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学位論文題目　Characterization of Confined Liquids by Resonance Shear Measurement and Synchrotron X-ray Diffraction Measurement (共振ずり測定と放射光X線回折測定による閉じ込め液体の構造・特性評価)
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Chapter 1 Introduction

Liquids confined in molecular-scale spaces show markedly different properties from the bulk due to the spatial limitation and the interaction with solid surfaces.[1] For example, relaxation time is prolonged, phase transition temperature shifts, and viscosity is enhanced. These phenomena become prominent as the confined space gets smaller. Until now, characteristic properties of confined liquids between two solid surfaces have been revealed with surface forces apparatus (SFA). However, for the diverse advanced technology and materials, much further study of confined liquids is required. In particular, the elucidation of the structure is imperative because the physical properties are closely related to its structure. In addition, the understanding of the influence of external field and temperature on confined liquids is important such as for the electromechanical devices and lubrication. In this study, to further investigate the confined liquids, new methodologies based on SFA were developed and applied to confined liquids with versatile properties.

Chapter 2 Structural Analysis of Confined Liquids

- Development of Synchrotron X-ray Diffraction Measurement for Confined Liquids –

The structural determination of confined liquids is important in advanced sciences and technologies. Although some measurements using X-ray have been performed for studying the structure of confined liquids between two solid surfaces, the previous measurements were limited to relatively thick (≥ ~0.5 μm) films[2] or did not unambiguously determine the structure.[3] In this study, to directly investigate the structure of confined liquids, we have developed synchrotron X-ray diffraction measurement with SFA by using a high brilliant and stable X-ray beam of SPring-8. Figure 1 shows the synchrotron X-ray diffraction measurement system. Due to a weak signal from ultrathin samples, reduction of the background scattering was desired. We succeeded in reducing the background scattering and could obtain the diffraction profiles from the confined liquids.

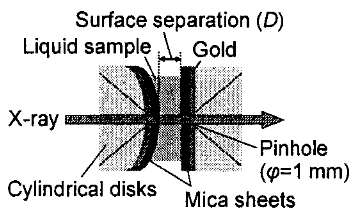

Fig. 1 Schematic illustration of synchrotron X-ray diffraction measurement system.

- Structure of Smectic Liquid Crystal Nanofilm Confined between Mica Surfaces –

At first, we used smectic liquid crystal (LC), 4-cyano-4'-octylbiphenyl (8CB), as a liquid sample because it has relatively high regularity. Surface separation (D) was adjusted to be 1.7 ± 0.5 nm and the normal pressure on 8CB was changed to be 0.38 MPa, 0.31 MPa, and 0.26 MPa.

Figure 2 shows the time course of diffraction profiles of 8CB confined between mica surfaces at D = 1.7 ±

0.5 nm under the normal pressure of 0.31 MPa. Just after injection of 8CB between mica surfaces, a diffraction peak at q = 1.99 nm^{-1}, corresponding to the lamellar spacing of 8CB, was observed. The diffraction pattern indicated that 8CB was highly oriented due to the flow caused in the approaching process. The intensity of diffraction peak gradually decreased with time, indicating the structure of 8CB relaxed. The decrease in the peak intensity at q = 1.99 nm^{-1} was found to depend on the normal pressure applied to 8CB. We could directly monitor the time course of the structural change in 8CB under molecular-scale confinement.

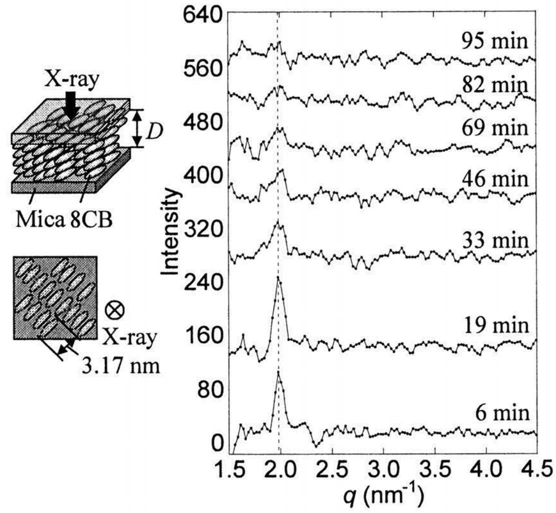

Fig. 2 Time course of the X-ray diffraction intensity profiles of 8CB confined between mica surfaces at D = 1.7 ± 0.5 nm after sample injection. Profiles were obtained with the exposure time of 11 min. The elapsed time from sample injection is denoted by the median of the collected data. Profiles are vertically sifted for clarity.

- Ionic Liquids Confined between Mica Surfaces –

Ionic liquids (ILs) have attracted considerable attention as a new class of materials. Although there are many studies of the bulk structure, for the applications of ILs, understanding of the structure in confined space is imperative because the surface and the spatial limitation play a crucial role in applications such as electrochemical systems and lubricants. In this study, to directly investigate the structure of confined ILs, synchrotron X-ray diffraction measurement with SFA was applied to two ILs, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ($[C_2mim][OTf]$) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ($[C_2mim][NTf_2]$).

Two diffraction peaks were observed for both ILs in a q-range from 2 to 20 nm^{-1}. Based on the crystal structure, the peak at low-q value was assigned to the spacing between cation-cation or anion-anion and the peak at high-q value was assigned to the spacing between cation-anion. By decreasing the surface separation from D = 1 μm to 3 nm, the increase in the integrated intensity of the diffraction peaks was observed, indicating the ratio of ordered structure increased by confinement.

Chapter 3 Confinement Effect on Electric Field Induced Orientation of Nematic Liquid Crystal

In LC devices, surfaces and electric field are two main factors to control the molecular orientation. Here, it would be interesting and important to know the influence of confinement on LCs oriented by the electric field. In this study, resonance shear measurement (RSM) was performed to investigate confined 6CB (4-cyano-4'-hexylbiphenyl) between mica surfaces under the electric field and the orientation of confined 6CB was determined by synchrotron X-ray diffraction measurement.

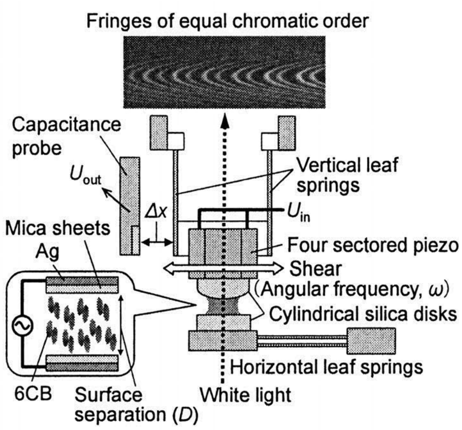

Fig. 3 A schematic of resonance shear measurement system

Figure 3 shows a schematic of RSM system. The upper surface was laterally oscillated with various frequencies, f, by applying the sinusoidal voltage (± U_{in}) to the piezo tube and was monitored by the capacitance probe as an output voltage (U_{out}). The resonance curves were obtained by measuring the normalized amplitude (U_{out}/U_{in}) as a function of angular frequency, ω (= $2\pi f$), of input voltage. RSM on 6CB was performed as a function of the surface separation with and without an electric field.

Figure 4 shows the damping parameter (b), which corresponds to viscosity, of 6CB obtained by analyzing the resonance curves. The behavior for $D < 17 \pm 2$ nm was quite different from that at $D > 17 \pm 2$ nm. For $D > 17 \pm 2$ nm, the b values obtained with the electric field (ac 1 kHz, 1.87 kV/mm, homeotropic orientation) were ca. 1.8 times larger than the values obtained without the electric field (0 kV/mm, planar orientation) due to the difference in the molecular orientation. On the other hand, for $D < 17 \pm 2$ nm, the b values of 6CB with the electric field were almost identical to those without the electric field, indicating 6CB both with and without the electric field were in the same orientation. The most likely orientation of 6CB was parallel to the surfaces because 6CB is originally in the planar orientation on the mica surfaces. In order to directly determine the orientation, synchrotron X-ray diffraction measurement was employed (Fig. 5). At average thickness of 12 nm, the diffraction peak corresponding to the long axis spacing of 6CB dimer was observed both with and without the electric field, indicating 6CB was in the planar orientation. Whereas, at average thickness of 20 nm, the diffraction peak corresponding to the long axis spacing of 6CB dimer was not observed with the electric field. These results directly showed that the orientation of 6CB cannot be changed when the confinement effect became significant.

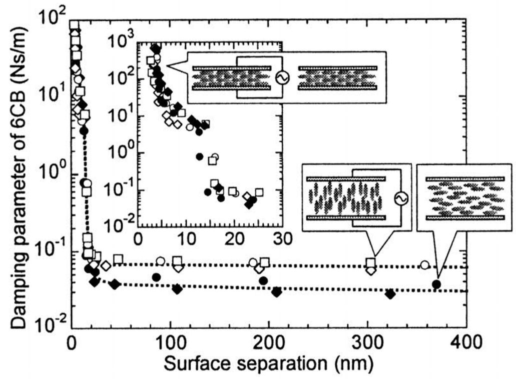

Fig. 4 Surface separation dependence of damping parameters of 6CB with the electric field (open symbols) and without the electric field (filled symbols). Inset shows magnified figure at short surface separations. Different symbols indicate data from different experiments. The dashed lines are guide to eyes.

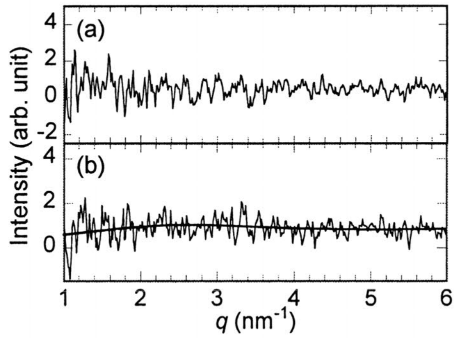

Fig. 5 Diffraction intensity profiles from 6CB confined between mica surfaces with the applied electric field. (a) D = 10 nm (average thickness of 20 nm) (b) D = 2 nm (average thickness of 12 nm). Bold solid line is fitting curves by Lorentzian function, $I(q) = I_0/[1 + 4((q-q_0)/w_0)^2] + aq + b$, where I_0 is the peak amplitude, q_0 is the center of the peak, and w_0 is the half-width.

Chapter 4 Characterization of Lubricant Confined between Mica Surfaces at High Temperature

Reduction in friction by lubricants is important for low carbon society and energy saving. Lubricants are used in confined space and are frequently used at high temperature. Therefore, elucidation of the properties of lubricants under confinement and at elevated temperature is desired. In this study, a heating system, which was used focused infrared light, was employed to RSM. The properties of perfluoropolyether lubricant, Zdol-2000s [$HOCH_2CF_2(OCF_2CF_2)_p(OCF_2)_qOCF_2CH_2OH$ p, q ≈ 10], under molecular-level confinement at room temperature to 60˚C were investigated.

Figure 6 shows the surface separation dependence of damping parameters of Zdol-2000s obtained at various temperatures. At $D >$ ~20 nm, the b values did not change with decreasing the surface separation and the b values were lower at higher temperature. At D = 5-10 nm, the b values increased drastically as decreasing the surface separation, indicating the occurrence of structuring. The drastic increase in b value was occurred at shorter

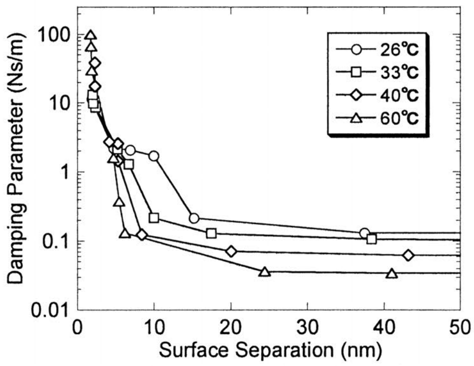

Fig. 6 Surface separation dependence of damping parameter of Zdol-2000s obtained at various temperatures.

distance with increasing temperature. This is due to the suppression of hydrogen bond at higher temperature. At hard-wall thickness (D = 1.7–2.3 nm), the b value was larger at higher temperature unlike the b values at large distances (D > ~20 nm).

Chapter 5 Summary and Conclusion

In this study, novel approaches using synchrotron X-ray diffraction measurement and RSM were developed and applied for characterizing the confined liquids. (1) The measurement using SFA combined with synchrotron X-ray diffraction measurement was developed and was applied to confined 8CB, [C_2mim][OTf], and [C_2mim][NTf_2] to directly investigate the structure. X-ray diffraction pattern from liquid nanofilm confined between solid surfaces was obtained for the first time. (2) RSM and synchrotron X-ray diffraction measurement were performed for 6CB with the applied electric field. It was found that the orientation of 6CB cannot be changed by applying the electric field when the confinement effect becomes significant. (3) RSM was performed for Zdol-2000s at high temperature. The temperature dependence of the behavior of confined Zdol-2000s was observed.

Reference

1) S. Granick, Science **253** 1374 (1991). 2) S. H. J. ldziak et al., Science, **264** 1915 (1994). 3) E. Perret et al., Europhys. Lett. **88** 36004 (2009).

論文審査結果の要旨

ナノメートルスケールの間隔の固体表面間に挟まれた液体は、表面との相互作用並びに閉じ込め効果によりバルクとは異なる特性を示す。このような閉じ込め液体の理解は、微細化・精密化が進む先端技術において重要となっている。著者は、閉じ込め液体についての理解を更に進めるために、放射光X線を使用し、固体表面間に挟まれた液体ナノ薄膜の構造評価法を新たに開発し、閉じ込め液体の構造評価に成功した。また、閉じ込め液体への電場の効果や温度の効果について新たに検討し、そのときの挙動を明らかにした。本論文はこれらの結果をまとめたもので、全編5章よりなる。

第1章は序論である。

第2章では、放射光X線を使用した閉じ込め液体の構造評価法の開発及びその測定法のスメクチック液晶とイオン液体への応用について述べている。まず、新たに開発した装置の構成について述べ、続いてバックグラウンド散乱の低減について検討している。次に、スメクチック液晶を試料として測定を行い、固体表面間に挟まれた分子レベルの厚みの液体からの回折像の測定に初めて成功している。そして、ナノ空間に閉じ込められたスメクチック液晶の構造緩和の観測及びその原因についての検討、ナノ空間に閉じ込められたイオン液体の構造評価について述べており、本測定法が有用であることを確認している。

第3章では、電場配向させたネマチック液晶への閉じ込め効果の影響について検討している。表面間の距離を連続的に変えながら粘性や潤滑性を評価できる“共振ずり測定”に新たに電場印加の機構を組み込み、表面間距離 17 nm 以上では、電場により液晶分子の配向を変えられるが、表面間距離 17 nm 以下では、閉じ込め効果が顕著になるため、電場を印加しても液晶分子の配向を変えられないという興味深い結果を見出している。また、表面間距離をフィードバック制御により一定に保つ機構を新たに導入し、電場を印加しての放射光X線回折測定を行い、ナノ空間に閉じ込められた液晶分子の配向を直接的に確認している。

第4章では、著者の所属する研究室において新たに開発された加熱システムを共振ずり測定に使用し、固体表面間に挟まれた潤滑油の温度による特性変化について検討している。水素結合を形成する潤滑油を試料とし、温度による構造化挙動の差、ナノ空間中においては高温ほど粘度が大きくなる様子など新たな挙動の観測に成功している。

第5章は総括である。

以上要するに本論文は、ナノメートルスケールの空間に閉じ込められた液体の構造を評価するための測定法の開発とその有用性、及び閉じ込め液体への電場や温度などの外部因子の影響について新たに検討したものであり、基礎科学的に重要であるとともに材料化学の発展に寄与するところが大きい。

よって、本論文は博士(工学)の学位論文として合格と認める。