

Influence of Alignment of Crystalline Confining Surfaces on Static Forces and Shear in a Liquid Crystal, 4'-*n*-Pentyl-4-cyanobiphenyl

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Received March 8, 2000. In Final Form: August 2, 2000

Static force–distance relations as well as linear and nonlinear viscoelastic responses to oscillatory shear were studied in 4'-*n*-pentyl-4-cyanobiphenyl (5CB) confined between two muscovite mica surfaces at 25 °C. The orientation of the crystallographic axes of the mica sheets was varied from close to perfect alignment to a twist angle of $\theta > 80^\circ$, and the sliding direction was kept parallel to the γ optical axis of one mica sheet. The layering was unaffected by twist angle when the film thickness exceeded three molecular layers of 5CB in a planar orientation, but for two and three layers the adhesive minima in the oscillatory force–distance curve decreased in magnitude with increasing θ . In the linear viscoelastic response (obtained with shear deformations of $< 20\%$ of the film thickness), an elastic response dominated at shear frequencies of 0.13–130 Hz and small θ , whereas a more liquidlike response appeared at low frequency for large θ . Apparent discrepancies between the shear responses of alkylcyanobiphenyl films obtained in other investigations were resolved: during shear deformations of large amplitude, either stick–slip or smooth sliding was observed, depending on the number of layers but not on the surface alignment. At the film thickness of two layers, we observed stick–slip above a maximum limiting strain of 0.5 (at the smallest θ), whereas at three layers, the sliding was continuous with shear thinning at strains larger than 0.7. The effective shear moduli and limiting shear stress decreased with increasing film thickness and misalignment. In contrast to the known friction behavior of muscovite mica in the absence of an intervening fluid layer, no local extrema were observed at $\theta = 30^\circ$ and 60° , indicating that the shear response resulted from the structure of the film of anisotropic molecules and not directly from the surface crystal lattice.

Introduction

The contact between two misaligned crystals typically consists of a region of defects (a grain boundary), where the crystal surfaces are unable to form the structure found in the bulk. In metals, moderate misalignment can be accommodated, because the interactions between atoms across the interface are of similar strength as the bonds within each surface, and can cause atoms or planes in the crystal to be moved from their original positions.^{1,2} Commonly, however, the interactions between surfaces are weaker than within them, and each surface retains its structure also in contact. Because of the defects in the plane of contact, the adhesion and friction between misaligned surfaces are lower than at perfect alignment.^{3–5}

Other atoms or small molecules (contaminants or lubricants) confined between the surfaces may become positionally ordered because of the structure of the crystal lattice. The resulting structure of this intervening film depends on the size of the molecules compared to the surface lattice and on the number of molecular layers.^{6–10}

For model monolayers consisting of atoms with the same size as those in the lattice, the ordering has been found to be maximized when the surface lattices are commensurate, and to decrease with increasing mismatch due to the conflicting ordering effect from each surface.^{6–8}

Several experimental studies on the angle-dependence of adhesion,^{11,12} and of friction with^{13–15} and without⁵ an intervening film, have concerned muscovite mica, a layered silicate in which repeating layers interact through van der Waals forces. These forces are weaker than the covalent bonds between silicon (or aluminum) and oxygen atoms exposed at each surface. It has been established that the muscovite surface has the same structure as a plane within the bulk crystal.¹⁶ Computer simulations of the effects of lattice registry on friction^{4,6–10} also assume rigid crystalline structures (typically face-centered cubic (100) or (111)).

Muscovite mica can be cleaved along its (001) plane to produce atomically smooth, flexible sheets that are 1–5 μm thick and up to 10 cm^2 in area. The structure of muscovite corresponds closely to a C_{2h}^6 ($C2/c$) symmetry, but a distortion, induced by an inner, octahedral structure,

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causes the oxygen atoms in the tetrahedral sheet exposed in the cleavage plane to have a ditrigonal symmetry composed of two interpenetrating triangles with side lengths of 3.9 and 5.1 Å, respectively.^{17,18} In the bulk crystal, K⁺ ions present in the cleavage plane are nearly hexagonally ordered,^{17,18} but upon cleavage they become randomly divided between the sites on the two newly created surfaces.^{16,19} The surface structure is pseudohexagonal so that the friction of two opposed surfaces under dry and clean conditions,⁵ and also their adhesion across water or KCl solution films with a thickness of only a few molecular diameters,^{11,12} show maxima both at perfect alignment ($\theta = 0^\circ$) and at a twist angle of $\theta = 60^\circ$.

In water and KCl solution, all adhesion maxima (at $\theta = 0^\circ$ and multiples of 60°) were found to have similar magnitude, and no distinct minimum with respect to a baseline adhesion was found.^{11,12} The experiments with bare, dry surfaces⁵ showed a minimum in the friction at $\theta = 30^\circ$, and also suggested that the local maximum at $\theta = 60^\circ$ was slightly smaller than the one measured at 0° . Other friction experiments at lesser twist angles ($\theta < 15^\circ$) across molecularly thin films of octamethylcyclotetrasiloxane^{13,14} (OMCTS) and tetradecane¹⁵ revealed that the friction forces also in these systems had a maximum at perfect alignment of the surfaces and decreased with misalignment,^{13,14} but did so less rapidly than the adhesion found in the static measurements in aqueous solution, where the maxima were found only within $\pm 1^\circ$ from $\theta = 0^\circ$ and multiples of 60° .^{11,12} A broad peak in the shear stress around perfect registry of model surfaces confining spherical molecules has been found in some computer simulations,^{8,9} whereas others showed a maximum only for the case of perfect alignment.¹⁰

Shear responses of confined, near-spherical molecules such as OMCTS and model films have been analyzed for the influence of their positional order in those cases when they lack direction with respect to the surface lattice or shear, but interact with each other and the surfaces.⁶⁻¹⁰ Alkane molecules are known to orient preferentially parallel to confining crystal lattices,^{20,21} but they interact with mica as weakly as OMCTS does, and they may already reorient in a weak shear field. To our knowledge, experimental data on friction between muscovite surfaces separated by well-characterized single-component thin films have not been shown previously for twist angles larger than 15° . Experiments showed no anisotropy in the friction of muscovite surfaces in ambient air,⁵ or in the adhesion in N₂ gas with a relative humidity of 33%,^{11,12} where a mixed layer of water and ions or contaminants was present on the surfaces.

In this paper, we investigate whether rigid, anisotropic molecules with stronger surface anchoring show a different static and dynamic behavior as a function of surface alignment. We have studied the effects of increasing twist angle between confining muscovite surfaces on the structure of 4'-*n*-pentyl-4-cyanobiphenyl (5CB) films with thickness of a few molecular diameters. It is known that on a clean muscovite surface in a dry atmosphere, the thermotropic liquid crystal 5CB adopts a planar orientation with its director (long axis of the cyanobiphenyl moiety) parallel to the surface.^{22,23} In a film confined

between two surfaces, positional ordering in the direction perpendicular to the surfaces (semioordered layers with a thickness corresponding to the mean diameter of the molecules in the direction perpendicular to their long axis) can be induced through strong confinement.²⁴ This behavior is also observed for molecules such as water,²⁵ OMCTS,²⁶ and linear alkanes²⁰ that, in the bulk, are isotropic liquids. Our experimental method gives information on layering and adhesion at different film thickness, which, together with rheological parameters obtained in oscillatory shear measurements, suggests differences in the film structure formed at different surface alignments. The results are compared to investigations on the static structure of 5CB^{24,27} and 4'-*n*-hexyl-4-cyanobiphenyl^{27,28} (6CB) films and to recent, apparently conflicting friction experiments^{29,30} on thin films of 4'-*n*-octyl-4-cyanobiphenyl (8CB) between aligned surfaces.

Methods and Materials

Instrumentation. The interaction forces and lateral shear of thin films were studied using a surface forces apparatus (SFA), in which two crossed, cylindrical surfaces can be brought toward or away from each other in a carefully controlled manner by means of motor-driven mechanical stages.³¹ The separation between the surfaces, D , was measured by multiple-beam interferometry³² with an accuracy of 1–2 Å. Attractive or repulsive forces between the surfaces cause a deflection of the double-cantilevered leaf spring supporting the lower surface. For a known spring constant, k (in our study $k = 930$ N/m), the magnitude of the interaction force, F , can be calculated from this deflection according to Hooke's law. Regions where dF/dD exceeds k are inaccessible to the technique, because the surfaces will at such points jump to or from each other to the next stable region. To allow comparison between different experiments, F is normalized by the geometrical average of the radius of the undeformed surfaces measured in two perpendicular directions, $R = (R_1 \cdot R_2)^{1/2}$. For elliptical contact positions, which are common in experiments where the surfaces are rotated with respect to each other, R_1 and R_2 must be measured along the axes of the ellipse to avoid an underestimation of R .³³

The measurements of shear moduli and stress at different surface separations (film thicknesses) and alignments of the confining surfaces were performed using a piezoelectric shear device, described in detail in refs 34–36 on which the upper surface was mounted. The shear response was detected in the same direction as the deformation of the film. The response to oscillatory shear at small amplitude (a few Å) was investigated in the frequency range $f = 0.13$ –130 Hz, and the response to increasing amplitude, 0.2–1900 Å, was investigated at a constant frequency of $f = 2.6$ Hz. The contact area was measured from the interference pattern, taking into account the elliptical shape of the contact.

Optical Measurements of Distance and Twist Angle. The surfaces were thin (2–3 μm) sheets of muscovite (ASTM V-2 Grade 3, obtained from Lawrence & Co., New Bedford,

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MA), cleaved from a thicker piece according to the procedure described in ref 12 to allow subsequent alignment of the crystallographic axes of two opposed sheets. The optical properties of muscovite^{31,37–40} and the measurements of separation distance³² and twist angle^{12,41} have been discussed extensively in the literature, and only those details essential for our experiment will be mentioned here.

Muscovite is birefringent in directions intersecting the cleavage plane, and these two almost-perpendicular optical directions, β and γ (with lower and higher refractive indexes respectively), give rise to two resonance wavelengths (doublet interference fringes) for each interference order. A preliminary determination of the optical axes of the mica pieces was made with crossed polarizing sheets (Leica) before cleaving (without distinguishing between β and γ at this point). The cleaved thin sheets were then cut along these directions according to the procedure described in ref 12. A heated platinum wire was used to make the cuts. The pieces obtained were silvered on one side for the interferometry. Small test pieces of each were silvered also on their other side, and the position of each optical axis was determined more precisely by observing the cancellation of the corresponding component (the β or γ fringe) of the constructively interfering light emerging from one such test piece. A sheet polarizer (Melles Griot) in a graded rotating holder, placed in the light path under the SFA, was used to make this observation. For a single sheet or two perfectly aligned sheets, the cancellation is complete only at certain distinct angles. The varying, incomplete cancellation shown in Figure 5 of ref 30 results from polarization mixing at nonperfect alignment of two mica sheets (cf. ref 41).

Matched pairs of back-silvered mica sheets of equal thickness were glued onto supporting half-cylindrical fused silica disks with a thermosetting epoxy glue, EPON 1004F (Shell). These disks were mounted in the instrument so that the γ axis of the mica on the upper (sliding) surface was aligned with the lateral shear direction to better than 5° . The γ axis of the mica on the lower surface, stationary during the sliding experiments, was aligned to similar accuracy with the supporting spring and was thus in the shear direction only at the best alignment obtainable (i.e., the smallest twist angle) between the two sheets. During the experiment, the upper surface was turned clockwise from perfect alignment (Figure 1) to different twist angles, θ , that were determined from measurements of the wavelength separation of the β and γ components of several fringes in the interference pattern according to¹²

$$\cos \theta = (\lambda_{\gamma,\theta} - \lambda_{\beta,\theta}) / \Delta\lambda_{\theta=0^\circ} \quad (1)$$

The maximum separation of β and γ needed for this calculation, $\Delta\lambda_{\theta=0^\circ} = \lambda_{\gamma,0^\circ} - \lambda_{\beta,0^\circ}$, is a function of wavelength and can be calculated for each fringe order from the difference in refractive index between the two directions. Strictly, the refractive indexes at the a priori unknown wavelengths $\lambda_{\gamma,0^\circ}$ and $\lambda_{\beta,0^\circ}$ should be used as input for the calculation, and $\Delta\lambda_{\theta=0^\circ}$ can then be found numerically,⁴² provided that the dispersions are known accurately. However, the refractive indexes of muscovite may occasionally vary³⁹ between different sources and even between different blocks (leading to differences in $\Delta\lambda_{\theta=0^\circ}$ that may, in extreme cases, affect the determination of θ by more than 10°).⁴³ These refractive indexes are not determined separately for the pieces used in our experiments.

For these reasons, $\Delta\lambda_{\theta=0^\circ}$ was not calculated from the refractive indexes reported in the literature, but was determined experimentally from the interference pattern of each test piece of mica that was silvered on both sides (cf. determination of optical axes above). In the wavelength interval of interest, the refractive indexes are slowly varying functions of wavelength,^{31,37–40} and

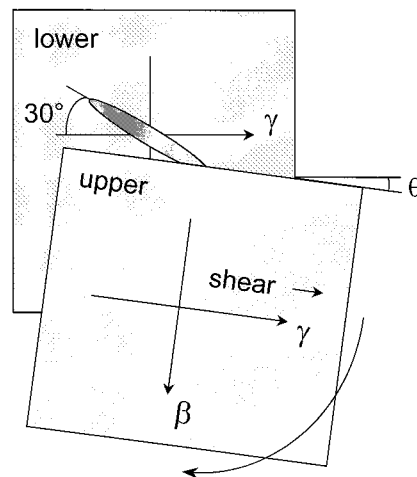


Figure 1. Schematic drawing of the orientation of the crystallographic axes (β and γ) of the two muscovite mica sheets and the shear direction (always along the γ axis of the upper sheet) at a twist angle θ from perfect alignment. On a single surface, the director (long axis of the cyanobiphenyl moiety) of 5CB in films thicker than a monolayer is oriented at ca. 30° from the γ axis (see text). Indicated on the lower surface is the approximately 30° clockwise orientation from γ observed in films $2.5\text{--}5\ \mu\text{m}$ thick between two surfaces at good alignment (smallest θ) in our experiments.

a practical method of obtaining $\Delta\lambda_{\theta=0^\circ}$ for a given wavelength is to plot $\lambda_\gamma - \lambda_\beta$ versus the middle point of the fringe doublet, $\lambda_{\text{ave}} = (\lambda_\beta + \lambda_\gamma)/2$, for several fringes arising from the single piece. From the equations for optical interference,³² one sees that for a single sheet, doublet fringes appear at the λ_{ave} where even order doublet fringes arise from two such sheets in contact at $\theta = 0^\circ$. (Within each sheet, weak interference also appears when two sheets are used, a phenomenon that can be observed as vertical, diffuse bands superimposed on the primary fringe pattern.⁴⁴) The average of the two wavelengths for each fringe, λ_{ave} , can be considered invariant with twist angle.¹² (For two sheets at $\theta = 90^\circ$, a single fringe is obtained at this wavelength as the two optical path lengths become equal.^{12,41}) The $\Delta\lambda_{\theta=0^\circ}$ corresponding to λ_{ave} measured for each fringe at arbitrary θ is then obtained with sufficient accuracy from the curve $\lambda_\gamma - \lambda_\beta$ versus λ_{ave} by interpolation, without the need to obtain refractive indexes and dispersion of each mica piece separately by other methods.

The influence of the liquid crystal on the determination of θ is small compared to the uncertainty arising from the wavelength measurement (cf. section on accuracy below) at a film thickness of $10\ \text{\AA}$ and $\theta > 30^\circ$, because at this separation, $\lambda_{\beta,\theta} - \lambda_{\gamma,\theta}$ is dominated by the contribution from the several μm thick mica.²⁷ However, because $\lambda_{\beta,\theta}$ and $\lambda_{\gamma,\theta}$ for a chosen fringe vary strongly with θ , the measurements of the film thickness (D above) at different alignments cannot be based on only $\lambda_{\beta,\theta}$, as is standard procedure in experiments where θ is not varied. Instead, because λ_{ave} can be considered invariant with twist angle, the separation distance can be determined with standard accuracy (above) by comparing the experimentally accessible λ_{ave} at arbitrary θ to the λ_{ave} from the wavelength calibration at $D=0$ (contact between the mica sheets without liquid crystal) and arbitrary θ .

Liquid Crystal Orientation. The liquid crystal was 4'-*n*-pentyl-4-cyanobiphenyl (5CB) purchased from Merck (British Drug House). A few mL of 5CB was centrifuged at 5000 rpm for 10 min to remove possible dust particles, and a drop (ca. 0.1 mL) was placed between the mica surfaces using a clean and dry glass pipet after the interference wavelengths of bare mica surfaces in adhesive contact in dry air had been measured to establish $D=0$ and the initial twist angle between the sheets. The surfaces were then brought to a separation of about $10\ \mu\text{m}$ and left for 1–2 h before any further measurements were conducted. The atmosphere of the instrument chamber was kept

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dry with P₂O₅ throughout the experiment, as in previous studies on 5CB,^{24,27} 6CB,^{27,28} and 8CB.^{29,30} Drying of the liquid crystal over molecular sieves, as in ref 30, was avoided, because such a procedure generally requires subsequent filtering to remove microscopic particles. All experiments were performed at 25 °C. At this temperature, bulk 5CB is in the nematic phase.⁴⁵

The anchoring of anisotropic molecules on crystalline substrates depends sensitively on the crystal lattice, on the chemical structure of the molecules, and on environmental factors such as humidity.^{19,23,46–48} On many ionic and molecular crystals, cyanobiphenyls orient with their director near-parallel to the surface (planar orientation) because of van der Waals and dipole–ion interactions.²³ The presence of other molecules due to humidity^{27,28,46} or contamination, or as a result of certain surface treatments (surfactant monolayers),^{24,29,48,49} may induce reorientation in the plane, or “homeotropic” orientation such that the director of the molecules is perpendicular to the surface.

The orientation of cyanobiphenyls relative to the crystallographic axes of muscovite has been studied using polarization microscopy^{19,27,46} and second-harmonic-generation²³ techniques. The latter has shown that in 5CB films thicker than one monolayer on a single surface, there is only one preferred orientation of the director, at ca. 30° from the γ axis of the mica. In contrast, in monolayer films (the upper surface being air or 5CB), more than 70% of the molecules are found in three near-planar alignment orientations: one at 30° from the γ axis and the other two at $\pm 144^\circ$ from this alignment orientation (not at $\pm 120^\circ$, as is expected for a pseudo-hexagonal or ditrigonal C_{3v} symmetry).²³ The remaining molecules in the monolayer are oriented perpendicularly to the surface. The reason for the complex alignment is that the anchoring of the liquid crystal is influenced by a thicker section of the mica (containing an asymmetrical structure of Al³⁺ ions and cavities) than only the oxygen atoms exposed at the surface.¹⁹ In the three near-planar orientations in the monolayer, the cyanobiphenyl moiety forms a small angle with the surface plane.²³ The single orientation in a thicker layer, which is parallel to the muscovite surface, is believed to result from the liquid crystal's minimizing its interaction with the monolayer.²³

The layered structure of muscovite consists of a stack of sheets, 10 Å thick, with alternating mirror planes (separated by an angle of 120° that is bisected by the β optical axis,^{23,46} cf. Figure 3 of ref 23). On each sheet, the alignment of a 5CB film (thicker than the monolayer) is along its mirror plane, and thus is at 30° clockwise from the γ axis on one type of sheet and at 30° counterclockwise on the other. Specifically, this alignment implies that when mica is cleaved so as to allow realignment of the optical axes of two sheets, a single preferred direction of the liquid crystal might appear in the confined film, at 30° either clockwise or counterclockwise from the γ axis when viewed through the sheets (as shown in Figure 1, in which the 30° clockwise direction observed at good alignment in our experiments is indicated). Polarization microscopy studies of cyanobiphenyl films confined between two muscovite surfaces show good agreement with these results, giving an orientation of the director at $(27 \pm 2)^\circ$ from the γ axis for 6 μm thick 5CB and 6CB films.²⁷ Our measurements on 2–4 μm thick 5CB films in the SFA, mode using a sheet polarizer (Melles Griot), gave an orientation of the director at $(26 \pm 5)^\circ$ from the γ axis. This relatively large uncertainty is due to absorption by the polarizer, which decreases the intensity of the light entering the spectrometer so that to the eye, there is an apparent complete extinction of the observed fringe over a slightly larger angle than that caused by the polarization direction alone. For 8CB, which forms dimers in all bulk phases⁵⁰ and also in a thin film,²⁹ conflicting data have been reported. A recent

study³⁰ at 25 °C (smectic) indicated that the director would be aligned with one of the crystallographic axes of the mica, whereas in polarization measurements identical to the ones we performed for 5CB, an angle of $(28 \pm 7)^\circ$ from the γ axis was obtained for 2.5–5 μm thick 8CB films at 35° (in the nematic phase).⁴³ Considering the unusually large scatter in the data in ref 30, we conclude that in the nematic phase, the director of these three cyanobiphenyl compounds on clean and dry muscovite is at approximately 30° from the γ axis. The discrepancy in assignment of the liquid crystal orientation in ref 30 complicates the interpretation of the corresponding shear results in that study as arising from liquid crystal sheared in directions along and perpendicular to the molecular long axis.

Accuracy of Alignment. The experiments contain two different alignments: the twist between the crystal lattices of the surfaces, θ , and the separate problem of aligning a particular lattice direction with the shear direction. The error in the latter arises mainly from uncertainties in using polarizers to determine the optical axes of the mica pieces, and, to a smaller extent, from errors in the mounting of the surfaces in the instrument. Typically, the γ -direction of the upper surface in our experiment was aligned with the shear direction to better than 5°.

The accuracy in determining the twist angle between the sheets, θ , is not affected by the uncertainty in aligning the sheets with the shear direction, and depends only on the accuracy in the measurement of wavelengths, i.e., on the spectrometer resolution. Typically, the wavelengths are measured manually with a micrometer-positioned grid; the resulting resolution is 0.015 and 0.033 Å/ μm for standard spectrometer gratings of 1180 and 590 grooves per mm grating, respectively. Because $\cos \theta \propto \lambda_{\gamma,\theta} - \lambda_{\beta,\theta}$ (cf. eq 1), an uncertainty of only 1 μm (i.e., an uncertainty of 0.015 Å in $\lambda_{\gamma,\theta} - \lambda_{\beta,\theta}$) in the positioning of the grid leads to an error of about 2° at small θ , while at, say, $\theta = 30^\circ$, the corresponding error is 0.1°. It is, however, possible to align the crystallographic axes with better accuracy than is implied by this large error in establishing small θ from optical measurements. Because large θ can be measured very accurately and the upper surface can be rotated with an accuracy better than 1°,¹¹ the crystallographic axes can be aligned to a chosen angle with an accuracy better than 1° (i.e., significantly better than the 10° claimed in ref 30) as soon as one θ at large mismatch has been established.

Such an aligning procedure was employed in this study: from an initial intentional mismatch of θ around 30° (actual θ measured to better than 0.3°), the upper surface was rotated back toward small θ . The large error in our best alignment, $\theta = (2 \pm 2)^\circ$, reflects the uncertainty in the measurement of three consecutive β – γ pairs of interference fringes; however, based on the rotation of the upper mount, the actual lattice mismatch at this position was only 1° clockwise from perfect alignment.

Results

Force versus Film Thickness. The static force between two mica surfaces separated by 5CB in a planar orientation consisted of several contributions. In a previous investigation²⁴ it was found that for $\theta = 0^\circ$ – 33° , there was a repulsive “medium-range” force with one invariant component (extending to $D \approx 600$ Å) and another that increased with θ . The second component disappeared at good alignment and on heating, and it was interpreted as a twist in the confined nematic film.²⁴ At $\theta < 40^\circ$ (including our best alignment) and $D > 100$ Å, we found a monotonically repulsive force (not shown) that increased with θ , but did so less strongly at small film thickness than was predicted from the twist elastic constant in the bulk, in good agreement with previous results.²⁴ Above $\theta = 40^\circ$, this force remained similar instead of rising further with increasing θ . However, the θ -dependent component disappeared only at the best alignment, but not at 60° as would be expected if the liquid crystal molecules were to reorient on a pseudo-hexagonal lattice.

We were interested mainly in the interactions across very thin films. After we subtracted the background

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"medium-range" force, an oscillatory force remained at $D < 50 \text{ \AA}$ for all twist angles. This "short-range" force is shown as a function of D for $\theta = (2 \pm 2)^\circ$ and $(60.4 \pm 0.3)^\circ$ in parts a and b, respectively, of Figure 2. In agreement with previous studies,²⁴ we found that the oscillations had a period of ca. 5 \AA , which closely corresponds to the mean diameter of a 5CB molecule in the direction perpendicular to its long axis, 4.3 \AA .⁵¹ The films having thicknesses of $(10 \pm 1) \text{ \AA}$ and $(15 \pm 1) \text{ \AA}$ thus correspond to two and three layers in planar orientation. In this system, a lesser force than is required for 8CB (cf. Figure 3 of ref 29) was needed to compress the film to these two film thicknesses. In the case of 8CB, $F/R > 150 \text{ mN/m}$ (causing considerable deformation of the surfaces) was necessary to go from a film thickness of 2 dimers ($16\text{--}18 \text{ \AA}$) to 1 dimer ($7.5\text{--}10 \text{ \AA}$).⁴³

At the smallest separations, the depths of the minima in the force–distance curve decreased with increasing misalignment, whereas the maxima of the repulsive walls during compression remained similar for all θ investigated, a phenomenon also observed in aqueous KCl solution.¹² Figure 2c summarizes the peak-to-peak heights of the oscillations in force curves at different twist angles between the same mica surfaces. Effects of twist angle are seen clearly only at separations of $(10 \pm 1) \text{ \AA}$ and $(15 \pm 1) \text{ \AA}$, where the peak-to-peak oscillation height decreased systematically with increasing θ , also at $\theta = 60^\circ$. In a previous investigation,²⁴ the oscillation heights at $\theta < 10^\circ$ were found to decrease exponentially with D , with the decay length of 10 \AA , as shown by the dotted curve in Figure 2c. We found this same result for our best alignment, $\theta = (2 \pm 2)^\circ$ (dashed–dotted curve in Figure 2c). The difference in absolute values between our data at $\theta = (2 \pm 2)^\circ$ and the dotted curve (from ref 24) is within the variation expected in measurements of oscillatory forces (such variations are believed to result from differences in the compression rate and possibly from previous compressions²⁶).

Linear Regime of Oscillatory Shear. Figure 3a,b shows the linear viscoelastic responses of films with thicknesses of $(10 \pm 1) \text{ \AA}$ and $(15 \pm 1) \text{ \AA}$ to oscillatory shear with an amplitude of a few \AA . The twist angles were the same as in Figure 2c. Several common features were observed for both film thicknesses. First, the elastic and viscous moduli were large and fairly constant at small θ (a rubberlike response) in the whole frequency range investigated ($f = 0.13\text{--}130 \text{ Hz}$), but they decreased systematically with increasing θ . This behavior is further illustrated in Figure 4, where average values of the low-amplitude shear moduli at $\omega = 8\text{--}33 \text{ rad/s}$ ($f = 1.3\text{--}5.2 \text{ Hz}$) are shown as a function of θ . Second, at low frequency and for $\theta > 40^\circ$, a region appeared in which the loss modulus exceeded the storage modulus (a liquidlike response). This region was observed at both film thicknesses (Figure 3). The response to small-amplitude shear differed between the cases of good alignment and $\theta = 60^\circ$. For a film thickness of $(10 \pm 1) \text{ \AA}$, an unusual minimum in the loss modulus was observed at the largest θ .

Nonlinear Responses to Large-Amplitude Shear. Figure 5a,b shows the viscoelastic responses to increasing deformation amplitudes ($0.2\text{--}1900 \text{ \AA}$) at constant frequency ($f = 2.6 \text{ Hz}$) as a function of the effective strain (deformation amplitude normalized by film thickness) for the film thicknesses of $(10 \pm 1) \text{ \AA}$ and $(15 \pm 1) \text{ \AA}$, respectively. The responses are shown at the same twist angles as in Figures 2c and 3. At small amplitudes a linear

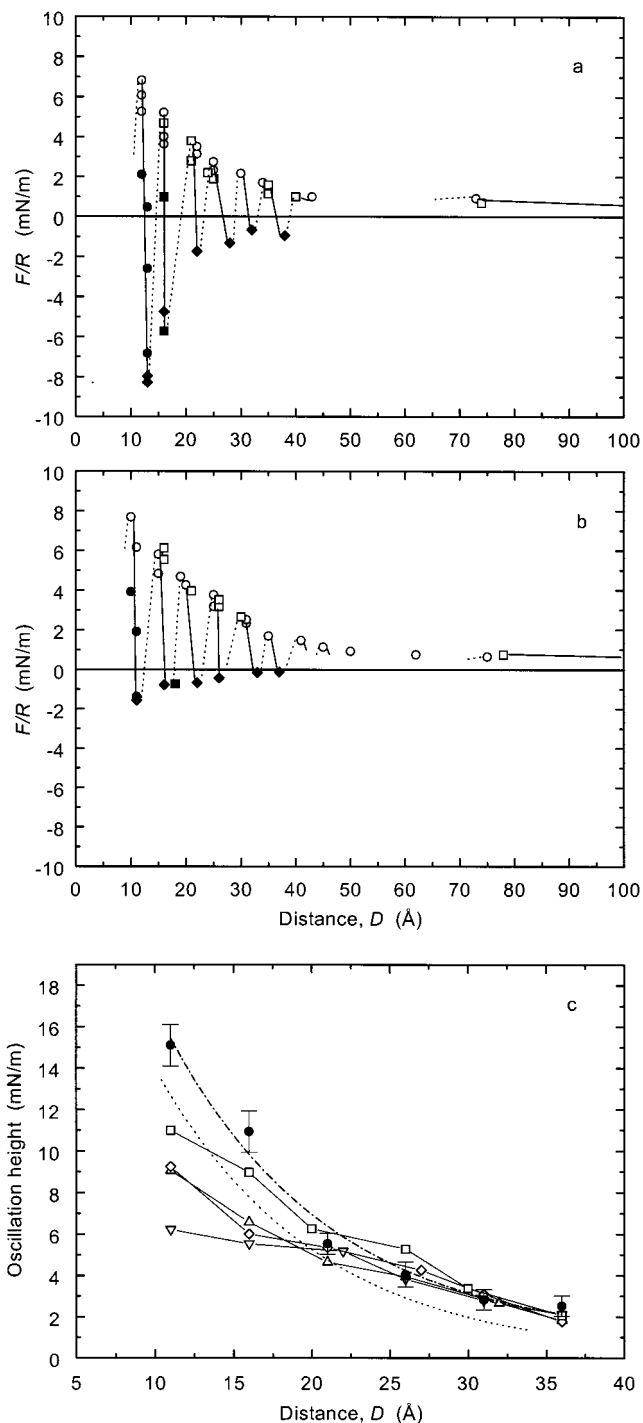


Figure 2. Static force (normalized by radius of curvature) as a function of film thickness of 5CB on approach (open symbols) and separation (filled symbols) of two mica surfaces at twist angles of (a) $\theta = (2 \pm 2)^\circ$ and (b) $\theta = (60.4 \pm 0.3)^\circ$. Diamond symbols indicate points from which the surfaces jumped apart on separation. The lines are intended as guides only. In (c), the peak-to-peak height of the oscillations in force curves at different θ , including the ones in (a) and (b), are plotted as a function of distance for (●) $\theta = (2 \pm 2)^\circ$; (□) $(19 \pm 1)^\circ$; (◇) $(40.2 \pm 0.5)^\circ$; (△) $(60.4 \pm 0.3)^\circ$; and (▽) $(72.6 \pm 0.1)^\circ$. At $\theta = (2 \pm 2)^\circ$, the oscillation height decreases exponentially (dashed–dotted curve) with a decay length of 10 \AA , in agreement with results at $\theta < 10^\circ$ from ref 24, indicated by the dotted curve. The error bars on the $\theta = (2 \pm 2)^\circ$ data indicate the typical variation in the oscillation height in different measurements.

viscoelastic response was obtained, in good agreement with the data in Figure 3. With increasing amplitude, the response differed according to film thickness: the com-

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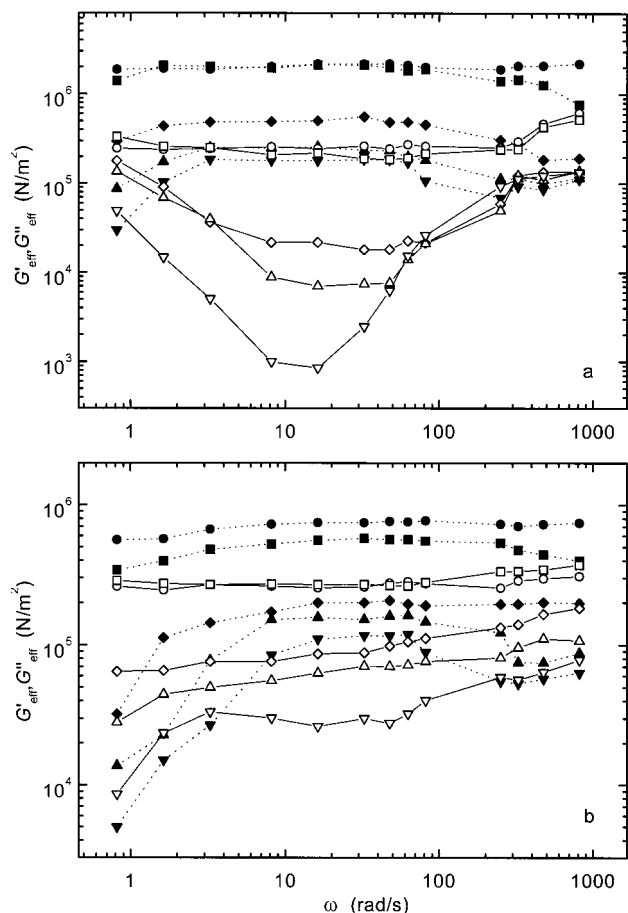


Figure 3. Response of confined films of 5CB with a thickness of (a) (10 ± 1) Å and (b) (15 ± 1) Å to small-amplitude shear. Filled symbols represent effective storage or elastic modulus (G'_{eff}) and open symbols effective loss or viscous modulus (G''_{eff}) as a function of angular frequency, ω ($\omega = 2\pi f$, $f = 0.13$ – 130 Hz) at twist angles of (●, ○) $\theta = (2 \pm 2)^\circ$; (■, □) $(19 \pm 1)^\circ$; (◆, ◇) $(40.2 \pm 0.5)^\circ$; (▲, △) $(60.4 \pm 0.3)^\circ$; and (▼, ▽) $(72.6 \pm 0.1)^\circ$ between the same pair of mica surfaces as in Figure 2. The lines connecting the data points are intended only as guides to the eye.

mencement of sliding in the (10 ± 1) Å film occurred as a slip (discontinuous transition from linear to nonlinear response) (Figure 5a), whereas the transition in the (15 ± 1) Å film was continuous, indicating smooth sliding (Figure 5b). The limiting strain was largest for the case of best alignment (with the exception of the value for $\theta = 72.6^\circ$ in Figure 5a), with maximum values of $\gamma = 0.5$ at (10 ± 1) Å and 0.7 at (15 ± 1) Å. The decreases in shear moduli after the transition can be described as shear thinning.

In Figure 6, the data in Figure 5 are shown as shear stress versus effective shear rate (defined as effective strain \times angular frequency). For both film thicknesses, the limiting shear stress decreased systematically with θ , and we observe that also in large-amplitude shear, the response at 60° was distinctly different from the one at $(2 \pm 2)^\circ$. Averages of the plateau values of the stress are plotted as a function of θ in Figure 7. As in Figure 4, these parameters decreased monotonically with θ . The absence of a minimum around 30° , or a maximum around 60° , stands in strong contrast to the friction when bare mica surfaces slide past one another.⁵

Discussion

Angle-Dependent Static Forces. The measurements of static interaction forces in Figure 2 show that, contrary

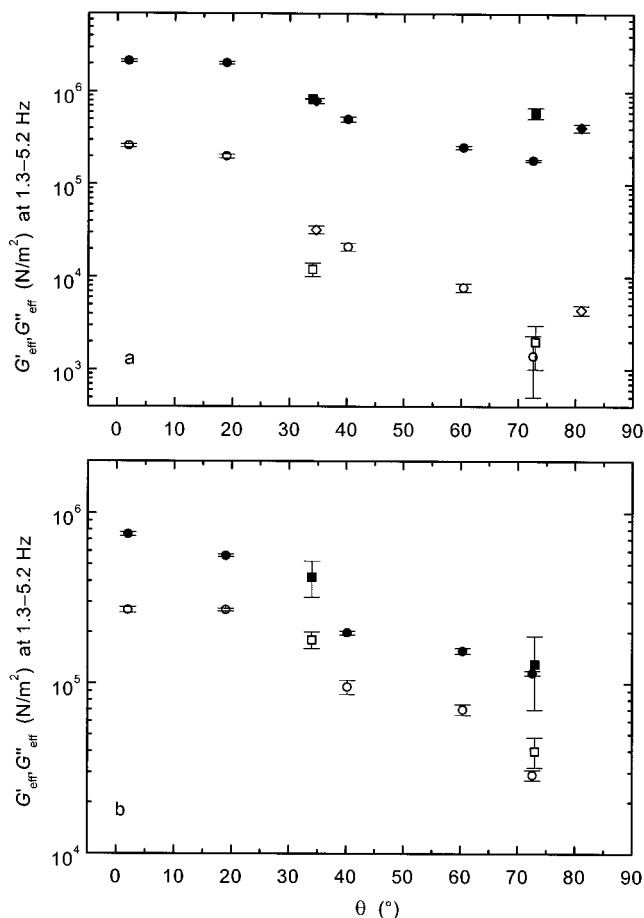


Figure 4. Average values of G'_{eff} (filled circles) and G''_{eff} (open circles) at $f = 1.3$ – 5.2 Hz ($\omega = 8$ – 33 rad/s), plotted as a function of twist angle, θ . The data are obtained from (a) Figure 3a, $D = (10 \pm 1)$ Å; and (b) Figure 3b, $D = (15 \pm 1)$ Å. Shown as squares and diamonds are additional data at these same separations from experiments using other pairs of mica surfaces.

to the intuitive expectation for pseudohexagonal surfaces, and also in contrast to observations of adhesion of mica separated by molecularly thin water and aqueous KCl films,¹² the forces measured in thin 5CB films were not the same at a surface orientation of $\theta = 60^\circ$ as at close to 0° . The reason is that the structure of the 5CB monolayer on muscovite²³ contains several alignment directions (cf. Methods and Materials section), so the mismatch between two unperturbed monolayers in contact or separated by a single layer would disappear only at $\theta = 0^\circ$, and not at multiples of 60° . The magnitudes of the oscillations in the force curve (measured out to between eight and nine layers with a period of 5 Å) decreased with θ only at $D = 10$ and 15 Å as a result of decreased adhesion (Figure 2), while the maxima in the force curves measured on compression remained similar at all θ studied. These results are consistent with observations in KCl solutions,¹² where the maxima in the force curve were unaffected at twist angles 1° away from the alignments at $\theta = 0^\circ$ and multiples of 60° .

It may be that the θ -dependence of interactions between muscovite surfaces in dry contact or separated by water and/or KCl solutions differs intrinsically from the case in which the surfaces are separated by larger molecules. Water molecules, H_3O^+ ions, and K^+ ions are small enough to fit the K^+ sites in the ditrigonal oxygen structure of the surface.¹² Between two contacting dry sheets, a redistribution might occur such that empty K^+ sites become filled.

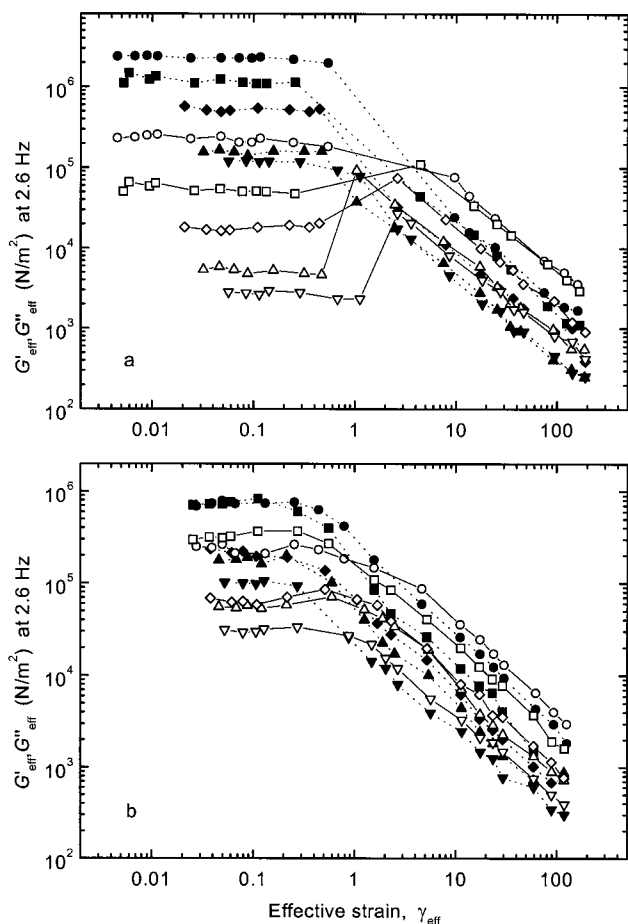


Figure 5. Responses to increasing deformation amplitude (0.2–1900 Å) at $f = 2.6$ Hz ($\omega = 16.3$ rad/s). The elastic and viscous moduli are plotted as a function of effective strain (deformation amplitude divided by film thickness) at the film thickness of (a) (10 ± 1) Å and (b) (15 ± 1) Å between the same mica surfaces as for Figures 2 and 3. Symbols and twist angles are as in Figure 3. The limiting strains at $\theta = (2 \pm 2)^\circ$ were $\gamma = 0.5$ and 0.7 in (a) and (b), respectively.

Unlike the ditrigonal oxygen structure, which would be aligned only at twist angles of 0° and $\pm 120^\circ$,¹⁷ the K^+ sites are very nearly hexagonally ordered in the (001) cleavage plane of the muscovite crystal.^{17,18} If these sites were occupied by small molecules or ions, the overall structure could be ordered also at twist angles that are multiples of 60° , whereas molecules large enough to cover several K^+ lattice sites might form a different structure. Experiments on large, near-spherical molecules at large θ would be instructive in testing this possibility.

For rigid anisotropic molecules, it is desirable to know whether misalignment causes disorder (randomness), a smooth twist, or an abrupt mismatch in the film between the surfaces, and how this is affected by shear. Some information on the orientation in thin 5CB films comes from static force measurements. It has been shown^{24,27} that an angle-dependent “medium-range” repulsive force in 5CB films between misaligned surfaces is superposed on a repulsive force with somewhat shorter range ($D < 600$ Å) that occurs also at perfect alignment. (A medium-range repulsive force at good alignment has also been seen in 6CB²⁸ and 8CB²⁹ films at temperatures where the bulk liquid crystal is nematic.) The angle-dependent force has been interpreted as a twist arising from the strongly physisorbed layer closest to the mica (discussed further below) aligning the adjacent layers. Observations of the interference pattern in SFA experiments on 5CB sug-

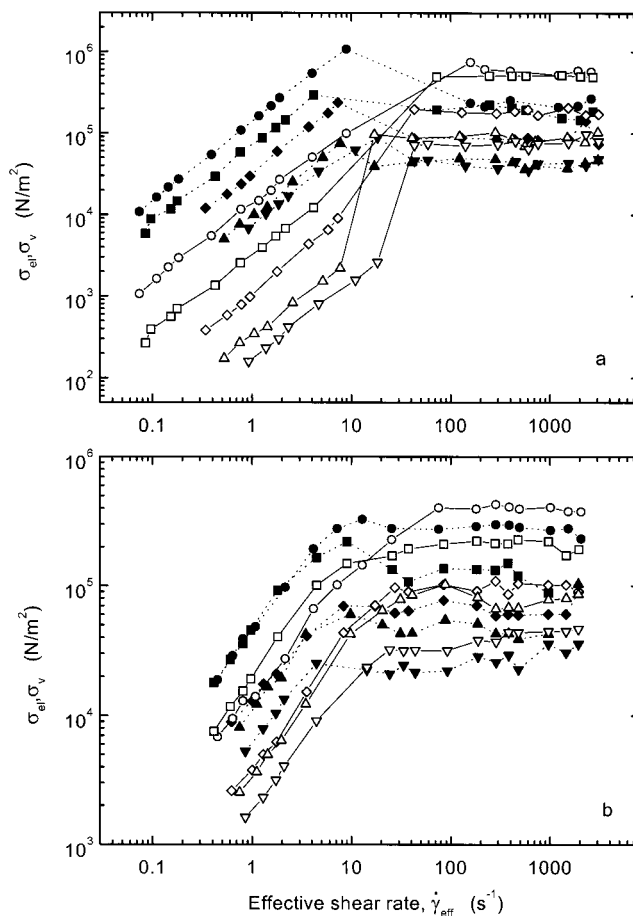


Figure 6. Elastic shear stress (σ_{el} , filled symbols) and viscous shear stress (σ_v , open symbols) as a function of effective shear rate (effective strain \times angular frequency ω , $\omega = 16.3$ rad/s) for 5CB films with a thickness of (a) (10 ± 1) Å and (b) (15 ± 1) Å at different twist angles (symbols same as in Figure 3) between the same pair of confining mica surfaces as in Figures 2, 3, and 5.

gested²⁴ that this conflicting alignment was not removed until only a single layer remained between the surfaces at high pressure. A calculated force based on the bulk twist elastic constant described the interactions at $\theta = 33^\circ$ well down to $D \approx 200$ Å, but the agreement was not as good at smaller separations.²⁴ A study of the interference fringes arising from 5CB films between mica surfaces suggested that the liquid crystal structure contained an abrupt mismatch at $D < 350$ – 500 Å and $\theta = 90^\circ$, but a continuous structure at smaller twist angles.²⁷ A film with a thickness of only a few molecular layers may not be able to accommodate a smooth twist.

It is known that in the bulk nematic phase,^{50,51} and in confined, homeotropically oriented films on surfactant monolayers,^{24,29} both 5CB and 8CB form dimers. In 8CB with a planar orientation, the period of the oscillatory force corresponds closely to the diameter of a dimer.²⁹ However, the period of the oscillatory force measured for 5CB in a planar orientation (ref 24 and this work) is comparable to the diameter of a single molecule in the direction perpendicular to its long axis.⁵¹ Furthermore, the molecules in a 5CB monolayer are known to form a small angle with the surface plane,²³ but the contact between two monolayers appears at 10 Å, even though the unperturbed monolayer on each surface would be expected to occupy a slightly larger volume (film thickness) than other layers. This difference in structure under

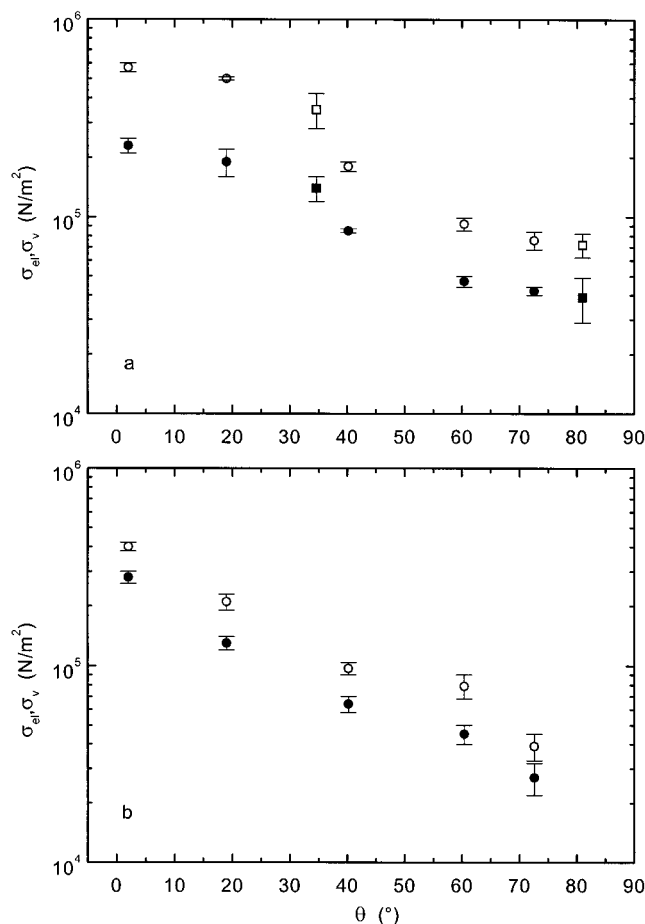


Figure 7. Average values of the viscous shear stress (σ_v , open circles) and elastic shear stress (σ_{el} , filled circles) at the plateaus found at the large shear rate in (a) Figure 6a, $D = (10 \pm 1) \text{ \AA}$; and (b) Figure 6b, $D = (15 \pm 1) \text{ \AA}$. The squares denote results from an experiment using a different pair of mica surfaces.

confinement in the planar orientation and its effect on the observed “background” force remain to be investigated.

Response to Oscillatory Shear. The shear responses showed lower shear moduli and lower limiting shear stress with larger film thicknesses. In addition, a larger limiting strain was observed at the larger film thicknesses; this can be interpreted to denote that the molecules were less strongly confined and ordered in the center portion of the thicker films. Similar results have been observed for OMCTS⁵² and in computer simulations^{6,8} of confined spherical molecules.

At film thicknesses of three or more layers of 5CB in planar orientation ($D \geq 15 \text{ \AA}$), and at large shear amplitudes, smooth sliding was observed (as for an 8CB layer of 16–18 Å thickness [ref 29] consisting of two layers of dimers in planar orientation). Stick–slip occurred only upon confinement to a film with a thickness of two molecular diameters ($D = (10 \pm 1) \text{ \AA}$) (Figure 5). The distinctly different shear behavior of the films with thicknesses of (10 ± 1) and $(15 \pm 1) \text{ \AA}$, and thus the significance of a thickness change of only a single molecular layer, is demonstrated in Figures 5 and 6. The occurrence of stick–slip thus appears to be a function of film thickness and not of degree of misalignment. The 10 Å thick film of 8CB reported in ref 30 also consisted of a layer that was two molecules (one dimer) thick. Such a layer with a thickness of 7.5–10 Å can be reached⁴³ in 8CB at compressive forces exceeding $F/R \approx 150 \text{ mN/m}$ (cf. Figure 3 in ref 29), at a load of about 2 MPa, which closely

corresponds to the “low-load” and “high-load” regimes studied in ref 30 and thus to a different pressure and thickness regime than the experiments in ref 29. Sliding at such large normal forces was not studied in ref 29 or in the present work on 5CB, because it is associated with very large deformations of the surfaces. Thus the different results in ref 30 as compared to those in ref 29 were not due to humidity, as was proposed in ref 30, but instead were attributable to different film thickness and normal force. Similar differences with increasing normal pressure and decreasing film thickness are also observed for confined quasispherical molecules.⁵²

In small-amplitude shear at both film thicknesses, a region was observed at low frequency and high θ where the viscous response dominated over the elastic, indicating a liquidlike response in contrast to the overall solid- or rubberlike response seen at good alignment or higher frequencies. Both this low-frequency response and the overall decrease in moduli and stress suggest that with increasing θ , the order within the film decreased. The shear data does not, however, give direct information on the location of the shear plane. On one hand, the results may reflect an abrupt mismatch across a shear plane between 5CB layers (decreasing the dipole–dipole interaction between 5CB molecules belonging to different layers). On the other hand, they may stem from a uniformly oriented 5CB film being sheared between increasingly misaligned mica surfaces, with the shear plane located at the mica–5CB interface.

The anchoring energy of liquid crystals on polar surfaces is on the order of 10^{-3} – 10^{-2} mJ/m^2 .⁴⁸ Both the static forces at the largest confinement²⁴ and the shear forces in our experiment are large enough to overcome this interaction if they are applied to a *single* layer of confined liquid crystal. However, in our experiments on films with a thickness of at least two molecular layers, it is likely that the dislocations between the misaligned surfaces, and the shear plane, were between the layers of 5CB and not at the interface between 5CB and mica, given that the interactions between molecular layers are weaker than the anchoring to the surface. A similar physical situation is seen in liquid crystal displays,⁵³ where anchoring to various surface layers induces a permanent pretilt of the liquid crystal, which is further aligned in an electric field. The alignment induced by the electric field does not, however, not propagate back to the first anchoring layer, which remains at the initial pretilt.

In liquid crystal films with a thickness of several molecular layers, it is likely that the molecules not in direct contact with the confining surfaces become shear-aligned. Reorientation at a shear rate of 30 s^{-1} has been demonstrated in X-ray experiments on 0.4 \mu m thick 8CB films between mica surfaces,⁵⁴ and such experiments might eventually give direct information on the orientation during shear of anisotropic molecules also found in much thinner films.

Conclusions

The effects of the twist angle of confining muscovite mica sheets on static forces and responses to oscillatory

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shear of molecularly thin 5CB films arise from the complex anchoring of the liquid crystal, and not directly from the ditrigonal structure of the oxygen atoms exposed at the mica surfaces. At good alignment between the mica sheets, and thus between the first (anchoring) layer of 5CB molecules on each surface, the structure of the confined film was solid- or rubberlike. At increasing misalignment, the lower limiting strain and shear stress suggested decreased interaction between molecules within the film,

possibly the result of a mismatch between molecular layers.

Acknowledgment. We thank E. Kumacheva, T. Gruhn, M. Schoen, B. Jérôme, J. Israelachvili, A. Berman, and L. Demirel for helpful discussions. This work was supported by the National Science Foundation (Tribology Program).

LA000350Z