Correlation Function

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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.

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.
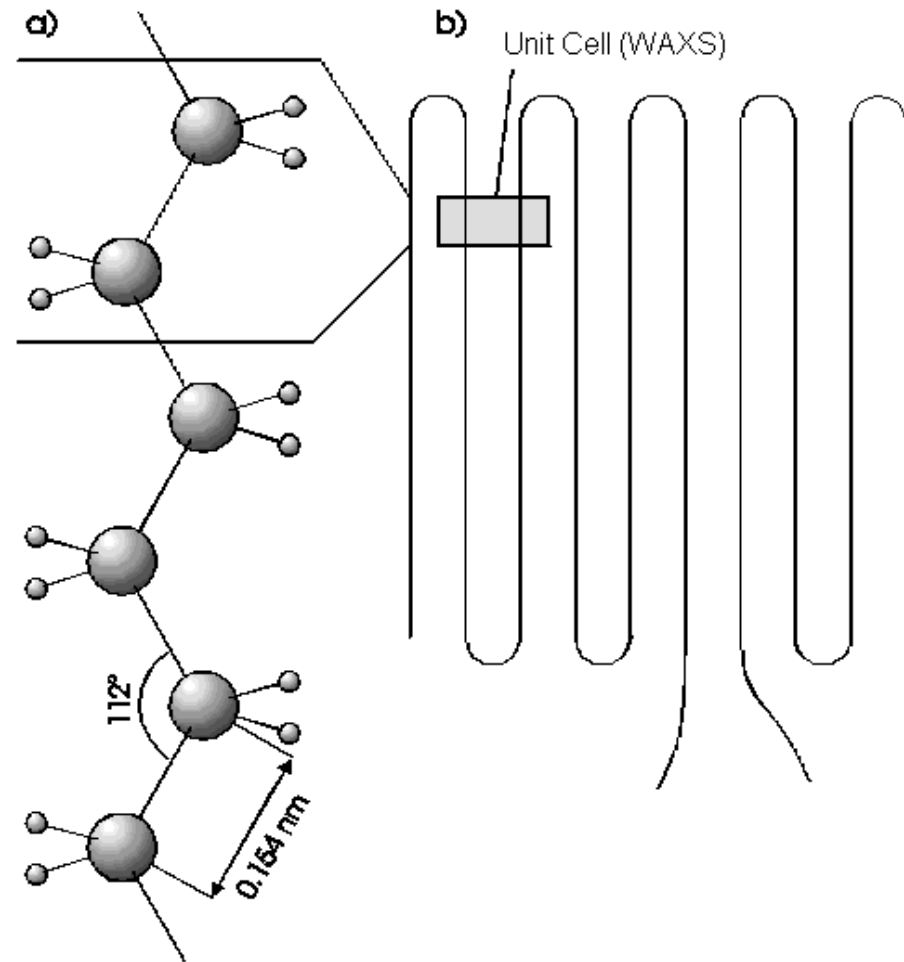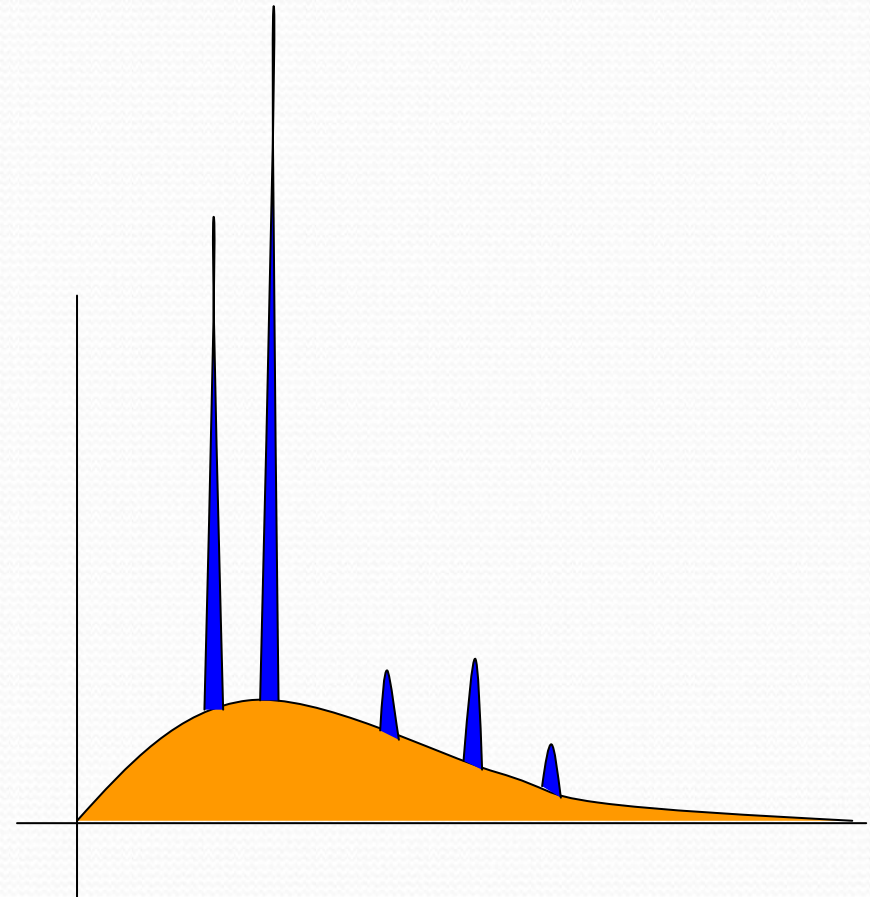
WAXS

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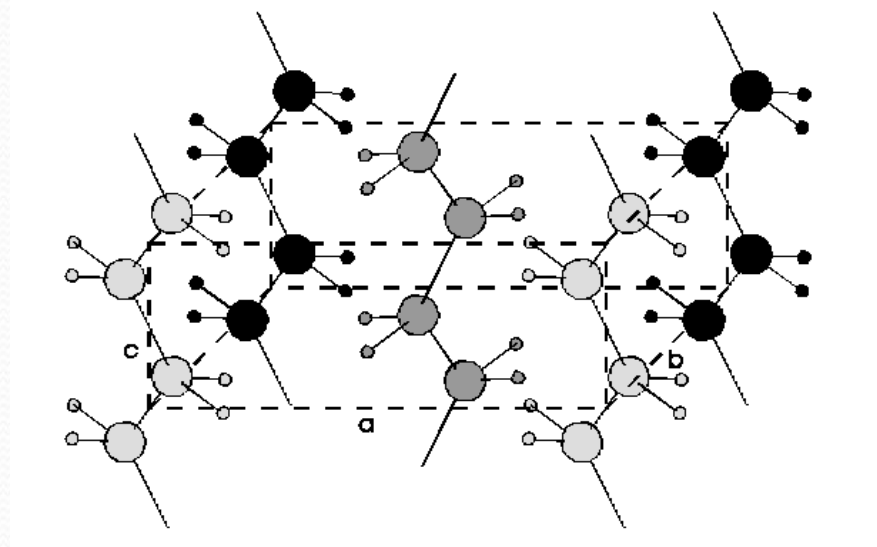
$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2}h^2 + \frac{1}{b^2}k^2 + \frac{1}{c^2}l^2$$

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 and possibly pole figures.
    - The performs a fit to the pattern and determines a,b,c and the predicted intensities.
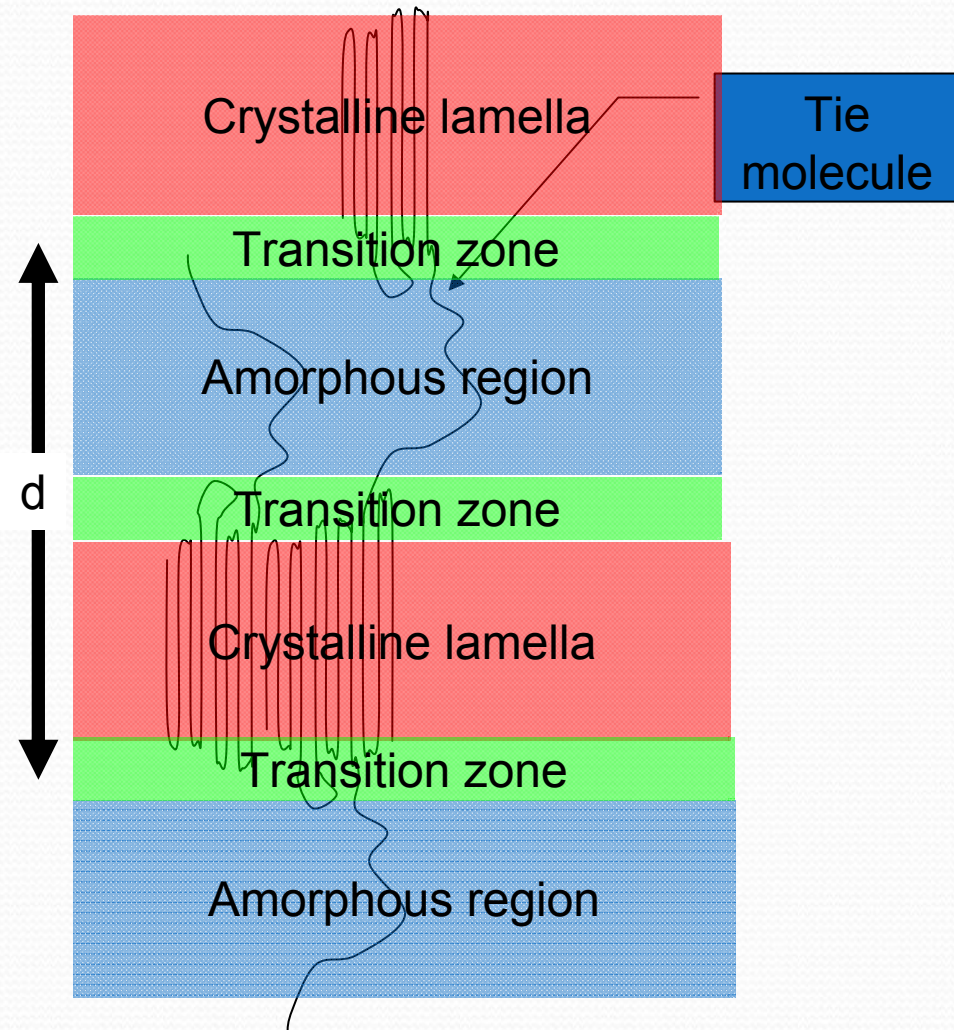
WAXS

- To perform any meaningful analysis via WAXS the polymer should be very crystalline.

- 70% is a very crystalline polymer

- 40% you will struggle to find more than one or two peaks

- Less than this and you are pushing the boundaries.

- There are some people who use WAXS to study amorphous systems, but I'm not one of them.

SAXS

- SAXS is ideal for studying polymers as the length scales of SAXS overlap those of semi-crystalline polymers.
- The following correlation function analysis is commonly applied to semi-crystalline polymers (see Strobl's book)
- However, it is equally applicable to any two phase system and is often used in polyurethane (PU)systems.
  - Ophir, Wilkes, *J Poly Sci Poly Phys Ed* 1980 **18** p1469
- It assumes a lamella morphology, but this is not as stringent as you may think, as PU is locally lamella.

Lamella

- 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

Crystalline lamella

Tie molecule

Transition zone

Amorphous region

d

Transition zone

Crystalline lamella

Transition zone

Amorphous region

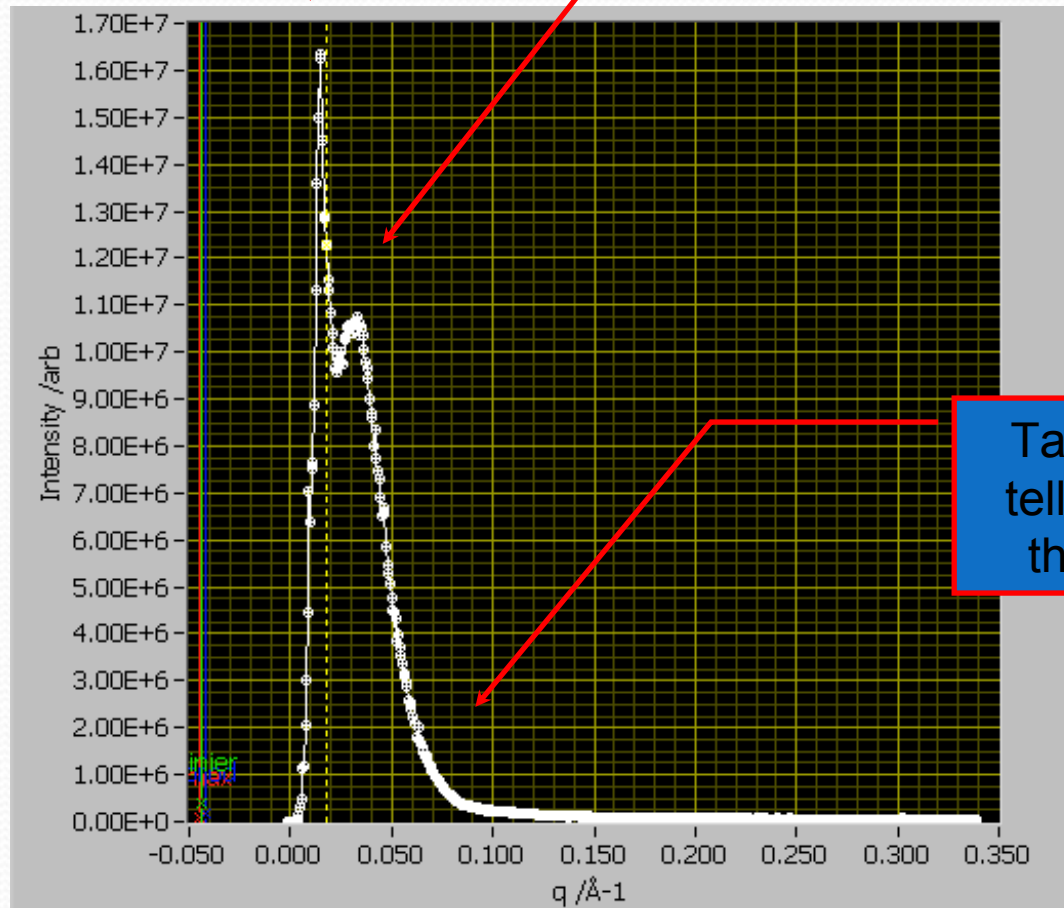# SAXS
(Small Angle X-ray Scattering)

- 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)
  - $1\text{Å} = 10^{-10}\text{m}$ (Angstrom) $1\text{Å}^{-1} = 10^{10}\text{m}^{-1}$
  - $1\text{nm} = 10^{-9}\text{m}$

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^2 first.
- This is termed the Lorentz correction.

Lorentz Correction
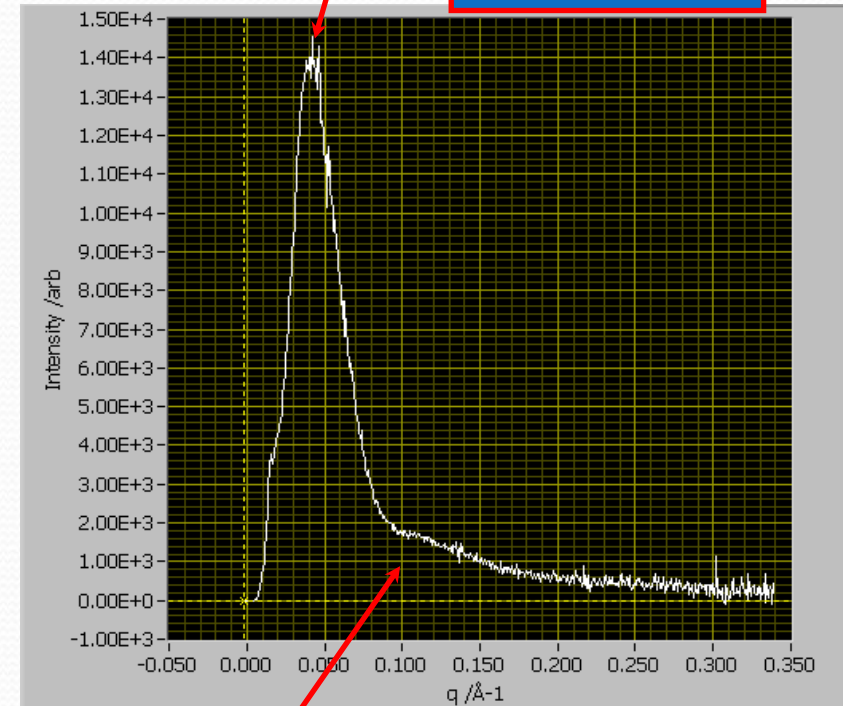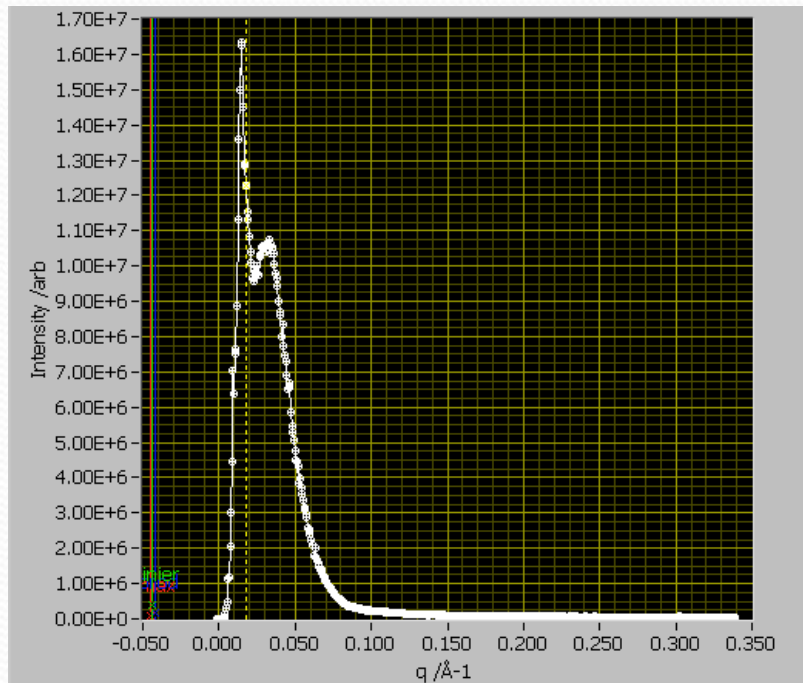
D spacing from this peak

Weak second order can now be seen

$D \approx 2\pi/q^* = 2\pi/0.045 = 155\text{Å}$

14

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

density

- 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.

Mean density

16
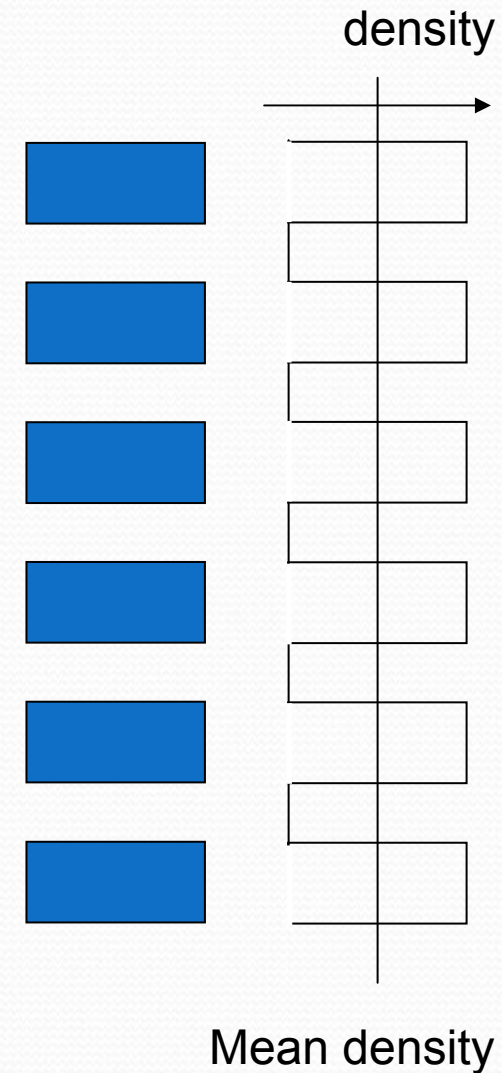
Correlation function

- 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.

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

LIMITS→ extrapolation of data is problematic.

Correlation function limits

- LOW Q
- Usually Guinier
- Ignore the first 5 points from the beamstop
- Check the output
  - Element of skill/experience

- HIGH Q
- Usually Porod
- Ignore the very high q
- Use tail end of a broad peak→ problems with sharp peaks.
- Check the output
  - Again experience

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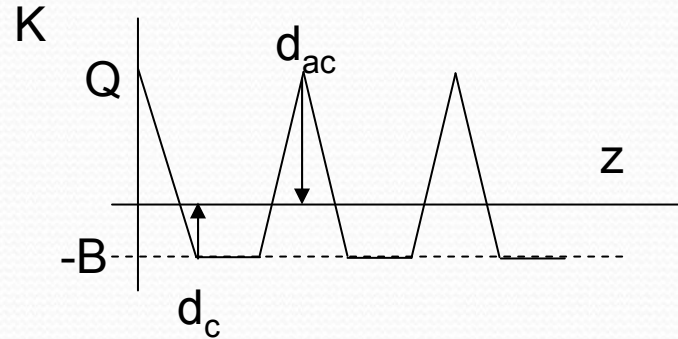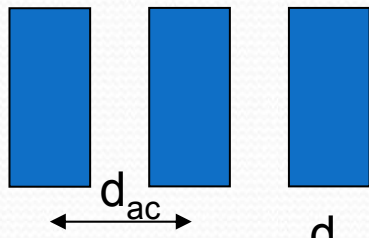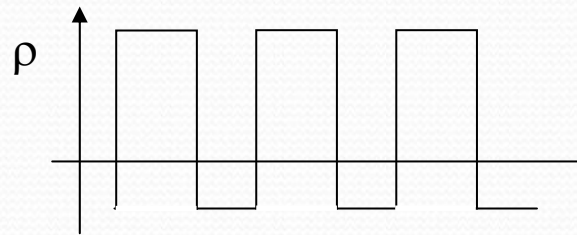
$$ -B = \phi_c^2 \left(\rho_{ec} - \rho_{ea} \right) $$

$$ Q = \phi_c \left(1 - \phi_c \right) \left(\rho_{ec} - \rho_{ea} \right)^2 $$
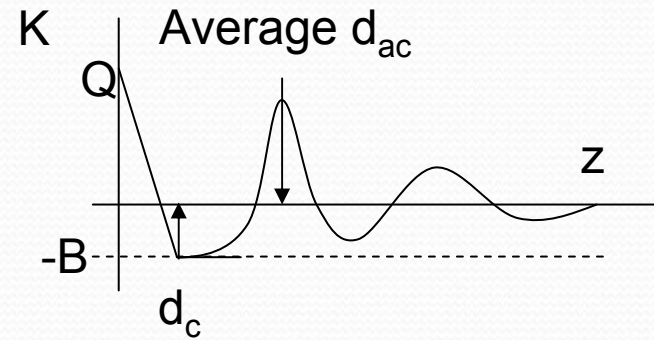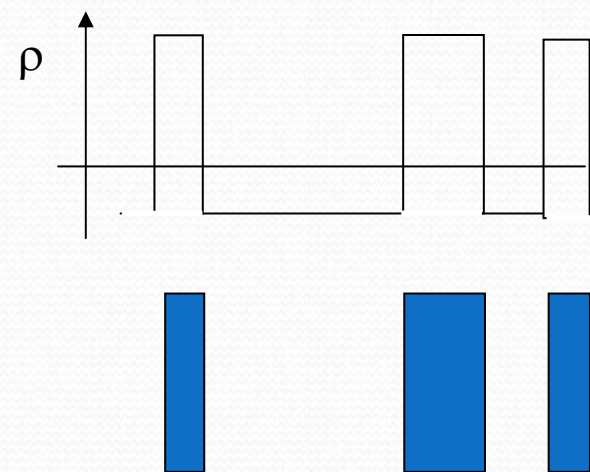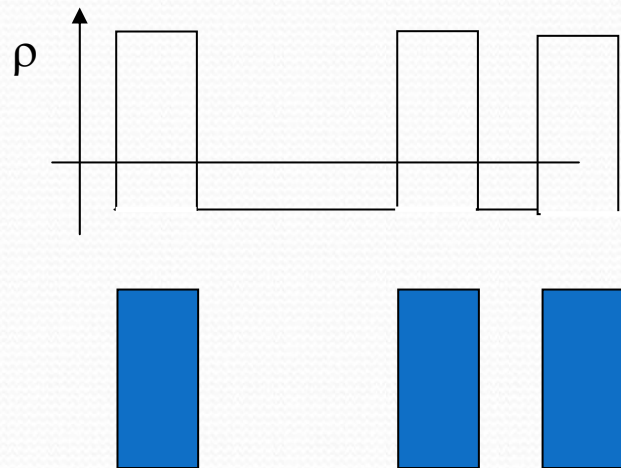
ρ_{ec} is the crystalline electron density
ρ_{ea} is the amorphous electron density
ϕ_c is the volume degree of crystallinity

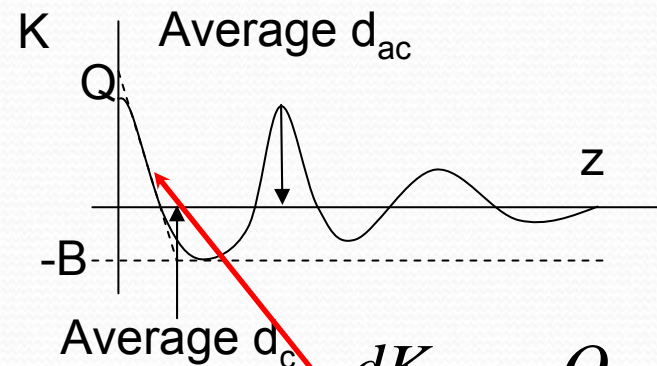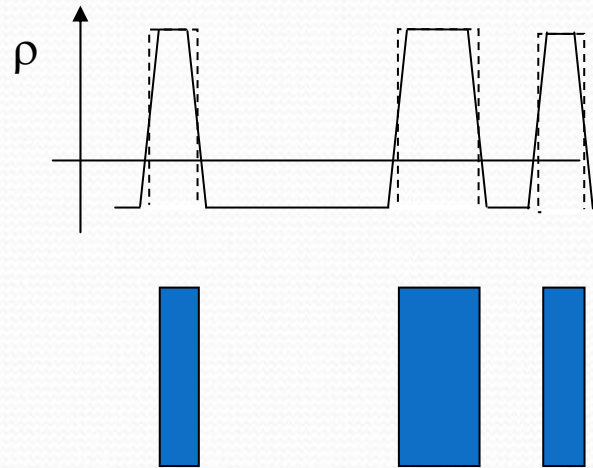Q has a maximum at 50% crystallinity, this means that you can't tell the difference between 40 and 60%.
Similarly you cannot distinguish between the amorphous and crystalline d.
However DSC or WAXS should give you a clue.

20

Correlation function 2
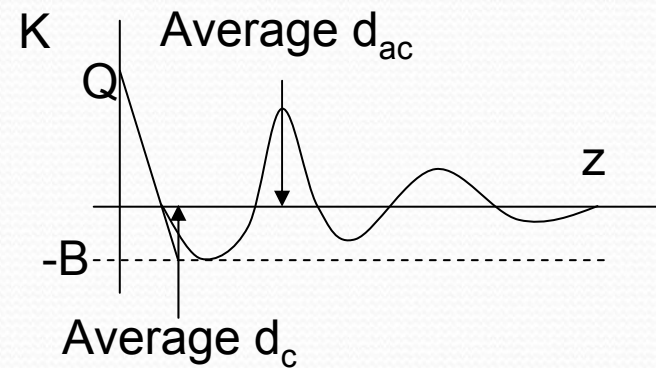
Correlation Function 3

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

Slope gives O_{ac} the "specific internal surface".
Area per unit volume of the interface separating crystalline and amorphous regions.

Good versus bad.

- A good correlation function will have 2-3 oscillations and asymptote to axis.

- If it does not asymptote then the Guinier probably is wrong→ move closer or further from the beamstop.

- Weak oscillations check the Porod fit and change the high q limit.

Crystallinity and WAXS

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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.

$q^2I(q)$

q /Å^{-1}
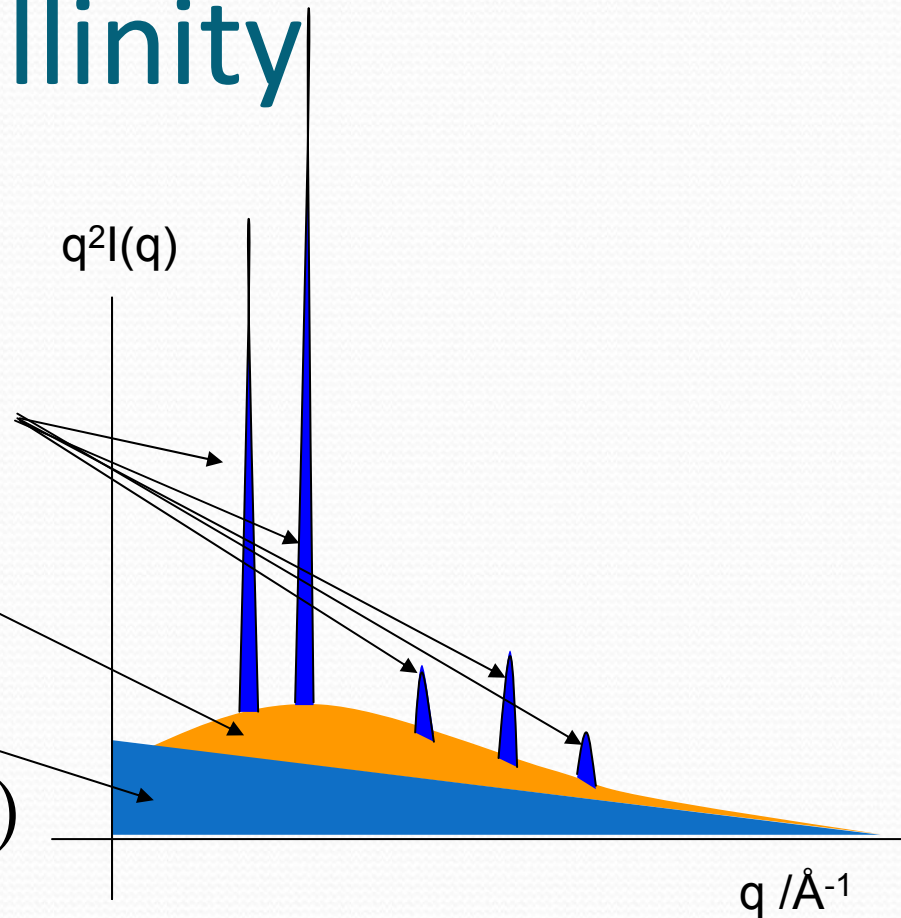
Degree of Crystallinity

- 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.

x 0.5
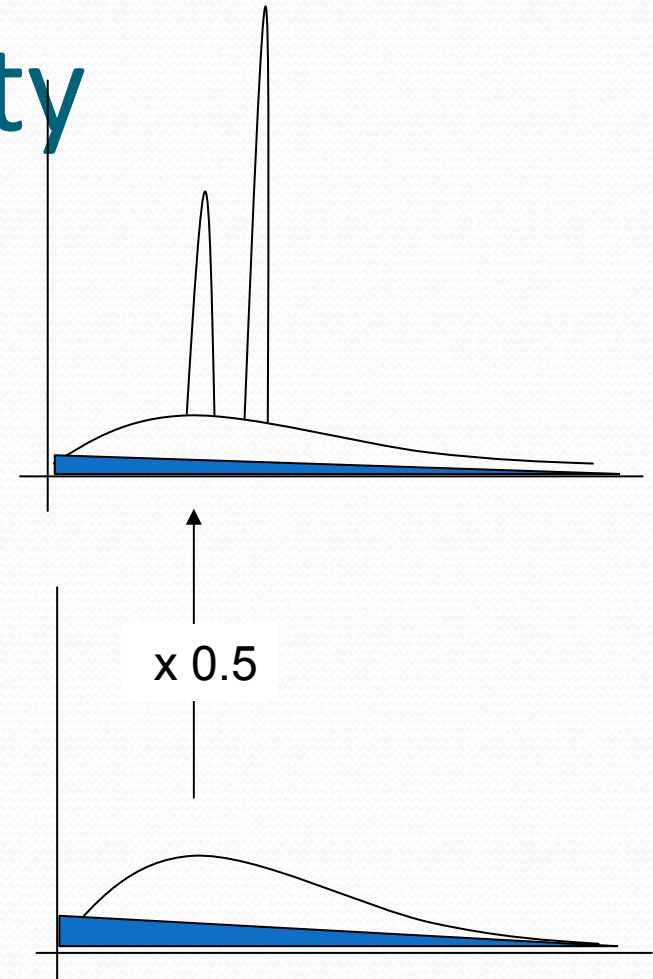
WAXS and Crystallinity

- Most people seem to think that WAXS is the best general technique for determining the degree of crystallinity
  - ITS NOT, it depends on the degree of crystallinity.
  - 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 start with DSC then WAXS/SAXS correlation function, and then density.
    - But of course this only works for a thermoplastic material, but most thermosets are amorphous anyway.
    - 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.

Reference Books

- Otto Glatter and Kratky: **Small Angle X-ray Scattering**
  - **The** book on SAXS.
- Leroy E. Alexander: **X-ray Diffraction Methods in Polymer Science**
- 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 (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
- **The Physics of Polymers: Concepts for Understanding Their Structures and Behavior by Gert R. Strobl**

  - This is good general polymer book and appendix A gives a good introduction to SAXS and the correlation function.
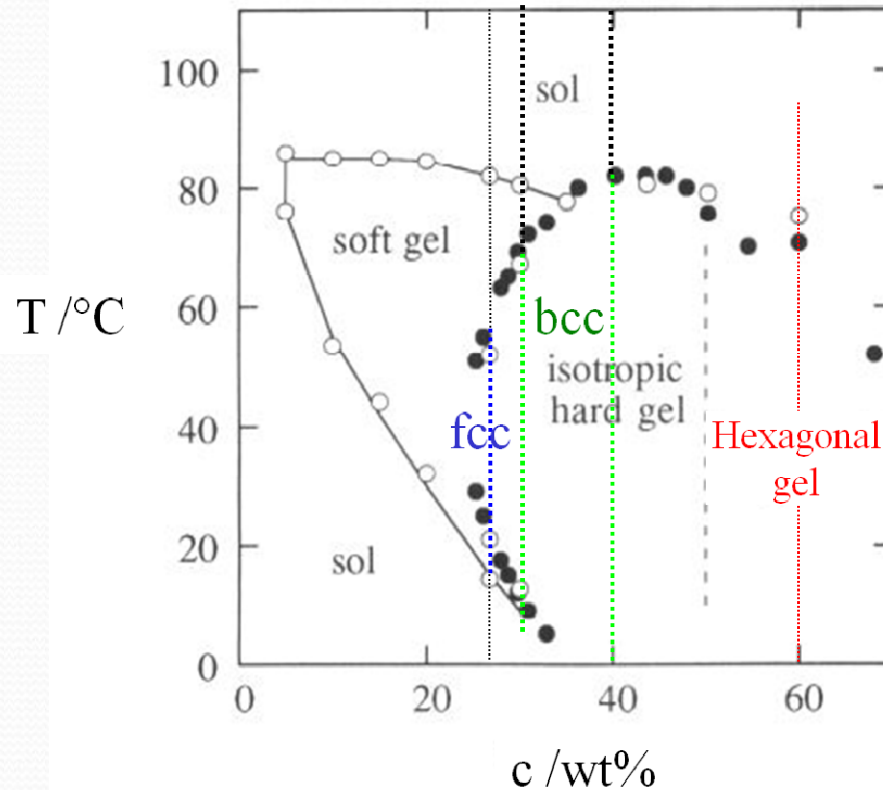
Block Copolymer Phases

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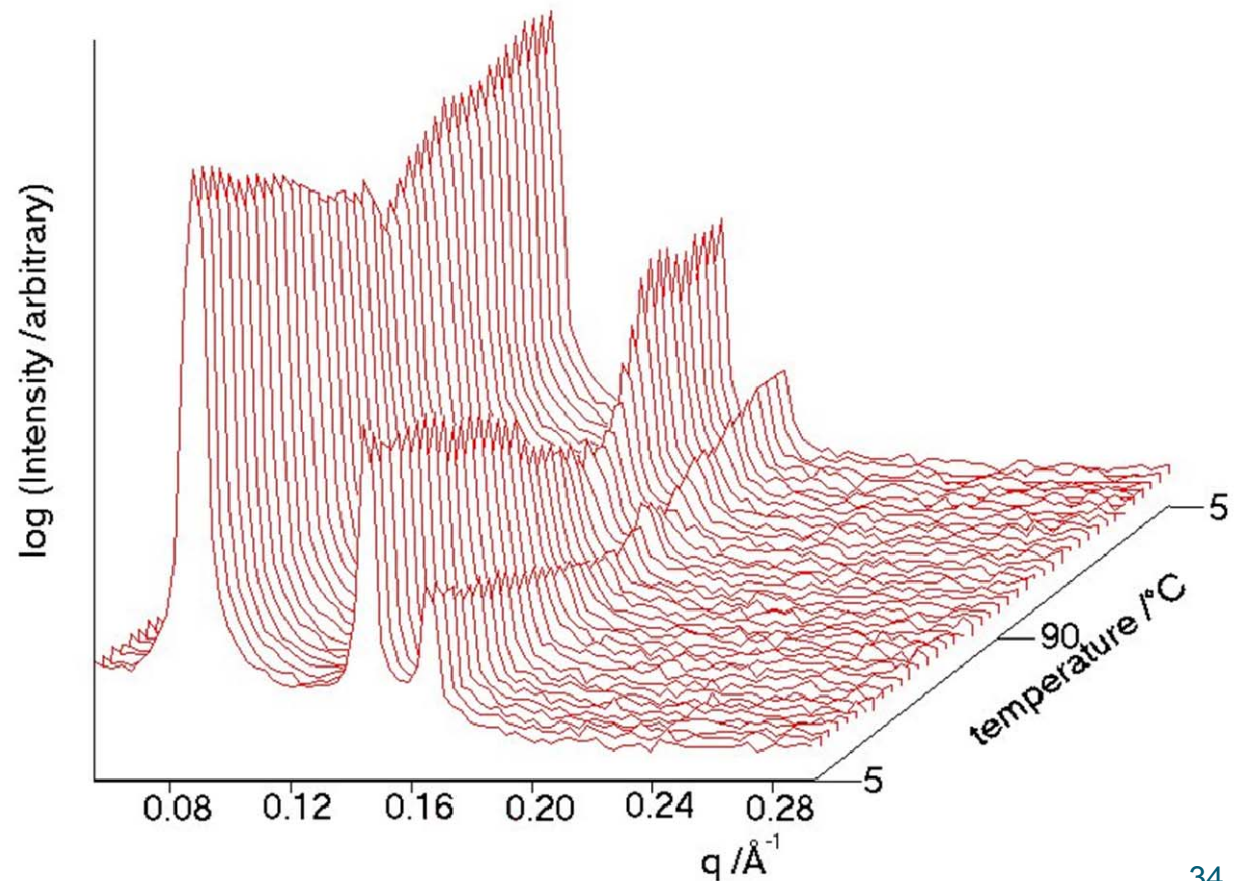# Block Copolymer/Lyotropic liquid Crystals.

- E=PEO water soluble
- B=polybutylene oxide water insoluble
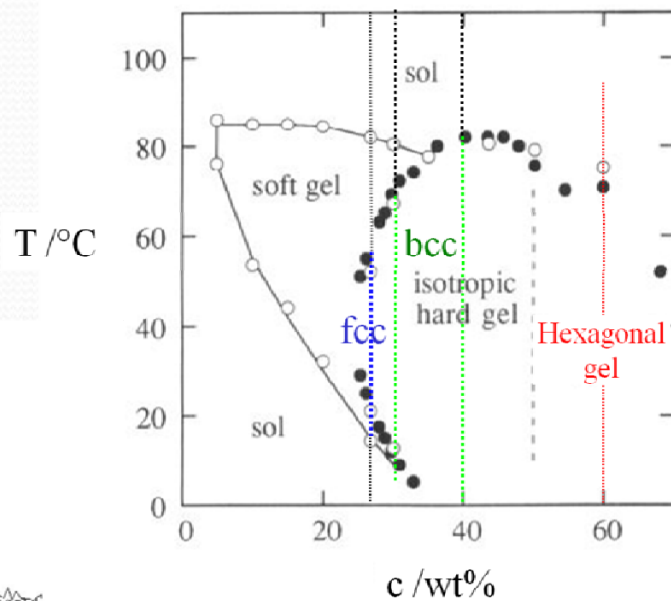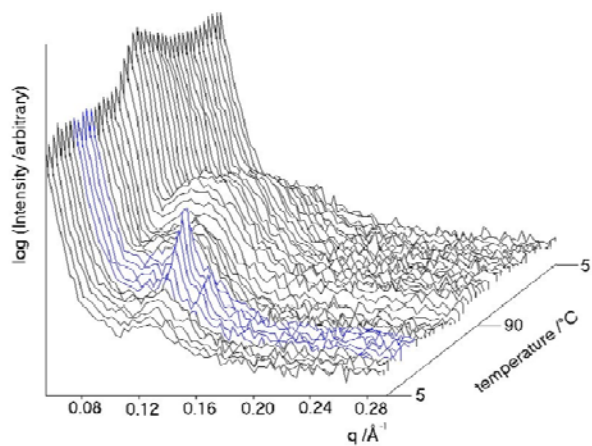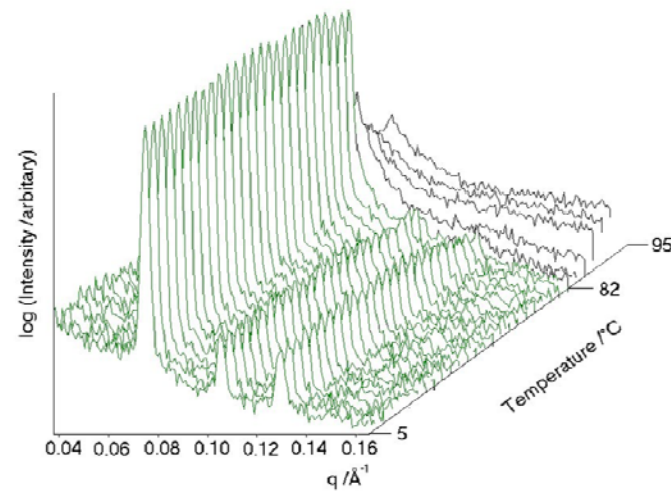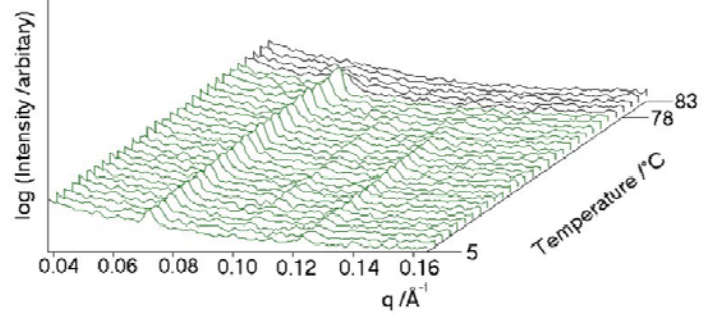- Forms ordered phases in water

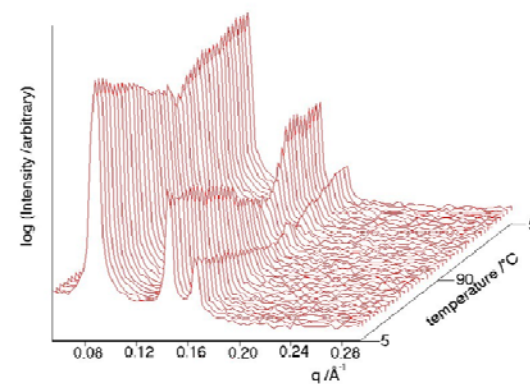
$E_{41}B_8$ in H_20

Hexagonal Phases

- 1°C /min
- Analyse via lfit
- Lfit UNIX based program runs on SUN
- Working on new version.

$E_{41}B_8$ in H_2O

Caution

- P(q) has minima
- If S(q) has a max at P(q) min then you loose the peak.
- Frequently occurs close to 50/50 volume fraction for lamella systems.

$$I(q) = S(q)P(q)\langle \eta^2 \rangle$$

The End

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