

## Structuring of Confined Liquid Crystal Films Studied by Shear Resonance Measurement

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The formation of molecular scale ordering was studied for 4-cyano-4'-hexylbiphenyl, confined between mica surfaces, in both the nematic and the isotropic phase. The shear force resonance method was employed. This resonance method has excellent sensitivity because the frequency and the intensity of the resonance peak change depending on the structuring of the confined liquids. The nematic and isotropic phases were set by controlling the temperature of the sample in the chamber. Shear resonance curves were measured with varying the thickness of the sample. For the nematic phase, the peak intensity began to decrease at a 12 nm film thickness due to structuring of the liquid crystal molecules, and the peak disappeared at 7 nm. However, for the isotropic phase the structuring effect was first observed only at 7 nm thickness, and the peak abruptly vanished at 5.3 nm.

Key words: Confined film, Liquid crystal, Shear resonance measurement, Temperature dependence

### 1. INTRODUCTION

The behavior of liquid molecules, confined in a nanometer scale space, is quite different from that in the bulk. Liquid molecules, that are caught in a pore of a porous crystal or located between two solid surfaces show peculiar properties such as the formation of an ordered structure and a phase transition unlike the bulk phase. This behavior originates from the interaction between the liquid molecules and solid surfaces. The effect of structuring at the interface has been observed in multitude of ways, over various field of applications such as micromachining, liquid crystal (LC) displays, catalysts and lubrication techniques. Therefore, the elucidation of the behavior of a liquid at the interface has become an important problem.

Especially, the demand on liquid crystal displays has recently significantly increased. Therefore, to improve the performance, the orientation control technology of liquid crystals is necessary [2]. Rubbing, that is the major technique at present, was developed in the 1970's as a basic technology for liquid crystal displays. However, problems such as static electricity, dust particles and nonuniformity of rubbing occur in this method. A more precise orientation control technology that replaces the rubbing method is required to produce a wide-range view angle and large size displays.

Research has been reported on liquid crystals oriented on the surface of a solid substrate by scanning tunnelling microscopy (STM) [3-5]. STM is a powerful tool to examine the dependence of the surface induced ordering of liquid crystals on the substrate. It is possible to sequentially monitor the packing and the orientation of the adsorbed molecules and the crystal structures of the

underlying substrate surface by STM. However, it can observe only molecules strongly adsorbed on the substrates, thus limiting the practical observation to single molecular layers.

Another standard method for studying liquid crystals on substrates is the measurement of the second harmonic generation (SHG) [6,7]. However, this method again is only sensitive to the high order induced by the substrate at a one-two molecular layer depth.

An experimental tool capable of investigating both the surface induced orientation of the LC samples from the monomolecular thickness to hundred nanometer scale is necessary. A potential tool for such an investigation is the surface forces apparatus (SFA) with and without a shear force device. The SFA is an instrument first developed by Tabor and Winterton in 1969 [8], which measures the force (surface force) that operates between two atomically smooth surfaces as a function of the surface separation distance. This method actually detected the oscillatory surface forces for thin liquid films with a several molecular layer thickness [9], and later for liquid crystal films [10, 11]. The period of the oscillation corresponds to the thickness of a molecular layer, thus characteristic of the orientation of the molecules.

To investigate the dynamic properties of the confined liquids or liquid crystals, one can simultaneously study the rheological and tribological characteristics by using the SFA with specific shear equipment [12-14]. Previous shear measurements were mostly limited to study the friction behavior of liquid (or liquid crystal) films with a several molecular layer thickness because of the sensitivity and the stability. The propagation mechanism of the orientation of the liquid crystal molecules in the vicinity of

the solid interface has not been known.

A new shear force resonance method was developed in our laboratory [15,16] in order to examine in detail the ordering behavior of liquid crystal molecules confined between two mica surfaces. The frequency and the amplitude of the resonance during shearing are highly sensitive to the long-range order within the confined liquid. This method is applicable up to a large separation range.

In this study, the shear resonance measurement was applied to study the structuring behavior of a liquid crystal sample (6CB) at different temperatures. It is known that 6CB between mica surfaces is orientated parallel to the surfaces [11,14,17]. The resonance curve was measured in the nematic phase and in the isotropic liquid phase of the liquid crystal while the film thickness was accurately monitored on a nanometer size scale. The surface separation dependence of molecular ordering between the mica surfaces was investigated for each liquid crystalline phase.

## 2. EXPERIMENTAL

### 2.1 Materials

4-cyano-4'-hexyl biphenyl (6CB)(BDH, Ltd.) was used without further purification. The molecular structure of 6CB is shown in Fig.1. 6CB is a thermotropic liquid crystal which shows a nematic liquid crystalline phase at 14.5~29 °C. It becomes crystalline below 14.5 °C and isotropic above 29 °C.

Mica sheets (1×1 cm<sup>2</sup>, thickness  $D < 5 \mu$ ) were freshly cleaved, and silver (silver shot, Rear Metallic Co., Ltd. 99.999 %) was deposited on one sides of them at a thickness of 50 nm using the standard procedure (at vacuum ca.  $5 \times 10^{-6}$  torr) [8]. The sheets were then glued onto cylindrical quartz disks (the radius of curvature of ca. 2 cm, ca. 1 cm diameter of the disk) by the silver covered sides down on the disk, and subjected to the experiments.

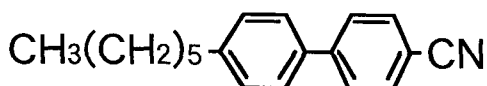


Figure 1. Structure of 4-cyano-4'-hexylbiphenyl (6CB).

### 2.2 Method

The home-built shear force resonance unit combined with the surface forces apparatus (SFA: Mark IV ANUTECH Co.) was described earlier (Fig.2) [8]. Therefore, we describe only the general method of the experiment. The horizontal movement of the surfaces arises from the periodic strain of a piezo element, which is driven by two amplifiers ( $U_{in}$ ) fed by a sine wave signal (frequency  $f$ ), through a pair of stiff leaf springs (Fig.2). In this case, the upper surface vibrates at a constant angular frequency  $\omega (=2\pi f)$ . The deflection ( $\Delta x$ ) of the leaf

spring was detected by a static capacitance probe ( $U_{out}$ ). The input ( $U_{in}$ ) and output ( $U_{out}$ ) signals were recorded by a personal computer (using the LabView program, National Instruments) through a digital oscilloscope (Gould, GRD 1602). The amplitude of the oscillation was then defined as the ratio  $U_{out}/U_{in}$ .

During the experiments, the amplitude of oscillation was first measured with the mica surfaces separated (SP) in air at a set of frequencies ( $f$ ), and the resonance frequency ( $f_0$ ) was determined. A similar set of measurements were performed for the surfaces in contact (MC), where the thickness of the mica sheets was characterized using the fringes of equal chromatic order (FECO) [8]. The liquid crystal sample ( $\sim 20 \mu$ l) was then dropped on the lower mica surface. The distance between the surfaces ( $D$ ) was monitored using the FECO with a resolution of 0.1 nm. The measurement started at  $D = 100 \sim 200$  nm. The resonance curve was recorded at each separation as the bottom surface approached to the other.

The temperature of the sample was controlled using a built-in heater (Tokyo Technical Laboratory Co., Ltd.) and a thermocouple (Nippon Rikagaku Kikai Co., Ltd.) attached near the upper silica disk. The measurement of the nematic phase was carried out at room temperature. The experiment on the isotropic liquid phase was started after heating the SFA chamber to 33 °C at a 2 °C/15 min speed, and waiting for more than 1 h to equilibrate the sample.

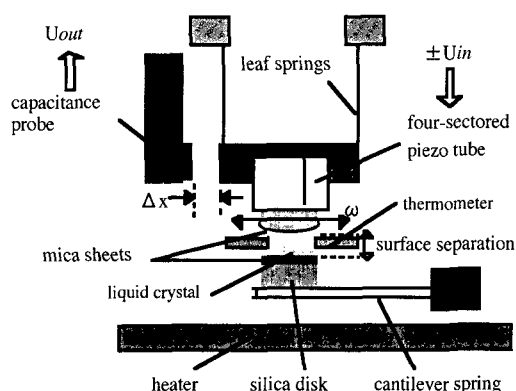


Figure 2. Schematic illustration of the unit for shear force measurement

### 3. RESULTS AND DISCUSSION

#### 3.1 Resonance measurements

Resonance curves obtained on 6CB in the nematic (room temperature) and in the isotropic phase (33 °C) are shown in Fig.3. The horizontal axis of the graph is the angular frequency ( $\omega$ ) and the vertical axis is the resonance amplitude ( $U_{out}/U_{in}$ ). In the nematic phase, at a thickness ( $D$ ) of 104 nm, the resonance peak appeared at a frequency of 212 Hz, which was the same as the frequency for SP, although the amplitude was lower than that for SP. Here, the presence of liquid crystal thin films did not help the two surfaces to move together. The lower amplitude of the resonance peak must be due to a higher viscosity of liquid crystals than that of air. This behavior did not change with the distance decreasing to 18 nm (date not shown). The amplitude of the resonant peaks started to decrease at  $D = 12$  nm. In the range from  $D = 7$  to 5.7 nm –the middle region- the resonant peaks completely disappeared. Here, due to structuring of the liquid crystals, the two surfaces were not independently moved unlike the resonance in air. Below  $D = 5.7$  nm, both the resonance amplitude and the frequency started to increase toward the MC peak (the frequency of 341 Hz). This indicated that as the structuring of liquid crystals progressed, the two surfaces were tightly bound by the film. The surfaces could be brought into contact down to a 4 nm film thickness without damaging the mica surfaces (flat contact). A possible mechanism behind the limited increase of the resonance peak at the contact side is the lubrication [15] of the mica surfaces, where the internal friction of the liquid crystal sample plays an important role.

The resonance peaks for the isotropic liquid state (at 33 °C Fig.3.b) are quite different from those of the nematic phase. Unlike the nematic phase, the resonance amplitude of the isotropic liquid phase at the separation side (SP) was almost equal to that of SP in air. There was no remarkable attenuation observed down to  $D = 7$  nm, (also measured using the 104 nm film thickness). This means that the viscosity of the isotropic phase was significantly smaller than those in the nematic phase. The resonant peaks (at SP) disappeared at the 5.3 nm film thickness, and the oscillation was damped. On the contact resonance side (MC), the resonance peaks appeared at as low as  $D = 3.5$  nm (already flat contact). The peak amplitude again indicated the lubrication behavior at the flat contact. It is interesting to detect that structuring of the liquid crystals even occurred in the isotropic phase.

#### 3.2 Resonance intensity dependence on the surface separation

The resonance intensity at the free resonance side (SP) is displayed as a function of the separation between the mica surfaces ( $D$ ), i.e., film thickness, in Fig. 4. The attenuation of the resonant peaks is different between the nematic phase and the isotropic liquid phase due to the

different sample viscosity. This is clearly indicated by the amplitude of the peaks at the high thickness values ( $D = 104$  nm). The observed value is 0.6 for the nematic sample, and 0.8 for the isotropic sample. The increase in the resonance peak at the contact side (MC) is due to the cross-link between the mica surfaces, and the contribution of the lower sample holder and double leaf spring. Both effects together decrease the amplitude of the free resonance.

Decreasing the thickness, the amplitude of the oscillation began to gradually decrease for the nematic sample, and it reached the middle region at about the  $D = 8$  nm thickness. The final minimum value was reached at  $D = 7$  nm, and did not significantly decrease down to  $D = 4$  nm. We can assume that the structuring gradually increases from where the resonance amplitude starts decreasing at about  $D = 12$  nm for the nematic case.

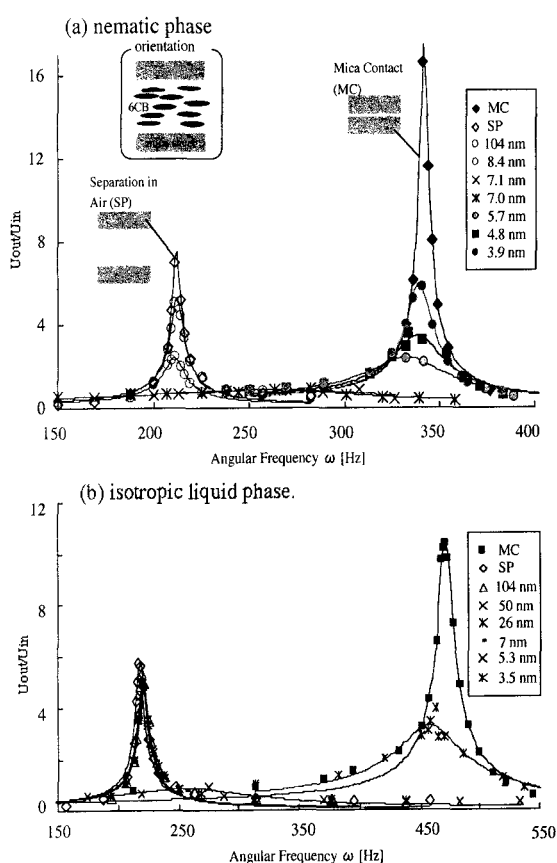


Figure 3. Shear force resonance amplitude curves of 4-cyano-4'-hexylbiphenyl (6CB). The liquid-crystal volume is  $\sim 20 \mu\text{l}$ . The measurement was carried out at room temperature [(a) nematic phase], and 33 °C [(b) isotropic liquid phase]. The vertical line is the resonance amplitude shown as the ratio of output voltage and input voltage.

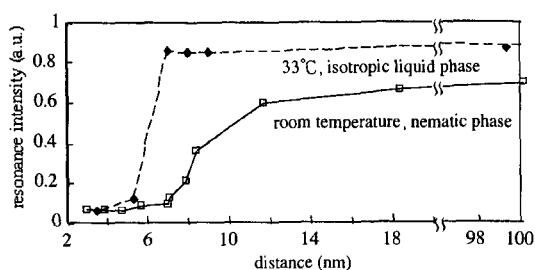


Figure 4. The resonance intensity change for the distance between surfaces. The broken line is the isotropic liquid phase, and the solid line is the nematic phase. The resonance intensity was respectively normalized by the value in air.

For the isotropic phase, there is only an abrupt variation at  $D = 5.3$  nm, and no long range effect was observed. This result indicates that the structuring of the liquid crystal was not pronounced compared to the nematic phases.

The observed thickness dependence on the shear resonance amplitude can be correlated to the fact that the liquid crystal in the nematic phase has long range ordering even in the bulk. However, for the isotropic liquid phase, we can expect only the ordering effect in the vicinity close to the solid-mica-walls.

#### 4. CONCLUSION

We have studied the structuring of nanometer scale liquid crystal (6CB) films in the nematic and the isotropic liquid phases using the shear resonance method. We found that in the nematic phase, the ordering of the liquid crystal began to rise at the 12 nm film thickness, and the resonance peaks changed from the separation side to the damping region at  $D = 7$  nm, a strong contact was reached at 3.9 nm. On the other hand, in the isotropic liquid phase, the intensity of the resonance peaks in the separation side was almost equal to that of the free resonance in air, indicating a very low viscosity for the isotropic liquid. The attenuation, like in the nematic phase, was recognized at approximately 7 nm film thickness and damping occurred at 5.3 nm. The thickness of the contact side was  $D = 3.5$  nm.

These results indicate that the longer range order is present in the nematic phase compared to the liquid isotropic one. However, significant ordering of liquids occurs in the vicinity close to the surfaces in both phases, reflecting strong interactions between the substrate and liquid crystalline molecules.

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