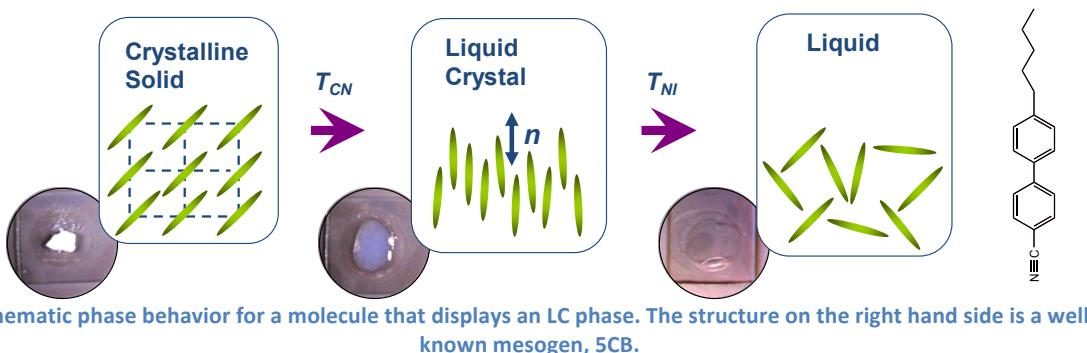


## 2D-Wide angle X-ray Scattering (WAXD) studies of Liquid crystals

### Introduction of Liquid Crystals

A large class of organic molecules display a series of intermediate transition states between solid and isotropic liquid state as there temperature is raised. These intermediate phases have properties in between crystalline solid and corresponding isotropic liquid state and hence the name liquid crystalline phases. Other name is ‘mesomorphic phases’ where mesomorphic means of intermediate form. According to de Gennes [ref], liquid crystal is an intermediate phase which has liquid like order in at least one direction and possesses a degree of anisotropy. Remember, all liquid crystalline phases are formed by anisotropic molecules (either elongated or disk-like) but not all the anisotropic molecules form liquid crystalline phases.



Non spherical (anisotropic) objects can possess different types of ordering giving rise to different liquid crystalline phases.

#### Nematic

The word nematic comes from Greek which means thread, and refers to the thread like defects commonly observed in the polarizing optical microscopy of these molecules. They have no positional order only orientational order in the direction of molecules denoted by  $n$  commonly referred as ‘director’ (figure...). The director  $n$  is bidirectional that means the states  $n$  and  $-n$  are indistinguishable.

#### Smectic phases:

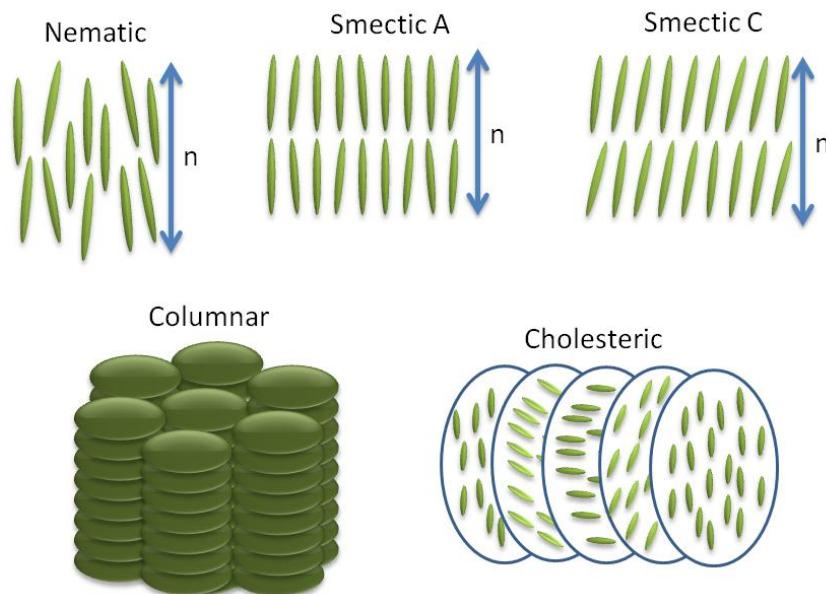
All the smectic phases are layered structures and are usually found at slightly lower temperatures than nematics. The three main types of smectics are : smectic A, smectic C and hexatic smectics. **Smectic A**: each layer is like a two dimensional liquid and the long axis of molecules is on average orthogonal to the layers (figure...). Just like nematics, the state  $n$  and  $-n$  are equivalent. They are made up of achiral and non polar molecules.

**Smectic C**: again is a layered but long axis of molecules is not along the layer normal instead it makes an angle ( $\theta$ , figure ). The tilt angle is an order parameter of this phase and can vary from 0 to 45-50 degrees. **Smectic C\***: these are smectic phases formed by chiral molecules. This extra constraint of chirality causes a slight distortion of Smectic C

structure. Now the tilt direction precesses around the layer normal and form a helical configuration.

### Cholesterics

Sometimes they are also referred as chiral nematic phase since in many regards they are similar to nematic phase. Many derivatives of cholesterol exhibit this type of phase. They are generally formed by chiral molecules or doping the nematic host matrix with chiral molecules. Adding chirality causes helical distortion in the system, which makes the director  $n$  rotate continuously in space in shape of helix with specific pitch. The magnitude of pitch in a cholesteric phase is a strong function of temperature.



Schematic of different types of liquid crystal phases.

## Introduction of 2D XRD

X-ray diffraction is one of the fundamental experimental technique to analyze the atomic arrangement of materials. The basic principle behind x-ray diffraction is the Bragg's Law. According to this law, x-rays that are reflected from the adjacent crystal planes will undergo constructive interference only when the path difference between them is an integer multiple of the x-rays wavelength.

$$2d\sin\theta = n\lambda$$

where,

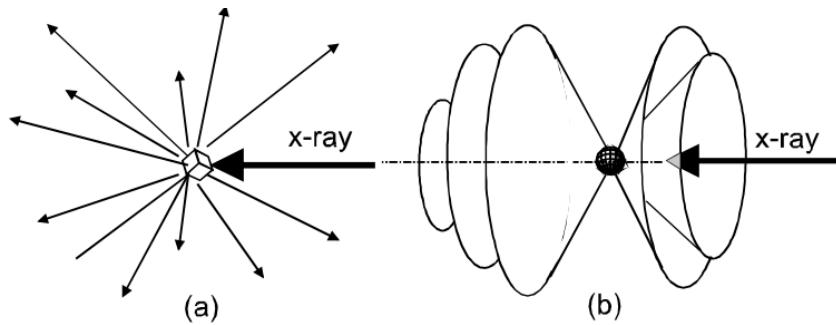
$n$  – integer

$d$ -spacing between the adjacent crystal planes

$\theta$ -angle between incident x-ray beam and scattering plane

$\lambda$ -wavelength of incident x-ray

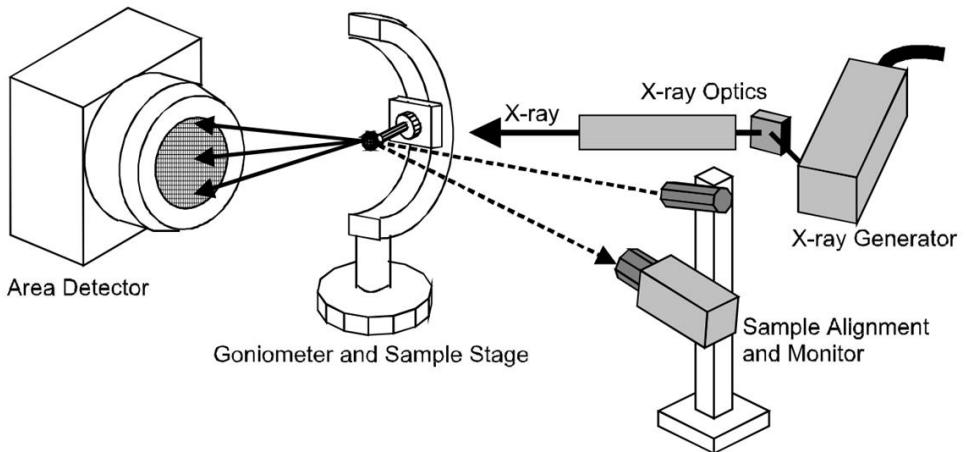
Now the atomic arrangement of molecules can go being extremely order like in single crystal to random like in liquid. Correspondingly the scattered x-rays form specific diffraction pattern particular to that sample. Figure --- shows the difference between x-rays scattered from a single crystal and polycrystalline (powder) sample. While in case of single crystal diffracted rays point to discrete directions but for polycrystalline sample they form a series of diffraction cones.



An two dimensional XRD system is a diffraction system with the capability of simultaneously collecting and analyzing the x-ray diffraction pattern in two dimension. A typical 2D XRD setup consists of five major components (figure...) (i) x-ray source, (ii)x-ray optics, (iii) goniometer, (iv)sample alignment and monitoring device and (v) 2D area detector.

The basic function of x-ray optics is to condition the x-rays generated from the x-ray source into the required wavelength, beam focus size and divergence. X-ray optics is a collective term used for x-ray tube, monochromator, collimator and beamstop. Function of a pinhole collimation is to control the size and divergence of a beam. A monochromator allows only a selected characteristic to pass through. Ideally, reflected beam from a monochromator will be a parallel beam.

The most common x-ray source are synchrotrons. They can be tune to generate a specific wavelength and they have much brighter luminosity for better resolution. For small laboratory scale x-ray generators, x-rays are emitted by bombarding metal targets with high velocity electrons accelerated by strong electric field. The most common used metal target is copper.



Schematic illustration of basic 2D WAXD setup (International Centre for Diffraction Data 2000, Advances in X-ray Analysis, Vol.43).

### **Mention advantages and disadvantages of 2D XRD as compared to 1D XRD.**

Figure ... shows the diffraction pattern from a polycrystalline sample. For illustration purpose only two diffraction cones are shown in the schematic. In case of conventional x-ray diffraction measurement, measurement area is confined within a plane represented as diffractometer plane. The 1D detector is mounted along the detection circle and variation of diffraction pattern in z direction is not considered. The diffraction pattern collected is an average over a range defined by a beam size in Z-direction. And the diffraction pattern measured is a plot of x-ray intensity at different  $2\theta$  angles. While in case of 2D XRD system, the measured diffraction pattern is not limited to the diffractometer plane. Instead a large portion of the diffraction rings are measured simultaneously. One such advantage is in the measurement of percent Crystallinity of a material. Determination of material crystallinity is required both for research and quality control {ref}. Scattering from amorphous materials produces a diffuse intensity ring while in case of polycrystalline samples , sharp and well-defined rings or spots are seen. The ability to distinguish between amorphous and crystalline is the key in determining percent of Crystallinity accurately. Since most crystalline samples have preferred orientation, depending on the sample is oriented it is possible to measure different peak or no peak using conventional diffraction system. On the other hand, sample orientation has no effect on the full circle integrated diffraction measuring done using 2D detector. An 2D XRD can measure percent crystallinity more accurately.

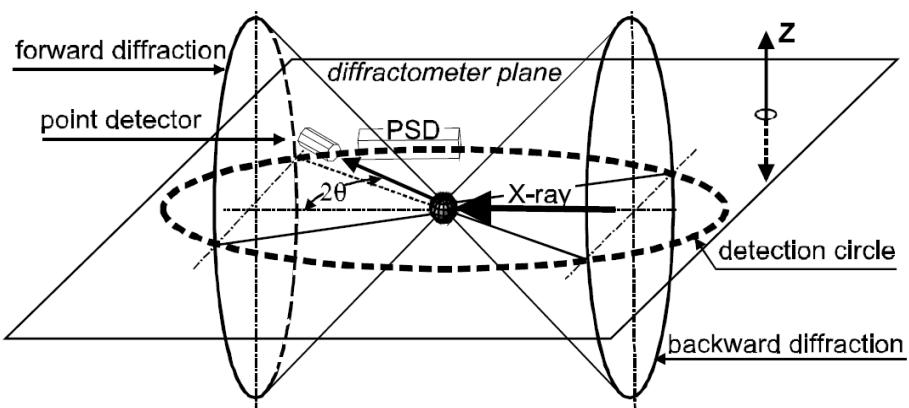


Figure : Diffraction patterns from a powder sample (International Centre for Diffraction Data 2000, Advances in X-ray Analysis, Vol.43).

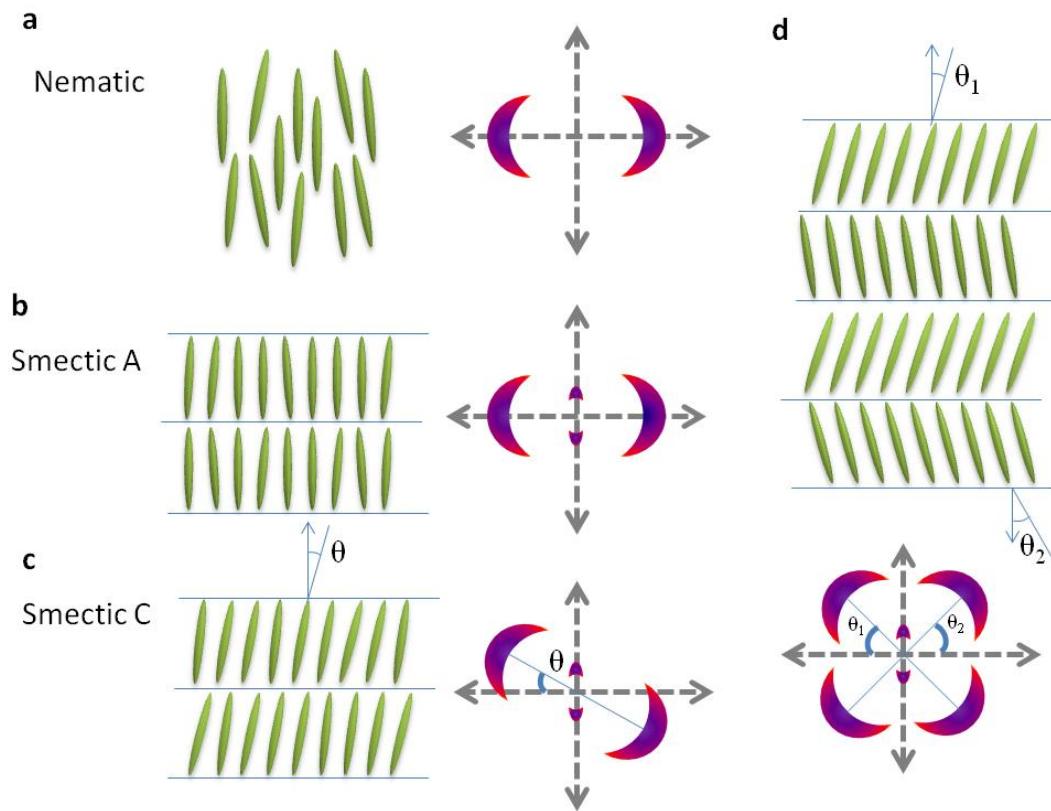
## 2D-WAXD patterns of LCs

As mentioned in the introduction section, liquid crystal is of an intermediate state between solid and liquid phase. And at temperatures above liquid crystal phase transition temperature, they become isotropic liquid i.e. absence of long-range positional or oriental order within molecules. Since an isotropic state cannot be aligned, its diffraction pattern consist of weak diffuse ring (figure . the reason we see any diffraction pattern in the isotropic state is because even in case of classical liquid s such as water there exists a short range positional order. The ring has of radius of  $4.5\text{Å}$  and it mostly appears at  $20.5$  degrees. It represent the distance between the molecules along their width.

Nematic liquid crystalline phase has only long range orientational order but no positional order. An unaligned sample of nematic liquid crystal has similar diffraction pattern as for isotropic case. But instead of a diffuse ring, it has a more sharper intensity distribution. For an aligned sample of nematic liquid crystal, x-ray diffraction pattern exhibit two sets of diffuse arcs (figure...). The diffuse arc at the larger radius ( $P_1$ ,  $4.5\text{Å}$ ) represents the distance between molecules along their width. Now under the presence of external magnetic field, samples with positive diamagnetic anisotropy aligns parallel to the field and  $P_1$  is oriented perpendicular to the field. While negative diamagnetic anisotropy samples aligns perpendicular to the field with  $P_1$  being parallel to the field. The intensity distribution within these arcs represents the extent of alignment within the sample generally denoted by  $S$ .

Similarly when an smectic phase is cooled down slowly under the presence the external field, two sets of diffuse peaks are seen in diffraction pattern (figure...). The diffuse peak at small angles condense into sharp quasi-Bragg peaks. While the peak intensity distribution at large angle is still not that sharp since molecules within the smectic planes are still randomly arranged. While in case of smectic C phase, the angle between smectic layer normal and director ( $\theta$ ) is no longer collinear (figure...). This tilt can be easily seen in the diffraction pattern as the diffuse peaks at smaller and larger angles are no longer orthogonal to each other.

At the smectic A-smectic C transition, it is possible that smectic layers can retain the same configuration as in smectic A phase but molecules start tilting both to the left or to the right of the X-ray beam. So two diffuse peaks at larger angle get split into four (figure...). This is generally help in looking at molecular rearrangement at phase transitions.



Schematic of diffraction of different types of liquid crystal phases (a) Nematic (b) Smectic A (c) smectic C and (d) mixture of two phases

## Sample Preparation

In general X-ray scattering measurements of liquid crystal samples are considered more difficult to perform as compared to crystalline samples. Following steps should be performed for diffraction measurement of liquid crystal samples:

1. The sample should be free of any solvents and absorbed oxygen. Since their presence affects the liquid crystalline character of the sample and their thermal response. This can be achieved by performing repeated melting and freezing cycle in vacuum to get rid of unwanted solvents and gases.
2. For performing measurements, liquid crystal sample can be filled inside a thin-wall glass capillary for low resolution experiments. The ends of capillary can be sealed by epoxy in case of volatile samples. The filling process tends to align the liquid crystal molecules along the flow direction.
3. For high resolution measurements, sample is generally confined between two rubbed polymer coated glass coverslips coated with an o-ring as a spacer. The

rubbing causes formation of grooves in polymer film which tends to align the liquid crystal molecules.

4. Aligned sample are necessary for identifying liquid crystalline phase of the sample. Liquid crystal sample can be aligned by heating above the phase transition temperature and cooling them slowly in presence of external electric or magnetic field. Magnetic field is effective in case of samples with aromatic cores as they have high diamagnetic anisotropy. Common problems in using electric field is internal heating which can interfere with the measurement.
5. Sample size should be sufficient to avoid any obstruction to the passage of incident x-ray beam.
6. Sample thickness should be around one absorption length of X-rays. This allows about 63% of the incident light to pass through and get optimum scattering intensity. For most hydrocarbons absorption length is approximately 1.5mm for copper metal target ( $\lambda = 1.5418 \text{ \AA}$ ). Molybdenum target can be used for getting even higher energetic radiation ( $\lambda = 0.71069 \text{ \AA}$ ).

## Data analysis

Identification of phase of a liquid crystal sample is critical in predicting its physical properties. A simple 2D x-ray diffraction pattern can tell a lot in this regard. Next critical information generally required is determining orientational order of a liquid crystal. This is important to characterize the extent of sample alignment.

For simplicity, rest of the discussion is for nematic liquid crystal phase only. In a unaligned sample, if we look macroscopically then there won't be any specific order in the system. But for micrometer size domains, molecules are all oriented in a specific direction, called a local director. Since there is no positional order in nematic liquid crystal, these local directors vary in space and assume all possible orientations. For example, in case of perfectly aligned sample of nematic liquid crystal, all the local directors will be oriented in the same direction. The specific alignment of molecules in one preferred direction in liquid crystal makes their physical properties also directionally dependent for example refractive index, viscosity, diamagnetic susceptibility.

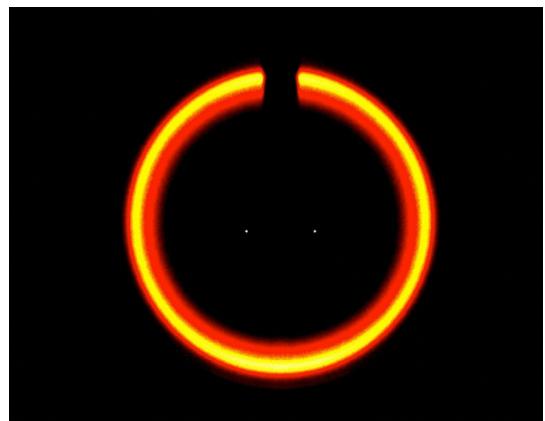
When a liquid crystal sample is oriented using external fields, local directors preferentially align along the field director globally. This globally preferred direction is referred as director and denoted by unit vector  $\mathbf{n}$ . Most commonly, extent of alignment within a liquid crystal sample is denoted by order parameter,  $S$

$$S = \langle \frac{3\cos^2\theta - 1}{2} \rangle$$

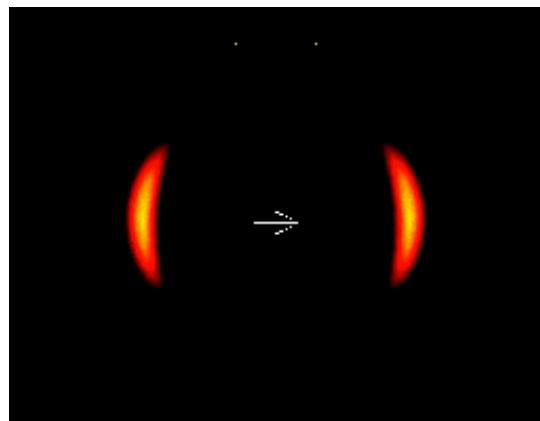
Where  $\langle \rangle$  means average value

$\theta$  is the angle between long axis of molecule and the preferred direction,  $n$ .

For isotropic samples, value of  $S$  is zero and for perfectly aligned sample it's 1.



(a)



(b)

2D WAXD data of (a) polydomain and (b) monodomain, nematic liquid crystal acquired using a Rigaku Raxis-IV++ equipped with an incident beam monochromator, pinhole collimation (0.3 mm) and Cu X-ray tube ( $\lambda = 1.54 \text{ \AA}$ ).  
The sample to detector distance was 100 mm.