

Apparatus for simultaneous observation of the electro-optic response and small angle x-ray scattering in liquid crystals

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A novel apparatus allowing the simultaneous observation of small angle x-ray scattering and time dependent birefringence changes of a dynamic system is described. The apparatus incorporates a monochromatic light source, polarizers, a fast photodiode detector, and electric field generating equipment, such that electro-optic response times between 10 μ s and 100 s may be measured. The electro-optic apparatus is incorporated in an x-ray camera sited at the Synchrotron Radiation Source at Daresbury Laboratory, UK. The x-ray apparatus allows the study of structures ~ 30 Å in dimension and the detector is time resolved with a minimum response time of 10 μ s. A hot stage and temperature controller are also incorporated into the apparatus, allowing the study of smectic liquid crystal devices. Results from the simultaneous acquisition of time resolved x-ray scattering data and electro-optic measurements from a thin film of smectic-A liquid crystal are presented. © 1995 American Institute of Physics.

I. INTRODUCTION

Small angle x-ray scattering (SAXS) allows the study of regular structures between 10 and 5000 Å. A wide variety of research fields within the biological, chemical, and physical sciences make use of this technique. While small angle x-ray scattering yields unique structural information from many different types of samples, a full description of a system frequently relies on combining x-ray information with that gained from other experiments. There are inevitably problems associated with correlating data obtained in two entirely different experiments, not the least of which is that they may have to be undertaken on different samples of material, often in different geographical locations. This is both time consuming and may contribute significantly to experimental errors which are difficult to reliably ascertain. Undertaking SAXS experiments concurrently with other measurements often maximizes the amount of information that a single experiment may yield, though doing so requires a special apparatus to be constructed. SAXS has been implemented in conjunction with techniques including pressure variation,¹ differential scanning calorimetry,² and reaction injection moulding.³ In this paper an apparatus suitable for the simultaneous observation of the time dependent electro-optic response and SAXS from a smectic-A liquid crystal device is presented.

SAXS is particularly well suited to the study of smectic liquid crystals where the layered structures typically have repeat distances of the order of 30 Å. X-ray scattering from smectic materials gives unique insight into their structures and the technique has to date focused on analyzing the polymorphism and symmetry of smectic systems. Recently there has been increasing interest in using x rays to examine the layer structure in liquid crystal devices rather than in bulk samples. A typical liquid crystal device consists of a thin sandwich of material (1–10 μ m thick) held between constraining glass surfaces. Smectic liquid crystalline materials scatter x rays only weakly and the study of liquid crystal

devices therefore requires a high x-ray flux, such as is available at a synchrotron source.

In a simplistic picture of a smectic liquid crystal device the layers are perpendicular to the glass walls of the device, as shown in Fig. 1(a). However, x-ray studies have revealed that even in well-aligned smectic materials, the layer structure in devices is usually far more complex than shown here. As an example, an extensive x-ray study of the layer structure found in chiral smectic-C (ferroelectric) liquid crystal devices has been carried out by Clark and Rieker,⁴ which shows the existence of chevrons [Fig. 1(b)]. Indeed, almost all x-ray studies on liquid crystal devices to date have been undertaken on chiral smectic-C (ferroelectric) devices. The discovery of the chevron structure in ferroelectric liquid crystal devices has proven vital to understanding the physics of their operation. More recently the formation of the chevron structure at the smectic-A to smectic-C phase transition has been investigated by Richardson and Taylor.⁵

Electric field effects are of great importance in liquid crystals. Liquid crystal electro-optic display devices are designed using materials which are ordered birefringent fluids responsive to electric fields. By coating the surrounding glass plates which form a liquid crystal device with an aligning agent, a predefined orientation is imposed on the liquid crystal director within a thin (~ 10 μ m) film of material. The molecules can be switched away from this predefined orientation by the application of an electric field (typically between 1 and 10 V/ μ m). The electro-optic device employs the change in birefringence associated with this reorientation of the molecules on application of the electric field. In static SAXS experiments, Isogai *et al.*⁶ and Oh-e *et al.*⁷ have examined the influence of electric fields on the chevron angle and the associated layer structure in ferroelectric liquid crystal devices.

While these static electric field experiments can yield information which is useful in the design of liquid crystal devices, a full understanding of the physics of such systems can only be obtained via a study of the dynamics of the

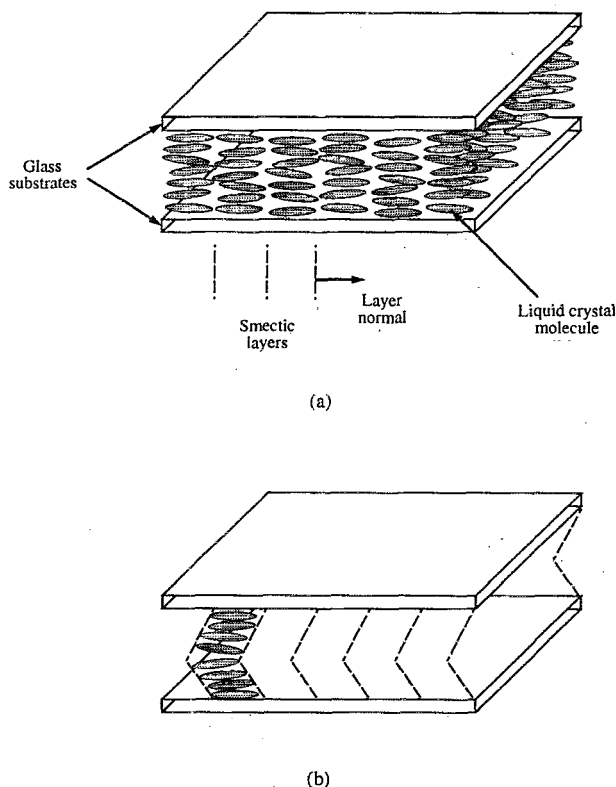


FIG. 1. A schematic showing the layer structure and cell geometry of (a) a positive dielectric anisotropy smectic-A liquid crystal device, and (b) a simplified view of the chevron structure observed in a ferroelectric liquid crystal device (Ref. 4). The diagram is not to scale; the glass substrates are typically $100\text{ }\mu\text{m}$ for x-ray experiments, while the thickness of the liquid crystal material is $\sim 10\text{ }\mu\text{m}$. The inner surfaces of the glass plates are coated with a transparent electrode and alignment layer.

switching. Switching times are usually short (depending on the device) and can vary from a few seconds in smectic-A devices to a few microseconds in ferroelectric materials, so fast timing resolution is required for dynamic studies of liquid crystal devices. To obtain information about the dynamics it is necessary to probe both the director and the layer structure throughout the switching process. Time resolved x-ray scattering studies of the switching mechanisms in smectic-A liquid crystals were pioneered by Gleeson *et al.*,⁸ where it was shown that the dynamics of liquid crystal device switching involves a complex coupled movement of the layers and the director. These studies were necessarily undertaken using separate experiments and hence suffered from the associated difficulties discussed earlier. In order to gain more complete information about the dynamics of the switching, a novel arrangement to allow simultaneous time resolved optical and x-ray observation of a specimen has been designed where the sample temperature and the applied electric fields to the sample are externally controlled. The dynamic movement of the layers is probed by time resolved x-ray experiments, while the dynamics of the liquid crystal director is monitored simultaneously via observation of the birefringence of the system using visible light. At present the instrument is designed for the observation of smectic liquid crystal devices but this arrangement may find applications in

other fields where simultaneous x-ray and optical observations are desirable.

II. THE INSTRUMENT

As liquid crystals scatter x-rays only weakly, the sample thickness within a device is necessarily small, and the time resolution employs short exposure times, a high flux x-ray source is required. The apparatus described in this paper is thus designed to be adapted to a beam line (station 2.1) of the Synchrotron Radiation Source at the Daresbury Laboratory, Warrington, UK.

A. The low-angle scattering station

This section summarizes only those characteristics of the beam line which are relevant to the present experiment. A crystal monochromator selects x-rays at a wavelength of $1.54\text{ }\text{\AA}$, giving a Bragg angle of 1.4 degrees for a typical layer spacing of $30\text{ }\text{\AA}$ as found in smectic liquid crystals. For optimum resolution at 1.4 degrees, a 1-m -long evacuated camera⁹ is used. The x rays are collimated to a $1\text{ mm}\times 2\text{ mm}$ beam, allowing the observation of areas of the liquid crystal device smaller than the individual domain structure. The scattered x rays are detected via a gas-filled area detector (multiwire chamber with wire spacing of 0.5 mm constructed at Daresbury Laboratory). The area detector allows variations in the layer spacing as well as the spread of the Bragg peak associated with layer disruption to be monitored during switching.⁸

The detection hardware is computer controlled using a system specifically designed for Daresbury Laboratory as described in detail elsewhere.⁹ The data acquisition system allows the user to define parameter files which control the time evolution of the detection for a specific experiment via a time frame generator (TFG). Data from the area detector is input to files in a series of frames; the length of each frame and the mark to space ratio being user defined within the parameter file. The timing of the system is extremely versatile, allowing each frame length to be defined from $10\text{ }\mu\text{s}$ to several hours with up to 120 frames per experiment. Thus, it is possible to distort the sample *in situ* by means of some external stimulus (in this case the application of an electric field), and monitor the time dependence of the subsequent SAXS data with an appropriate choice of the timing interval and number of time frames collected. The TFG controlling the data acquisition system can also output programmable TTL level pulses to synchronize the apparatus providing the external stimulus to the liquid crystal and to the x-ray data acquisition system. A timing diagram for a typical experiment is shown in Fig. 2. An analogue signal from the simultaneous experiment (in this case the electro-optic response) can be input to the data acquisition system, digitized, and stored together with the x-ray data in the data files.

B. The visible light optics

For simultaneous x-ray and electro-optic measurements it is necessary to combine the incident visible-light and x-ray

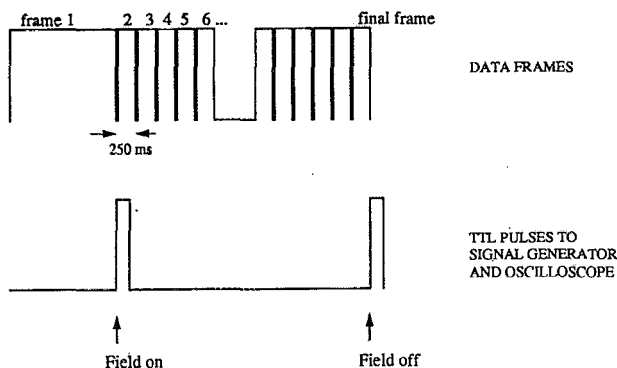


FIG. 2. A timing diagram showing the typical evolution of a time resolved x-ray experiment studying smectic-A liquid crystal devices. The first frame is 2.5 s long, and all subsequent frames are 250 ms long. There is a wait time of 10 μ s between frames.

beams at the same point in the specimen. Following scattering, the visible light has then to be separated from the main x-ray beam prior to detection.

The layout of the visible light optics is shown in Fig. 3. The 670 nm visible light is from a collimated 5 mW laser diode (Sumichem Optoelectronics Ltd.). The light beam is polarized using a sheet polarizer and brought collinear to the x-ray path by reflection on a pellicle beamsplitter (model 03BPL003/02, Melles Griot). The beamsplitter is a tough, extremely thin (5 μ m) elastic membrane of cellulose nitrate stretched taut over an optically flat aluminum alloy frame, and reflects approximately 45% of the laser light at 45° incidence. The x-ray absorption by the pellicle membrane is weak and is insignificant in the experiments described here.

Inside the evacuated camera, the visible light beam is

reflected at a small mirror placed on the lead x-ray beam stop and is directed onto a Radio Spares BPX65 medium area photodiode detector. The detector and a second sheet polarizer are mounted on an aluminum cradle of the same radius as the tube of the camera. The first polarizer placed after the laser, and the second polarizer prior to the detector are crossed in order to monitor the birefringence of the liquid crystal. The optics are aligned with the rear of the x-ray camera removed and the whole system is at atmospheric pressure, allowing access to the mirror, second polarizer, and detector. The position of the cradle on the camera and the orientation of the mirror on the beam stop are adjustable in order to allow detection of the light beam without obstructing the relevant scattered x rays. The signal from the light detector is amplified using an EF351N operational amplifier circuit with a response time $<10 \mu$ s, then directed to a Hewlett-Packard 54502A digital storage oscilloscope for monitoring. The analogue electro-optic signal is also routed to the x-ray data acquisition system to be digitized and stored with the x-ray scattering data from individual frames.

C. The specimen cell

The specimen cell must be transparent to both visible light and x rays. A review of cell design for optical and x-ray studies of liquid crystals is given by Rieker and Clark.⁴ The cells used for the present experiment are prepared in our laboratory and consist of two 100- μ m-thick glass plates coated with a transparent layer of indium-tin oxide (ITO) 0.01 μ m thick.¹⁰ The plates are held parallel by 12- μ m-thick Kapton spacers. The thickness of the ITO electrodes, as well as the glass thickness are kept to a minimum in order to reduce attenuation and stray scattering of the x rays. A buffed film of polyvinyl alcohol (PVA) is applied on the inner faces

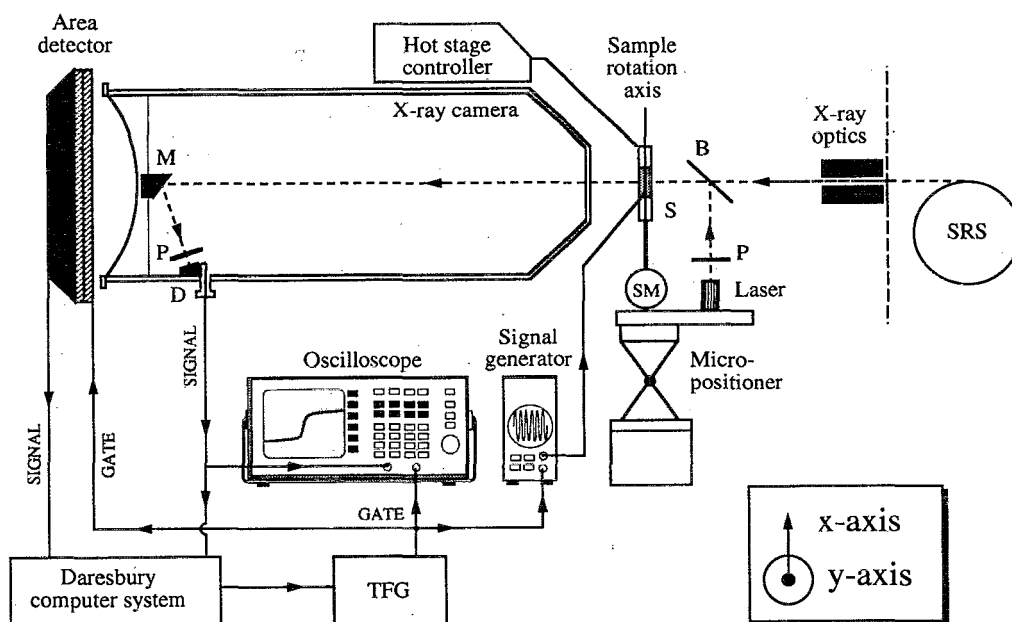


FIG. 3. The general layout of the simultaneous electro-optic and time resolved small angle x-ray apparatus. M: beam stop and mirror, P: polarizers, D: photodiode detector, S: sample and oven (see Fig. 4 for detail), B: beamsplitter, SM: stepper motor and gears. The stepper motor rotates the oven and sample about the rotation axis shown (x axis). The micropositioner allows translation along both the x and y axes shown. The x-ray camera length is 1 m.

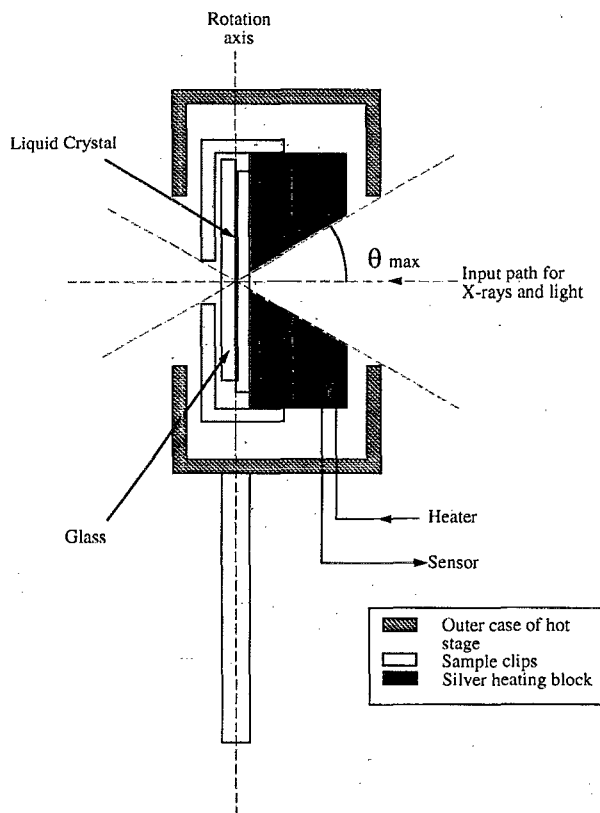


FIG. 4. A cross-section through the center of the hot stage and sample holder. The hot stage and sample holder may be rotated about the rotation axis shown. $\theta_{\max}$ defines the angle of the cone which has been removed from the silver heating block and is the maximum angle through which the sample may be rotated without blocking the incident and Bragg scattered x-ray beams. The central aperture through the hot stage is 2 mm in diameter.

of the cell to induce unidirectional planar alignment of the molecules in the liquid crystal. Once assembled the cell is capillary filled with the liquid-crystalline material in its isotropic phase and is then sealed. The electrical connections for the application of the electric field are soldered to the ITO electrodes using pure indium.

The specimen cell is mounted in the specially modified oven (Linkam THMS600 series) as shown in Fig. 4. To observe the x-ray diffraction from an oriented liquid crystal sample, the experimental geometry must correspond to the Bragg condition and it is therefore necessary to be able to rotate the liquid crystal sample around an axis of liquid crystal symmetry. The shape of the silver heating block and the slots on the thermal shield allow a 30 degree rotation of the oven without obstruction of the scattered beams. The temperature of the specimen can be regulated using the Linkam TMS91 control unit from ambient to 600 °C with an accuracy better than 0.2 °C.

III. THE LAYOUT OF THE EXPERIMENT

The general layout for the experiment is shown in Fig. 3. The oven containing the specimen is mounted on a single axis goniometer allowing the oven and thus the specimen to be rotated about an axis perpendicular to the x-ray beam. The rotation is finely controlled with a stepper motor (M061-

FD03) and reduction gear box (type 3D 90:1) from Bede Scientific Instruments, which is computer controlled using Bede Scientific Software (Double Crystal Control Program V1.2). The sample is oriented within the oven such that the smectic layer normal lies at right angles to the axis of rotation and in the Bragg condition with respect to the incident x-ray beam [the device is almost normal to the beam for the layer orientation shown in Fig. 1(a)]. The position of the specimen cell inside the oven can be adjusted to select the area of the specimen to be observed, ensuring that a well-aligned monodomain area of sample is studied. The monodomain of high quality is selected initially by examining the cell within the oven using polarized microscopy. The goniometer, laser diode, defining polarizer, and the pellicle beam-splitter are mounted on the same rigid frame. A fine adjustment of the optical path of the laser beam is possible using two mutually perpendicular linear translation stages for positioning with respect to the x-ray beam. The rotation axis of the goniometer is initially brought coincident with the x-ray beam. The exact point at which the x rays are incident on the sample is determined using x-ray sensitive paper which shows a color change in areas exposed to x rays. The collimated laser beam is then brought collinear with the x-ray beam by adjustment of the beamsplitter mount. Once the specimen and the light beam are aligned with the incident x-ray beam, the evacuated camera is opened to position the light detector and to cross the analyzing polarizer with the polarizer defining the incident light beam.

The ac voltage applied to the specimen is provided by a programmable function generator (Thurlby-Thandar TG1304) and amplified using an in-house wideband voltage amplifier (EW1896/4). The voltage applied to the liquid crystal device can be adjusted to 160 V rms at frequencies up to 5 MHz. The function generator oscillator is gated using a pulse from the TFG. The gate is opened at the second time frame (see Fig. 2) so that information about the specimen prior to the application of the electric field can be recorded in the first time frame. The gate is shut at the end of the last time frame. The storage oscilloscope, also triggered by the TFG at the second time frame, is used for immediate observation of the electro-optical response.

IV. EXPERIMENTAL DATA

Concurrent observation of time resolved SAXS and electro-optic responses was initially made on a smectic-A liquid crystal device. The liquid crystal specimen was S3 from Merck¹¹ which has positive dielectric anisotropy and exhibits the phase sequence:

54.5 °C 59 °C
smectic-A → nematic → isotropic.

The high temperature nematic phase responds well to the surface alignment techniques used here, allowing a monodomain smectic-A sample to be produced at low temperatures. A voltage of 27 V rms at a frequency of 1 kHz was used to switch the sample, which was held at a constant temperature of 53.4 °C. The sample switches fully from the planar orientation to a homeotropic state in approximately 6 s under these conditions. The time evolution of the experi-

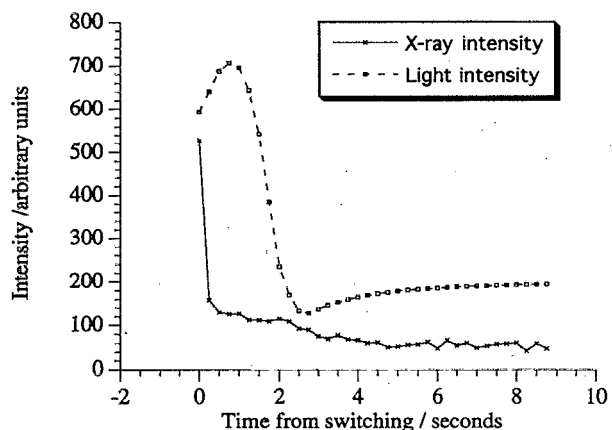


FIG. 5. Simultaneously acquired SAXS and electro-optic data from the sample S3. The sample was mounted at an angle corresponding to the Bragg condition of the system.

ment is as depicted in Fig. 2. The time interval of 250 ms used for x-ray detection following the application of the electric field was determined in previous experiments⁸ which had shown that the minimum exposure time allowing the x-ray scattering data to have reasonable accuracy to be 250 ms.

Figure 5 shows the simultaneously recorded intensities of the Bragg peak and the transmitted light as a function of time, following the application of the electric field to the sample. It can be seen that the decay of the x rays follows a quite different behavior from the optical response of the system. The x-ray intensity reduces to approximately 20% of its initial value in the first 500 ms, implying that the majority of the smectic layers move away from the Bragg position within this time. The slow decay of the x-ray signal over the remainder of the experiment corresponds to the slow motion of the residual 20% of the layers out of the Bragg condition. The electro-optic response (dashed line) is quite different. There is an initial increase in the detected light intensity following the application of the field, which may be related to the production of scattering defects in the sample. This is followed by a reduction in intensity over approximately 1 s, indicating that during this time the majority of the change in birefringence of the sample takes place. The slight increase in birefringence observed >2 s after the application of the field is thought to be due to a coupling of the rotation of the layers which remain in the Bragg condition during the latter part of the experiment⁸ to the molecular reorientation. A direct comparison of the two data sets is impossible without determining the evolution of the layer structure within the device more completely on application of an electric field. The complete evolution of the layer deformation which occurs on application of the field is obtained by repeating the experiment at various angles, in small ($\sim 1^\circ$) steps. Such an experiment brings the layers which are deformed and rotated in response to the electric field into the Bragg condition for some rotation angle. The data set shown in Fig. 5 allows the electro-optic response of the sample to be directly related to the decay of the layer structure at one angle, thereby allow-

ing correlation of the data between the experiments. A full analysis of the layer structure and its evolution during switching is presented in Morse *et al.*¹²

The time resolution of the experiment described here is limited by the total integration time necessary to obtain accurate x-ray scattering data (250 ms) from the smectic-A sample, rather than due to limitations in the apparatus. The time resolution could in principle be improved by repeating an identical experiment, adding data from shorter time frames such that total accumulation time for the data in each frame is at least 250 ms. Such an experiment would in practice be extremely difficult in a smectic-A system as the switching from the planar to the homeotropic state is not fully reversible, the sample requiring the addition of a heating and cooling cycle through the nematic phase following each application of the electric field to the sample to return it to a reproducible initial condition.

The apparatus was specifically designed for use at the Synchrotron Radiation Source at Daresbury, though the optics could be readily adapted for use with other suitable high flux x-ray sources. It should be noted that in these experiments which examine the switching characteristics of smectic-A devices, the optical and x-ray beams are required to be collinear. For other liquid crystal devices, e.g., ferroelectric systems, the geometry is more complicated, due to the complex nature of the layer structure. In these cases it is necessary to align the incident laser beam normal to the cell, while the x-ray beam must be incident at approximately the chevron angle (the Bragg condition for such devices). The apparatus described here could be modified to allow the optics to rotate coaxially with the cell rotation as the cell itself is rotated with respect to the x-ray beam by employing a second goniometer. Such an apparatus is currently under construction. Finally, although the apparatus described here was designed for use with liquid crystal devices, it could readily be used to monitor birefringence changes concurrently with SAXS for many other systems where the combined data yield enhanced information about processes taking place in response to external stimuli.

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