CHM6201
Scattering from Polymers

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Semi-crystalline polymers

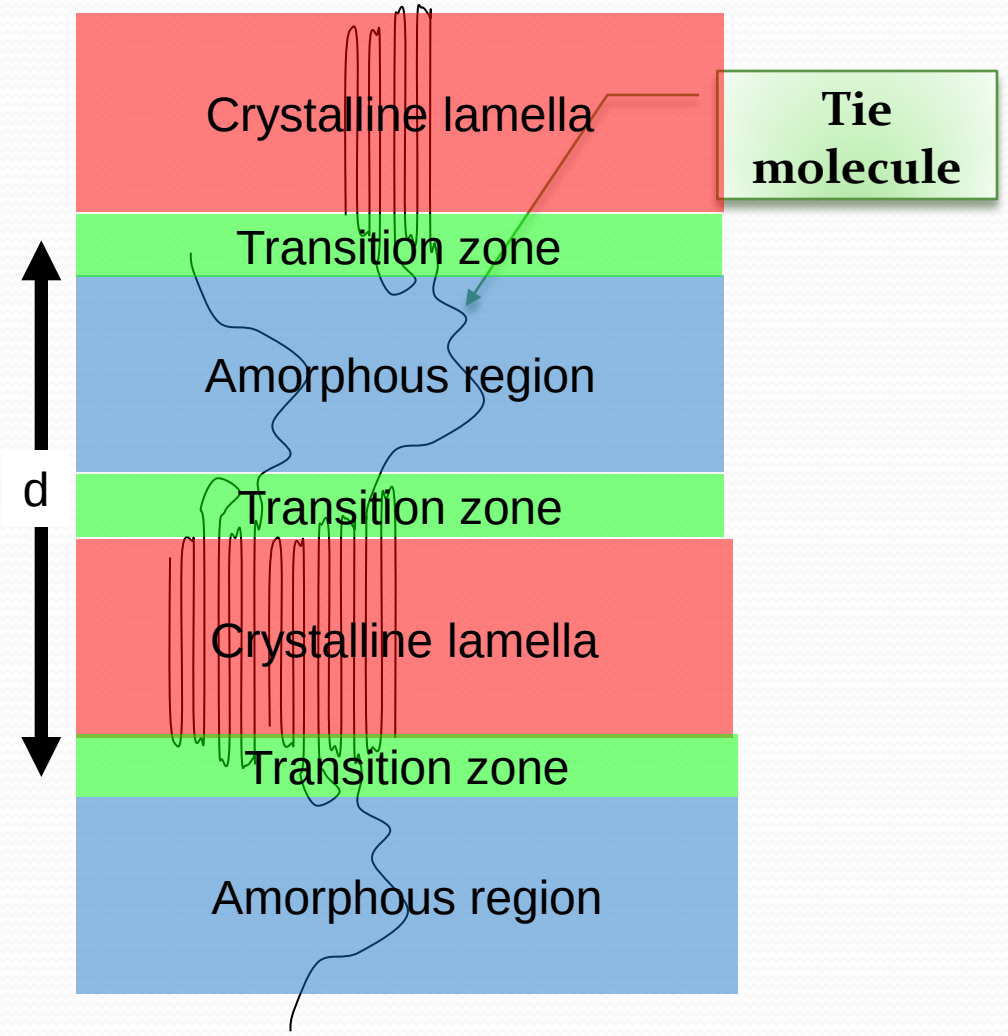
Thermoplastics

Semi-crystalline Polymers

- Most commercial thermoplastic polymers are part amorphous, part crystalline.
  - Semicrystalline.
  - Crystalline lamellae, separated by amorphous regions.
  - Gives the ability to maintain shape but resist impact.
  - On heating the lamellae melt and the polymer flows, usually with a high viscosity due to chain entanglement.

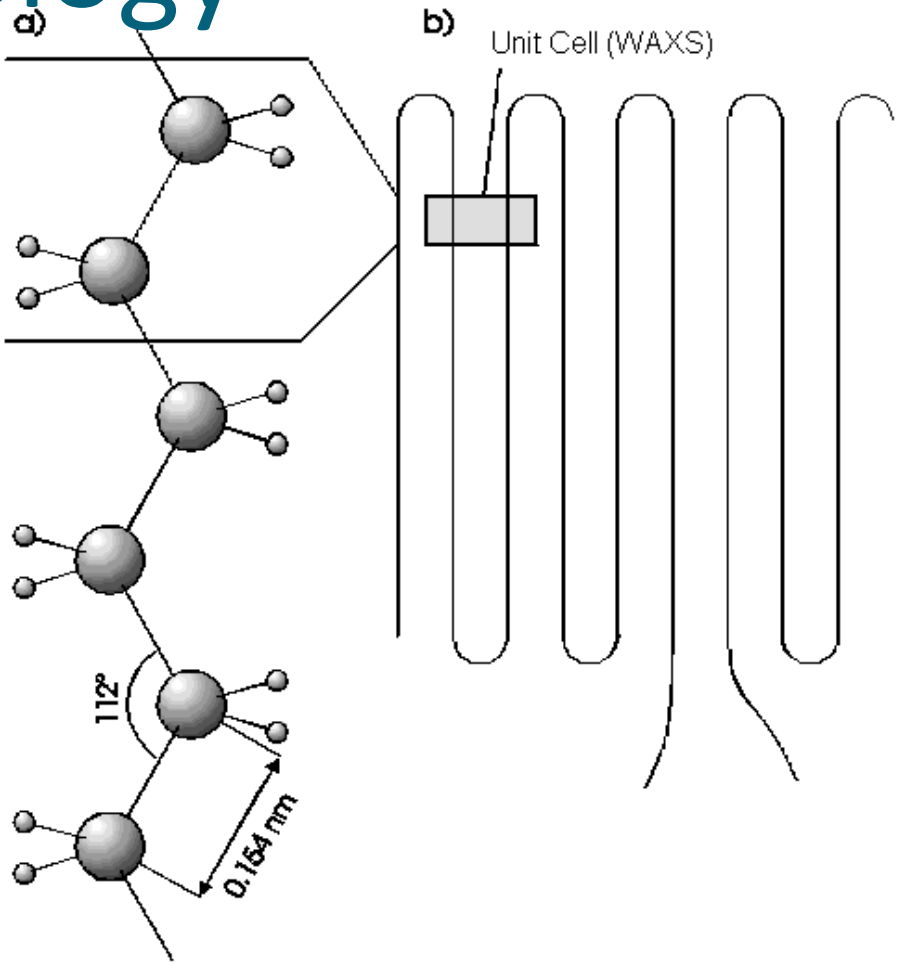
Lamella

- Crystalline and amorphous regions
- The crystal does not have perfect edges, they are made up of folded chains
- There is a small transition zone from pure crystal to amorphous (greatly exaggerated on this slide)
- In addition not all the lamella will be the same size.



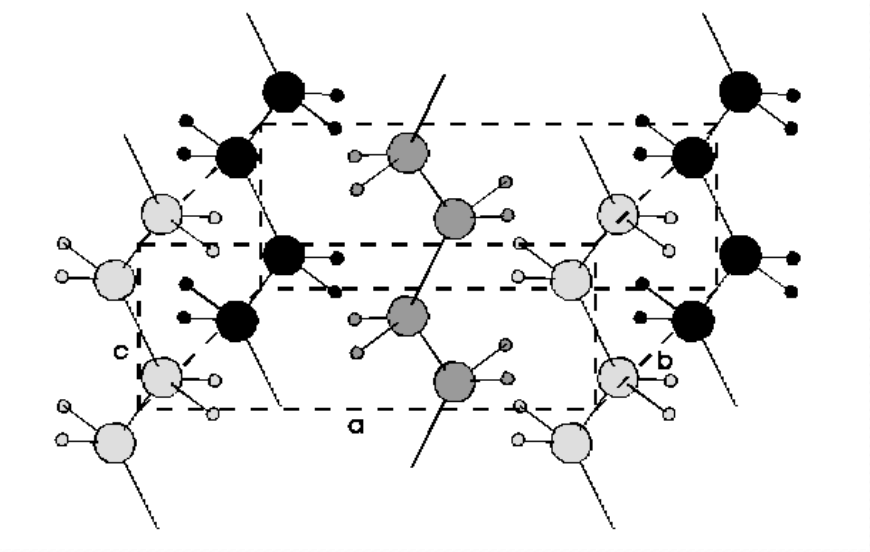
Polymer morphology

- A semi-crystalline polymer has a hierarchical structure.
- Some parts of the polymer chain crystallise.
  - These regions give rise to a WAXS (Wide angle X-ray, XRD) diffraction pattern.



WAXS

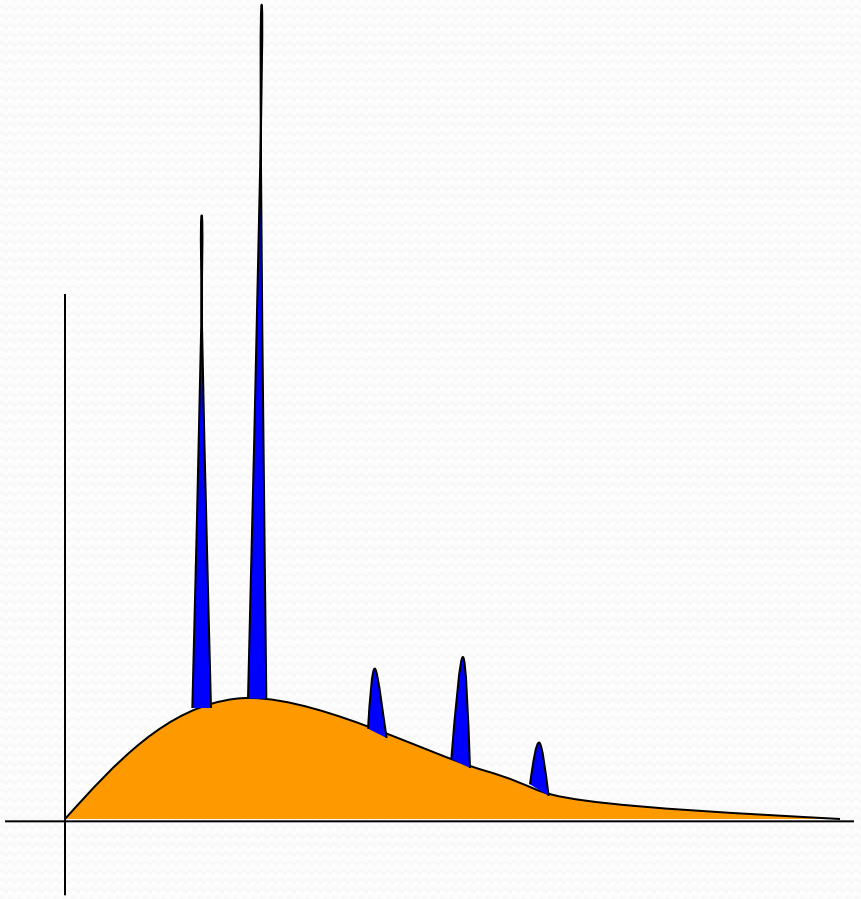
- WAXS measures the interatomic spacings within the unit cell.
- The PE unit cell is orthorhombic (all angles 90° all sides different lengths).
- The plane separation for an orthorhombic cell is given by
  - a,b,c are the lengths of the sides.
  - h,k,l are the Miller indices of the planes.
- Different unit cells have different formula.



$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2}h^2 + \frac{1}{b^2}k^2 + \frac{1}{c^2}l^2$$

WAXS

- The degree of crystallinity can be calculated from WAXS.
- The degree of crystallinity is related to the area under the crystalline and amorphous peaks.

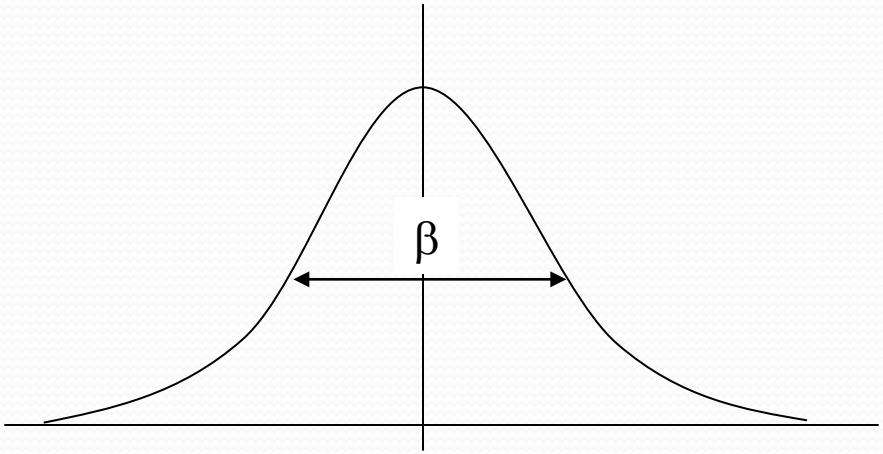


WAXS

- Therefore WAXS will give you structural information about the unit cell.
  - This is normally prior knowledge as most polymer structures have been determined. Its rare you get a completely new polymer to work on.
  - WAXS gives a check on the structure and points to preferred orientation of the crystal lamella and the degree of crystallinity.
  - To determine this you would run a Rietveld analysis.
    - The performs a fit to the pattern and determines a,b,c and the predicted intensities.

Peak Width

- The peak width increases
  - due to instrument resolution
  - if the crystals are under strain
  - If the crystal size reduces
    - Scherrer equation gives an estimate of the crystal size from the width of the peak.
    - β is the full width at half height
    - λ is the wavelength of the x-rays
    - t is the thickness of the crystal
    - And 2θ is the scattering angle
    - K is a constant close to one that accounts for the particle shape (usually about 0.95) for most systems.

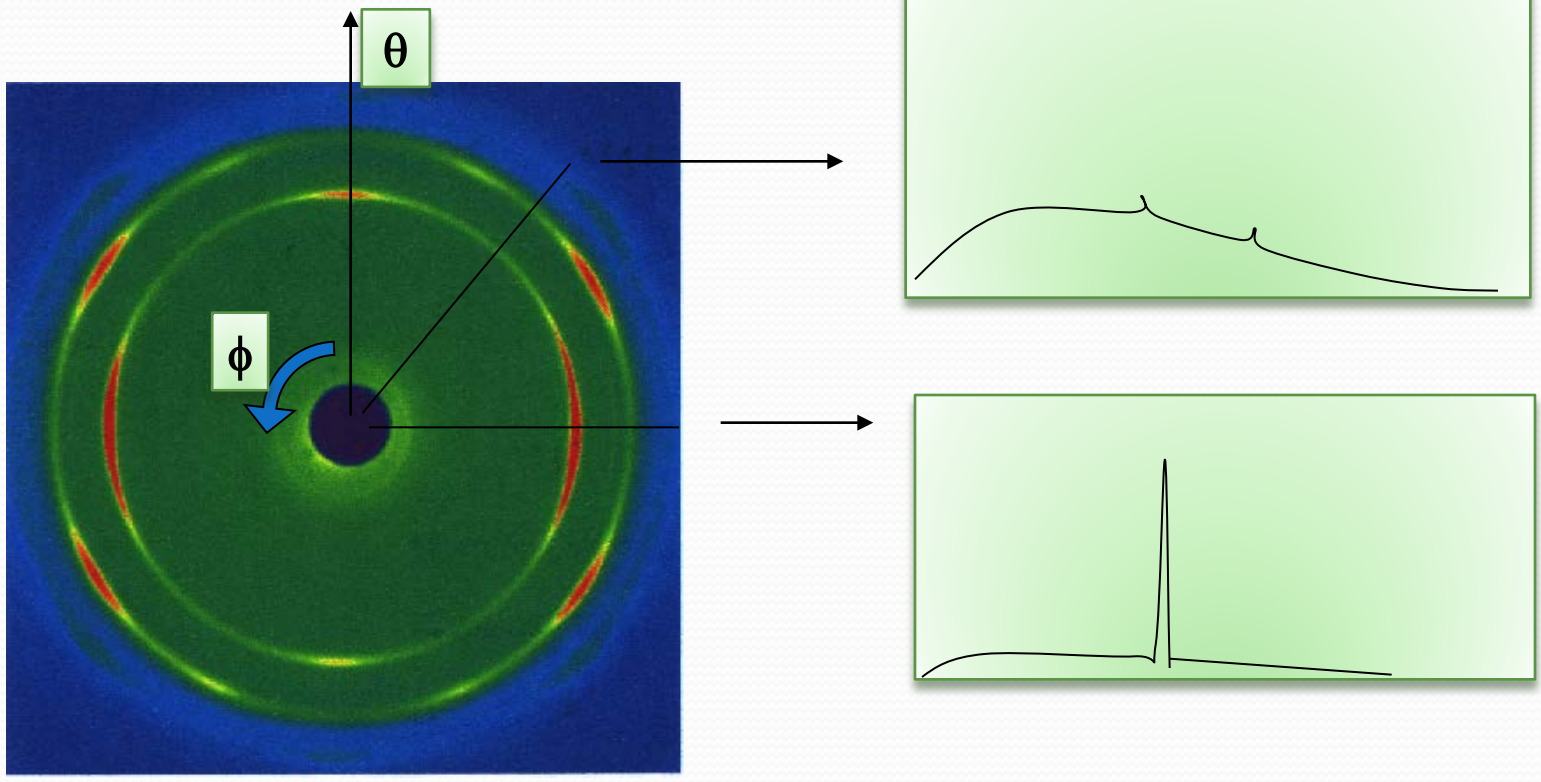


$$\beta = \frac{K\lambda}{t\cos\theta}$$

WAXS

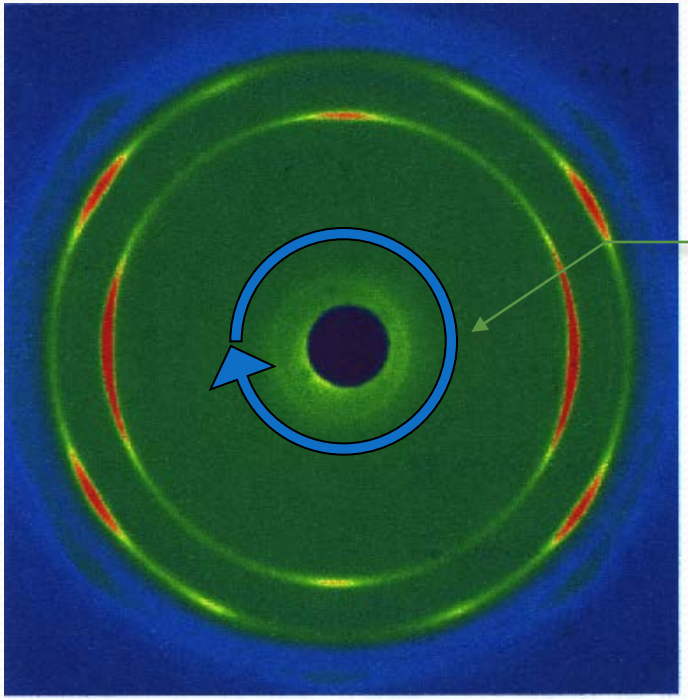
- WAXS or XRD is the most common form of scattering you will encounter.
- The equipment is in most research labs.
- Most equipment will collect “powder” patterns.
  - That means it relies on there being no preferred orientation within the material.
  - This is a BIG problem for polymer materials
    - Any form of deformation results in chains becoming elongated.
  - Its much better to collect the full pattern if possible.

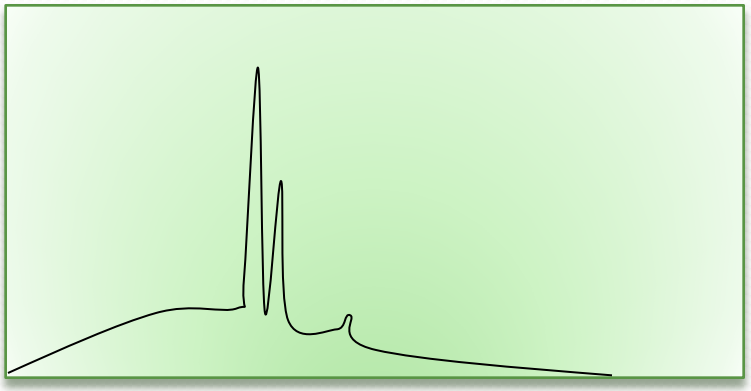
PEO Pattern



Which is correct?

PEO pattern





A f integration is a solution but you loose all the orientation information.

This corresponds to what the database says PEO looks like, but it tells you nothing beyond it is PEO

Polymer crystal structure

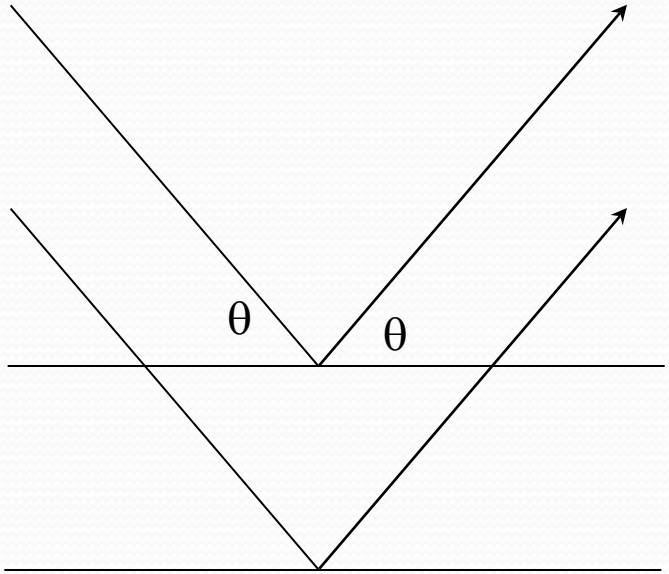
- WAXS is used to determine the crystal structure.
- The principle is basically that due to Bragg
- That a series of crystal planes gives rise to a scattering maxima (spot) in reciprocal space
- The position of these spots is given by the Bragg equation.

$$n\lambda = 2d_{hkl}\sin\theta$$

λ is the wavelength
n is the order 1,2,3,4…
d_{hkl} is the interplanar spacing for indices hkl
θ is the angle between the incident beam and the scattering plane, which is the same as the angle between the scattered beam and the plane.

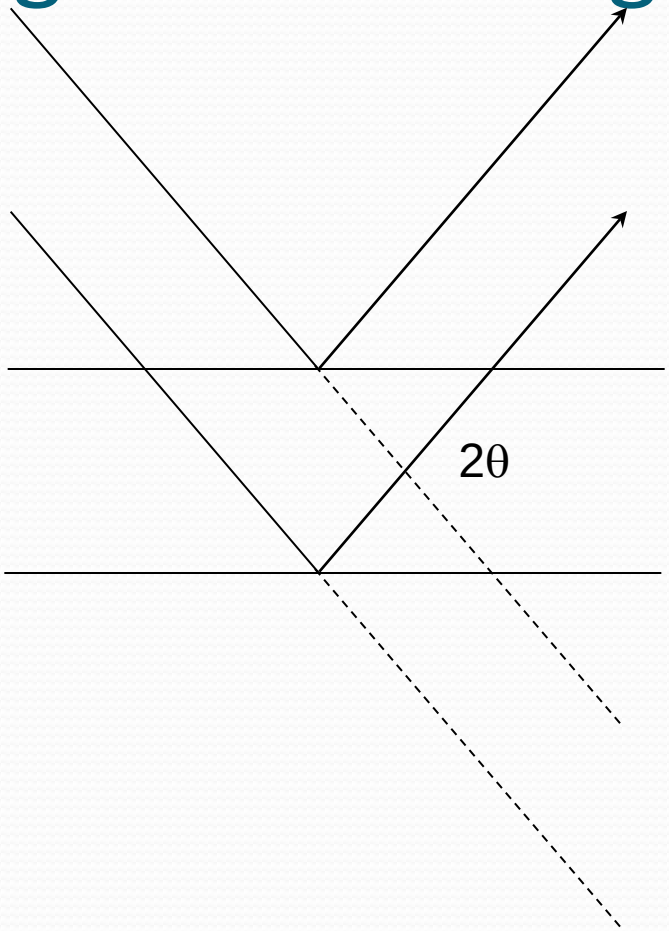
θ or how to confuse things in scattering

- Often in WAXS the same notation is used for two different things the most common case is the use of the Greek symbol θ (theta).
- For Braggs law



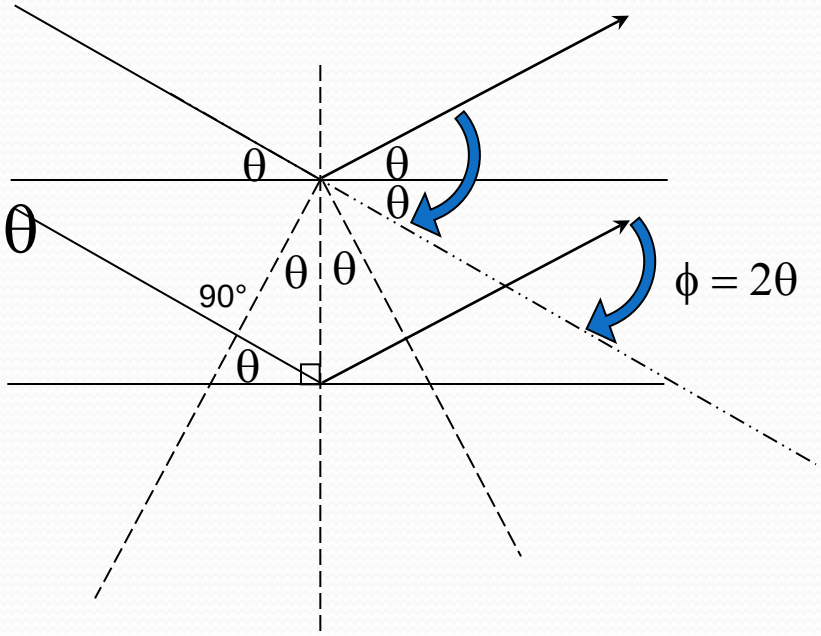
θ or how to confuse things in scattering

- For SAXS
- The scattering angle is defined as 2θ.
- In fact they are the same thing.



θ and 2θ

- Using simple trig.
- It is relatively easy to show that if the incident angle is θ then the scattering angle is 2θ.

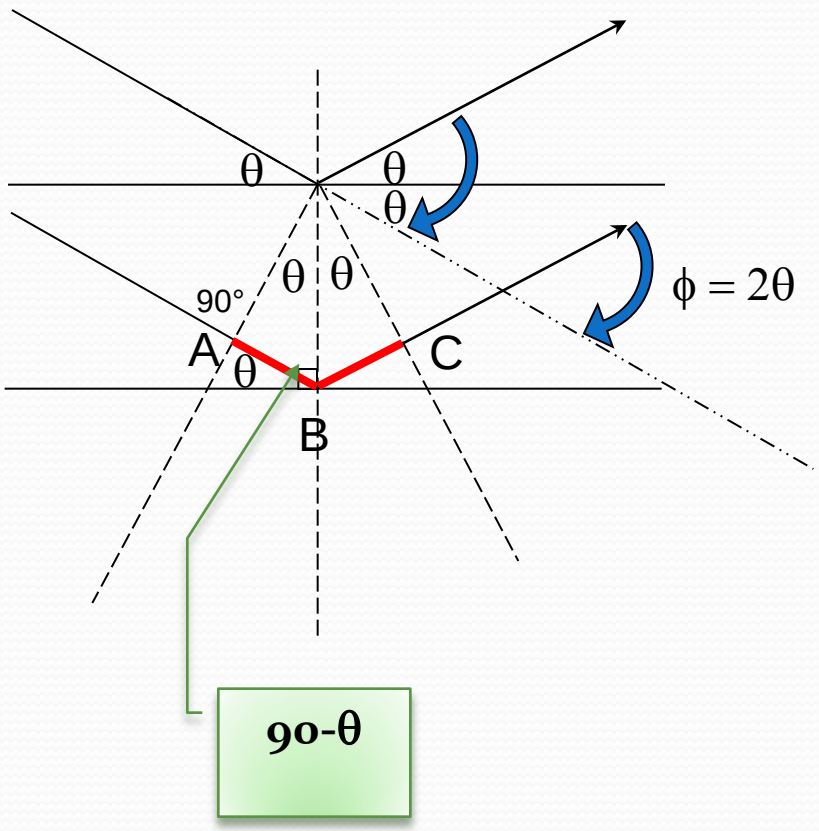


Back to Bragg

- So the scattering maxima (reflections) are dependent on the layer spacing of the planes.
- These planes have different discrete spacings depending on the lattice geometry.
- This results in missing reflections and these tell you about the internal structure of the unit cell.

Braggs law

- The extra path ABC is dsinθ.
- If this is a integral number of wavelengths (nλ)
  - Then there will be constructive interference.
- Therefore, a given reflection can be indexed to a diffracting plane

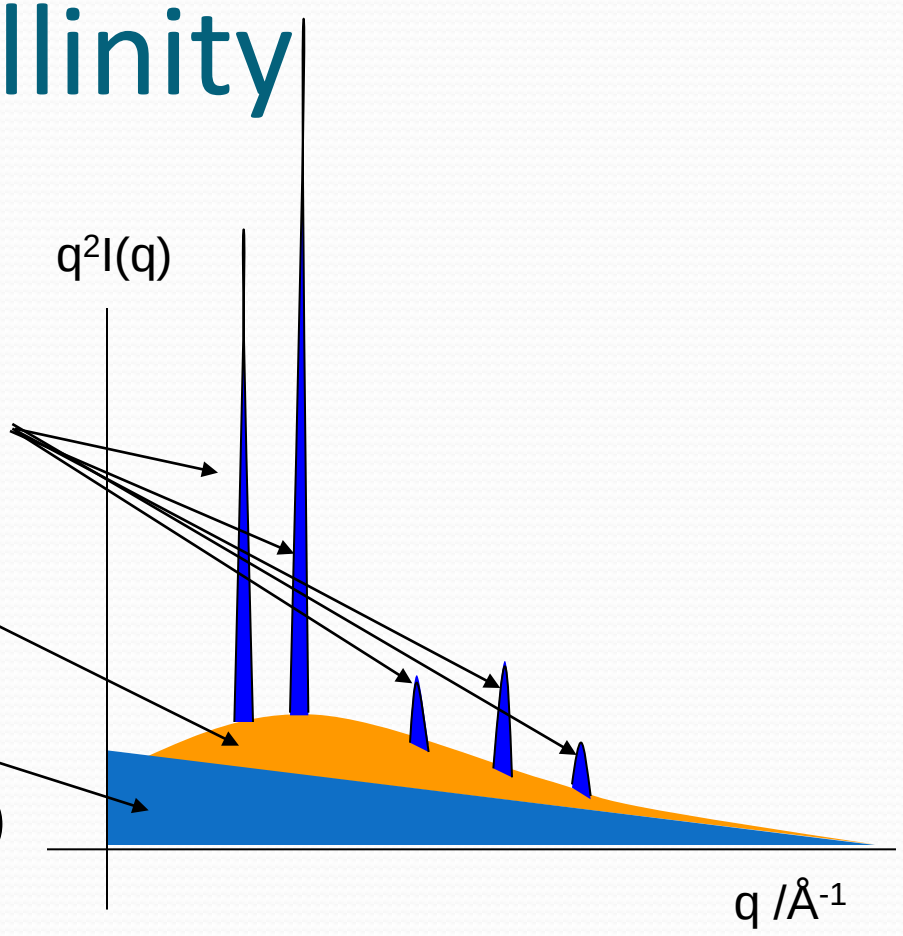


Degree of Crystallinity

- If the Bragg peaks are from the crystal then you should be able to calculate he degree of crystallinity from the WAXS pattern.
- In principle this is possible however the accuracy is not that good and its best limited to comparable measures.
- SAXS, density and DSC give more reliable answers.

Degree of Crystallinity

- The idea is that you can break the scattering up into regions.
  - One from the crystals (C)
  - One from the amorphous (A)
  - And one from incoherent scatter. (IS)
- Then the ratio of C/(C+A) gives the degree of crystallinity.

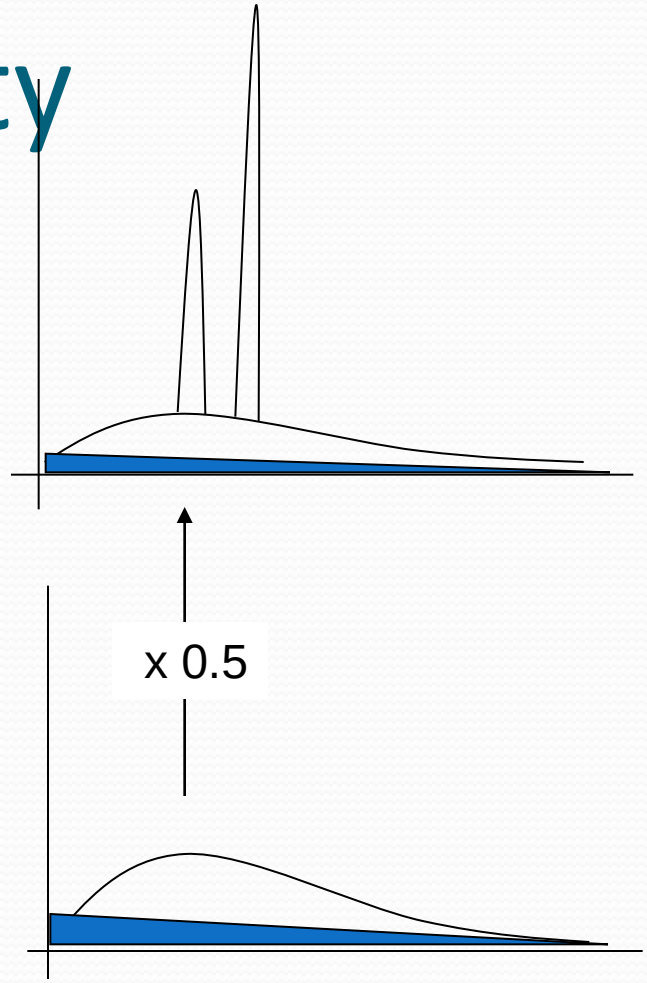


Degree of Crystallinity

- The problem with this method is that its difficult to determine the exact curve of the incoherent scatter.
- Ruland does give a functional form
  - W. Ruland Acta Cryst 14 1180 (1961)
- But this is not exact.
- Therefore the method is best limited to comparing the effects of processing on a given material.

Degree of Crystallinity

- The next option is to measure a completely amorphous sample (quenched from high temperature)
- Use this as a background to establish the correct form of the amorphous halo and the incoherent scatter.
- Then perform the calculation of crystallinity as before.



WAXS and Crystallinity

- Most people seem to think that WAXS is good at determining the degree of crystallinity
  - ITS NOT.
  - Because of the uncertainty in the incoherent scattering.
  - There have been many attempts to overcome this with varying degrees of success.
  - If I were asked to determine the degree of crystallinity I would use a DSC.
    - But of course this only works for a thermoplastic material, but most thermosets are amorphous anyway. In this case use SAXS and correlation function.

WAXS and Structure

- What WAXS is very good at is structure
  - Not the amount of structure
  - But what structures you have
    - How the atoms pack in the crystal
    - How big the crystals are
    - What orientation the crystals are in
    - What preferred growth directions occur in the crystals.
  - For this information POLE figures are required.
    - Pole figures have a reputation as a specialist technique and require a 3 circle goniometer for the diffractometer.

Orientation in polymers

- Terms:
  - For an extruded film:
    - Machine direction: Direction the film/fibre comes out of the extruder (MD)
    - Transverse direction: Perpendicular direction, parallel to the film surface (TD)
    - Normal direction: Perpendicular direction normal to the film surface (through the film) (ND)
    - For a blow moulded film MD and TD show similar orientation as the extension occurs simultaneously.
    - For stenter films MD usually shows more orientation than TD
  - For a cast sample
    - Flow direction: Not as well defined as for films as flow tends to be divergent in a die.
  - To determine orientation of crystals POLE figures are used.

Small Angle X-ray Scattering

SAXS
(Small Angle X-ray Scattering)

- SAXS can measure the lamella spacing in a semi-crystalline polymer.
  - SAXS can do much more but due to time limitations this will be the main subject.
- SANS can also measure it.
- The position of the diffraction maximum is related to the lamella d spacing.
- The larger d the smaller the angle the scattering appears at.

SAXS

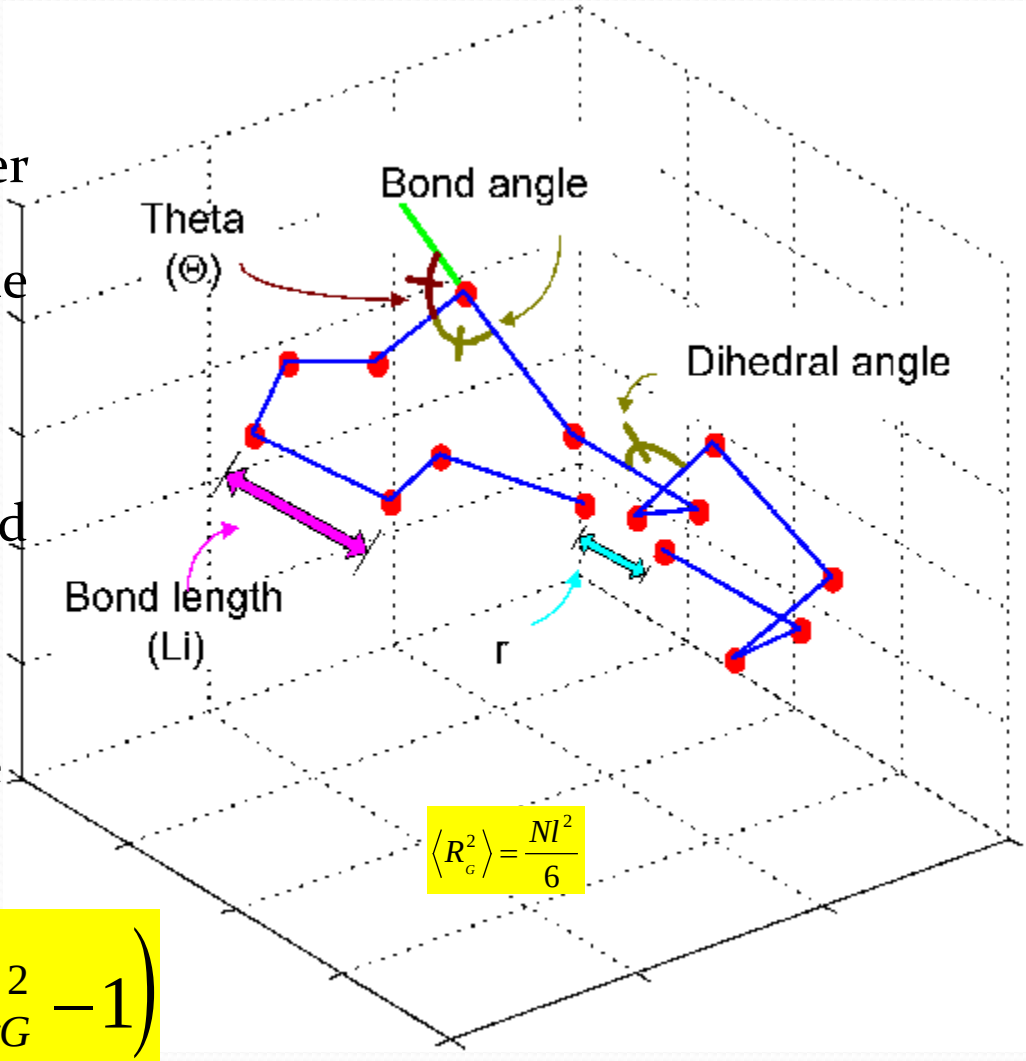
- In SAXS you would normally measure the scattered intensity (I) as a function of q rather than θ (angle).
- Usually q has units of $Å^{-1}$ or nm^{-1} (reciprocal Angstrom or reciprocal nanometres)
  - $1Å = 10^{-10}m$ (Angstrom) $1Å^{-1} = 10^{10}m^{-1}$
  - $1nm = 10^{-9}m$

Guinier Model

- Ideal Chain (in the melt or in solution)
  - Freely jointed chain
  - Self avoiding random walk
  - Restricted bonds
  - Real chain

Polymer Coil

- The simplest model of a polymer is the freely jointed chain. Here the bond angles can be any value (even 0°).
- It's chemically not particularly accurate but it does give a reasonable model of the size and shape of a polymer molecule.
- R_G is the radius of gyration, and measures the average distance from a point on the chain to the centre of mass.



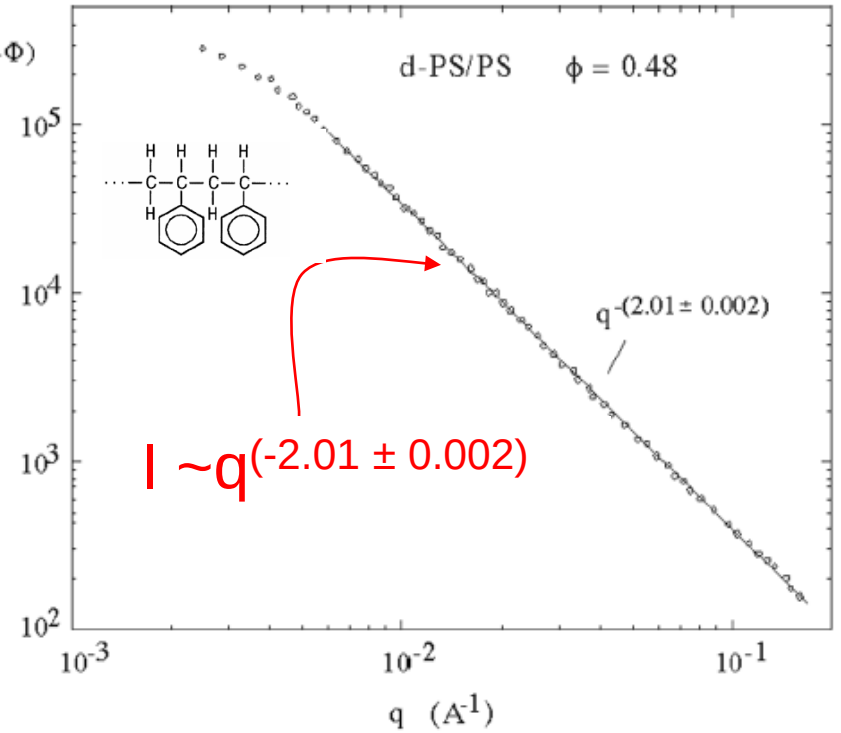
$$P(q) = \frac{2}{\left(q^2 R_G^2\right)^2}\left(e^{-q^2 R_G^2} + q^2 R_G^2 - 1\right)$$

Debye (1947)

Guinier Approximation

- For qRg<<1 (very much less than 1, i.e. 0.1 or less)
- Clearly the intercept is only valid if the Intensity units are absolute.
- You can calculate the size of the chain in solution.
- SANS: You can calculate the size of a hydrogenous polymer in a deuterated one: Natural size of the polymer.
- Gradient gives -$Rg^2/3$

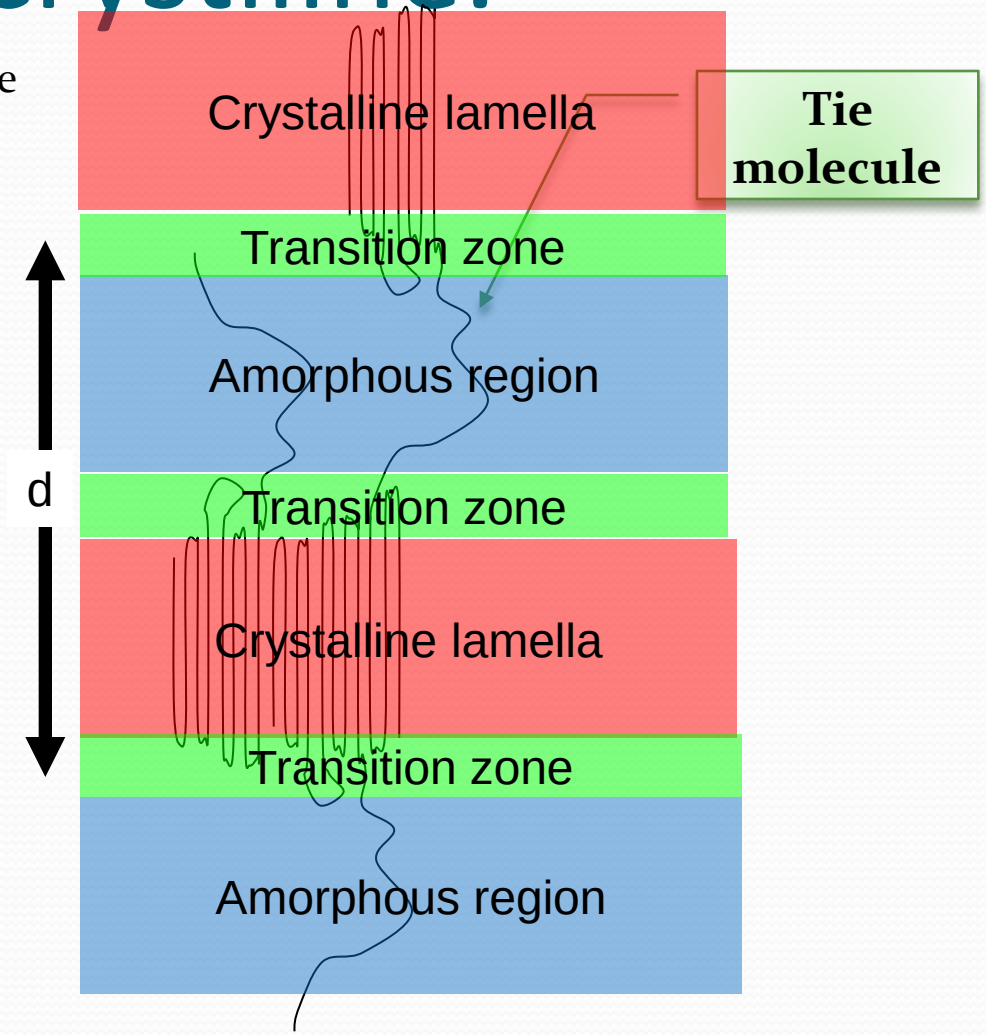
$$\ln(I(q)) \approx \frac{-q^2 R_G^2}{3} + M\frac{\phi(\eta)^2}{N_A \rho}$$



scattered intensity for a melt of h- and d-polystyrene (from Schwahn, 1991 using SANS)

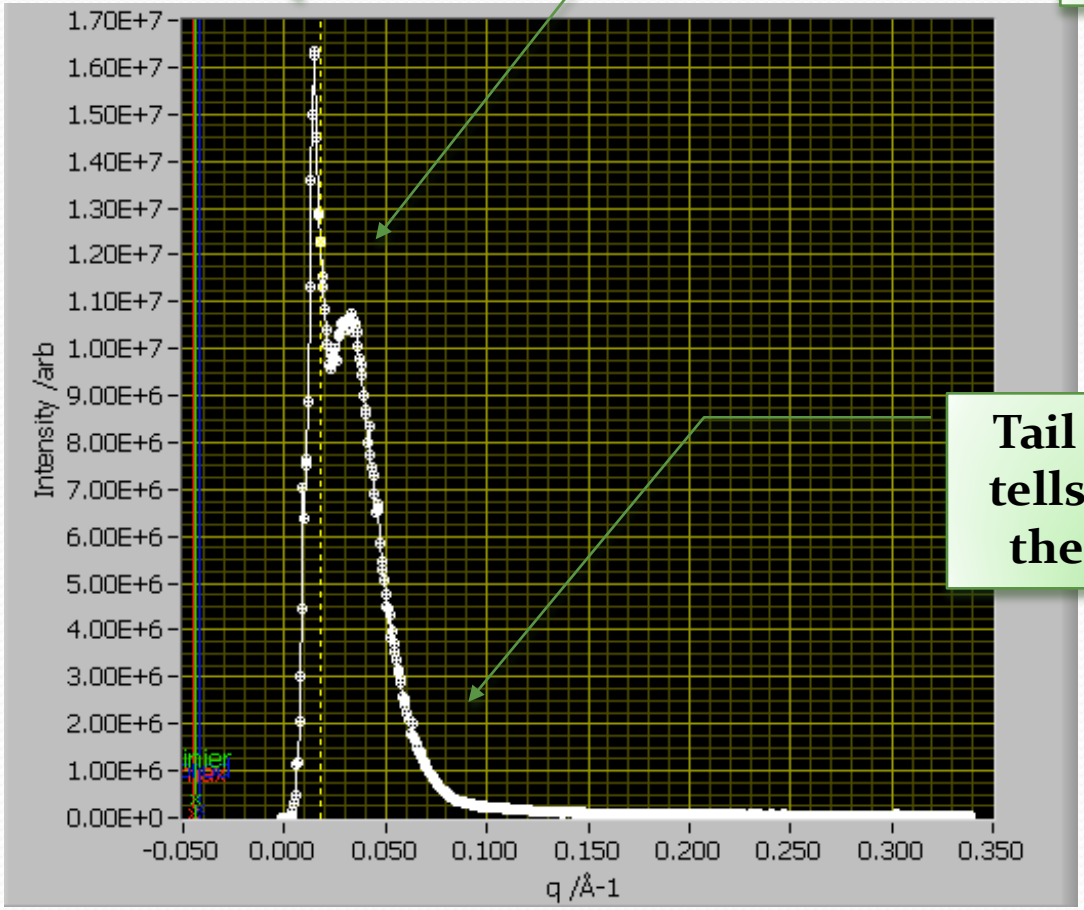
Lamella Semi-crystlline.

- SAXS measures the d spacing (d in the picture)
- The crystal does not have perfect edges, they are made up of folded chains
- There is a small transition zone from pure crystal to amorphous (greatly exaggerated on this slide)
- In addition not all the lamella will be the same size.
- As a result the SAXS peak is broadened.
- To determine the crystal morphology the correlation function is used.
  - See Strobl, G. R. and Schneider, M. J., *Polym. Sci.* (1980) **18**, 1343-1359
  - Also Strobl: The Physics of Polymers: Concepts for Understanding Their Structures and Behavior



Scattering close to beam stop not a real peak

Scattering peak due to lamella structure

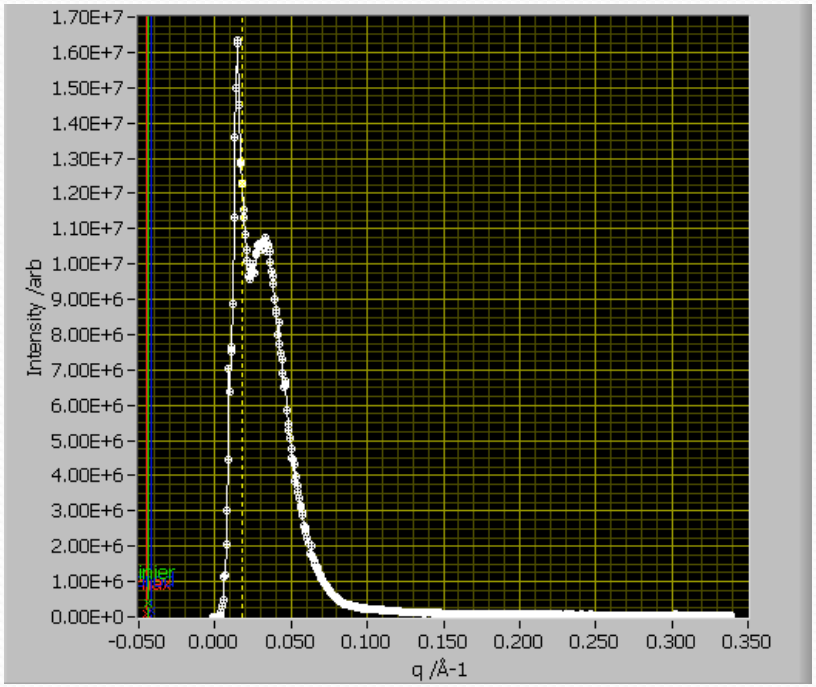


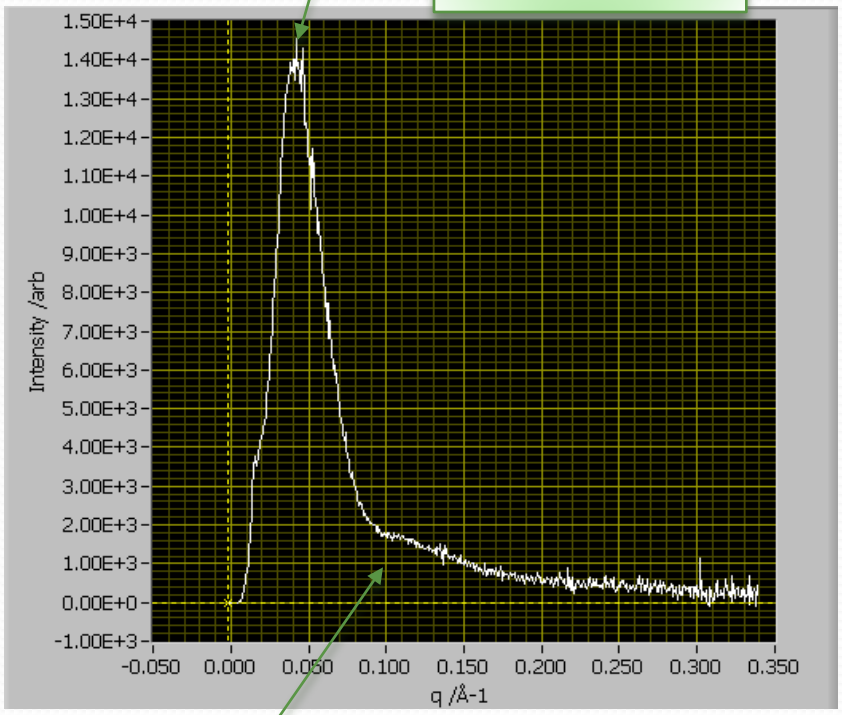
Tail scattering tells you about the interface

Lorentz Correction

- There is a problem with scattering from 1 D stuff.
- Scattering is a 2D representation of a 3D system.
- Therefore the I(q) data from SAXS will give the wrong structural information.
- To resolve this issue the data must be multiplied by q^2first.
- This is termed the Lorentz correction.

Lorentz Correction





D spacing from this peak

Weak second order can now be seen

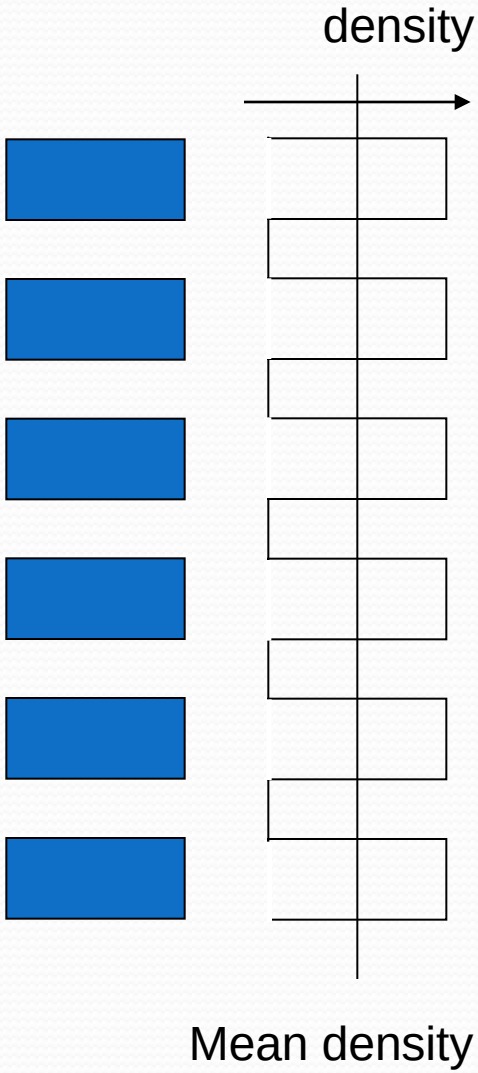
$D=2\pi/q^* = 2\pi/0.045 = 155Å$

SAXS

- But just finding the d spacing tells you very little and you are throwing away a lot of information if this is all you do.
- To extract more information you should run a correlation function analysis.

Correlation function

- The one dimensional correlation function is useful for determining the structure of a semi-crystalline polymer.
- It assumes that the scattering is due to a linear arrangement of lamella stacks.
  - While this may not always be the case it can still be applied to most semi-crystalline polymers.



Correlation function

- As the system only shows contrast in the z direction that's all we need to be concerned with.
- We need to perform a Fourier transform on the scattering data to obtain the correlation function.

$$K(z) = \frac{1}{k}\int_{\infty}^{0} e^{iq.z}\, 4\pi q^2 I(q) dq$$

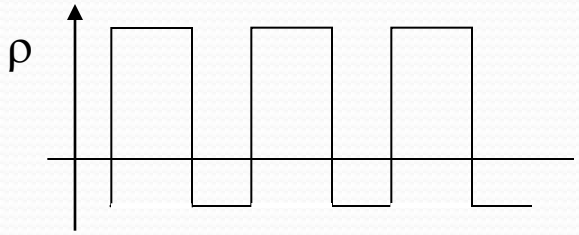
Symmetry

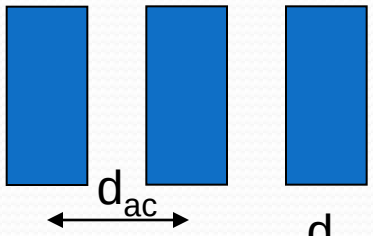
- As the structure is periodic in the z direction we can fold it in half and simplify the maths.
- This cosine transformation relies only on the fact that the structure is periodic.

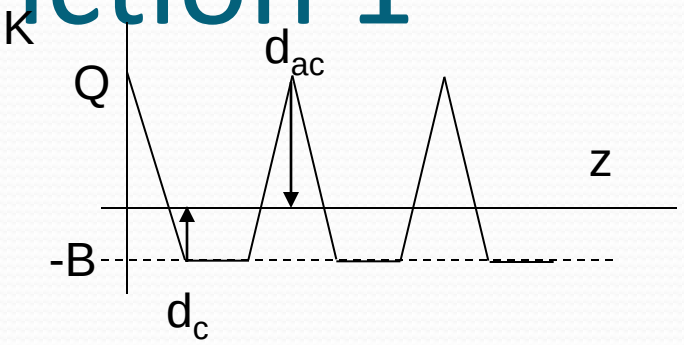
$$K(z) = \frac{1}{k}\int_{-\infty}^{\infty} e^{iq.z}\, 4\pi q^2 I(q)\, dq$$

$$= \frac{2}{k}\int_{0}^{\infty} \cos(q.z)\, 4\pi q^2 I(q)\, dq$$

Correlation function 1







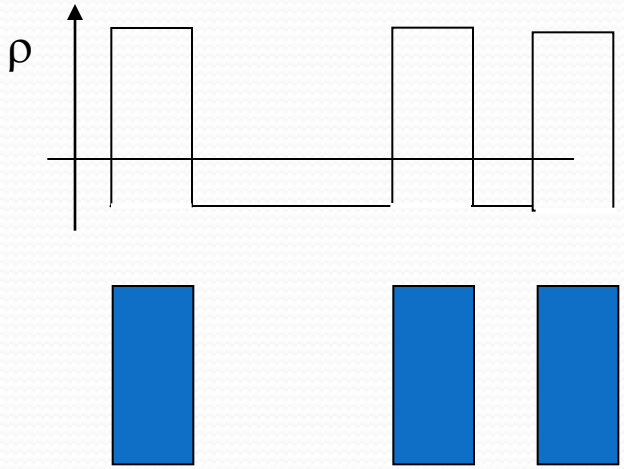
$$-B = \phi_c^2\left(\rho_{ec} - \rho_{ea}\right)$$

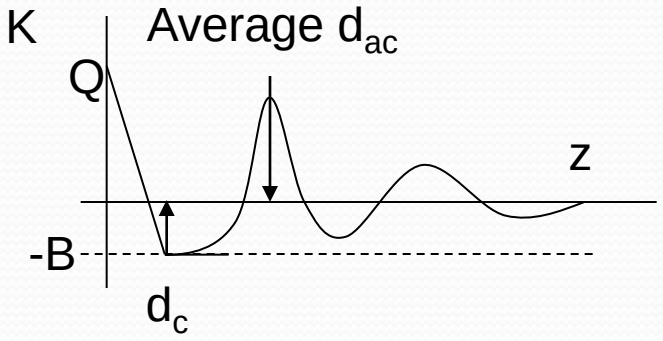
$$Q = \phi_c\left(1-\phi_c\right)\left(\rho_{ec} - \rho_{ea}\right)^2$$

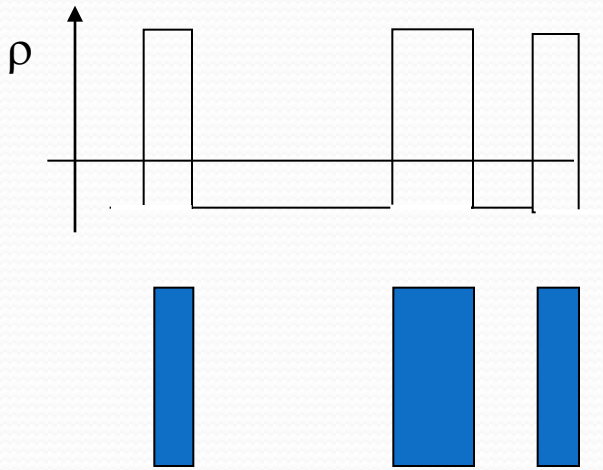
ρ_{ec} is the crystalline electron density
ρ_{ea} is the amorphous electron density
ϕ_c is the volume degree of crystallinity

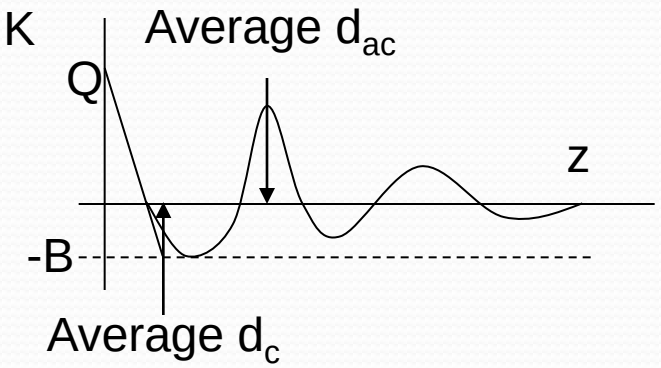
Q has a maximum at 50% crystallinity, this means that you can't tell the difference between 40 and 60%.
Similarly you cannot distinguish between the amorphous and crystalline d.
However DSC or WAXS should give you a clue.

Correlation function 2

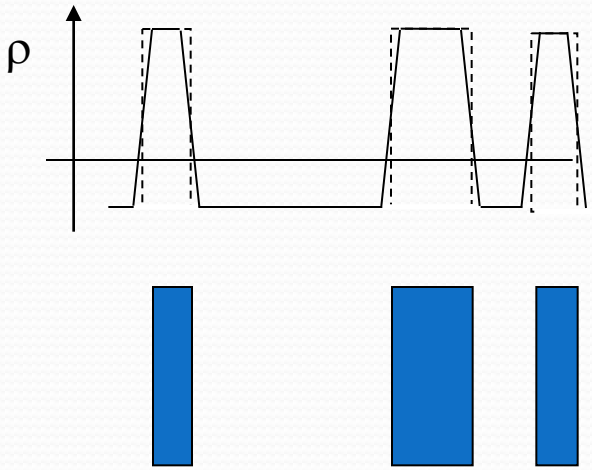


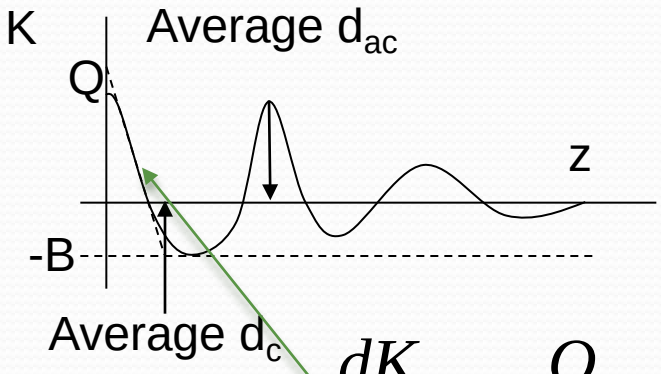






Correlation Function 3





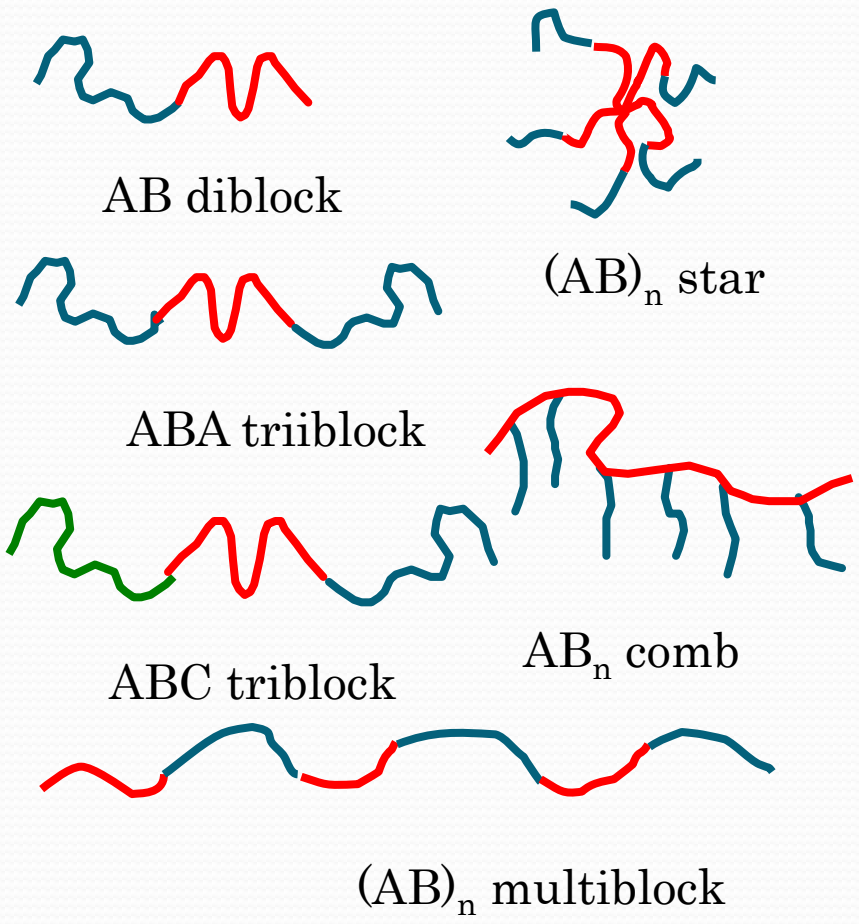
$$\frac{dK}{dz} = -\frac{O_{ac}}{2}\left(\rho_{ec} - \rho_{ea}\right)^2$$

Slope gives Oac the "specific internal surface". Area per unit volume of the interface separating crystalline and amorphous regions.

Block Copolymers

Block Copolymers

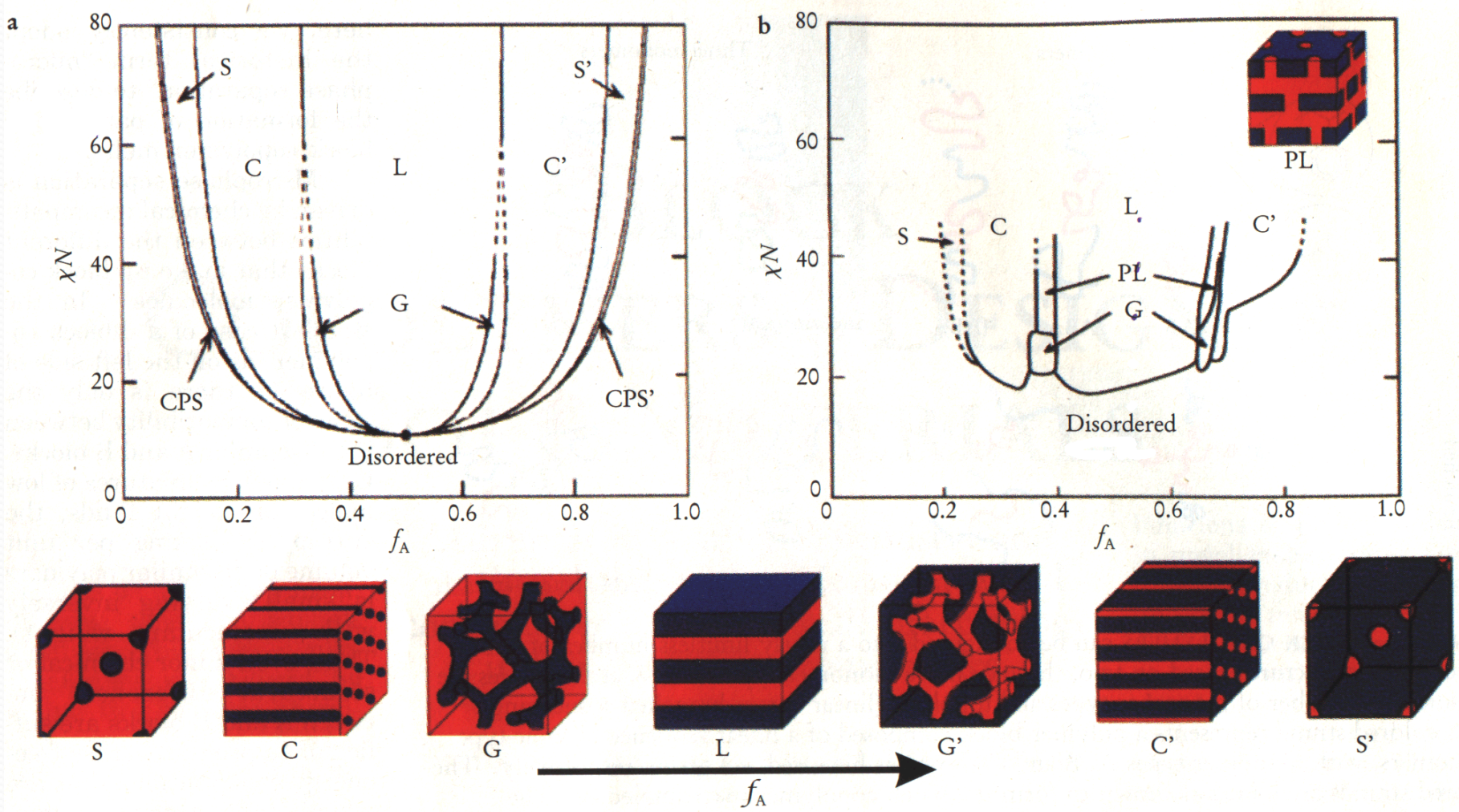
- Chemically linked polymers
  - Polymers phase separate
  - Linked so separation is limited
  - Microphase separated
    - Domains are few nanometers in size
  - Heat them up and they mix → ODT
    - If Mn is not too big



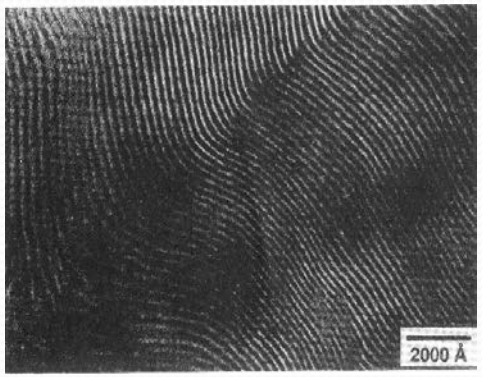
AB-Diblock copolymer phases

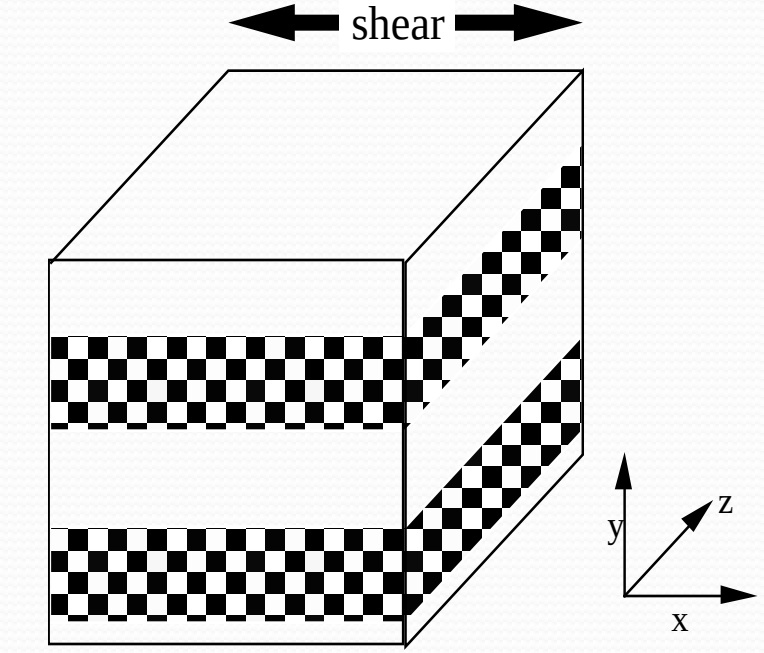
Matsen et al Macromolecules 1994,1996

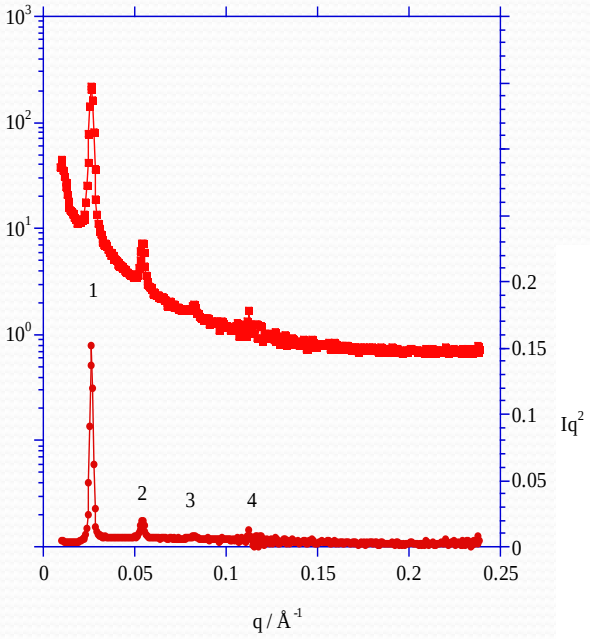
Khandpur et al Macromolecules 1995

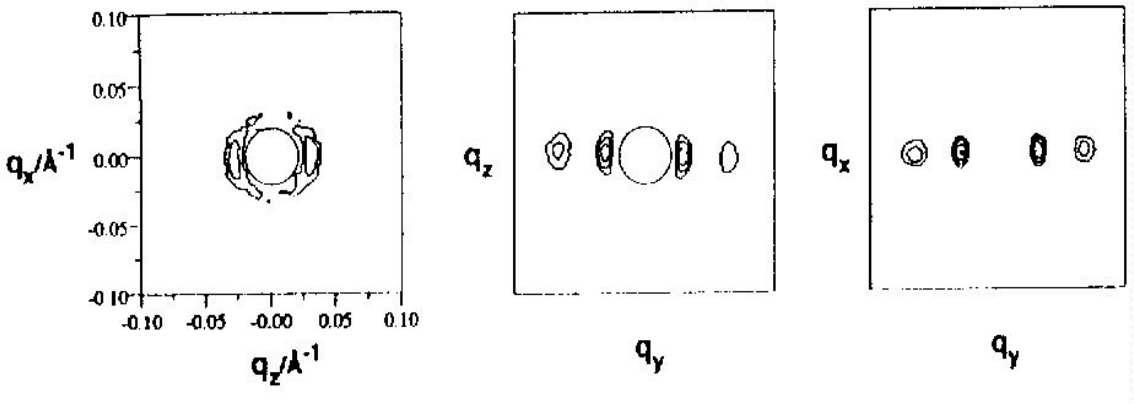


Lamellar





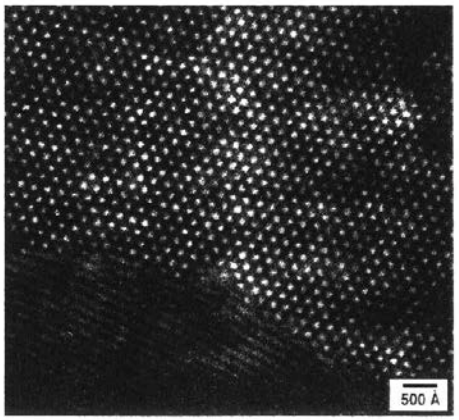


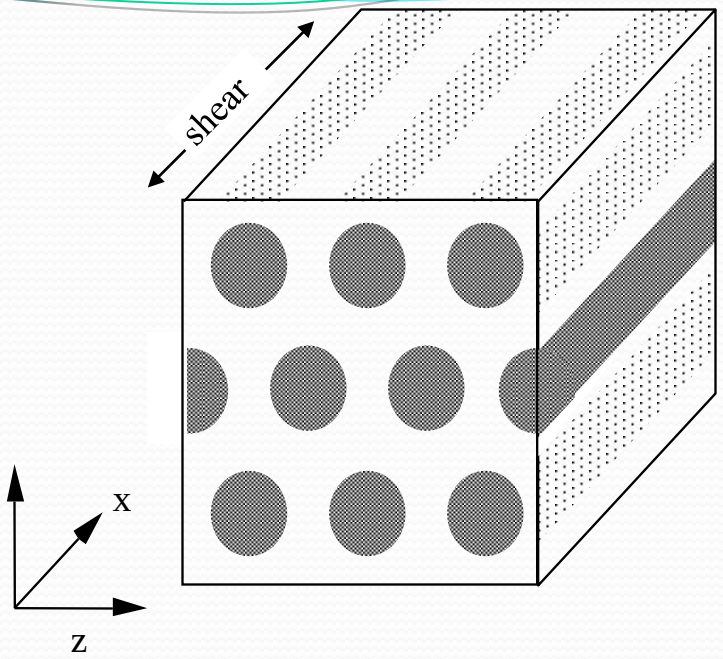


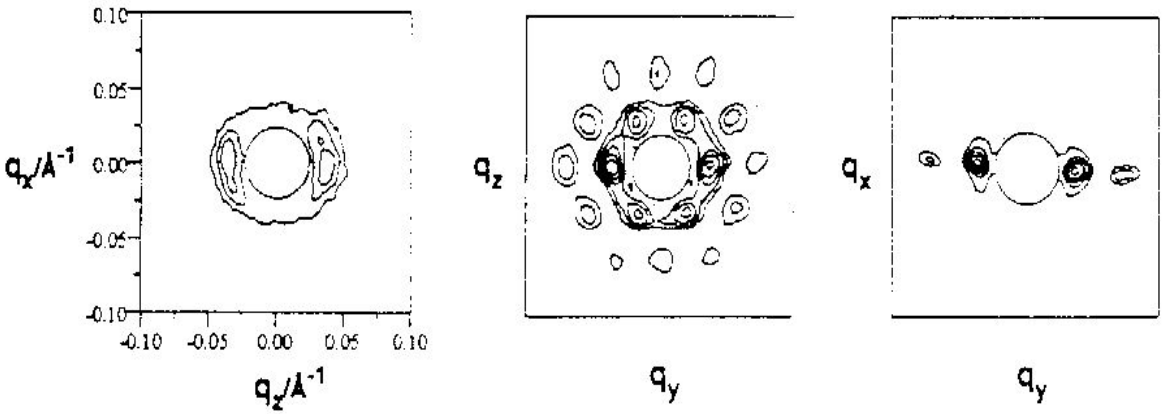
Schultz et al Macromolecules 1995

Hexagonal

- $q^*, \sqrt{2}\,q^*; \sqrt{3}\,q^*; \sqrt{4}\,q^*$

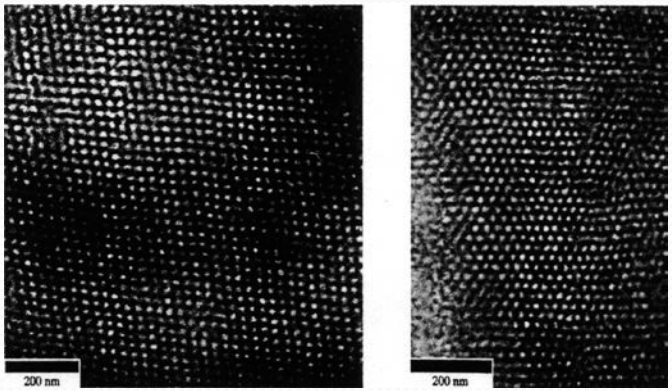




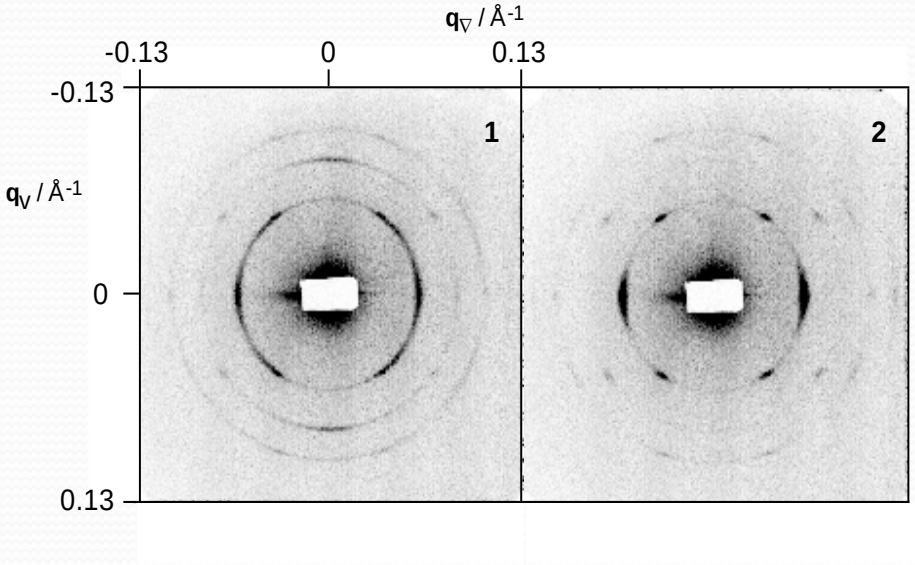


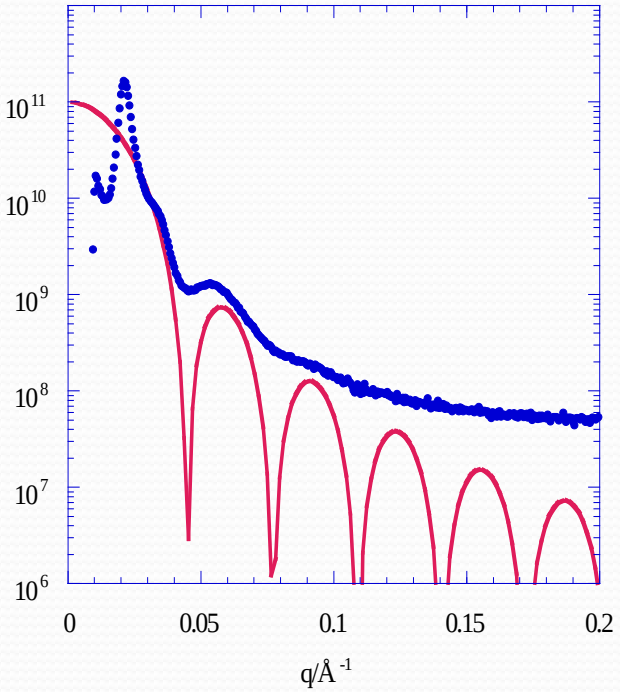
Schultz et al Macromolecules 1995

BCC Cubic

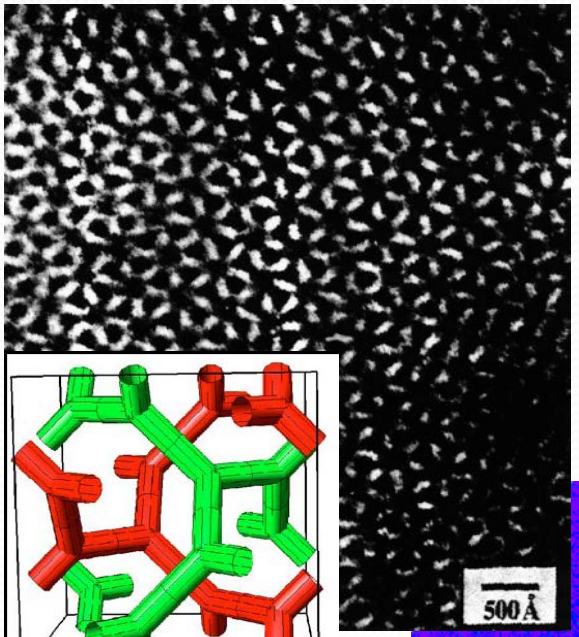


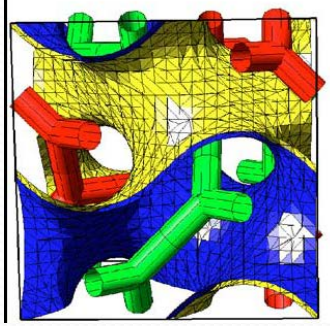
- $I(q)=S(q)P(q)\eta^2$
- BCC "sum is even"
- 110 = q*; 200 =$\sqrt{2}$ q*;
- 211 =$\sqrt{3}$ q* etc…

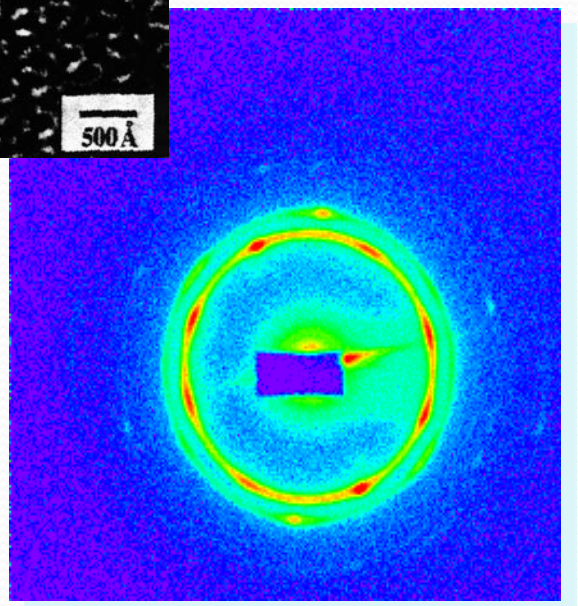




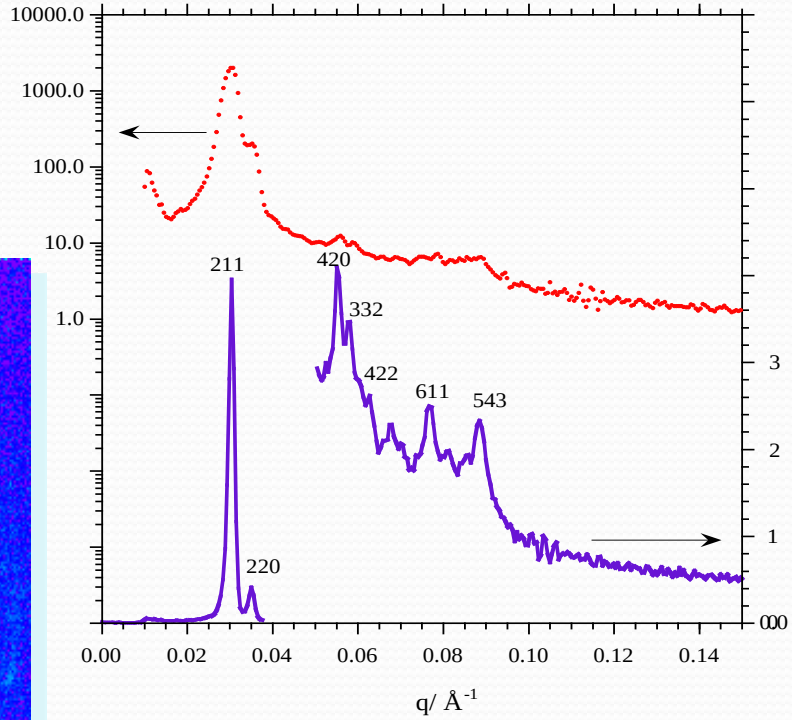
Ia3d “gyroid”





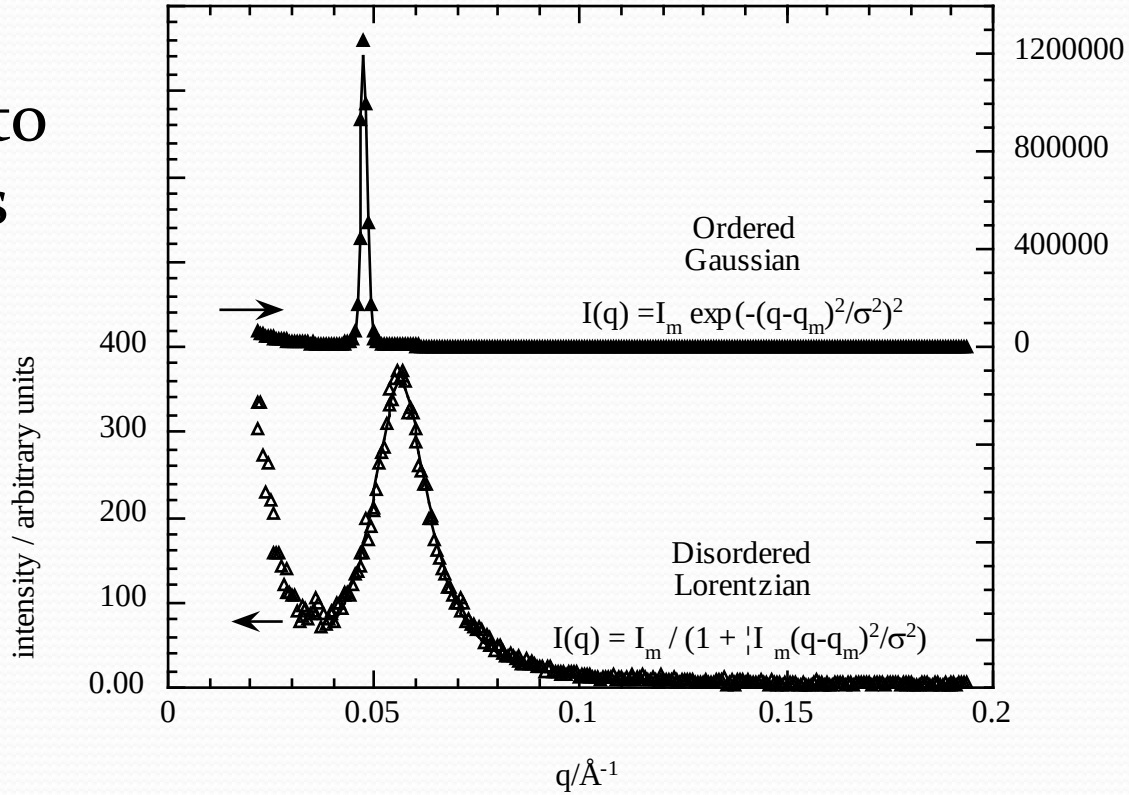


- Beware the “eye of faith”



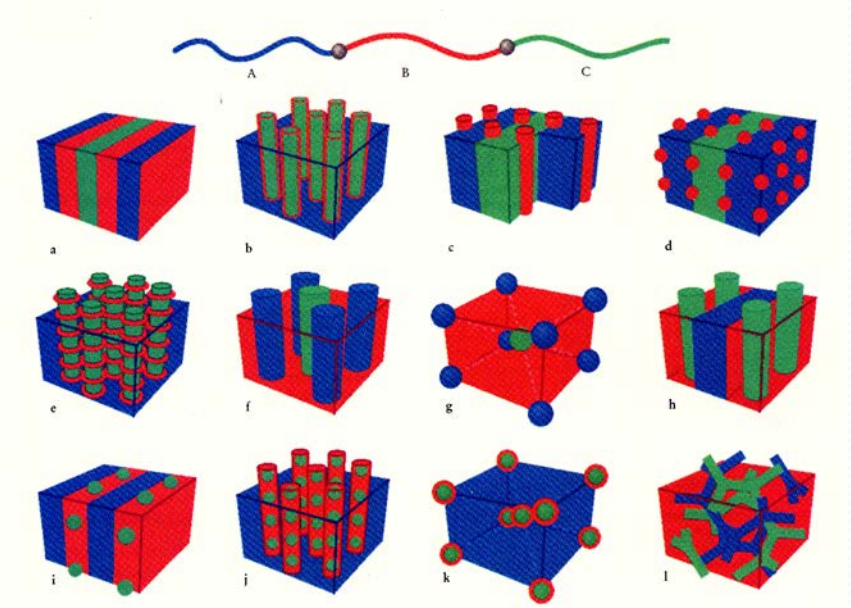
Order to Disorder

- Not always this clear
- Glassy: eg PS tends to produce broad peaks that change slowly.
- Why only one peak
- Interface: sine wave



ABC phases

- ABC triblock.
- Stamp collecting to some degree
- But good for volume of papers.



Reference Books

- Leroy E. Alexander: X-ray Diffraction Methods in Polymer Science
- Otto Glatter and Kratky: Small Angle X-ray Scattering
- H.P. Krug and L.E. Alexander X-ray Diffraction Procedures
  - All of these are old and out of print.
  - But any good library will stock at least two of the three.
- I have yet to find a good new book (one still in print) on the subject.
  - **Methods of X-ray and Neutron Scattering in Polymer Science (Topics in Polymer Science S.)**
    by Ryong-Joon Roe is OK
- Light Scattering: From Dover publications old but still available:

The End

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