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Systematic study of pretransitional orientational order at the free surface of *n*CB liquid crystals ($n = 5$–12) in the isotropic phase

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A high precision rotating ellipsometer was used to perform a systematic study of the pretransitional orientational order induced by the free surface of *n*-alkylcyanobiphenyl liquid crystals ($n = 5$–12) in the isotropic phase. All the compounds of this series show a complete wetting behaviour at the free surface. The temperature dependence of the surface order parameter was determined via calculations based on the Landau–de Gennes theory and the results show an even–odd behaviour. Moreover, we used a neural network recognition algorithm to reconstruct the order parameter profile $S(z)$ near the surface. The results of this model-independent analysis are compared with the model based calculations.

1. Introduction

The study of surface-induced ordering in liquid crystals is of special importance, not only for technological applications but also from a fundamental scientific point of view. The phenomenon of the orientation of bulk liquid crystals in one of the mesophases, by a properly treated surface, is called *anchoring* and is of crucial importance in display technology. However, it is well known that a treated surface can induce specific structures near the interface while the bulk is still in the isotropic phase. The growth of such a layer with enhanced order is usually described by *wetting* theories [1–3]. The influence of the surface is treated by a short range potential and the wetting behaviour depends on the relative strength of the intermolecular and the molecule–surface interaction: if the temperature approaches the bulk phase transition temperature T_c from above, the thickness of the wetting film is expected either to diverge (i.e. complete wetting) or to remain finite (i.e. partial wetting). In order to describe this orientational wetting behaviour the adsorption parameter Γ is introduced, and defined as

$$\Gamma = \int_0^\infty (S(z) - S_b)\,dz, \tag{1}$$

where $S(z)$ and S_b are the order parameters in the surface layer and in the bulk, respectively. The wetting behaviour is then predicted to depend on the ratio S_0/S_c, where S_0 is $S(z=0)$ and S_c is the order parameter of the bulk at the transition temperature; if $S_0/S_c > 1$ (or $S_0/S_c < 1$), Γ diverges (remains finite) as $T \to T_c$ and the wetting is complete (partial).

Recently several authors [4–7], using birefringence and ellipsometry techniques, investigated pretransitional wetting behaviour of liquid crystals near surfaces treated with various coatings which induce planar or homeotropic alignment. However, studies proved that the free surface of a liquid crystal can also show a strong anchoring behaviour, so induced pretransitional ordering is also expected for free surfaces. Nevertheless, experimental studies investigating wetting phenomena near the liquid crystal–air interface are rare. Complete wetting was found for 5CB by Beaglehole [8], and for PCH5 and PCH7 by Immerschitt *et al.* [9]. Here we report on a systematic study of the pretransitional orientational order, induced by a free surface, in the isotropic phase of members of the homologous series of alkylcyanobiphenyl liquid crystals (*n*CB, $n = 5$–12). Applying an accurate method of analysing experimental data acquired by reflection ellipsometry, we investigated the reflection of polarized light, varying the temperature of the samples and angle of incidence of the light. For the analysis of the data a model proposed by Sheng was used [2]. We determined the wetting behaviour and temperature dependence of the surface order parameter for all the samples in order to investigate the influence of the alkyl chain length. Furthermore, we performed a model-independent analysis of experimental data using a neural network recognition algorithm [10]. It is well known that neural networks are powerful tools in the determination of physical properties from experimental

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data when there is a complex relationship between the signal and these properties. From the polarization signal we reconstructed the order parameter profile $S(z)$ near the surface via a neural network and compared this with the model-based calculations.

2. Measuring method

Reflection ellipsometry [11] has proven to be a very adequate technique to investigate surface properties. We used a dynamic photometric ellipsometer (figure 1), consisting of a 3 mW He–Ne laser and a polarizing prism in the transmitter unit, and a rotating polarizing prism driven by a stepper motor in the receiver unit. The ratio of the complex reflection coefficients r_p and r_s [associated with light polarized parallel (p) and perpendicular (s) to the plane of incidence] is determined by Fourier analysis of the modulated detector signal. This ratio is expressed as $r_p/r_s = \tan(\Psi)\exp(i\Delta)$. The intrinsic measuring accuracy of the ellipsometer is 0·002°. For a step profile in dielectric constant (as at an air/isotropic liquid interface) Ψ varies as a function of the angle of incidence θ, from 45° for $\theta = 0°$, over zero at the Brewster angle to 45° for $\theta = 90°$. However, when the temperature of an isotropic liquid crystal sample approaches T_c the formation of the ordered wetting layer causes the minimum of Ψ to differ from zero and to shift towards smaller angles [figure 2 (*a*)]. This angular dependence $\Psi(\theta, T)$ is determined by the dielectric properties of the air above the sample, the substrate (isotropic bulk liquid crystal) and the surface layer at temperature T. However, instead of considering $\Psi(\theta, T)$, the accuracy of the experimental data can be substantially improved by considering the difference $\delta\Psi(\theta, T) = \Psi(\theta, T) - \Psi(\theta, T_{iso})$ where T_{iso} is a temperature above T_c, where the entire liquid crystal is isotropic [figure 2 (*b*)]. Because Ψ is strongly dependent on θ, it is crucial that both terms in $\delta\Psi$ are taken at the same angle of incidence. To exclude any inaccuracy originating from a mismatch of θ in both terms, we have carried out temperature scans at fixed angles of incidence, starting from a high value T_{iso} down to T_c. Afterwards we reconstructed, for an arbitrary temperature T between T_c and T_{iso}, the angular dependence of $\delta\Psi(\theta, T)$ and these data are used to determine the layer profile at temperature T.

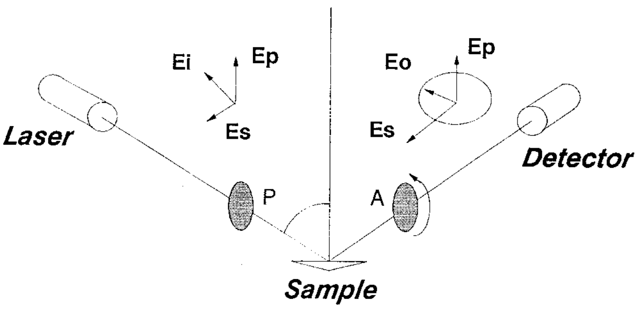

Figure 1. Optical path of the rotating analyser ellipsometer, used in reflection mode: P is a polarizing prism, A is the rotating analyser.

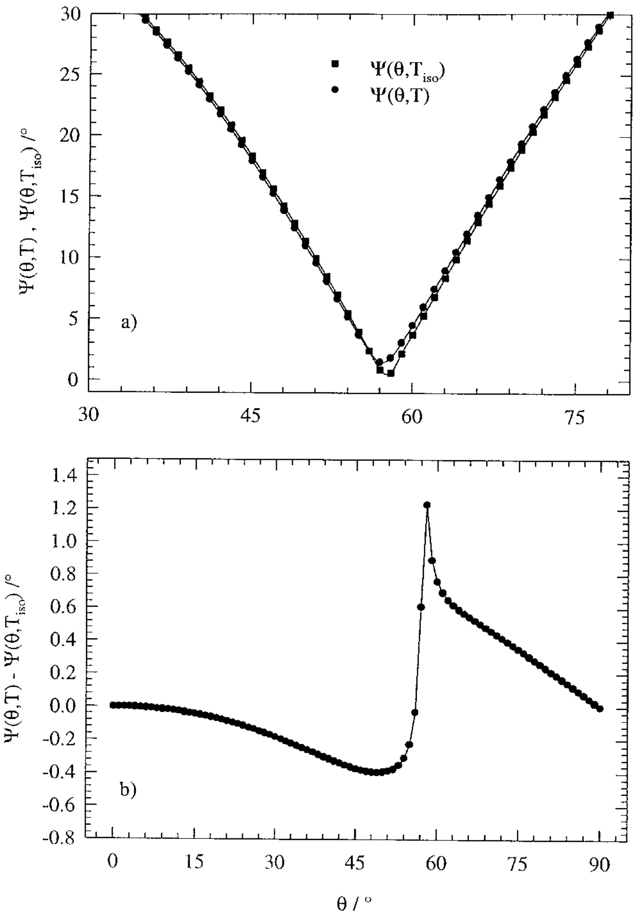

Figure 2. (*a*) The angular dependence of Ψ for an air/isotropic liquid crystal configuration—$\Psi(\theta, T_{iso})$, and the angular dependence of Ψ for a temperature T near T_c, when an ordered layer has formed on top of the isotropic bulk—$\Psi(\theta, T)$. (*b*) Normalized signal $\delta\Psi(\theta, T) = \Psi(\theta, T) - \Psi(\theta, T_{iso})$. These simulations are for 6CB with $T_{iso} = T_c + 3{\cdot}0$ K and $T = T_c + 0{\cdot}1$ K.

Typical temperature scans for 6CB are shown in figure 3. For angles below the Brewster angle θ_b, $\Psi(\theta, T)$ decreases with decreasing temperature, otherwise $\Psi(\theta, T)$ increases on approaching T_c. The scans were performed using a two-stage oven, which allows a temperature stability within 1 mK. We examined the experimental $\Psi(\theta, T)$ curves on possible scanning rate dependence, and since no influence on the measured curves was detected, we used a linear decreasing scanning rate—starting with steps of 0·05 K and ending with steps of 0·005 K—in order to be able to measure a relatively large temperature interval and to determine T_c with a satisfactory accuracy (0·01 K). The scans were started at approximately 3 K above T_c where the liquid crystal, as is clear from figure 3, is completely isotropic. In this way, for each sample, scans were performed at about 20 angles of incidence between 30° and 80°. The liquid crystals were obtained from Merck (UK). For 5CB–9CB, we investigated the induced ordering near the isotropic–nematic phase transition; for 10CB–12CB, which have no nematic phase, the isotropic–smectic A phase transition was studied. Experiments revealed that, over long periods, the measured $\Psi(\theta, T)$ curves slowly shifted with time, due to ageing of the samples. For this reason the whole set of temperature scans for each compound was executed in three days, in which period no measurable change in the signal was detected. In this context, we used a *steel* conic sample holder, which induces less ageing than a copper reservoir. The reservoir was made conic, to exclude any disturbing reflections from the bottom side. We also checked the signal for possible influences of the presence of the surface curvature due to the filling level of the reservoir, but no measurable effects on the experimental signal were detected.

3. Model-based data analysis

Because of the homeotropic alignment of the liquid crystal molecules, the induced ordered layer has a uniaxial symmetry with the optical axis (z-direction) perpendicular to the surface (xy plane). Therefore the dielectric profile throughout the boundary layer can be described by:

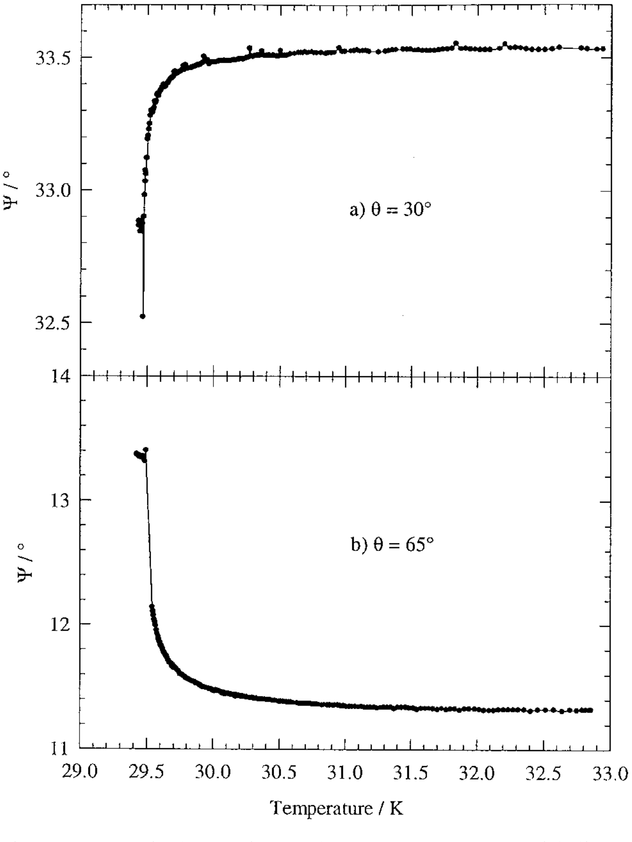

Figure 3. Typical experimental temperature scans with linear decreasing scanning rate. (*a*) Scan for 6CB at an angle of incidence $\theta = 30°$ ($<\theta_b$); (*b*) scan for 6CB at an angle of incidence $\theta = 65°$ ($>\theta_b$).

$$\varepsilon_x(z)=\varepsilon_y(z)=\varepsilon_b-\frac{1}{3}\Delta\varepsilon_{\max}S(z) \qquad (2)$$

$$\varepsilon_z(z)=\varepsilon_b+\frac{2}{3}\Delta\varepsilon_{\max}S(z) \qquad (3)$$

with ε_b the dielectric constant of the isotropic bulk liquid crystal (i.e. for $S=0$) and $\Delta\varepsilon_{\max}$ the dielectric anisotropy of a perfectly ordered system (i.e. for $S=1$). The model used to calculate the order parameter profile was proposed by Sheng [2], who introduced a surface potential $V=-G\delta(z)S$, where G is the strength of the potential and $\delta(z)$ is a delta function. Via the Landau–de Gennes expansion [12] of the free energy density, the total free energy is given by:

$$\Phi=\int_0^\infty\left[f(S)+\frac{L}{2}\left(\frac{\mathrm{d}S}{\mathrm{d}z}\right)^2\right]\mathrm{d}z-GS_0, \qquad (4)$$

with S_0 the surface order parameter $S(z=0)$ and

$$f(S)=\frac{a}{2}(T-T^*)S^2-\frac{b}{3}S^3+\frac{c}{4}S^4 \qquad (5)$$

where a, b, c, T^* and L are the expansion parameters. The equilibrium form of $S(z)$ is determined by minimization of this free energy. Tarczon and Miyano [3] derived an analytical expression, given by:

$$S(z)=\frac{2a(T-T^*)Z}{Z^2+\frac{1}{2}bZ+\frac{1}{9}b^2-\frac{1}{2}ac(T-T^*)}, \qquad (6)$$

where $Z(z)=R(S_0)\exp(z/\xi)$. Here ξ is the Landau-correlation length and $R(S)$ is determined by

$$R(S)=\frac{1}{S}[2a(T-T^*)]^{1/2}\left[\frac{a}{2}(T-T^*)-\frac{b}{3}S+\frac{c}{4}S^2\right]^{1/2}+\frac{a}{S}(T-T^*)-\frac{b}{3}. \qquad (7)$$

To relate this profile with the experimental data we used a 2 × 2 matrix algorithm, which allows a calculation of Ψ for a nonabsorbing, stratified medium with uniaxial symmetry, as shown by Lekner [13]. We will give here only a very succinct description of the algorithm. The inhomogeneous, anisotropic surface region is approximated to by a large number (N) of homogeneous layers $(z_{n-1}, z_n)_{n=1\ldots N}$, with dielectric constants ε_x^n and ε_z^n. Matching the wave amplitude and derivative at the boundaries, each of the layers is characterized by a *layer matrix* M_n, which depends on the thickness of the layer and its dielectric properties. For the s-wave one has:

$$M_n = \begin{pmatrix} \cos\delta_n & \sin\delta_n / q_s^n \\ -q_s^n \sin\delta_n & \cos\delta_n \end{pmatrix}, \tag{8}$$

where $\delta_n = q_s^n(z_{n+1} - z_n)$, q_s^n is the component of the s-wavevector normal to the interface, and

$$(q_s^n)^2 = \varepsilon_s^n \frac{\omega^2}{c^2} - K^2$$

(K is the component of the wavevector along the interface). For the p-wave one similarly obtains:

$$M_n = \begin{pmatrix} \cos\delta_n & \sin\delta_n / Q_p^n \\ -Q_p^n \sin\delta_n & \cos\delta_n \end{pmatrix}, \tag{9}$$

where $\delta_n = q_p^n(z_{n+1} - z_n)$, q_p^n is the z-component of the p-wavevector, $(q_p^n)^2 = \varepsilon_x^n \omega^2 / c^2 - \varepsilon_x^n / \varepsilon_z^n K^2$, and $Q_p^n = q_p^n / \varepsilon_x^n$. Finally the profile is characterized by a profile matrix

$$\boldsymbol{M} = M_n \ldots M_1 = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} \tag{10}$$

and the reflection coefficients for the s- and p-waves are given by:

$$r_s = \exp(2i\alpha) \frac{q_a q_b m_{12} + m_{21} - i q_b m_{11} + i q_a m_{22}}{q_a q_b m_{12} - m_{21} + i q_b m_{11} + i q_a m_{22}}, \tag{11}$$

$$r_p = -\exp(2i\alpha) \frac{Q_a Q_b m_{12} + m_{21} - i Q_b m_{11} + i Q_a m_{22}}{Q_a Q_b m_{12} - m_{21} + i Q_b m_{11} + i Q_a m_{22}}, \tag{12}$$

where the indices a and b refer to the wavevectors in the air and bulk liquid crystal, respectively. With these equations, together with equation (2) for the dielectric profile, which is determined by $S(z)$, we can calculate the angular spectrum $\Psi(\theta, T)$ at each temperature. The parameters in the model are the Landau-expansion coefficients a, b, c, dielectric constants ε_b and $\Delta\varepsilon_{\max}$, and surface order parameter S_0. The values for the material parameters a, b, c, ε_b and $\Delta\varepsilon_{\max}$ were taken from Coles [14]. In this way we are able to perform a one-parameter least-square fitting procedure to determine S_0.

4. Neural network calculations

A suitable alternative for the fitting procedure described in the previous paragraph is the application of a neural network to reconstruct the order parameter profile $S(z, T)$ from the angular spectrum $\Psi(\theta, T)$. The main advantage of this method is the generation of a model-independent profile, which can be compared with the results derived from the model as described above. Details of the neural network reconstruction algorithm will be published elsewhere [15]; thus we will confine ourselves to a brief description of the procedure. The general concept is to train the network to recognize profile properties by using a large number of generated, representative profiles together with the corresponding calculated angular spectra. On the condition of a good signal–profile relation and with an appropriate training, the network is then able to recognize immediately profile features from spectral data.

The training profiles ($N_{tr} = 500$) were characterized by a number ($N_0 = 40$) of values $S(z_i)$, restricted between 0 and 1, and linearly interconnected at equally spaced depths z_i between 0 and 500 Å (for $z > 500$ Å the profile was assumed to be constant, $S = 0$). Using equations (2) and (3), and the matrix model for stratified media, equations (8)–(12), N_I (=40) Ψ-values at angles of incidence between 30° and 80° were calculated for each training profile together with the angular spectrum for a uniform air/isotropic liquid crystal configuration, $\delta\Psi(\theta)$. Gaussian noise of 0·03° was then added to these data in order to obtain more realistic signal data and to prevent overtraining. For each profile parameter $S(z_i)$ a neural network was trained with these N_{tr} sets of profile-signal, by minimizing the training error ε_{tr}:

$$\varepsilon_{tr}(S(z_i)) = \left[\sum_{k=1}^{N_{tr}} (S_k(z_i) - S_k^{est}(z_i, \delta\Psi(\theta_1), \ldots \delta\Psi(\theta_{N_I}), W_*))^2 / N_{tr} \right]^{1/2}. \tag{13}$$

In this expression $S^{est}(z_i)$ is the profile value estimated by the network, based on the signal data $\delta\Psi_j$, via N_u (=2) hidden tangent hyperbolic units and one linear output unit:

$$S^{est}(z_i) = W_{0,i}^{2} + \sum_{u=1}^{N_u} W_{u,i}^{2} \tanh\left(W_{0,i}^{1,u} + \sum_{j=1}^{N_I} W_{j,i}^{1,u} \delta\Psi_j \right), \tag{14}$$

where Ws are weight values which are adjusted to optimize the training error. Afterwards, the performance of the networks was tested by using known profile–spectrum pairs, which were not used during the training process, by calculating in a similar manner the generalization error ε_{gen}, which is a measure for the quality of the reconstructed profiles. Finally, applying the trained networks on the experimental spectra provides us then with a $S(z)$ reconstruction method without any *a priori* knowledge of profile characteristics.

5. Results and discussion

The temperature scans shown in figure 3 are characteristic for all the compounds of the cyanobiphenyl series. This means that an ordered layer appears not only at the isotropic–nematic phase transition (5CB–9CB), but also for the isotropic–smectic A phase transition (10CB–12CB). This is in contrast to a previous result

[4], where the wetting behaviour was studied near a polyamide-coated glass surface, which induces planar alignment. In that study, no pretransitional order was observed for 10CB, 11CB and 12CB.

After normalization with the isotropic value $\Psi(\theta, T_{\text{iso}})$, the angular spectra at an arbitrary temperature T were reconstructed. For some compounds of the series experimental curves $\delta\Psi(\theta, T)$ are shown in figure 4, for different values of $T - T_c$, where T_c is the experimentally determined bulk phase transition temperature of the compound. The experimental error of the measured $\delta\Psi$ data is estimated to be situated between 0·01° and 0·02°. All the curves have the expected shape [figure 2(*b*)] with an increasing amplitude for decreasing temperature, which is a visual indication of the formation of the wetting layer. In figure 4 the solid lines represent the theoretical curves, resulting from a fitting procedure based on equations (2)–(7). As mentioned before, the only parameter in the fits is the surface order parameter S_0. Results of these calculations for $T - T_c = 0{\cdot}1$ K are given in the table, together with the values used from reference [14] for the bulk order parameter S_c at the phase transition. From a comparison of the values for S_0 and S_c and following the criterion of the ratio S_0/S_c as explained before, it is immediately clear that all the compounds show a complete wetting behaviour. This result is also opposite to the conclusion in reference [4], where a partial planar wetting behaviour was observed for 5CB–9CB near the polyamide-coated glass surface.

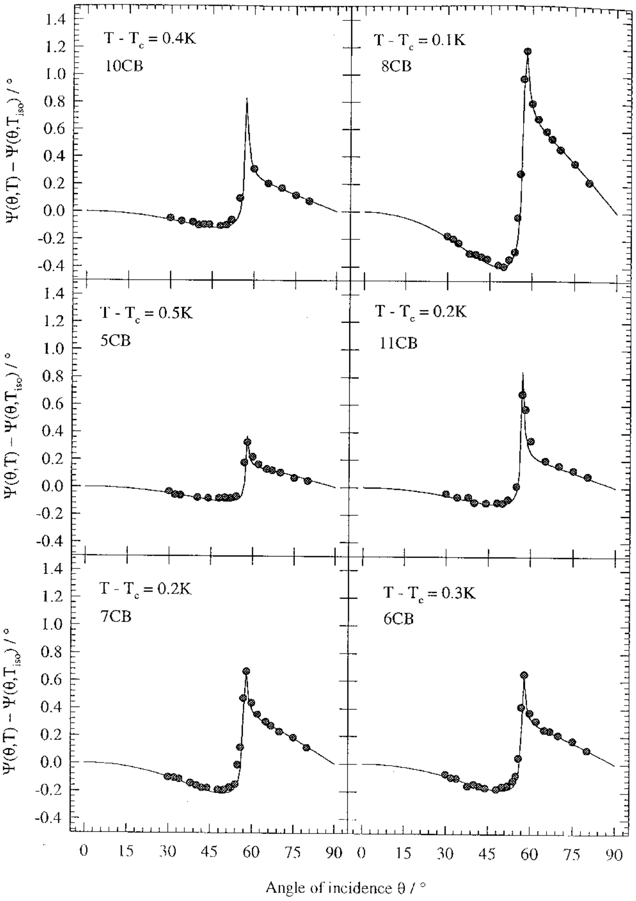

Figure 4. Some examples of experimental data $\delta\Psi(\theta, T)$ [symbols] for several temperatures and for different compounds in the homologous series. Solid lines represent theoretical fits following equations (2)–(7).

In some previous studies [1, 3, 4] equation (6) was used to fit experimental data with S_0 assumed to be independent of T. However, in the temperature region studied here, this assumption is not valid in general. Our experimental method allows us to determine the surface order parameter at each temperature between T_c and T_{iso}. In figure 5, values for $S_0(T)$ are shown for each compound at different temperatures. It is clear that, indeed, there is a gradual but significant decrease of the surface order parameter with increasing temperature. This result is in agreement with the observations of Chen *et al.* [6], who determined via evanescent-wave-ellipsometry a slightly decreasing surface order parameter for *n*CB liquid crystals near a glass substrate coated with silane surfactant molecules. However, looking at the value of S_0 as a function of the alkyl chain length in the compounds of the *n*CB series, as shown in figure 6 for $T - T_c = 0{\cdot}2$ K, we can see a typical alternation, which is known as the even–odd effect in homologous series (a similar figure can be drawn for any temperature above T_c). This effect has been described by Marcelja [16], and originates from the molecular structure and disposition of the end groups, enhancing or reducing the molecular anisotropy and hence the molecular order. A similar effect was experimentally observed [17–20] for a number of properties, e.g. isotropic–nematic transition temperatures, entropies and latent heats along a homologous series. The theory of Marcelja also predicts that the order parameter should depend on the end chains of the liquid crystal molecules

Table Surface order parameter S_0 for $T - T_c = 0{\cdot}1$ K determined with equations (2)–(7) and order parameter S_c at the bulk phase transition.

Parameter	5CB	6CB	7CB	8CB	9CB	10CB	11CB	12CB
S_0	0·32	0·39	0·35	0·42	0·36	0·71	0·54	0·64
S_c [12]	0·27	0·25	0·27	0·30	0·29	0·54	0·50	0·61

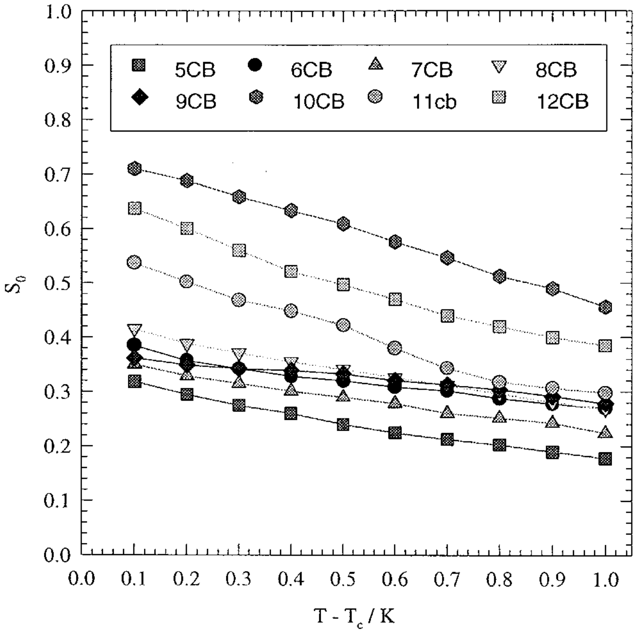

Figure 5. Temperature dependence of the surface order parameter S_0 as deduced from the fitting procedure, using the profile given by equation (6).

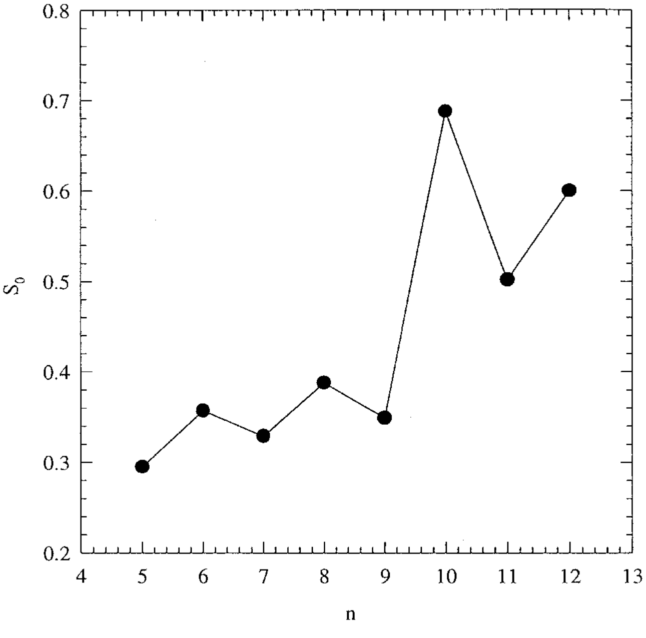

Figure 6. Surface order parameter S_0 for $T - T_c = 0{\cdot}2$ K as a function of the alkyl chain length of the different compounds in the homologous series. The line is a guide for the eye.

and exhibit the even–odd effect, which was indeed observed by Pines *et al.* [21]. Nevertheless, to our knowledge this effect has not yet been observed for the pretransitional order induced by a surface. So, our results represent the first observations of the even–odd effect in the wetting behaviour of a homologous series.

Finally, we describe the results of the calculations with the neural network algorithm. Figure 7 shows a comparison between, on the one hand, profiles obtained with equation (6) using best-fit values for S_0, and on the other hand, neural network reconstructed profiles for 6CB at different temperatures above T_c. Keeping in mind that no condition at all is imposed, neither for the starting value at $z = 0$, nor for the general shape of the curves, the agreement of each set of profiles is very satisfactory. In figure 8 the experimental data corresponding to these profiles are compared with the least-square fits following equations (2)–(7) and with angular spectra which are calculated *a posteriori* from the neural network reconstructed profiles. Again, the agreement of these curves is quite good, which confirms the consistency of the neural network results. The correspondence of the curves in figures 7 and 8 is not only a confirmation of the model-based results derived above, but is also evidence for the very interesting abilities of neural network profile recognition, which need not be restricted to this specialized optical application [22].

6. Conclusions and perspectives

We have presented an accurate method to analyse experimental data for the surface of liquid crystals, obtained by a rotating analyser ellipsometer. The results could be well described by the model proposed by Sheng.

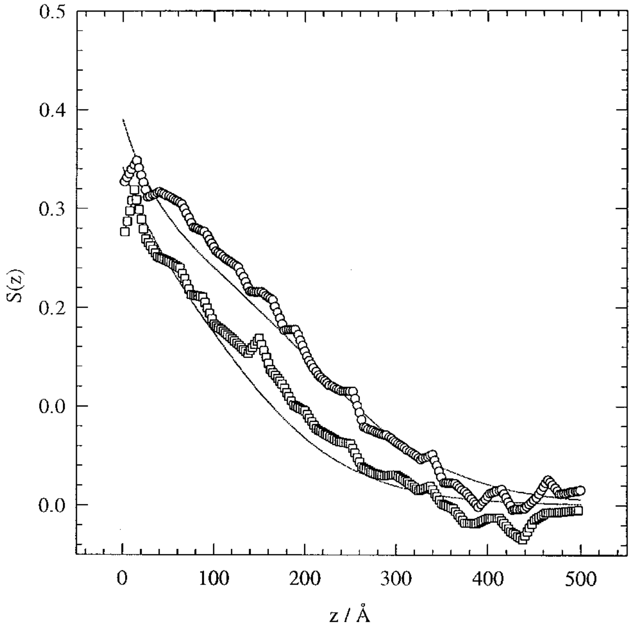

Figure 7. Order parameter profiles reconstructed with the model of Sheng (lines), in comparison with neural network generated profiles (symbols). Profiles are shown for 6CB at $T - T_c = 0{\cdot}1$ K (circles) and at $T - T_c = 0{\cdot}3$ K (squares).

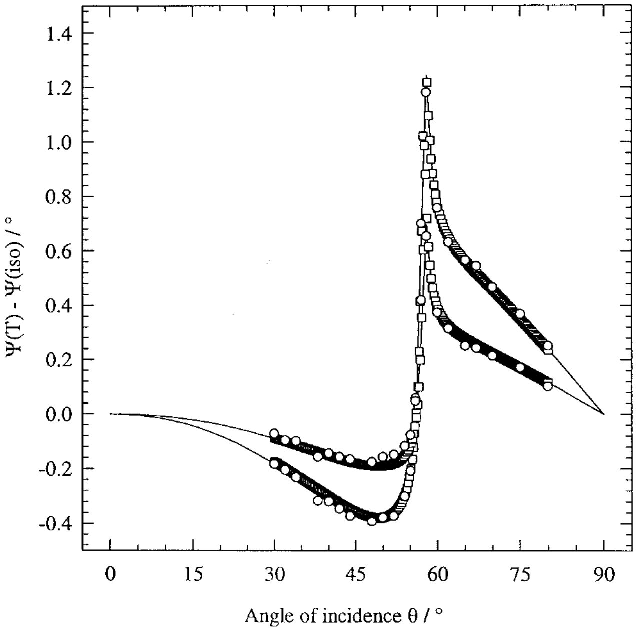

Figure 8. Circles represent measured angular spectrum for 6CB at $T - T_c = 0\cdot1$ K and at $T - T_c = 0\cdot3$ K; squares are the signal, calculated *a posteriori* from the neural network reconstructed profile. The full line is the least square fit to the measured data following equations (2)–(7).

All the compounds of the cyanobiphenyl series, the nematics as well as the smectics, exhibit a complete wetting behaviour at the free surface on approaching the bulk phase transition temperature. This is consistent with the fact that the surface tension in the nematic phase is smaller than in the isotropic phase [23]. We have determined the temperature dependence of the surface order parameter, which decreases monotonically with increasing temperature. Moreover, we report for the first time an even–odd effect in surface-induced pretransitional order. Finally, we used a neural network profile recognition algorithm to reconstruct independently the surface layer ordering in 6CB. The correspondence between the profiles obtained in this way and the model-based profiles is a confirmation of the theoretical model and an illustration of the promising capabilities of neural networks in the determination of profile characteristics.

The field of pretransitional wetting of liquid crystals is one with much experimental work yet to be done. Until now, studies of surface-induced ordering have been concerned only with planar or homeotropic alignment of the samples. We plan a study of the wetting behaviour of molecules that show less tendency than the cyanobiphenyl compounds to align homeotropically at the free surface. It would also be interesting to investigate the influence of external fields on the wetting behaviour.

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