

Structural characterization of nano-confined liquids by synchrotron X-ray diffraction measurement

The properties of liquids confined between solid surfaces with a nanometer-scale gap (nano-confined liquids) are known to be different from those of bulk liquids owing to the restriction of their motions and interactions with solid surfaces [1-5]. The measurements of both the surface and shear forces using a surface force apparatus (SFA) have been performed to study various liquids confined between solid surfaces taking advantages of the ability to freely changing the surface separation distance (D) [1-4,6]. Generally, nano-confined liquids exhibit solid-like properties, i.e., the effective viscosity increases more than several orders of magnitude. This significant change has been ascribed to the decrease in the freedom of movement as a result of the confinement of liquid molecules in a nanospace, similar to the effect of the decrease in temperature. However, the molecular-level understanding of nano-confined liquids is still limited because of the lack of techniques appropriate for characterizing the structure of the nano-confined liquids.

For example, the surface force measurement revealed the formation of layered structures of simple liquids, e.g., a quasi-spherical molecule (octamethylcyclotetrasiloxane (OMCTS)) and n -alkane, when they are confined between atomically smooth mica surfaces at D 's less than about 10 molecular diameters [4]. These reports prompted a discussion about the solidification mechanism of confined liquids; however, information on the in a plane structure parallel to the surfaces is imperative for understanding. Also, the structural variation of the liquid molecule and the properties of confining surfaces make the behavior of the confined liquids complicated [5].

One of the most effective techniques for understanding the specific properties of nano-confined liquids is a structural analysis with X-ray diffraction (XRD) measurements used in combination with an SFA, which enables the investigation of the structures in a plane parallel to the confining surfaces. However, this technique was only applied to liquids in a submicron-scale thickness range until recently [7]. We have established the X-ray diffraction measurement of nano-confined liquids by using the high-brilliance synchrotron X-ray beam of SPing-8 BL40B2 [8]. This technique has enabled us to obtain new insights into nano-confined liquids, e.g., (i) changes in diffraction peak intensity revealed that a nano-confined liquid crystal (4-cyano-4' octyl biphenyl (8CB)) exhibited a 10^{10} -fold slower diffusion than did the bulk 8CB [8];

(ii) the specific organization of cations and anions of confined ionic liquids could help to determine the mechanism behind the specific lubricity of nano-confined ionic liquids [9].

Recently, we developed a device for the XRD measurement of nano-confined liquids under shear and investigated the effects of shear on the orientational behavior of a room-temperature smectic-A liquid crystal 8CB confined between mica and silica surfaces (Fig. 1) [10]. As shown in Fig. 2(a), the X-ray diffraction intensity profiles of 8CB confined between mica surfaces measured at the hard wall thickness ($D = 1.7$ nm) showed the two centrosymmetric diffraction spots corresponding to spacing (d) = 3.13 nm. This result demonstrated the uniaxial orientation of the lamellar axis of 8CB most probably due to the preferential alignment of its long axis along the crystallographic axis (a -axis) of the mica. On the other hand, the ring diffraction pattern observed for 8CB confined between silica surfaces ($D = ca. 2$ nm) demonstrated the omnidirectional orientation of the lamellar axis of 8CB in-plane (Fig. 2(b)). These results clearly demonstrated the significant effects of surface properties on the structure of nano-confined liquids and should be important for liquid crystal applications such as optical devices and lubricants in which the effects of surface properties are becoming more significant for finer and smaller devices.

As shown in Fig. 3(a), the two centrosymmetric diffraction spots for the nano-confined 8CB between mica surfaces were rotated only $ca. 3$ degrees within the plane parallel to the surface by applying shear. The ring diffraction pattern of 8CB confined between silica surfaces showed almost no change on applying shear. These results demonstrated, for the first time, that the effect of shear on the orientation of 8CB was significantly suppressed when the surface

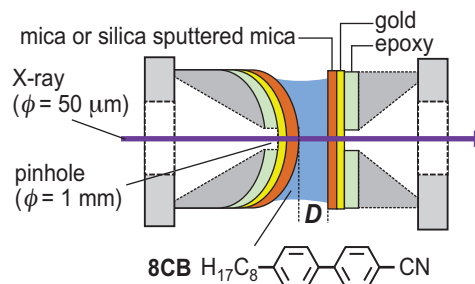


Fig. 1. Schematic diagram of XRD measurement of nano-confined 8CB.

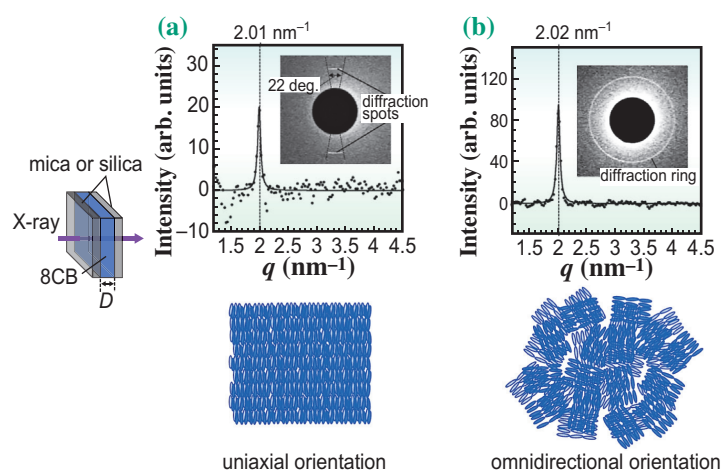


Fig. 2. (a) X-ray diffraction intensity profiles of 8CB confined between mica surfaces whose crystal axes were adjusted to be parallel to each other at $D = 1.7$ nm. (b) X-ray diffraction intensity profiles of 8CB confined between silica surfaces at $D = ca. 2$ nm. Filled black symbols are the obtained diffraction data, and solid lines are the fitting curves of the Lorentz function. The insets show the diffraction images at $q < ca. 2.5$ nm⁻¹.

separation distance (D) was at the nanometer scale regardless of the types of surface examined. On the other hand, when shear was applied to 8CB at a large $D (= 3.3 \mu\text{m})$ that was then returned to $D = ca. 2$ nm, the orientation of 8CB confined between mica surfaces was rotated, and the diffraction ring pattern of 8CB confined between silica surfaces disappeared. These results indicated that 8CB was significantly rotated or

disordered by the shear applied at a large D where the mobility of 8CB was not suppressed.

The X-ray diffraction measurement of confined liquids has great potential to advance the molecular-level understanding of confined liquids, which exhibit complex behavior, and can also provide useful information for the innovative design of materials such as lubricants, micro/nanofluids, and nanomolds.

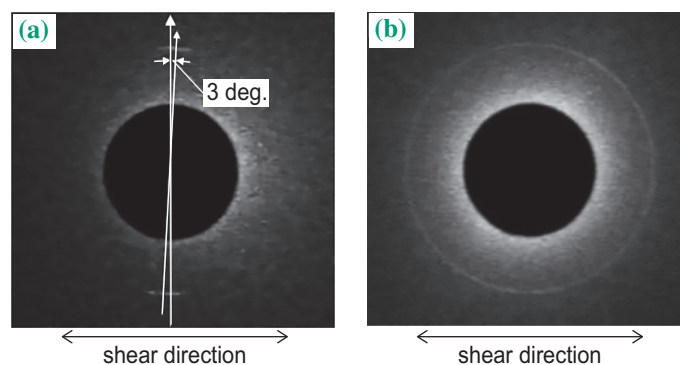


Fig. 3. X-ray diffraction images of 8CB under shear confined between (a) mica surfaces at $D = 1.7$ nm and (b) silica surfaces at $D = ca. 2$ nm.

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