

Using neutron reflection to understand the structural origin of liquid crystal lubrication.



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Liquid crystals and their tribology

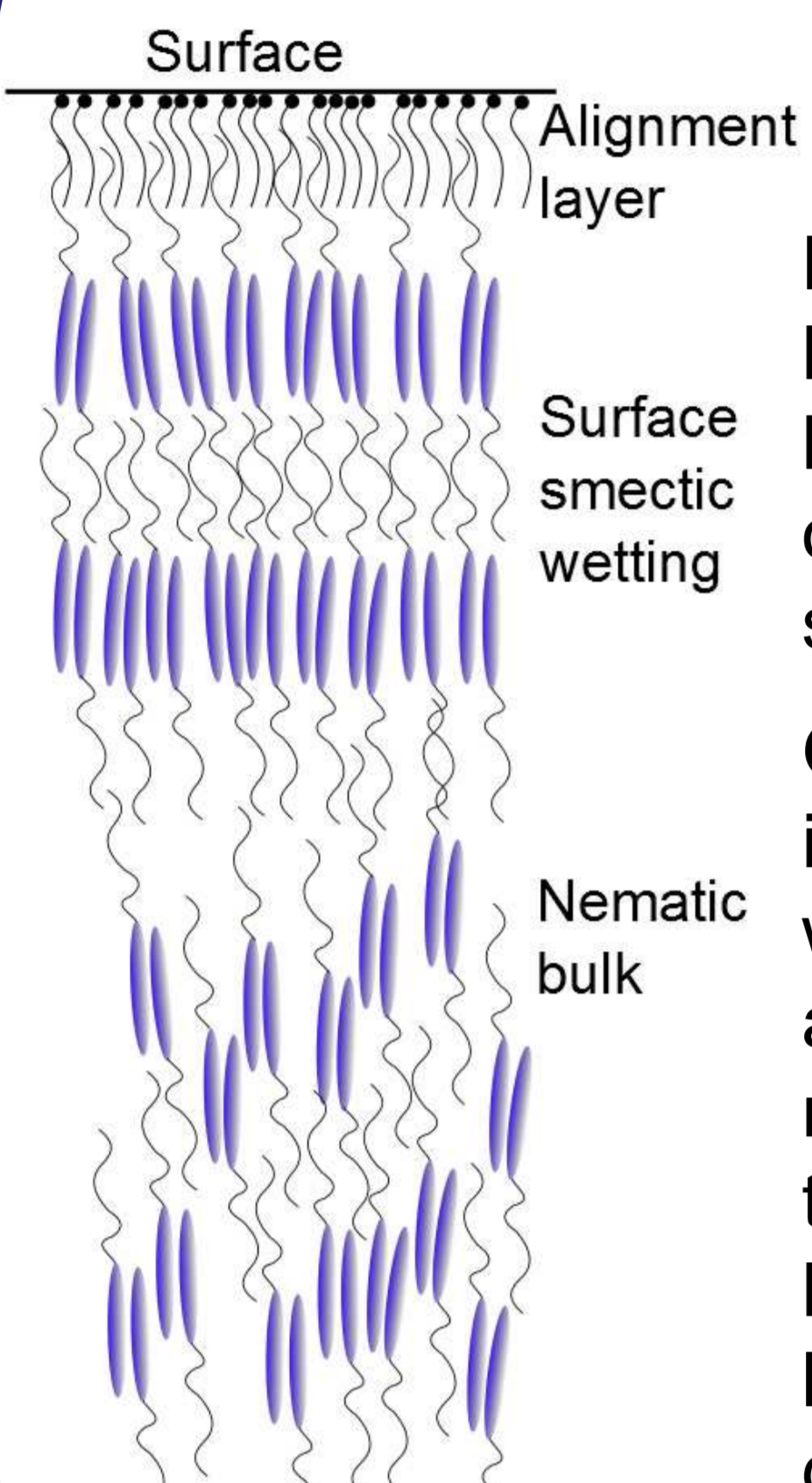


Figure 1 Schematic of smectic wetting in a nematic LC.

Liquid crystal (LC) lubrication is a well known phenomena. Their tribology has been an ongoing area of research for over two decades.^{1,2} However the structural origin is yet to be understood.

One explanation which we aim to investigate is the surface smectic wetting. This has been observed against a bulk nematic already³. If this were the reason for the tribological behaviour then when a thin film of LC is confined between two surfaces (such as in a lubricated system) an increase in the depth of smectic layering would be expected.

Neutron reflection

The technique of neutron reflection is particularly useful for investigating thin layers at buried interfaces^{3,4} due to the penetrating nature of the radiation and wavelengths available. The reflected intensity (reflectivity) varies with the composition (scattering length density, ρ), thickness and uniformity of the layer.

Many features can be determined from the reflectivity profile: interference fringes are from the overall layer thickness; the two bulk materials either side of the layer determine the critical edge and repeating layers parallel to the interface which have a difference in hydrogen and deuterium content cause Bragg peaks.

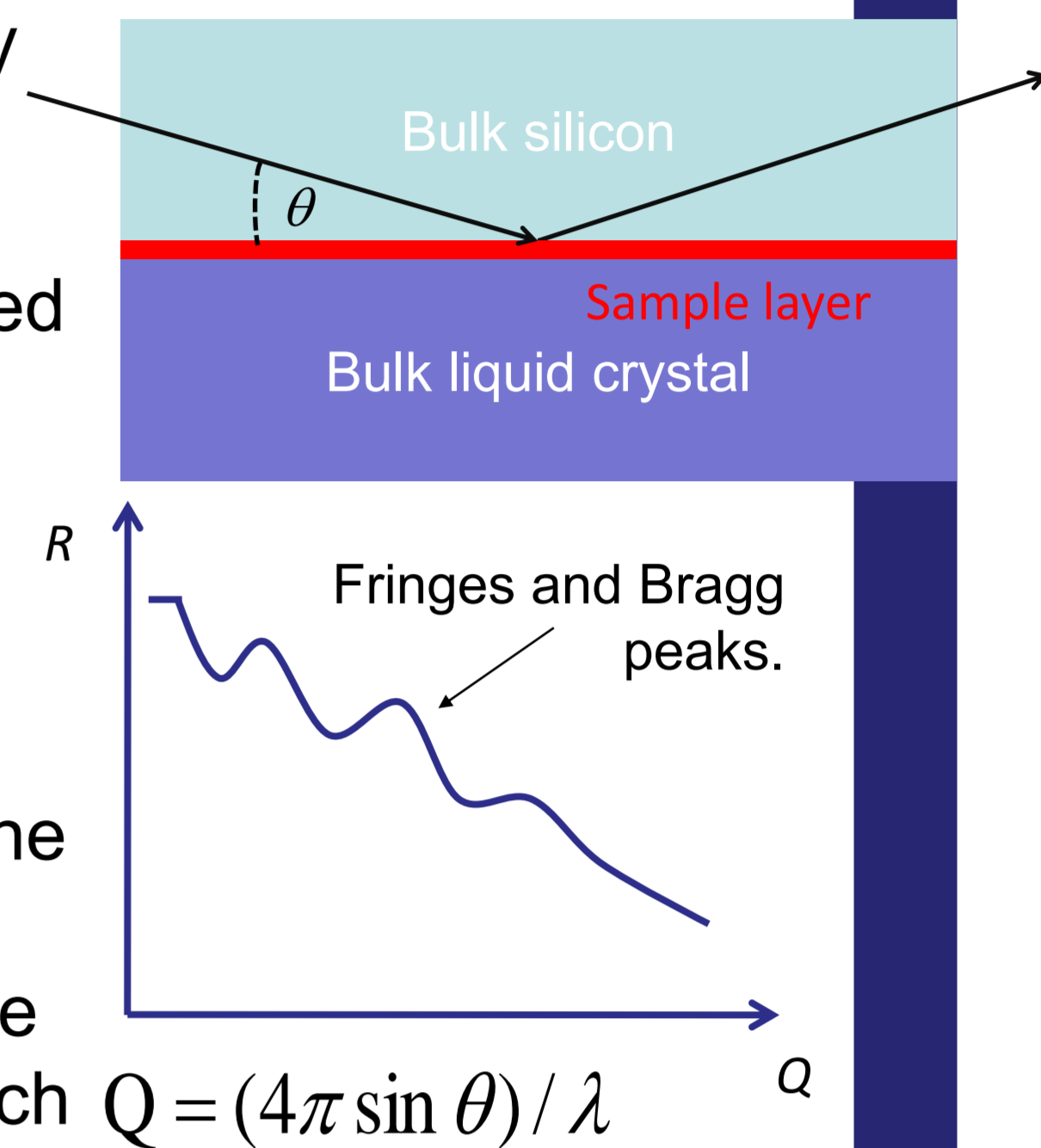


Figure 2 A general overview of neutron reflectivity.

Sample environment

The silicon block with liquid crystal spread on its surface was held in our confinement sample environment⁵, figures 3 and 4. The sample is confined between the silicon block and a plastic, Melinex (PET), membrane which is inflated using N₂ and held at a constant confining pressure.

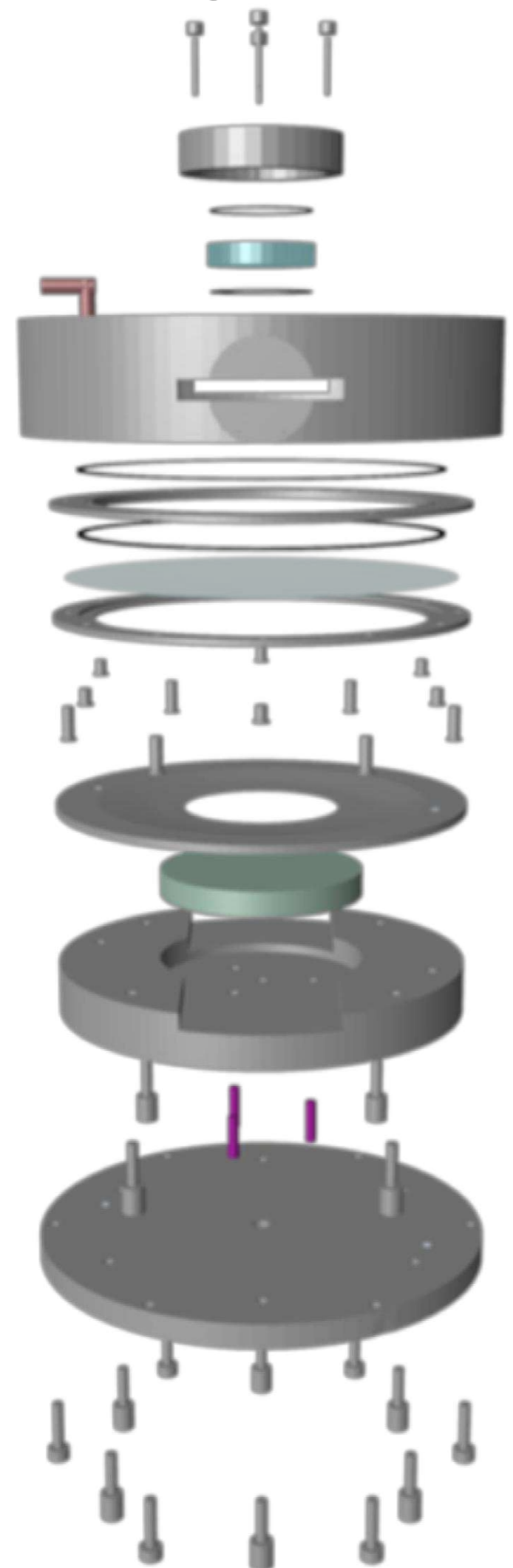
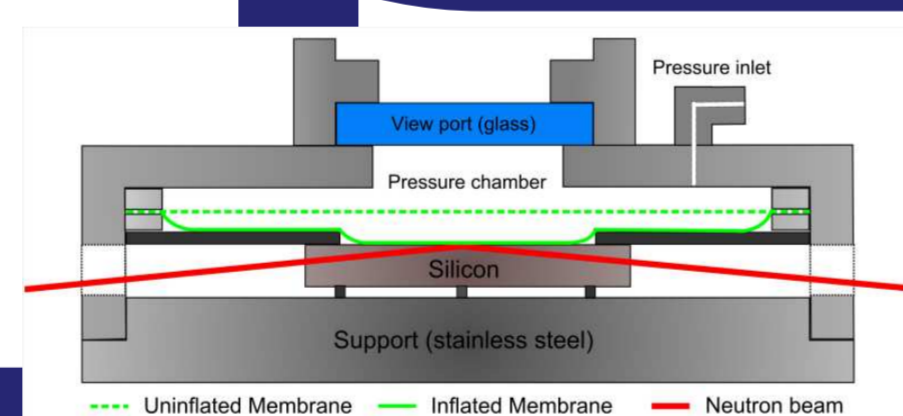


Figure 3: Expanded schematic of the confinement sample environment for neutron reflection

Neutrons are then reflected off the Si/LC interface and measurements taken for a number of pressures. The temperature of the sample, and hence the LC phase, is also controlled using a copper heat exchanger.

Figure 4: Schematic of the assembled confinement sample environment for neutron reflection

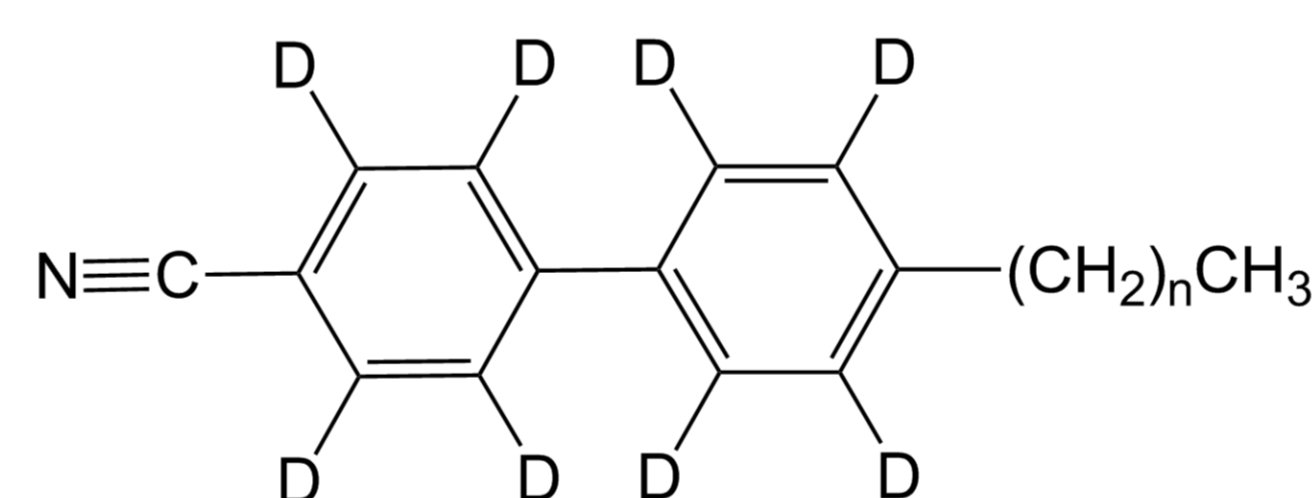


Experimental details

An experiment was recently performed using the INTER reflectometer at the ISIS neutron facility, STFC, Oxfordshire.

A silane alignment layer (DMOAP) was deposited on the surface of silicon blocks. This treatment causes director anchoring in the liquid crystal perpendicular to the surface, thus smectic layers which grow from the surface will be in the correct orientation to produce Bragg peaks.

Contrast within the layers was introduced by using core deuterated cyanobiphenyls with hydrogenous alkyl chains 6, 8 and 10 carbons long. The LC phases these materials have are nematic only, both nematic and smectic and smectic only, respectively for increasing alkyl chain length (6CB, 8CB, 10CB).



Structure of core deuterated alkyl cyanobiphenyl: $\Delta\rho_{\text{core-chain}} \sim 5.5 \times 10^{-6} \text{ \AA}^{-2}$

Future experiments

Neutron reflection has shown promising initial results for liquid crystal and other systems (polyelectrolyte multilayers⁵ and stacks of hydrated lipid bilayers). However there are some disadvantages, such as deuteration to provide contrast.

We have recently built a new sample environment, using the same principles, for use with X-ray reflection (XRR) measurements.

Key differences for XRR: sample environment is smaller, substrate is diamond, inherent contrast from electron densities within the LC, hence no need for deuteration, higher flux leads to quicker measurements, radiation damage may be suffered.

The first experiment with this cell will be carried out at beamline I07 at Diamond, RAL. The alkyl cyanobiphenyls will again be confined under a range of pressures and temperatures.

Results so far

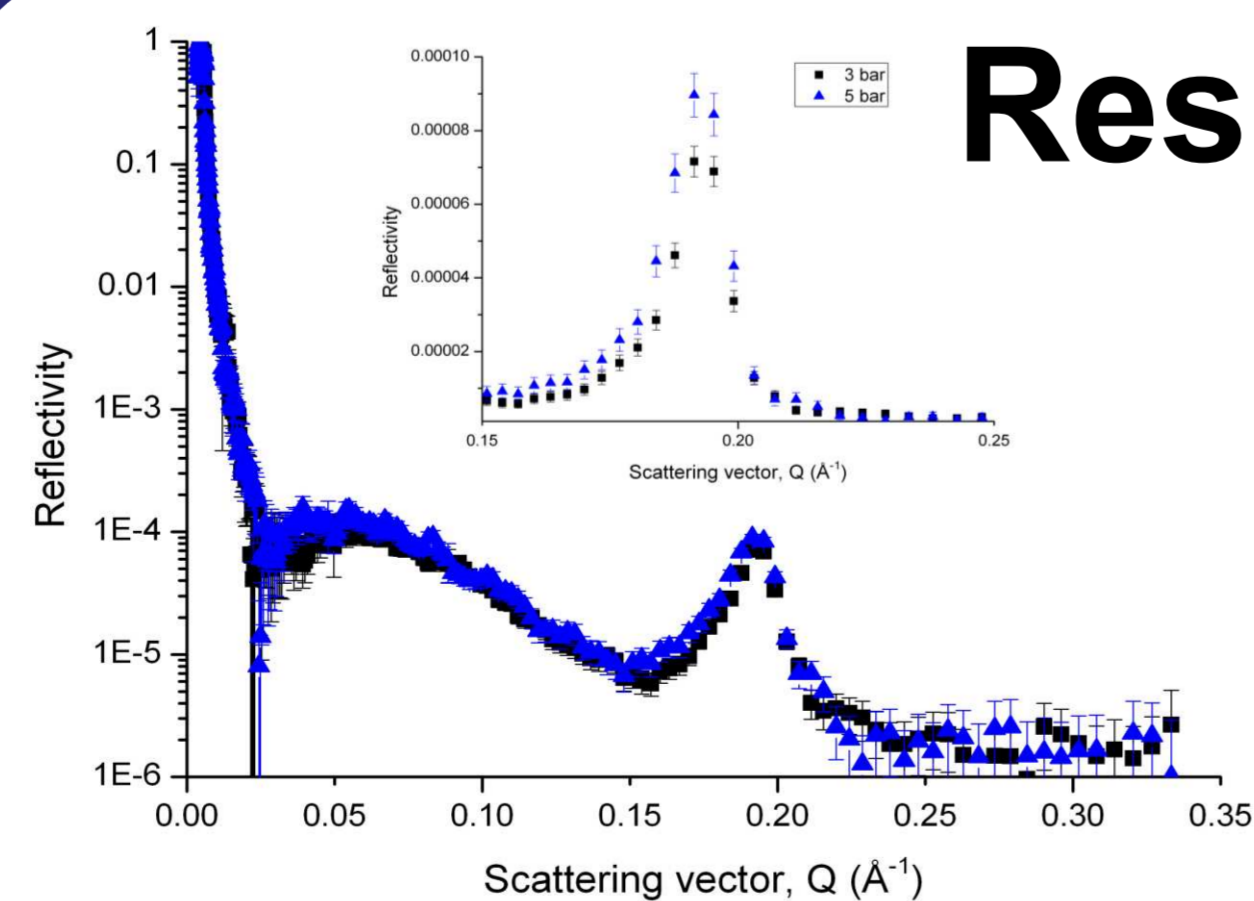


Figure 5 8CB in nematic (34.8°C) shows a very small increase in Bragg peak intensity with an increase in confinement, this will be investigated further in future experiments. 6CB did not show any smectic wetting in the small range of conditions tested.

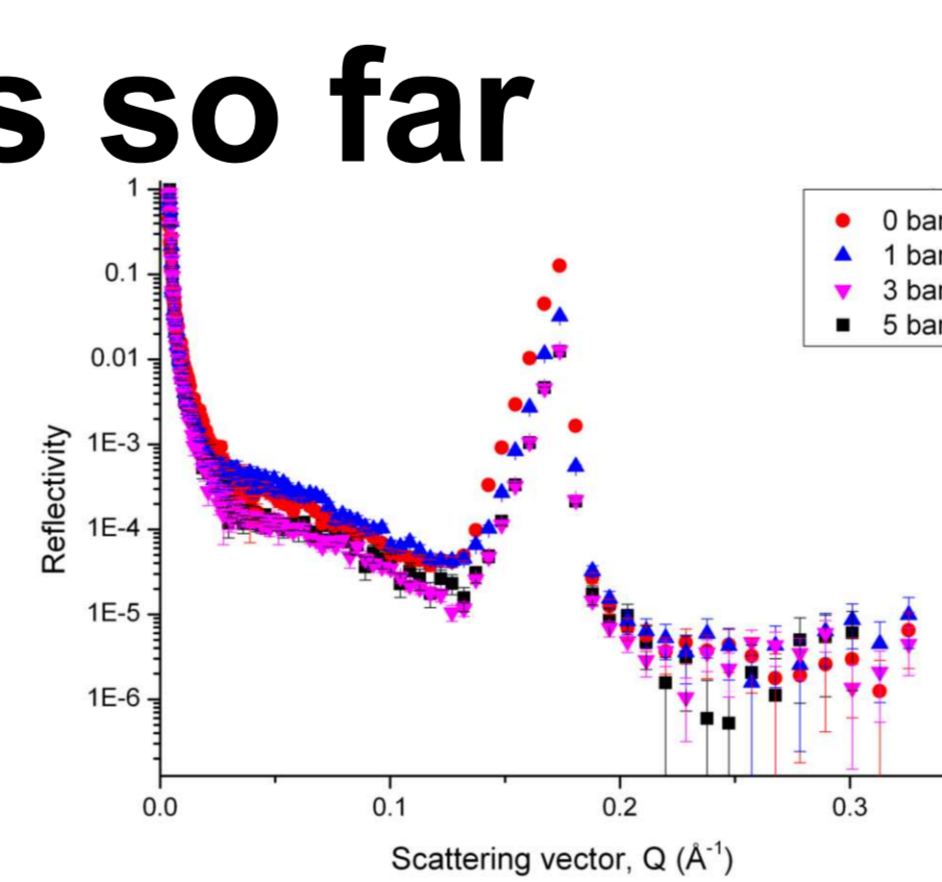


Figure 6 10CB shows a decrease in Bragg peak intensity as material is pushed out with increasing confinement. No change in interlayer spacing. Analysis is ongoing.

References:

- [1] Cognard, J. Lubrication with liquid-crystals. In *Tribology and the Liquid-Crystalline State*. ACS Symposium Series, 441; Biresaw, G., Ed.; American Chemical Society: Washington DC, USA, 1990; pp. 1-47.
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