

Optorheological Studies of Sheared Confined Fluids with Mesoscopic Thickness

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Fluids of mesoscopic thickness can be sheared and their molecular orientation probed concurrently with the new instrument described in this paper. The fluid is confined between parallel optically flat windows whose spacing is controlled, using piezoelectric inchworms, from submicrometer thickness to $\sim 500 \mu\text{m}$, with no essential lower limit apart from surface roughness. Capacitance sensors or optical interferometry is used to monitor spacing between the windows with submicrometer accuracy. Piezoelectric bimorphs are used to apply periodic shear displacements with amplitude $0.1\text{--}10 \mu\text{m}$ and frequency $0.1\text{--}700 \text{ Hz}$. Shear-induced molecular alignment during sinusoidal shear cycles is determined, with up to $5 \mu\text{s}$ time resolution, using step-scan time-resolved infrared spectroscopy. To demonstrate capabilities of this new instrument, we describe an experiment in which shear and electric fields were applied in orthogonal directions to 5-cyanobiphenyl (5CB), a simple nematic liquid crystal. Provided that the molecule lacked the time to relax during the period of oscillation, the molecule tilted back and forth around the equilibrium orientation under the action of small-amplitude oscillating shear. The shear alignment appeared to be proportional to the shear displacement, not to the effective shear rate.

Introduction

The alignment of fluid molecules in a field (shear field, electric field, temperature gradient, etc.) is traditionally studied in the bulk, but in numerous practical problems a fluid is confined. Examples include technologies such as lubrication of magnetic disks, high-speed coating operations, dispersion of highly filled polymer composites, and melt processing. Though traditionally it was supposed that materials properties in a confined geometry, such as the viscosity, are essentially the same as for the same bulk fluid, recent experiments and computer simulations point instead to much more sluggish viscoelastic relaxation in nanometer-sized films^{1,2} and even to shifts of the glass transition temperature in micrometer-sized films of polymers.^{3,4}

Owing to the technical difficulties of performing the experiment in existing apparatuses, direct measurements of the field-induced orientations of confined molecules have been few. Among the exceptions are measurements of fluorescence depolarization,⁵ X-ray diffraction,^{6,7} and shear-induced optical anisotropy of sheared dye monolayers^{8,9} within suitably modified surface forces apparatuses. These are special cases, however, and it is clear that for bulk samples there are many additional

alternative methods to study molecular orientation. For example, the evaluation of dichroism is often used to determine the mean segmental orientation of solid polymer films using ultraviolet, visible, or infrared (IR) spectroscopy (depending on the adsorption characteristics of the sample and its pertinent functional groups). The recent development of two-dimensional infrared spectroscopy (2D-IR) has also made it possible to measure segmental orientation as a function of time at discrete times during stimulation such as oscillatory deformation.^{10,11} For stimulation provided by an electric field, the alignment of liquid crystals has been studied extensively using time-resolved infrared spectroscopy (TRS).¹²

There are several difficulties in applying these methods to study shear-induced orientations of fluid samples. One is that conventional rheometers are difficult to modify for spectroscopic measurements; they are constructed of metal parts, which are opaque to optical transmission, and in addition the implementation of an effective optical path through a commercial rheometer is not simple. A second difficulty, if the sample is thick, is that too much light may be absorbed. Third (unlike solid samples that, before measurements, can be quenched to a temperature where they cease to relax), measurements of deformed liquids must be made in situ.

Here we describe a new experimental platform to measure molecular orientation of thin-film fluid samples during the course of dynamic mechanical viscoelastic measurement and other external fields. The apparatus, originally developed by Dhinojwala,¹³ has three main functions. One function produces parallel optically-flat windows whose separation can be varied continuously with no essential limitation on the lower limit apart from surface roughness. A second function is that because the

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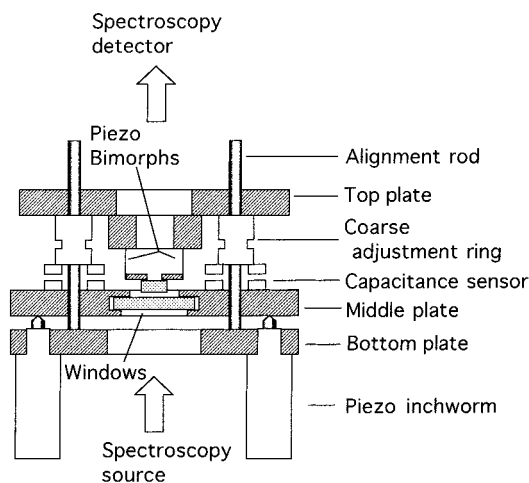


Figure 1. Schematic illustration of the micrometer-gap optorheometer. Of the three alignment rods and piezoelectric inchworms, only two are shown. Some optional components are also omitted: a polarizer (set just below the lower windows), a focusing mirror (set below the lower window), and a reflector (set above the top plate).

windows are mounted separately, they can be moved relative to one another. Here we slide one window parallel to the other and measure shear forces, in-phase and out-of-phase with the shear displacement. A third function of this apparatus, described in this paper for the first time, is that with the choice of appropriate window materials, transmission spectroscopies and dichroism measurements are possible using ultraviolet, visible, and infrared radiation. Molecular orientation is measured directly as a function of time during cyclic shear. In a word, this apparatus can be described as a liquid cell for transmission spectroscopy during shear.

We expect this new experimental platform to be useful in various systems, especially polymers, biopolymers, and colloids. To demonstrate the capabilities, here we describe experiments where shear and electric fields were applied in orthogonal directions to 5-cyanobiphenyl (5CB), a simple nematic liquid crystal.

Apparatus

Positioning Parallel Windows at Micrometer-Sized Gaps. Figure 1 shows a schematic illustration of the main unit of the apparatus. This consists of three plates (usually steel or aluminum):

The bottom plate has two main functions. First, it serves as mount for three finely polished steel rods (one not shown for clarity) along which the middle and top plate slide up and down. Smooth motion along these rods is facilitated by axial ball bearings mounted within the two upper plates. A second function of the bottom plate is to support three piezoelectric inchworms.

The middle plate holds an optical window. The tilt of this plate is controlled by adjusting the piezoelectric inchworms that serve as a tripod support for this plate.

The upper plate holds a second optical window, separated from the middle plate by three spacers that provide coarse adjustment of the spacing between the two windows (the inchworms provide fine adjustment). This top optical window is not attached directly to the top plate, but hangs as a boat from two piezoelectric bimorphs. These bimorphs, through which shear force can be applied and displacement detected, operate on the same principle

described previously for shear in a modified surface forces apparatus.^{14,15}

The windows are aligned in the following steps. First, by turning coarse adjustment screws, the upper window is brought manually to a position within a millimeter or so of the bottom window. Next the spacing is further reduced using piezoelectric inchworms to push the lower window upward. Parallel alignment is achieved using either capacitance sensors (if the windows are opaque) or interferometry (if the windows are translucent to visible or infrared light). The alignment procedure is described in detail elsewhere¹³ and is summarized in the section that follows.

Optical Components. The optical path is normal to the center of the two windows. Light usually enters the apparatus from below from an IR or halogen light source; it is reflected to the vertical direction, passes through an optical polarizer and then through the sample, and is again reflected to an infrared detector or a spectrometer with a CCD (charge-coupled detector) camera. For the experiments described below, the light source was a Fourier transform infrared spectrometer (FTIR) and the IR detector was a mercury-cadmium-telluride (MCT) detector. Windows of Si or Ge were employed, 2.5–5.0 cm diameter and 3–15 mm thickness for the bottom window and 1.0–1.27 cm diameter and 2–10 mm thickness for the upper window.

There is no fundamental limitation on the window material or shape; these can be selected freely for the purpose of the experiment and the light wavelength. But generally it is desirable to minimize surface roughness to achieve small surface-surface spacing, and we have employed optically flat Si, Ge, or ZnSe (for IR spectroscopy) or optically polished quartz (for visible light). In the case of quartz, to determine the window spacing and alignment, we found it convenient to sputter-coat the window with a 60 nm thick silver layer sputtered onto the quartz surfaces. This is thin enough to transmit visible light but causes interference between the two windows which can be used to determine gap thickness and the degree of parallel alignment. When using IR light, we found that Si, Ge, and ZnSe windows naturally provide interference fringes. When using these windows, IR fringes were used for distance calibration.

Electric fields can easily be applied between the Si, Ge, and ZnSe windows because all of these IR-translucent windows are also sufficiently conductive for this purpose. This has three benefits. First, by measuring capacitance between these windows, we can estimate the window separation without coating the window by metal (see above). Second, they provide convenient substrates between which dielectric measurements of the intervening material can be made. Finally, experiments under a dc bias are also possible. This is especially useful for liquid crystal samples.

The apparatus is also designed to allow X-ray and neutron reflectivity experiments. For this, the bottom window can be raised above its mounting plate to provide a clear path of access by the beam from the side. In the experiments described below, it was more convenient to sink the bottom window slightly beneath its mounting plate to produce a liquid reservoir.

Calibration of the Window Spacing. When interferometry is used, calibration of the gap distance and tilt is essentially the same as for the surface forces ap-

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paratus,¹⁶ especially when white light is employed, though (as noted) it is convenient to use IR interference when using Si, Ge, or ZnSe windows.

An advantage of using capacitance measurements instead^{17,18} is that sensitivity increases, the smaller the gap. To measure capacitance, we employ the bridge method. The window spacing (d) then follows from the textbook equation

$$d = \epsilon A / C \quad (1)$$

where ϵ is the dielectric constant of the medium between the surfaces, A is the window area, and C is the capacitance.

Equation 1 can become problematical to use since ϵ itself will change when shear-induced alignment causes the material between the surfaces to be anisotropic. To approach this issue, a third method was developed to determine the gap distance. In Figure 1, one notices that each of the vertical alignment rods carries an air-gap capacitance sensor (the sensors were home-built). The upper plate of each capacitor is attached to the coarse adjustment screw. The bottom plate of each capacitor sits on the mounting plate onto which the lower window is attached. Thus, as the lower window is translated up and down, the capacitance at the three sensing positions can be monitored. While the accuracy of these air-gap capacitors is not so high as that measured between the windows themselves, because the gap separation is larger, and the measured distances are relative rather than absolute, these capacitance readings are always independent of the window material and the dielectric properties of the sample.

Linearity of these measurements, and the use of capacitance sensors at four separate spots to achieve parallel surface alignment, are demonstrated elsewhere.¹³

Measurement of dynamic viscoelastic response.

Shear is generated and measured using a piezoelectric bimorph assembly with the same design that we use to measure interfacial rheology in a modified surface forces apparatus.^{14,15} This assembly hangs from the top plate as shown in Figure 1; fastened to a metal stage, the top surface hangs from a pair of piezoelectric bimorphs. When a periodic voltage is applied to one bimorph (the "sender"), it bends and the upper window is sheared relative to the lower window. The motion is not rotation; it is in a single direction. The motion that results from the applied force is sensed from the voltage that is induced in the symmetrically mounted second bimorph (the "receiver"). The amplitude and phase of this voltage are detected by a lock-in amplifier or spectrum analyzer. For a sinusoidally alternating electric field, the frequency-dependent viscoelastic response of the sample can be calculated by comparing the phase and amplitude of the sending and receiving signals. A typical frequency range is 0.1–700 Hz, with shear displacement amplitude 0.1–10 μm . The bimorph assembly is easily detached, allowing one to select dimensions of the piezoelectric bimorphs according to the purpose of the experiments. In practice, one varies these dimensions to vary sensitivity and resonance frequency by adjusting the bimorph stiffness.

FTIR Spectroscopy. To quantify molecular orientation in a shear field, we employ IR dichroism. Infrared

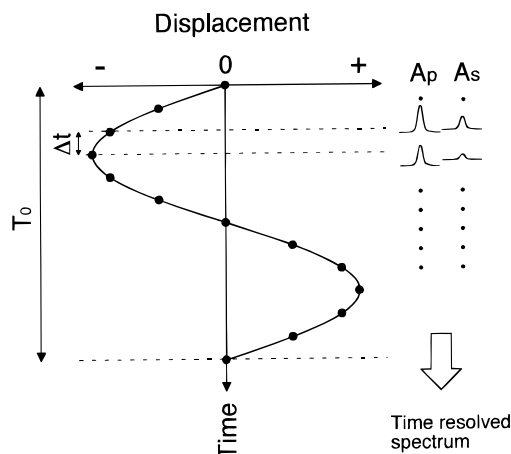


Figure 2. Principle of time-resolved spectroscopy under shear. The solid line shows oscillatory shear displacement of the upper window under the action of piezoelectric bimorphs. The symbol T_0 denotes the period of shear motion. The solid circles denote sampling times of the FTIR step-scan measurement. For each point, IR spectra are collected in both parallel and perpendicular polarization in order to provide information about molecular orientation at discrete points during the shear cycle.

spectra are collected using a Bio-Rad FTS6000 Fourier transform infrared spectrometer (FTIR). The IR beam from the spectrometer is directed onto a focusing mirror below the apparatus and reflected vertically. After the beam passes through a KRS-5 polarizer, it is focused on the sample position. The IR beam is again reflected by a flat mirror that sits above the apparatus and is focused onto a dc-coupled MCT (mercury–cadmium telluride) detector that sits beside the apparatus. The spot diameter of the IR beam at the sample is approximately 5 mm (small relative to the window size).

The electric field of the IR beam can be polarized parallel to the shear direction (we call this the p direction) or perpendicular to it (we call this the s direction). The infrared absorbance (A_p , A_s) is measured for both polarizations. Procedures to deduce molecular orientation from A_p and A_s are well established.¹⁹ Here we use a simple measure, the dichroic ratio

$$D = A_p / A_s \quad (2)$$

to quantify the molecular orientation.

The function and mechanism of time-resolved spectroscopy (TRS) using step-scan FTIR are well-described in several papers^{12,20–22} and their references. Figure 2 shows a schematic diagram of TRS under a sinusoidal shear motion. The horizontal axis corresponds to shear displacement of the upper window. The vertical axis shows time. As time elapses the upper window slides cyclically left (negative) and right (positive), causing shear in the sample. In a time-resolved manner, IR spectra are collected in p and s directions with time resolution Δt , allowing one to deduce the dichroism at discrete times during the shear cycle.

There are two benefits to measuring dichroism at discrete times rather than an average value. First, this approach picks up rapid changes; if orientation relaxes rapidly to a low level, it can still be detected. Second, and

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usually more importantly, it is desirable to know the phase of the orientation relative to that of the shear drive. For example, for a pure solid in sinusoidal shear the maximum orientation will be attained at the point of maximum displacement. But for a pure liquid it will occur at the minimum displacement (i.e., maximum velocity). The TRS approach permits one to quantify these and intermediate responses.

Experiments with a Nematic Liquid Crystal

In the remainder of this paper, to show feasibility of measurement, we report the results of applying this new experimental platform to a prototypical nematic liquid crystal, 4-pentyl-4'-cyanobiphenyl (5CB, E. M. Industries). The sample was kept in the nematic phase by temperature in the range 24–26 °C, which is well below the order–disorder temperature of 35 °C. Several IR bands can be used to determine the orientation of 5CB,^{22–25} and all of these were actually measured during the experiments. Here we discuss mainly the CN stretch band, centered at 2226 cm⁻¹, whose dipole moment is parallel to the long axis of the 5CB molecule.^{23–25}

The windows were Ge as in previous IR studies.^{23–25} The window spacing, determined from IR interference fringes, was 9.5 μm and kept fixed during these preliminary experiments. This spacing was relatively large for this apparatus, but since most previous comparable experiments were performed at ~10 μm spacing,^{23–25} it was convenient to select this for comparison; during these exploratory experiments, we did not attempt to go to lesser separation. dc voltages up to 15 V were applied to the Ge windows. The resulting electric field normal to the surface competed with the orthogonal shear field.

Shear was studied at sinusoidal frequencies 25–400 Hz with 0.24 μm shear amplitude, corresponding to a strain amplitude of 2.5%. TRS step-scan spectra were collected at 50, 100, 200, and 400 Hz; they were acquired during approximately only 50% of the shear cycle to minimize acquisition time. The start of sampling was timed to match zero displacement of the upper window. The resulting measurements of the time-dependent intensity of the CN band were fitted to the function

$$A(t) = \Delta A \sin[2(2\pi t/T_0 - \varphi)] + A_0 \quad (3)$$

where $A(t)$ is the observed polarized intensity of the IR band, T_0 is the period of the shear cycle at the given frequency, and ΔA , φ , and A_0 are fitting parameters to express amplitude, phase, and dc offset, respectively. In eq 3, the extra factor of 2 inside the sine function expresses the fact that shear-induced dichroism is symmetric for positive and negative shear displacements.

Orientation under dc Electric Fields. We begin with comparison to previous studies that dealt with the influence of electric field on 5CB orientation.^{23–25} In Figure 3, the absorbance of the CN stretch is plotted against dc voltage for p and s polarization. Ideally one should expect no polarization dependence, since the Ge was not treated to induce surface alignment in any preferred direction (as, for example, by rubbing); the observed difference at low voltage may reflect the history of flow as the cell was loaded with sample and may also reflect surface scratches or some other unintended surface defect. The absorbance data in Figure 3 show no dependence on voltage up to 2

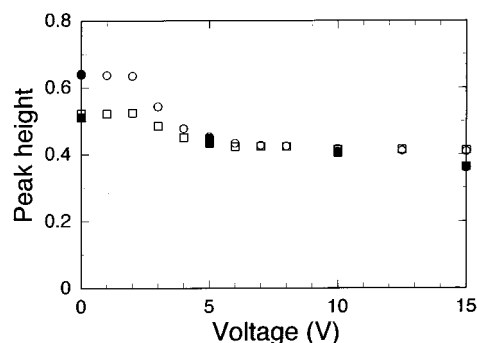


Figure 3. Infrared absorbance of 5CB (CN stretch at 2226 cm⁻¹; this band is parallel to the long direction of the molecule) plotted against magnitude of dc electric field between Ge windows spaced at 9.5 μm. Square symbols indicate p-polarized absorbance (electric field parallel to the shear direction); circle symbols indicate s-polarized absorbance (electric field normal to the shear direction and also normal to the electric field). The open symbols are taken in the direction of increasing dc voltage with an equilibration time of 5 min. The filled symbols are taken at much longer times, after the TRS experiment at each voltage, as a control experiment to check for sample stabilization. The good agreement shows that the data refer to steady state.

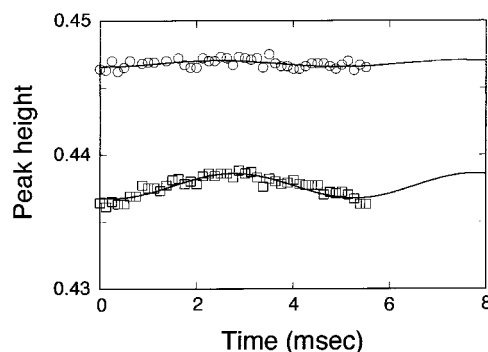


Figure 4. Time-resolved measurements of infrared absorbance under oscillatory shear with 5 V of dc bias applied normal to the shear field, plotted against elapsed time during a shear cycle at 100 Hz (period, 10 ms). The data refer to the CN stretch at 2226 cm⁻¹; this band is parallel to the long direction of the molecule. The shear amplitude was 0.24 μm and the gap thickness 9.5 μm. The solid lines show fits to the sinusoidal expressions in eq 3: squares, p-polarization; circles, s-polarization. The fit to A_s is essentially a flat line at $A_{s0} = 0.4468$. The fit to A_p gives $dA_p = 0.000924$, $A_{p0} = 0.4377$, and $\theta = 0.96$ rad s⁻¹.

V and thereafter a decrease with increasing voltage up to 5–6 V. Above 6 V, IR absorbance was the same in p and s polarization and ceased to decrease with increasing voltage, indicating saturation with the molecular axis perpendicular to the surface (homeotropic alignment).

These observations—especially the critical voltage to switch the direction of molecular alignment—agree well with previous studies in which 5CB was deliberately aligned by a rubbing treatment to the surface.^{23,24} As in Figure 3, absorbance started to decrease above 2 V and reached a steady value around 6–8 V.

Time-Resolved Spectroscopy during Shear. In Figure 4, absorbance of the CN stretch is plotted against time during shear at 100 Hz; in this figure, 5 ms corresponds to the period of half a cycle of oscillation. Time $t = 0$ identifies zero displacement of the upper window. TRS spectra were collected during 60% of the shear cycle with 62.5 μs time resolution. A dc voltage of 5 V, sufficient to produce homeotropic orientation, was applied throughout. The slight excess of A_p and A_s in

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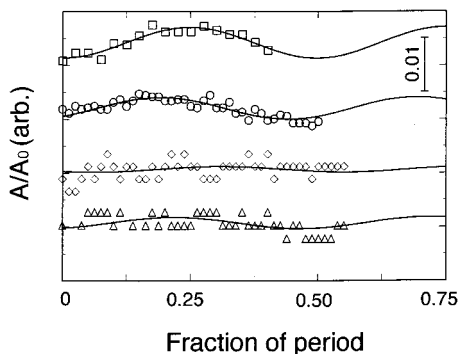


Figure 5. Time-resolved measurements of relative infrared absorbance under oscillatory shear and 10 V of dc bias applied normal to the shear field, plotted against the fraction of the oscillation period during shear cycles at variable frequency from 50 to 400 Hz: squares, 400 Hz; circles, 200 Hz; diamonds, 100 Hz; triangles, 50 Hz. The absorbance is normalized to the mean. To avoid overlap, each data set is shifted 0.01 on the vertical axis.

Figure 4 compared to Figure 3 reflects sensitivity to how the cell was loaded with sample during independent experiments.

We focus here on the time dependence, which was the main concern of this experiment. In Figure 4, it is apparent that A_s was nearly constant while A_p oscillated with shear, though the changes in A_p amounted to no more than 1% at this small strain amplitude. From this one can conclude that the oscillatory shear induced no overall change in average orientation but rather a small motion around the equilibrium position. This kinetics information would average out in a normal transmission experiment. To observe it is one of the benefits of the TRS function.

Other IR bands whose dipole moments were also parallel to the molecular axis, such as the phenyl C–C stretch at 1606 and 1496 cm^{-1} ,^{23,24} also showed these changes. On the other hand, bands whose dipole moments are predominantly perpendicular to the molecular axis, such as the CH_2 stretch at 2928 and 2857 cm^{-1} and the phenyl CH wag at 812 cm^{-1} , showed no changes.

On the quantitative side, fits to eq 3 (the solid lines in Figure 3) indicated that the amplitudes A_{s0} and A_{p0} were almost the same as in the rest state, indicating that molecules retained the homeotropic state under shear. The fit to A_s is essentially a flat line. For A_p , the phase change (φ) scattered somewhat between different experiments, so that we cannot discuss an exact phase shift, but roughly it can be considered to be close to $\pi/4$. The maximum level of A_p occurred near the point of maximum displacement, $t/T_0 = 0.25$. In Figure 4, this point falls at 2.5 ms. Otherwise stated, absorbance in p polarization was synchronized to displacement rather than velocity.

This might seem paradoxical since a liquid crystal is fluid, but it emerged that the phenomenon depends on frequency. In Figure 5, relative changes in A_p (expressed as A_p/A_{p0}) are plotted against time normalized by the period of one oscillation. The corresponding A_s data are not shown since A_s was essentially flat. The data taken at 400 and 200 Hz are of the same type as in Figure 4, but the relative change of A_p is larger, the higher the frequency. On the other hand the oscillation of molecular orientation during shear is not so clear at 100 and 50 Hz; though fitting always produces some result from scattered data, we consider the data at 50 Hz to be essentially flat. Parenthetically, we remark that the lack of quantitative agreement with the absorbance levels in Figure 3 reflects variability between independent experiments. In future work this will be remedied by rubbing the surfaces to

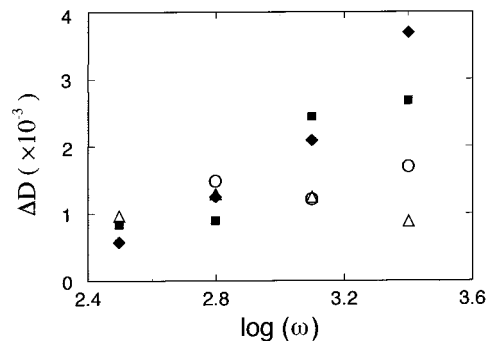


Figure 6. Infrared dichroism amplitude (order of magnitude 10^{-3}) plotted against logarithmic shear frequency (units of rad s^{-1}) for several levels of dc bias normal to the shear field: diamonds, no dc voltage; circles, 5 V; squares, 10 V; triangles, 15 V. The data refer to the CN stretch at 2226 cm^{-1} ; this band is parallel to the long direction of the molecule. The shear amplitude was 0.24 μm and the gap thickness 9.5 μm .

induce well-defined homogeneous alignment (parallel to the surfaces) even in the absence of dc bias. Regardless, the main point in Figure 4 is clear (see also the further studies described in the following section): periodic tilt in the shear direction was more prominent, the higher the frequency, and tended to disappear at the lowest frequencies.

Dependence on dc Bias Voltage. To explore the frequency dependence more systematically, similar experiments were repeated at other levels of dc bias applied normal to the shear direction. The shear amplitude and the window spacing were the same as previously. In this section we describe these data as the dichroic ratio, $D \equiv A_p/A_s$, and fit $D(t)$ to the function

$$D(t) = \Delta D \sin[(2(2\pi t/T_0 - \phi))] + D_0 \quad (4)$$

This has the same form as eq 3 and the symbols φ and D_0 have the same significance. The quantity ΔD measures the intensity of molecular alignment in the shear direction.

In Figure 6, D is plotted against shear frequency at several levels of dc voltage. The higher the voltage, the less effective shear was in inducing orientation in the orthogonal direction—the data confirm one's intuitive expectation in this respect. It is more significant to notice that the phase lag was close to $\pi/4$ in most cases (with the proviso of the scatter noted above), indicating that the maximum alignment was synchronized with maximum displacement. In the cases that $\Delta D < 0.001$, we note that the fits were not meaningful: these data must simply be recognized as too small to be resolved reliably. Altogether, the data in Figure 6 serve to generalize those in Figure 5: the higher the frequency, the more the molecular alignment. While it might be tempting to argue that this reflects the higher effective shear rate of high-frequency motion at fixed amplitude, this would be inconsistent with the observation that dichroism was in phase with displacement, not with velocity.

A more likely explanation lies in competition between the frequency of shear and the natural Brownian relaxation time. Under slow shear, molecules could relax to their undisturbed orientation during the shear cycle and showed only small ΔD . Analogous effects are familiar in everyday life: honey flows smoothly at low rates, but becomes elastic and can even snap when deformed rapidly enough.

Interesting opportunities will come, in future experiments, from more quantitative analysis of phase responses. For the present, we simply note the qualitative

trend that at zero dc bias the phase lag increased, the higher the frequency, meaning that the orientation was less able to follow shear motion at these relatively high frequencies. It also seems that phase values tended to be somewhat smaller, the higher the dc bias, suggesting that the dc bias voltage stiffened the oriented structure. No quantitative interpretation is offered at present; the matter remains to be followed up in future experiments.

Dynamic Oscillatory Viscosity. The preceding discussion has revolved around the relations between shear drive and molecular orientations. At the same time, the forces that *resist* shear motion were also measured. By Newton's law of viscosity, forces in phase with the shear rate are viscous; by Hooke's law of solids, forces in phase with the shear displacement are elastic. Our experiments are unable at present to resolve elastic forces (this will be improved by isolating the piezoelectric bimorphs from humidity in the ambient atmosphere) but found pronounced viscous forces. Using textbook relations²⁶ we report these viscous forces as a frequency-dependent dynamic oscillatory viscosity, $\eta'(\omega)$.

A sample of nematic liquid crystal, being anisotropic, flows with a viscosity that depends on the direction of shear relative to the director orientation; there are three viscosity coefficients.²⁷ With increasing dc bias, the molecule orients increasingly in the vertical direction and one expects the measured shear viscosity to increase. The expectation is confirmed in Figure 7, where η' is plotted against drive frequency (ω) on log-log scales. Similar effects occur when an electric field is applied to liquid crystal polymers dissolved in nematic solutions:²⁸ the electric field acts to resist shear-induced tilt.

Marked dependence on frequency is also evident in Figure 7; $\eta'(\omega)$ diminishes with increasing frequency, implying that the sample stored significant elastic energy at these frequencies.²⁶ This confirms the conclusion from an earlier section of this paper (based upon dichroism measurements), that a longest relaxation time was exceeded over this frequency range.

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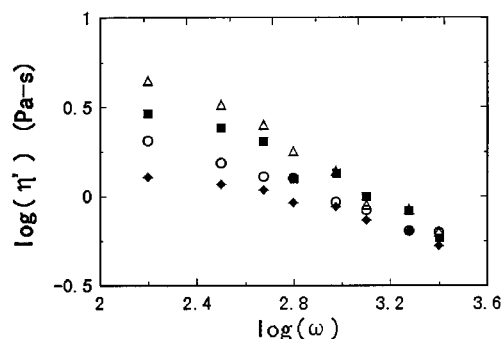


Figure 7. Small-amplitude dynamic oscillatory viscosity of 5CB plotted against oscillatory frequency (units of rad s^{-1}) on log-log scales for several levels of dc bias normal to the shear field: diamonds, no DC voltage; circles, 5 V; squares, 10 V; triangles, 15 V. The shear amplitude was $0.24 \mu\text{m}$ and the gap thickness $9.5 \mu\text{m}$.

But on the quantitative side, it is still unclear why the low-frequency $\eta'(\omega)$ in Figure 7 exceeds the literature value²⁷ of $\eta' \sim 0.12 \text{ Pa s}$ for 5CB at this temperature and this alignment of the nematic director with respect to the shear direction. Since our viscosity measurements of silicone oils, using this same apparatus, agreed with the known viscosity of calibrated standards,¹³ we are reluctant to dismiss the present discrepancy as an experimental artifact, yet a sound explanation is not yet in hand. The matter is under continuing investigation and may be related to similar effects observed with other cyanobiphenyl liquid crystals.²⁹

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