$

The temperature T_{NI} is the temperature of the nematic-isotropic transition and the coefficients a and b relate to the surface coupling constants in Landau–de Gennes free energy expansion. The solid lines in Fig. 2 are best fits of this theoretical model to the experimental data. In the case of azimuthal anchoring, the fitting parameters are $a=(1.42\pm0.06)\times10^{-3}$ J$^{1/2}$/m and $b=(0.60\pm0.02)\times10^{-3}J^{1/2}$/m K$^{1/2}$, whereas in the case of zenithal anchoring, the obtained values are $a=(1.70\pm0.08)\times10^{-3}$ J$^{1/2}$/m and $b=(0.79\pm0.04)\times10^{-3}$ J$^{1/2}$/m K$^{1/2}$.

As seen in Fig. 2, the theoretical description is in a very good agreement with the data in the wide temperature range of the nematic phase. The zenithal anchoring shows a very good agreement even in the vicinity of the transition, whereas the azimuthal anchoring shows a slight deviation of ≈0.5 K below the *N-I* transition. Recently, a theoretical model has been proposed by Barbero and Zvezdin [36] based on the mean-field approach, which fits our data on azimuthal anchoring very well even up to ≈0.1 K below the transition [26].

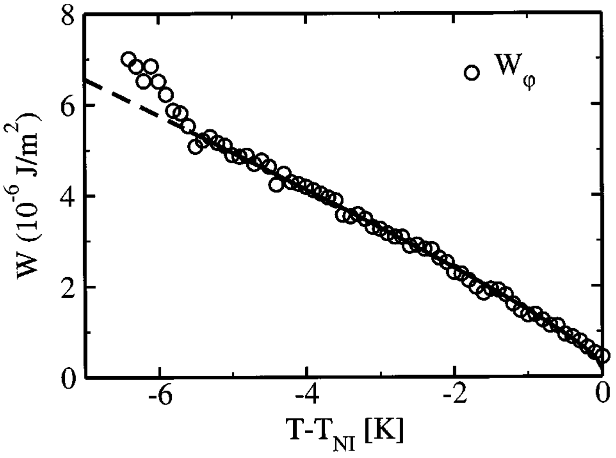

FIG. 3. Azimuthal anchoring energy coefficient W_φ measured by dynamic light scattering for nematic 8CB as a function of temperature. The solid line is the best fit of Eq. (4) to the data, except in the region where the influence of the approaching smectic-*A* phase becomes too strong.

In Fig. 3 the temperature dependence of the azimuthal anchoring coefficient W_φ for 8CB is presented. The aligning layer was prepared in the same way as for the measurements using 5CB. Despite a faster decrease of W_φ with increasing temperature in this case, the value of W_φ at the nematic to isotropic transition is finite. The strong increase of anchoring observed at ≈5.5 K below T_{NI} which is absent in 5CB can be associated with the approaching onset of the smectic-*A* phase as in this temperature range the elastic constant K_2 exhibits a pretransitional increase. The parameters a and b of the phenomenological model described earlier for 8CB are $a=(0.39\pm0.03)\times10^{-3}$ J$^{1/2}$/m and $b=(0.82\pm0.07)\times10^{-3}$ J$^{1/2}$/m K$^{1/2}$. The parameter a for 8CB is thus smaller than for 5CB for a factor of about 4, whereas b for 8CB is slightly larger than the corresponding coefficient for 5CB.

A particularly interesting result of the present study is the ratio of the two anchoring coefficients in the whole range of the nematic phase. So far, it has been generally believed [7] that there is one or even two orders of magnitude difference between the two anchoring coefficients. Our measurements show that the difference is less than a factor of 2. In fact, if we calculate the ratio between the two anchoring coefficients as a function of temperature, an almost constant value of approximately 1.5 ± 0.15 is observed for 5CB as shown in Fig. 4. Moreover, if the ratio W_ϑ/W_φ is compared to the ratio between the corresponding Frank elastic constants K_1/K_2 taken from the literature [33], the match is almost perfect in the whole regime of the nematic phase. The corresponding extrapolation lengths are almost equal for zenithal and azimuthal anchoring and they show only weak temperature dependence (Fig. 5). For liquid crystal 8CB, the zenithal anchoring coefficient could only be determined in a narrow temperature interval of ≈1 K just below the *N-I* transition and thus the comparison could be made only in this regime. The ratio is found to be the same as for 5CB, i.e., 1.5

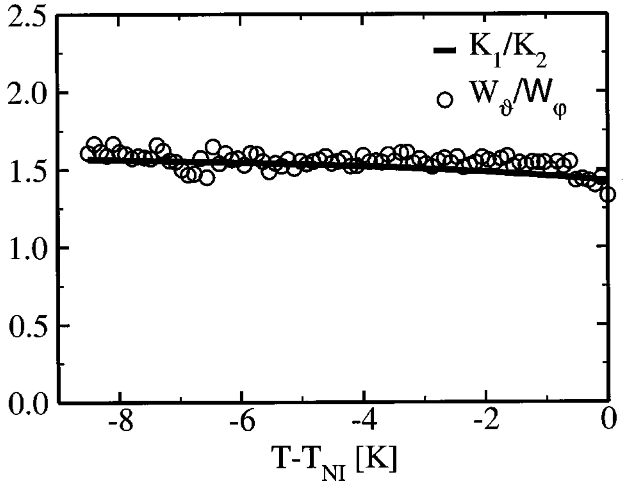

FIG. 4. Ratio between the measured zenithal and azimuthal anchoring strengths, W_ϑ/W_φ (circles), compared to the ratio of the Frank elastic constants, K_1/K_2 (solid line), for 5CB plotted as a function of temperature. The elastic constants are taken from the literature [33].

± 0.4, and is also within experimental error in agreement with the ratio of the elastic constants K_1/K_2 for 8CB [37].

The fact that the ratio of the anchoring coefficients has the same value as the ratio of the Frank elastic constants indicates that the anisotropy in the obtained anchoring coefficients originates in the anisotropic intrinsic LC molecular interactions rather than interactions of LC molecules with the aligning substrate. The experimentally observed macroscopic surface anchoring energy can be thus interpreted in the following way: the boundary induces changes in the LC order parameter close to the surface and due to the microscopic roughness and partly oriented polymer-surface microdomains the surface order parameter is smaller than order parameter in the remaining sample. The spatially varying order parameter results in a nonhomogeneous profile of the Frank elastic constants, and the surface free energy density of such a system can be written in simplified form as

$$F=\frac{1}{2}\int K_1(z)\left(\frac{\delta\vartheta}{\delta z}\right)^2 dz.$$

The parameter z denotes the direction perpendicular to the LC-substrate boundary and $K_1(z)$ is equal to bulk value far away from the surface and is smallest at the substrate. Minimizing the free energy and calculating at which distance ϑ is effectively zero (this distance corresponds to the extrapolation length), it is found that λ is proportional to the reduction of the elastic constant at the boundary. The difference in the anchoring energy coefficients results thus from the differences in the elastic constants. When measuring the anchoring energy coefficients with methods that are not sensitive to the phenomena in the first monomolecular LC layer at the substrate surface, such as light scattering experiment, this means that the macroscopic anchoring is actually observed. It is related to the elastic properties of the liquid crystal and not directly to the interaction between the molecules of the substrate and liquid crystal.

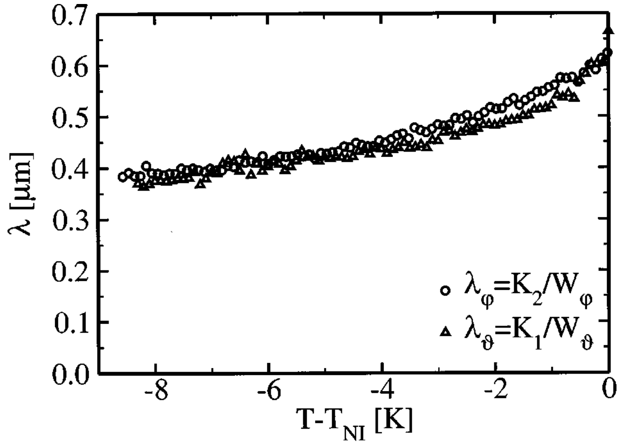

FIG. 5. Temperature dependence of the obtained azimuthal and zenithal extrapolation lengths λ_φ and λ_ϑ for nematic 5CB.

IV. CONCLUSIONS

To summarize, the azimuthal and zenithal anchoring coefficients of the nematic 5CB and partly for the nematic phase of the nematic 8CB have been measured using dynamic light scattering. The temperature dependence of the coefficients has been determined in a wide temperature range. The anchoring coefficients show smooth decreasing behavior with increasing temperature and no divergence is observed at the transition into the isotropic phase. A comparison of the experimental data with a phenomenological model is made and all measured anchoring coefficients can be well described. It was also found that for both alkylcyanobiphenyl liquid crystals aligned on rubbed nylon the ratio between the two anchoring coefficients has the same value as the ratio between the corresponding Frank elastic constants. This shows that the observed anisotropy in the measured anchoring energy coefficients is a consequence of the anisotropy in the intermolecular interactions within the liquid crystal and that the actual interactions between the aligning layer and the first LC molecular layer are not observed when measuring the macroscopic anchoring strengths.

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