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Alignment of Liquid Crystals by Grooved Surfaces†

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Abstract—We have observed alignment of nematic, cholesteric and smectic liquid crystals in directions depending on the orientation of submicroscopic, parallel grooves in adjacent glass and fused quartz surfaces. The alignment can be explained on the basis of elastic strain energy in the bulk of the liquid crystal that would be increased if the long axes of the molecules were aligned by the surface but were not approximately parallel to the groove direction. We have also observed alignment parallel to grooved surfaces but skewed with respect to the grooves, apparently when long molecules become attached to the surface in a direction that causes a competing torque on the director of adjacent liquid crystal molecules.

1. Introduction

We recently reported the observation of alignment of some thin nematic liquid crystal samples between two glass or fused quartz surfaces that had been lapped with diamond powder or cerium oxide in one direction and then cleaned and baked to remove organic material.(1) We have since learned that Zocher(2) performed very similar experiments in 1925. The mechanism of the alignment was not well understood at that time. We attributed the alignment to an elastic energy minimum that occurs when the directors are parallel to the grooves scored by the lapping process. If the directors were not paralleled to the grooves there would be bend and splay in the region above the surface where the directors change from orientation defined locally by the surface to parallel orientation. This strain would result in an increase of Oseen(3)–Frank(4) elastic energy.

In this paper we will give details of the derivation of the Oseen–Frank elastic energy for a simplified model of the nematic. We will

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† Presented at the Fourth International Liquid Crystal Conference in Kent, Ohio, August 21–25, 1972.

also describe observations of the alignment of a smectic C sample and of cholesteric samples by the same mechanism, without giving a detailed analysis of the elastic forces, which would be more complicated for those cases. We will also describe experimental evidence that alignment forces by the Oseen–Frank elastic energy mechanism may compete with alignment forces of comparable magnitude due to oriented molecules adsorbed to the surface, to yield alignment of nematics in intermediate orientations.

2. Elastic Energy Estimate for Nematics

We first derive an approximate expression for the Oseen–Frank elastic energy for a nematic oriented at some arbitrary angle with respect to a grooved surface. Frank's expression$^{(4)}$ for the elastic free energy in a strained nematic liquid crystal may be written

$$g = \tfrac{1}{2}[k_{11}f_1 + k_{22}f_2 + k_{33}f_3 - (k_{22}+k_{24})f_4]. \tag{1}$$

The f's are derivative functions of the " director ", L, of the liquid crystal, defining splay, twist, bend and splay-twist cross terms, respectively. The k's are elastic constants. In cartesian coordinates,

$$f_1 = \left(\frac{\partial L_x}{\partial x} + \frac{\partial L_y}{\partial y} + \frac{\partial L_z}{\partial z}\right)^2 \tag{2}$$

$$f_2 = \left[L_x\left(\frac{\partial L_y}{\partial z} - \frac{\partial L_z}{\partial y}\right) + L_y\left(\frac{\partial L_z}{\partial x} - \frac{\partial L_x}{\partial z}\right) + L_z\left(\frac{\partial L_x}{\partial y} - \frac{\partial L_y}{\partial x}\right)\right]^2 \tag{3}$$

$$\begin{aligned} f_3 = {} & \left(L_x\frac{\partial L_x}{\partial x} + L_y\frac{\partial L_x}{\partial y} + L_z\frac{\partial L_x}{\partial z}\right)^2 \\ & + \left(L_x\frac{\partial L_y}{\partial x} + L_y\frac{\partial L_y}{\partial y} + L_z\frac{\partial L_y}{\partial z}\right)^2 \\ & + \left(L_x\frac{\partial L_z}{\partial x} + L_y\frac{\partial L_z}{\partial y} + L_z\frac{\partial L_z}{\partial z}\right)^2 \end{aligned} \tag{4}$$

and

$$\begin{aligned} f_4 = {} & 2\left(\frac{\partial L_x}{\partial x}\frac{\partial L_y}{\partial y} + \frac{\partial L_y}{\partial y}\frac{\partial L_z}{\partial z} + \frac{\partial L_z}{\partial z}\frac{\partial L_x}{\partial x}\right) \\ & - 2\left(\frac{\partial L_y}{\partial x}\frac{\partial L_x}{\partial y} + \frac{\partial L_z}{\partial y}\frac{\partial L_y}{\partial z} + \frac{\partial L_x}{\partial z}\frac{\partial L_z}{\partial x}\right) \end{aligned} \tag{5}$$

We assume that we may neglect any variations of the director of the liquid crystal along the direction of the grooves, which we shall designate as the y direction. (See Fig. 1.) Then all derivatives with respect to y disappear from the expressions for the f's. Next, we define two angles, θ and φ (see Fig. 1), which determine the director L through the equations

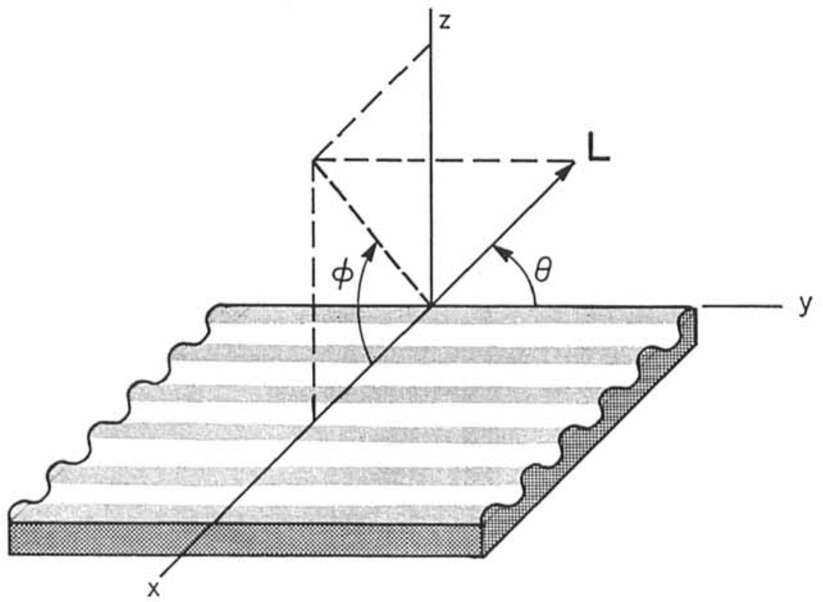

Figure 1. Director, L, and grooved surface with reference coordinates.

$$L_x = \sin\theta \cos\varphi \tag{6}$$

$$L_y = \cos\theta \tag{7}$$

$$L_z = \sin\theta \sin\varphi \tag{8}$$

We now make the first simplifying assumption, which is reasonable if the sides of the grooves are not too steep. We assume that θ, the angle between the y axis (groove axis) and the director, is approximately constant. That is, we will neglect changes of θ with x and z, as well as y. Then we find that

$$f_1 = \sin^2\theta\left(-\sin\varphi\frac{\partial\varphi}{\partial x} + \cos\varphi\frac{\partial\varphi}{\partial z}\right)^2 \tag{9}$$

$$f_2 = \sin^2\theta\cos^2\theta\left(\cos\varphi\frac{\partial\varphi}{\partial x} + \sin\varphi\frac{\partial\varphi}{\partial z}\right)^2 \tag{10}$$

$$f_3 = \sin^4\theta\left(\cos\varphi\frac{\partial\varphi}{\partial x} + \sin\varphi\frac{\partial\varphi}{\partial z}\right)^2 \tag{11}$$

and

$$f_4 = 0. \tag{12}$$

If we make a second simplifying assumption, that $k_{11} = k_{22} = k_{33} = \bar{k}$,† which is not very realistic but allows us to make semi-quantitative estimates of energies involved, we get the free energy expression

$$g = \frac{\bar{k}}{2}(f_1+f_2+f_3) = \frac{\bar{k}\sin^2\theta}{2}\left[\left(\frac{\partial\varphi}{\partial x}\right)^2 + \left(\frac{\partial\varphi}{\partial z}\right)^2\right] \tag{13}$$

Such an expression for free energy density occurs when the angle φ obeys the two-dimensional Laplace equation,

$$\frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial y^2} = 0. \tag{14}$$

Consider the following solution to Laplace's equation:

$$\varphi - \varphi_0 = \sum_j (P_j A_j)\cos[P_j(x - x_j)]\exp(-P_j Z). \tag{15}$$

If all $P_j A_j$ are small, then a surface that makes approximately a constant angle φ_0 with respect to the director is given by

$$Z(x) = \int_{\bar{x}}^{x}(\varphi - \varphi_0)\,\mathrm{d}x \approx \sum_j A_j\sin(P_j(x - x_j)). \tag{16}$$

We conclude that if a solid surface with contour $Z(x)$ has the property that local molecular forces cause the director of immediately adjacent nematic liquid crystal molecules to lie at an orientation φ_0, θ with respect to the surface, then the directors elsewhere in the liquid crystal will have orientations with φ given by Eq. (15). A Fourier analysis of the solid surface contour $Z(x)$ gives the coefficients A_j.

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† Grabmaier *et al.*⁽⁵⁾ have recently presented an analysis of strain energy density immediately adjacent to a grooved surface that does not require the approximation that $k_{11} = k_{22} = k_{33}$. They have also performed some experiments similar to ours.

If we insert Eq. (15) into Eq. (13) we obtain the following expression for the local strain energy density at any point within the liquid crystal.

$$g = \langle g \rangle + \tilde{g} \tag{17}$$

where

$$\langle g \rangle = \frac{\bar{k}\sin^2\theta}{2} \sum_j A_j^2 P_j^4 \exp(-2P_j z) \tag{18}$$

and

$$\tilde{g} = \frac{\bar{k}\sin^2\theta}{2} \sum_{j \neq k}\sum A_j A_k P_j^2 P_k^2 \exp(-(P_j + P_k)z) \cdot \{\sin[P_j(x - x_j)] \sin[P_k(x - x_k)] + \cos[P_j(x - x_j)] \cos[P_k(x - x_k)]\}. \tag{19}$$

If the surface contour were sinusoidal, as illustrated in Fig. 1, then there would be only one amplitude A with wave-number $P = 2\pi/l$, where l is the length of the fixed sinusoidal surface waves. In that case,

$$g \equiv \langle g \rangle = 8\pi^4 \bar{k} \sin^2\theta (A^2/l^4) \exp(-4\pi Z/l) \tag{20}$$

This expression for free energy density is equivalent to Eq. (4) of Ref. 1. Since there are no cross terms in the square, the energy density is constant everywhere for this simple case. The short-wave components of a Fourier transform of the surface contour contribute much more than the long wave components, for a given ratio of amplitude to length, as indicated by the factor A^2/l^4.

If we suppose that surface waves of length $l \approx 1000$ Å and amplitude $A \approx 200$ Å make the dominant contribution to energy, then the mean energy density $\langle g \rangle$ at the surface ($z \approx 0$) will be about $4 \times 10^{11} \bar{k} \sin^2\theta$ ergs per cubic centimeter. Electron micrographs of surfaces rubbed with 1-micron diamond powder$^{(1)}$ suggest that these are conservative estimates of reasonable groove parameters. (See Fig. 2.) In para-azoxydianisol (PAA), $\bar{k}$ is about 10^{-6} cgs units,$^{(4)}$ and we get $4 \times 10^5 \sin^2\theta$ ergs/cm^3 for the energy density as a function of disorientation angle, θ. A sufficiently strong electric or magnetic field of appropriate orientation should be capable of orienting molecules of nematic normal to, rather than parallel to a grooved surface because of the dielectric or magnetic

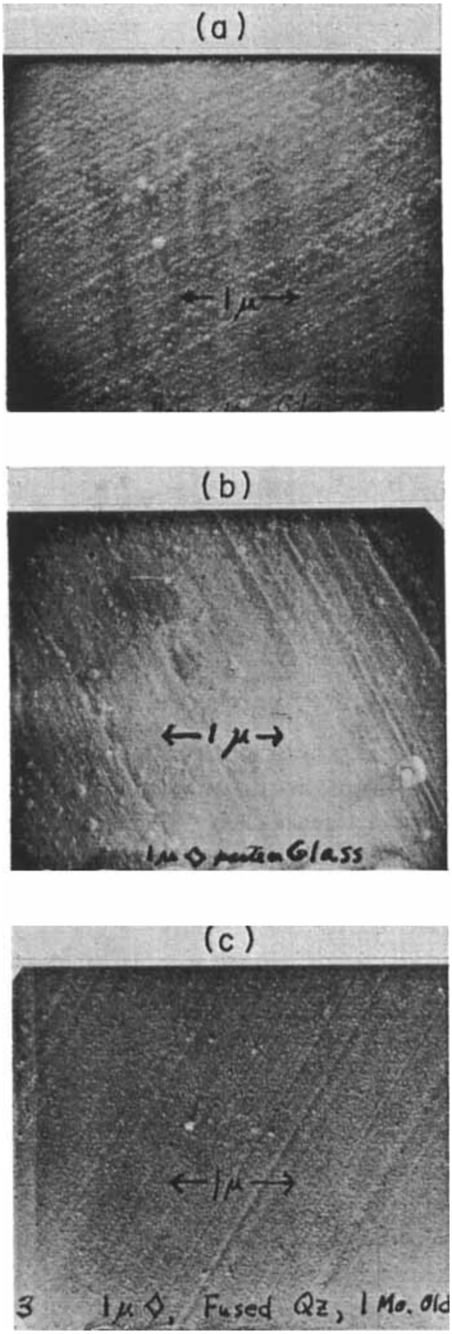

Figure 2. Electron micrograph of gold-shadowed replica of grooved surfaces formed (*a*) on glass microscope slide with " barnsite " on beeswax lap; (*b*) on glass microscope slide with 1 micron diamond powder in oil on hard leather lap; (*c*) on fused quartz slide with same treatment as (*b*), except that lap was tin.

anisotropy of the material. The strength of such a field would be such that the energy anisotropy is at least as large as $\langle g \rangle$ at the surface. In Gaussian units the expressions for such energy anisotropy are

$$u = E^2(\epsilon_2 - \epsilon_1)/8\pi \quad \text{(electric)}$$

and

$$u = H^2(\mu_2 - \mu_1)/8\pi \quad \text{(magnetic)}.$$

Maier and Meier⁽⁶⁾ give the values $(\epsilon_1, \epsilon_2) = 5.6,\ 5.9$ for PAA. Using these values of ϵ, a field E of 5×10^6 V/cm is required to make u as large as 4×10^5 ergs/cm³, which would make PAA lie across the grooves at equilibrium in our example, in spite of the additional elastic strain energy. Similarly, using the number $\mu_2 - \mu_1 = 2.4 \times 10^{-7}$ (Massen, Poulis and Spence⁽⁷⁾) we find that the magnetic field strength required to obtain the same energy anisotropy is 6×10^6 Oersteds. These two figures indicate the extremely strong orienting effect of surface grooves of reasonable dimensions.

Another interesting number is the total elastic strain energy density per unit area,

$$\langle p \rangle = \int_0^\infty \langle g(z) \rangle \, dz. \tag{21}$$

It is not unreasonable to suppose that for many substances the layer of molecules adjacent to the surface will have one relative minimum in surface energy per unit area for normal or homeotropic alignment and another for parallel alignment relative to the surface, with one minimum being slightly deeper than the other. A liquid crystal that aligns normal to a flat surface of a particular material might well have a higher total energy if it is normal to a grooved surface of the same material than if it changes to the other (parallel) alignment minimum because of the bulk strain energy $\langle p \rangle$ (Eq. (21)) associated with the normal alignment. If the energy minima are not sharp, there will be some tendence for the angles of the molecules at the surface to vary somewhat to reduce the strain energy in the bulk, thus requiring $Z(x)$ to be somewhat, but probably not much, larger than the value given by Eq. (16) to give the same strain.

In the case of the sinusoidal surface previously considered with PAA, Eq. (21) gives an energy of about 0.4 erg/cm². We have observed that certain liquid crystals may lie perpendicular to a grooved surface having about the suggested average groove dimensions if a monolayer of an appropriate surfactant that favors homeotropic alignment is applied over the surface, although the same liquid crystals align parallel even to ungrooved surfaces of the same material without the surfactant. This means that the energy required to overcome the alignment by the surfactant is over 0.4 erg/cm^2. This is a measure of a sort of surface tension anisotropy between normal and parallel alignment, amounting to 0.4 dynes/cm. Our observations also suggest that on glass cleaned in such a way that one would expect to get homeotropic alignment of certain liquid crystals above a flat surface, a well grooved surface may give parallel alignment.† Differences in surface tension depending on director orientation adjacent to the surface can apparently be less than the order of 0.4 erg/cm^2 for those liquid crystals and surfaces. Experiments with grooves of varying dimensions might give more accurate values for surface tension anisotropy for particular liquid crystals and surface or surfactant materials.

In our earlier paper(1) we speculated that if a surface were rough in both the x- and y-directions, there might be a preference for orientation of the directors of nematics normal to the overall surface. Such preference would exist only if the elastic forces tending to make molecules lie normal to the surface were weak, so that a local tilt with respect to a tilted region of the surface would produce little increase in energy at the surface. Such a small energy might be expected from long molecules with surface bonding sites on the tips of very flexible tails. With a surface that is rough in both directions there is no other orientation that can reduce elastic strain energy. However, we do not feel that we have conclusive evidence that such cases actually exist.

3. Experiments

We have performed experiments that are intended to demonstrate the existence of liquid crystal alignment that depends on the surface shape effect and not on short range forces by oriented molecules on

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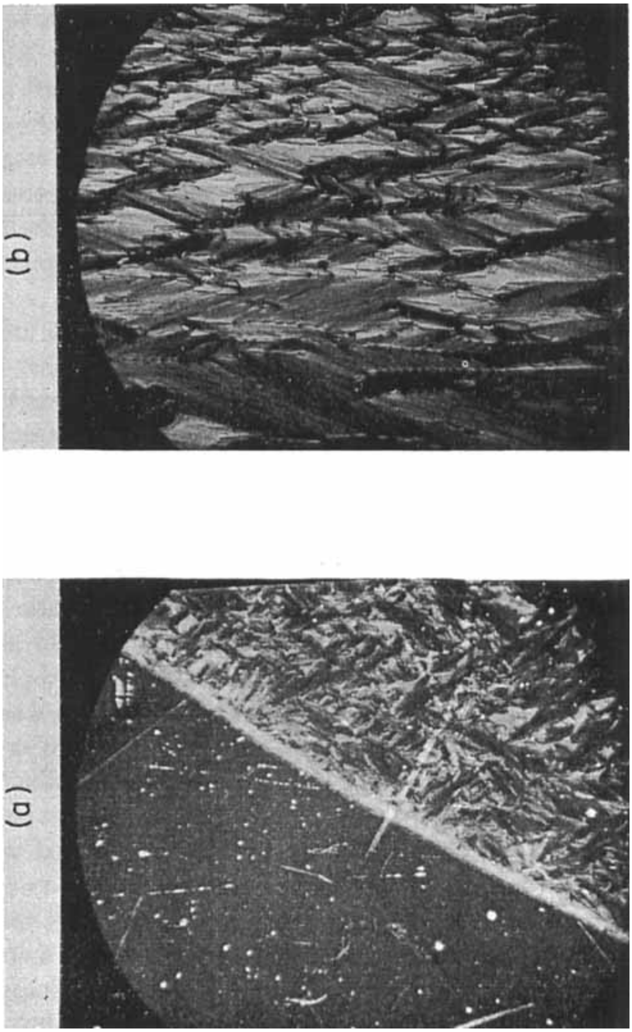
† In paper 20 of the Fourth International Liquid Crystal Conference, at Kent State, Creigh and Kmetz reported that parallel alignment of nematics on flat glass usually indicates a residual trace of carbon or hydrocarbon material left on the glass from the cleaning process.

the surface. In the process we have found evidence that the surface shape and oriented molecules on the surface may compete for control of the orientation of the overlying liquid crystal when the two are not parallel. To avoid intrinsic molecular alignment in the solid surface we have used glass and fused quartz as the grooved solid materials. We have heated them to very high temperatures after the grooves were made and after the surfaces were washed with various solvents, with the intent of removing, or at least disordering, any possible residue of molecules that might have become ordered on the surface by the grooving process. We learned recently that Zocher *et al.* performed very similar experiments starting in 1925 with similar results, though apparently with less understanding of those results.

Our first experiment was performed with two ordinary soft glass microscope slides. Each slide was rubbed parallel to its long axis by hand for about a minute with a piece of cork that had been dipped in beeswax and then in a slurry of " barnsite " (rare-earth oxide) polishing powder in water. The slides were then washed with soap, rinsed with water and acetone, then washed with benzene, rinsed again with acetone and water, agitated in chromic and concentrated sulfuric acid glass cleaner for about two minutes, rinsed again with running water and then distilled water, dried with dry air and finally baked in a kiln at about 500 °C for half an hour. An electron micrograph of a gold-shadowed carbon replica of a similarly prepared slide is shown in Fig. 2(a). When PAA was flowed between the two slides at 100 °C and observed between crossed polarizers under a microscope, very good alignment parallel to the direction of rubbing was observed. We tried similar experiments using a pitch lap with variable success. Then we tried using one micron diamond powder mixed with oil and rubbed onto a hard leather lap. We obtained extremely good alignment with all slides rubbed with this lap for a minute or more. The grooves in a slide rubbed with this lap are shown in Fig. 2(b). They are perhaps a little deeper and smoother than those obtained with barnsite. Then we tried using fused quartz slides because they are harder and could presumably withstand harder scrubbing in the cleaning process without altering the surface contour. To groove these slides we used a lap of soft tin that had been lightly impregnated with one micron


(b)
(a)

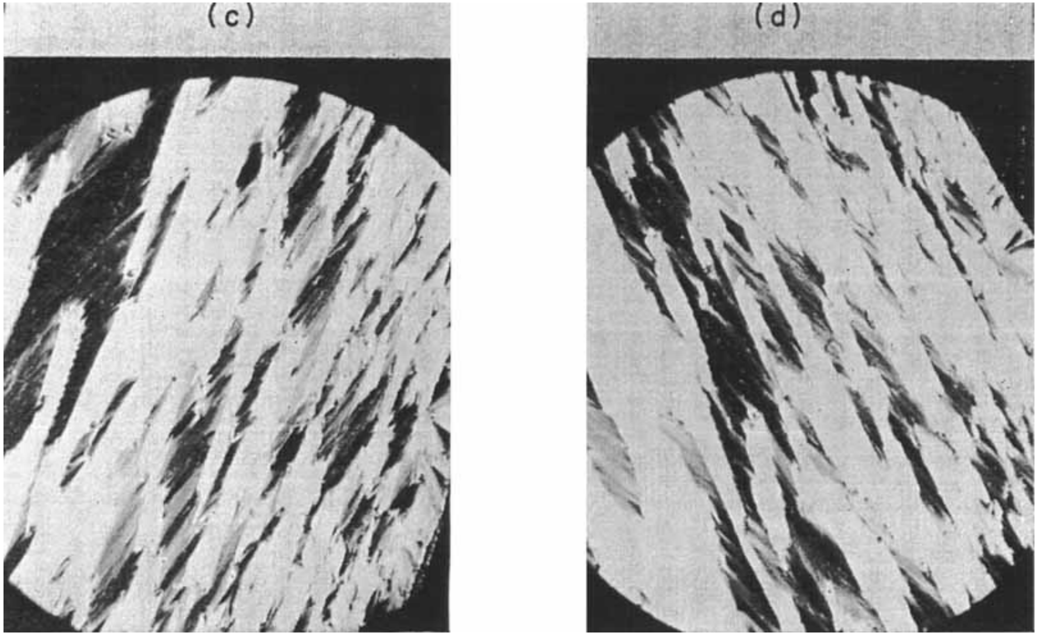


Figure 3. (a) Heptyloxyazoxybenzene at 122.6 °C, about 10 μ thick, between grooved quartz plates. Grooves are vertical, polarizer is vertical and analyzer is horizontal on figure. Solid melted to smectic " C " and then to nematic on lower right where mottled pattern exists, then flowed in the nematic phase to upper left where extinction is very complete except around flaws. Pattern in region of former smectic phase had a range of extinction angles of about $\pm 2°$. (b) Same sample cooled again to smectic *C* phase at 89 °C. (c) and (d) Same sample rotated to ± 21.5 degree angles between polarizer and analyzer showing extinction in complementary domains at those angles in smectic *C* phase.

diamond powder in oil and then rubbed in with a large piece of flat glass to push the particles into the surface and assure its flatness. An electron micrograph of one of the fused quartz slides rubbed on this lap for about two minutes is shown in Fig. 2(c). The grooves are smooth and not as deep as in glass. The alignment with these slides was the best we observed, and the slides could be recleaned and reused without apparent degradation of the grooves. The one shown in Fig. 2(c) had actually been grooved about a month earlier and cleaned and baked five times for various experiments without repolishing before the electron micrograph was made. Among the experiments done with that slide are the ones with heptyloxyazoxybenzene to be described in more detail. We also observed good alignment, by these slides, of PAA at 100 °C, and of MBBA at room temperature. In addition, sharp Grandjean–Canot discontinuities, indicating good alignment, were obtained using these slides with cholesteryl nonanoate after it had been heated to the isotropic phase and then cooled to the cholesteric phase. We would not expect good alignment of a cholesteric if the grooves were not much shallower and narrower than the cholesteric pitch length. The electron micrographs indicate that the grooves are only about a thousand Angstroms wide and a few hundred Angstroms deep.

Although the approximate theory we described applies only to nematics and perhaps, if the grooves are narrow and shallow compared to the pitch, to cholesterics, it seems likely that similar effects might occur in smectics. We have observed interesting alignment effects of heptyloxyazoxybenzene (HOAB) in both its nematic and its smectic *C* phase with the grooved quartz slides just described.

The slides were cleaned as described and baked at about 500 °C. When they had cooled to about 100 °C they were transferred to a Mettler hot stage under a Leitz polarizing microscope. A small amount of HOAB powder was then introduced between them. By then they had cooled so that the HOAB apparently went into its smectic *C* phase. This phase was originally in the lower right region shown in Fig. 3(a). We raised the temperature above 123 °C so that the HOAB became nematic and then isotropic and flowed out into a region " untouched " by the smectic *C* phase, in the upper left of Fig. 3(a). The sample was then cooled to the nematic phase. Figure 3(a) was made at 100 °C. As the figure shows, the alignment is essentially perfect in the nematic phase between the previously untouched surfaces. There is a mottled pattern in the lower right region where the smectic *C* phase was, but rotating the sample between the crossed polarizers revealed that the range of angles of orientation in this region was only about ±2 degrees from the direction of the grooves. The spots and lines are dust particles and scratches that show their effects only at sample orientations very near total extinction between the crossed polarizers. Then we cooled the sample to 93 °C, whereupon it returned to the smectic *C* phase shown in Fig. 3(b) with two extinction orientations at ±21° angles from the groove direction. The grooves are up and down in

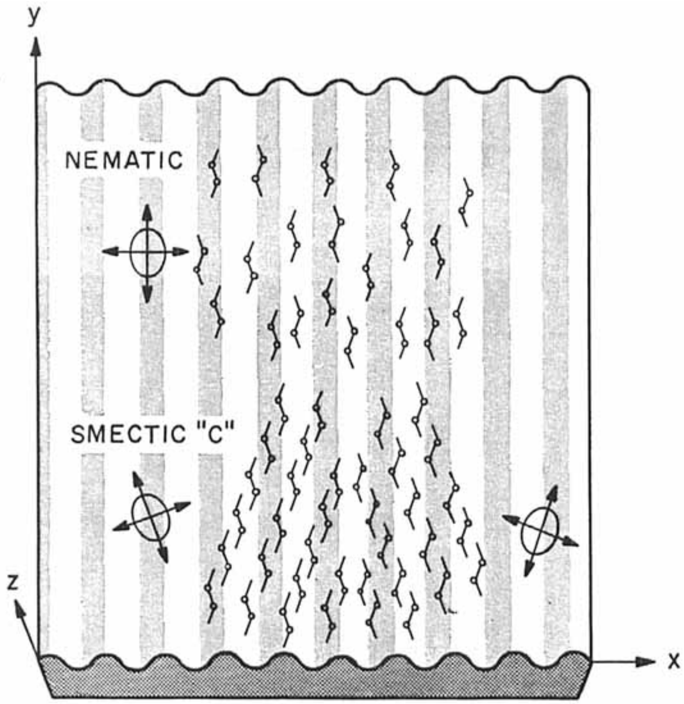
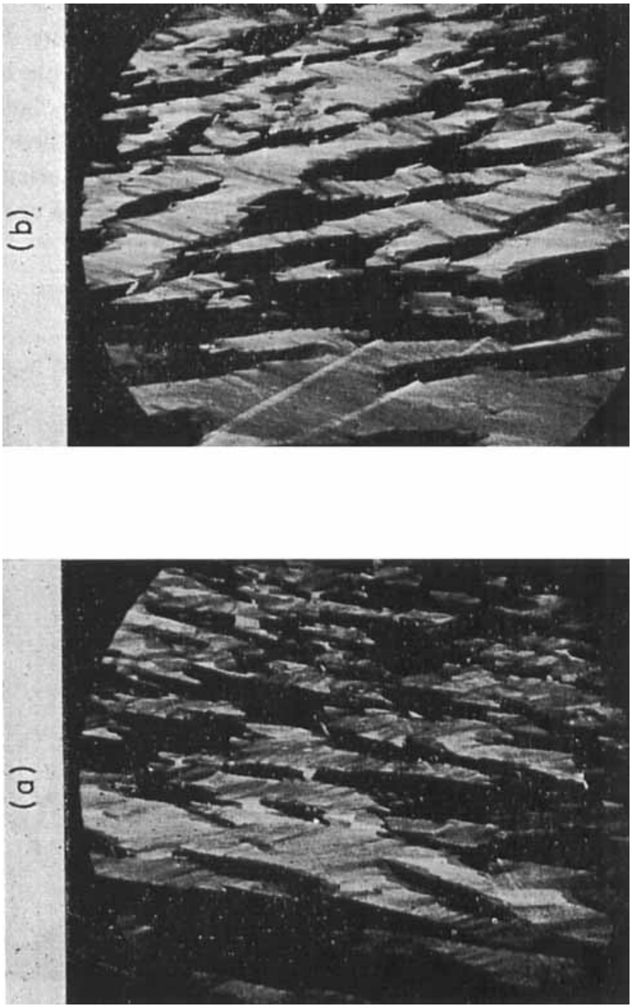


Figure 4. Diagram of molecules and optic axes above a grooved surface in the nematic phase (top) and in two complementary zones of proposed model of the smectic *C* phase (bottom right, left). In proposed model of smectic *C* phase, planes of molecules are normal to plane of figure and parallel to striations shown in Fig. 2(*b*).


(b)
(a)

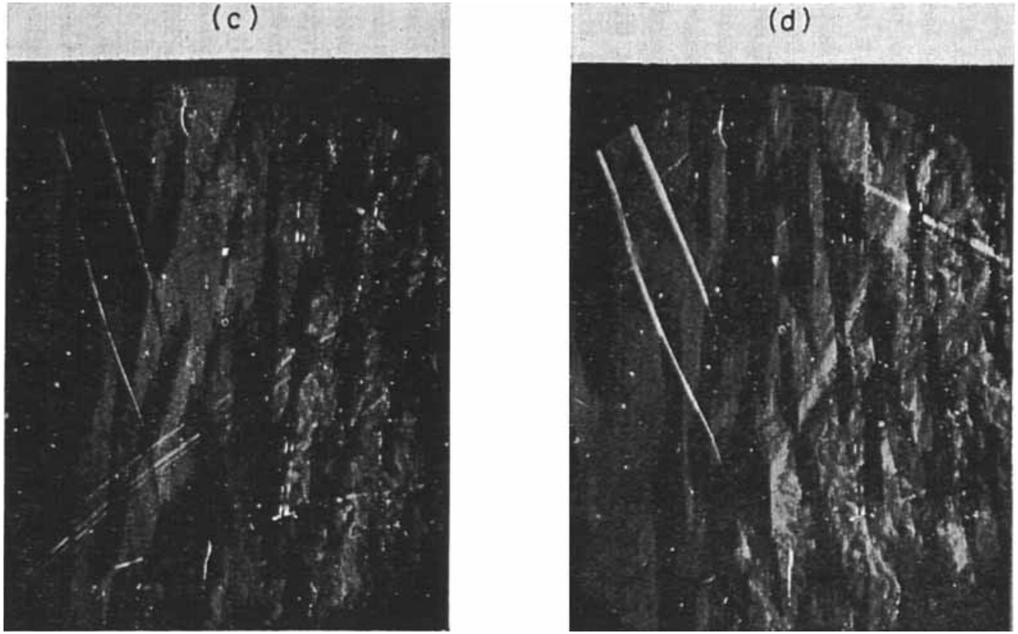


Figure 5. (a) and (b) Same sample as in Fig. 3(c), reheated to the nematic phase at 95 °C, showing extinction at angles of ±7.5° to grooves, indicating alignment perturbation due to molecules attached to surface in smectic phase and not yet loosened by thermal agitation. (c) and (d) Same sample after heating to 135 °C (isotropic) for about 20 minutes and recooling to nematic phase, showing extinction at ±2.5°, indicating that most of the attached molecules became detached from the surface during heating. Residual pattern from original melting through smectic phase is also visible (cf. Fig. 2(a)).

Fig. 3(b). Comparison of Figs. 3(c) and 3(d) shows conjugate zones of opposite orientation. The pattern remained essentially unchanged at 85 °C.

We believe that the two molecular orientations in the smectic *C* phase may be somewhat like that shown in the two zones at the bottom of Fig. 4. (The two small circles in each molecule are supposed to represent the two benzene rings in HOAB, but the scale is not very good.) The smectic *C* phase is supposed to be composed of monomolecular (or perhaps dimolecular) layers of molecules, tilted with respect to the layer surfaces. These surfaces are supposed to lie normal to the page and make an angle of about 25° with respect to the grooves, parallel with the striations shown in Fig. 3(b). The optic axes of the molecules are perhaps almost parallel to the axes between the two benzene rings but the direction of minimum strain energy over the grooved surface is different, resulting in the differences between the alignment of the planes, the grooves and the extinction directions. In the nematic phase the molecules rotate so that they have only one average preferred direction, which is parallel to the grooves and to the optic axis of the liquid crystal, as shown at the top of Fig. 4.

Next, we reheated the liquid crystal to the nematic phase. Instead of aligning parallel to the grooves, it remained in two zones oriented at about ± 7.5° from the grooves over the whole nematic temperature range, as shown in Figs. 5(a) and (b). We then heated the sample to 135 °C for 20 minutes, well above the isotropic transition at 122.6 °C, and recooled to the nematic phase. As shown in Figs. 5(c) and (d), there are still two zones, but they are only at about ± 2.5 degree angles from the grooves. (A faint residual pattern from the original smectic *C* material also shows in the lower right in these figures.)

We believe that the disorientation shown in Fig. 5 is due to oriented molecules that become loosely bonded to the surface when the HOAB is in the smectic *C* phase. We do not know whether these bonded molecules are HOAB or some impurity. However, the direction of minimum energy for adjacent HOAB in the nematic phase is clearly not parallel to the grooves but is strongly influenced by the orientation of the bonded molecules, which may also be oriented as shown at the bottom of Fig. 4. When the material is heated, we believe that thermal agitation slowly removes or randomizes the orientation of the molecules bonded to the surface so that the surface shape effect eventually becomes the governing force in aligning the nematic.

4. Conclusions

We believe we have demonstrated the existence of two factors that may influence the alignment of thin layers of nematic liquid crystals between rubbed surfaces. One is a purely geometrical effect that can arise from elastic strain energy if the surfaces are grooved. Such energy is minimized when the nematic director is parallel to the grooves. The other is the influence of short-range molecular forces by molecules aligned in some preferred direction on the surface. The geometrical factor probably determines the equilibrium orientation of a nematic adjacent to a grooved surface but molecules accidentally or intentionally attached to the surface in some other orientation may strongly disturb the alignment so long as they remain.

Acknowledgements

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