**Quiz 1 XRD 092706**

Diffraction involves constructive interference between waves that emanate from structurally organized matter such as from atoms in a crystal. X-ray diffraction uses a relationship of the angle that radiation is diffracted and the wavelength of the radiation to describe the structural size, d-spacing, associated with a diffraction peak.

1) Write Bragg's Law and sketch the diffraction experiment showing source, collimation (pinholes), sample, detector and the scattering angle.

2) Using the example of a halogen lamp and a pen laser, explain what a collimated beam of electromagnetic radiation is. Why is collimation important to Bragg's Law?

3) Explain the error in the following statement: "a laser beam is a focused beam of monochromatic light".

4) X-rays are electromagnetic radiation of higher energy compared to visible light. If you could see X-rays in the same way you can see light would they appear brighter than light? Explain.

5) Write an equation for the amplitude (electric field vector) for a wave based on complex numbers and show that the intensity $I = AA^*$ is not a complex number (A^* is the complex conjugate of A).

ANSWERS: Quiz 1 XRD 092706

1) $d = (\lambda/2)(1/\sin(\theta))$ where θ is half of the scattering angle 2θ.

2θ

2θ
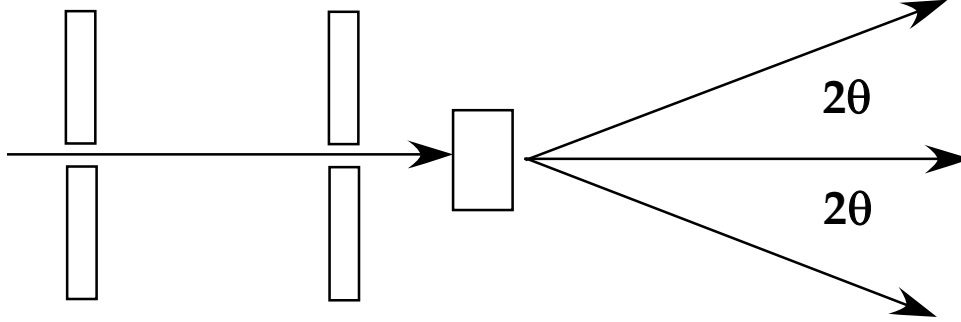
2) Collimated means that the component beams all travel in the same direction. A halogen lamp has divergent beams meaning that the beams emit in directions that serve to spread out the light. Collimation is important to Bragg's Law since the angle can only be measured with precision if the beam is well collimated. Diffraction with a divergent beam is not possible.
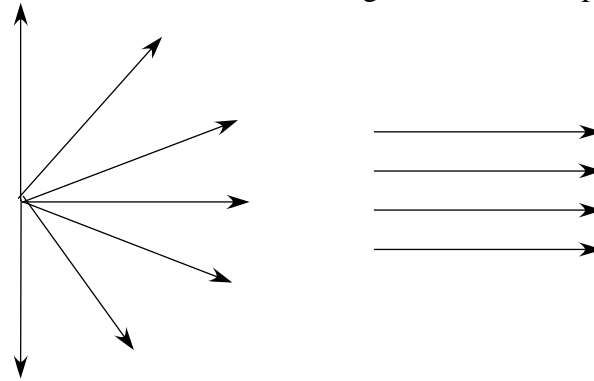
divergent   **collimated**

3) A laser is not focused. Focused means convergent so the beams concentrate to a focal point.

4) Energy, $E = h\nu$, reflects the capacity of a photon of the radiation to do work. Since the interaction of radiation with matter involves collisions of photons with atoms and molecules and transfer of this energy, the energy decides what the radiation can physically do. The brightness or flux is the number of photons per area per time. The energy does not have to do with the brightness.

5) $A = A_0 (\sin(\delta) - i\cos(\delta))$ where $d = 2\pi(t\nu + x/\lambda)$

$AA^* = A_0{}^2 (\sin(\delta) - i\cos(\delta))(\sin(\delta) + i\cos(\delta))$

$\quad = A_0{}^2 (\sin(\delta)^2 + i\sin(\delta)\cos(\delta) - i\sin(\delta)\cos(\delta) - i^2\cos(\delta)^2)$

$\quad = A_0{}^2 (\sin(\delta)^2 + \cos(\delta)^2) = A_0{}^2$

061004 XRD Quiz 2

1) Sketch an X-ray tube showing the a) source of electrons, b) source of X-rays, and c) explain how the two knobs on the front of the X-ray generator control the X-ray output in the tube.

2) a) Explain the difference between bremstralung radiation, white radiation and the continuous spectrum. b) Are these radiations made in an X-ray tube? c) How or Why?

3) a) What is the dependence of X-ray absorption coefficient on wavelength? b) In order to calculate the thickness of lead needed to shield an X-ray generator using a copper target and running at 20 mA and 50 kV what wavelength would you used to determine the absorption coefficient.

4) a) If the intensity of diffracted X-rays is proportional to the thickness of the sample, for a pinhole measurement, and the diffracted X-rays must obey Beer's Law, show how you can determine the optimum thickness for a transmission sample. b) If the optimum thickness for a polymer sample is 2 mm what is the linear absorption coefficient?

5) For a copper anode show a plot of intensity versus wavelength (the emission spectrum) for an X-ray tube for excitation at 3kV 100 mA; 6kV 100 mA; and 30 kV 100 mA. Give the wavelength of the characteristic lines and of the short wavelength limit as well as the relative intensity of the characteristic lines for Kα and Kβ radiation.

ANSWERS: 061004 XRD Quiz 2

1) Filament at the top is the source of electrons. The target (anode) at the bottom is the source
   of X-rays. The voltage knob adjusts the potential drop from the filament to the anode.
   The current knob adjusts the tube current from the filament to the anode through a servo
   controller that adjusts the filament current.
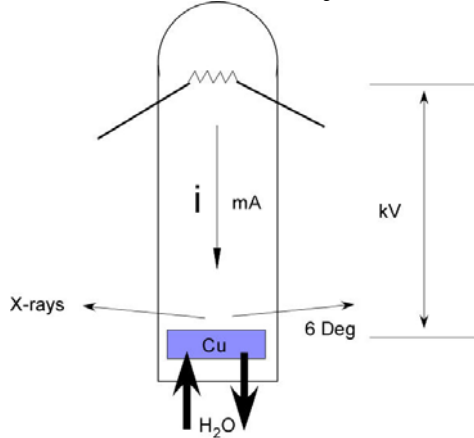
2) a) Bremstralung, white and continuous radiation are the same thing. b) c) This refers to the
   spectrum produced by electrons as they impact the target (anode) atoms and convert their
   momentum to X-rays in the process. Yes they are made in the X-ray tube.

3) a) $\mu = k \rho \lambda^3 Z^3$ between absorption edges. At the absorption edge the coefficient drops in a
   step manner
   b) $\lambda_{SWL} = 12.4/50kV = 0.25$ Å. This is the highest energy radiation to shield.

4) a) $I_{diffraction} = C \, x \exp(-\mu x)$. At the optimal thickness, x^*, $dI_{diffraction}/dx = 0$.
   $dI_{diffraction}/dx = C(\exp(-\mu x^*) - \mu x^* \exp(-\mu x^*)) = 0$
                or
   $1 - \mu x^* = 0$
                so
   $x^* = \mu$.
   b) 0.5 mm^{-1}

5) $\lambda_{SWL,3kV} = 12.4/3kV = 4.1$ Å; $\lambda_{SWL,6kV} = 12.4/6kV = 2.1$ Å; $\lambda_{SWL,30kV} = 12.4/30kV = 0.41$ Å
   $\lambda_{K\alpha} = 1.54$ Å and $\lambda_{K\beta} = 1.4$ Å   and these are about 100x and 20x the intensity of the white
   radiation.
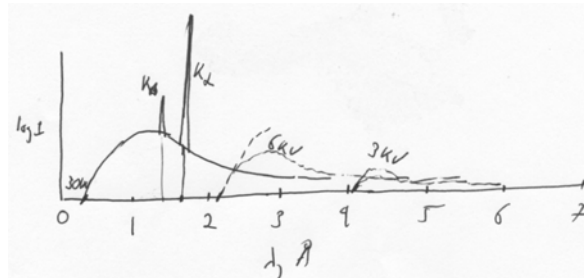
061011 Quiz 3 X-ray Diffraction

This week we discussed Synchrotron radiation briefly (Doug Kohls lecture) and Stereographic projections including the Wulff Net and Pole Figures.

1) What are the advantages of synchrotron radiation over a lab x-ray source? (at least 4)

2) [100] indicates the direction 100 (u,v,w). What do (100), {100} and <100> refer to?

3) What are the 3 reference frames (coordinate systems) of importance to the study of orientation of crystals in an x-ray diffraction measurement?

4) Sketch and describe how a Wulff Net is constructed. Which reference frames are related in a Wulff Net?

5) Sketch and describe how a Pole Figure is constructed. Which reference frames are related in a Pole Figure.

ANSWERS 061011 Quiz 3 X-ray Diffraction

1) Synchrotron radiation is collimated, coherent, usually monochromatic and of much higher brilliance compared to a lab source. The synchrotron beam can deliver extremely high fluxes in a small area (typically a 20 micron beam for instance).

2) (100) indicates the plane whose Miller indicies are h=1 k = 0 l = 0. {100} refers to the family of planes and <100> refers to all directions of the type [100], [100],[010] & [001] for a cubic system.

3) a) Crystallographic Frame. b) Sample Frame Machine direction/Transverse Direction/Normal direction. c) Laboratory Frame of Reverence, NS EW.

4) The Wulff Net relates the Lab frame to the crystallographic frame.

Figure 2-30 The stereographic projection
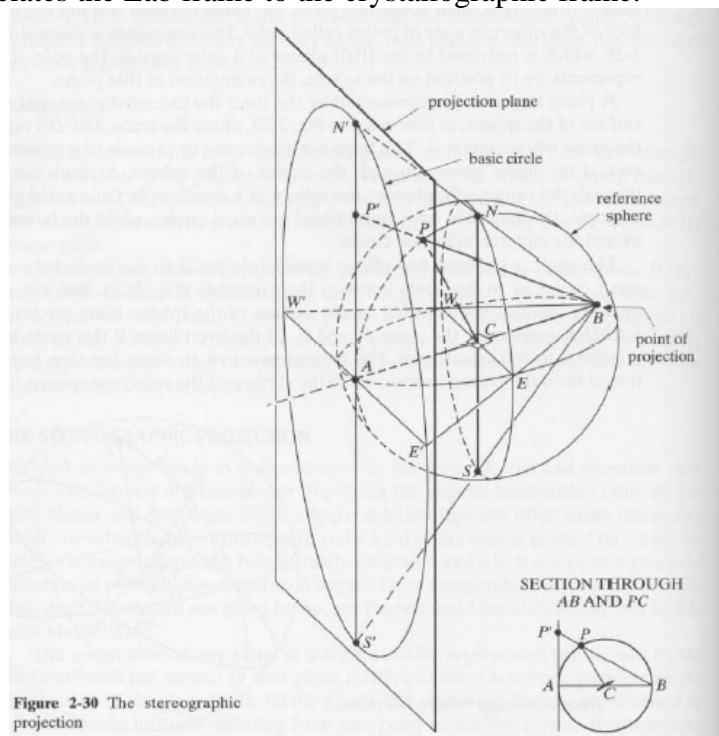
5) A pole figure relates the sample frame to the crystallographic frame.
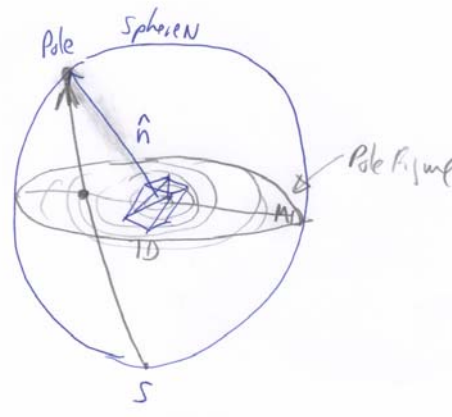
1) Derive Bragg's law assuming mirror-like behavior. Show all steps and give a description of what you must do.

2) Give the crystal structure and number of atoms in a unit cell for copper, aluminum, zinc, magnesium.

3) Give the crystal structure and number of atoms in a unit cell for α-iron, γ-iron, silicon, diamond.

4) Give the crystal structure and number of atoms in a unit cell for sodium chloride, potassium bromide, lead, nickel.

5) FCC and HCP both occupy 74% of the volume for touching spheres. What other similarities exist for these two crystal structures? Give details on the similarity and difference between FCC and HCP structures.

1)
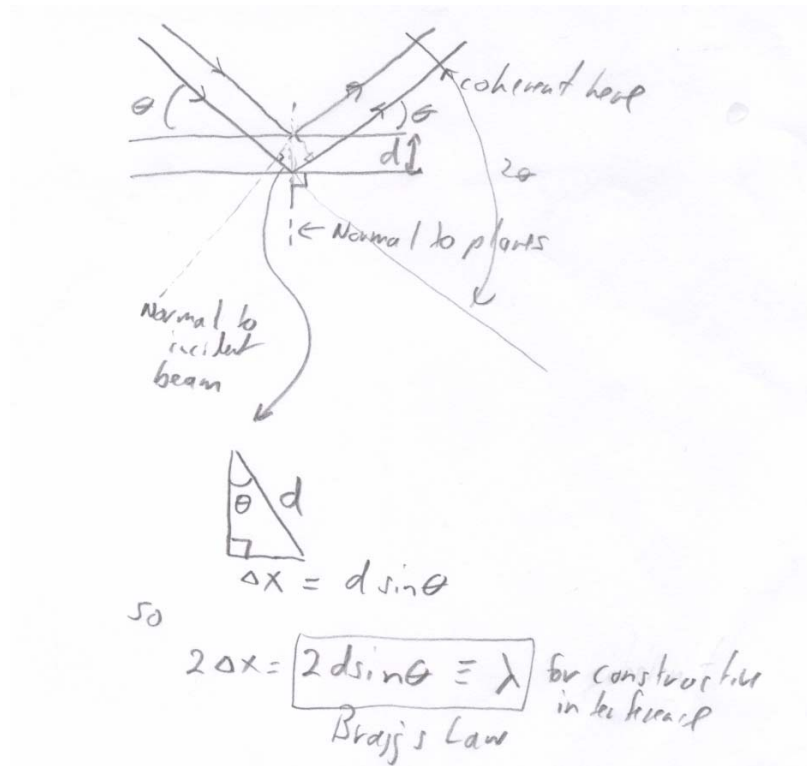
2) Copper FCC 4; Aluminum FCC 4; Zinc HCP 6 or 2; Magnesium HCP 6 or 2.

3) α-iron BCC 2; γ-iron FCC 4; Silicon FCC (diamond type) 8; diamond FCC 8

4) NaCl FCC 8; KBr FCC 8 (NaCl type); Lead FCC 4; Nickel FCC 4.

5) The FCC (111) plane is hexagonal and in the [111] direction the first two planes of atoms are the same as the HCP structure in the [100] direction. The next layer is difference in FCC leading to the ABCABCABC repeat. HCP displays a repeat of ABABABABABA in the [100] direction.

061025   Quiz 5 XRD

1 & 2) It was mentioned in Lab 1 that the diffraction pattern observed on a film or screen is the Fourier transform of the structure. Explain how a diffraction pattern with one peak (one d-spacing) is related to the real space structure of a crystal using the pairwise correlation function (rod throwing probability) and a Fourier transform of this function.

3) Show how the phase difference, $\phi = 2\pi/\lambda \ (\mathbf{S} - \mathbf{S_0}) \cdot \mathbf{AB}$ can be obtained from a sketch of the diffraction from atoms A and B.

4) Construct the Sphere of Reflection by sketching a reciprocal lattice with an origin, (000) and the center of the diffraction measurement indicating 2θ and $(\mathbf{S} - \mathbf{S_0})/\lambda$. Why are only a few peaks seen when a perfect crystal diffracts with a single wavelength x-ray radiation?

5) Construct the limiting sphere and explain why Debye-Scherrer rings are seen from a powder pattern in a 2D photographic measurement such as was done in lab 2.
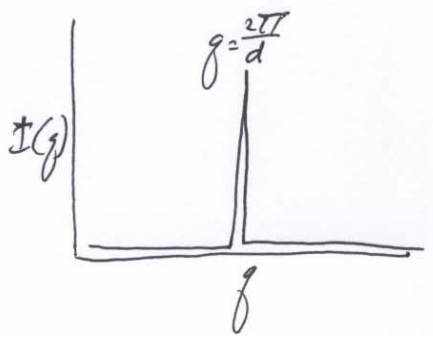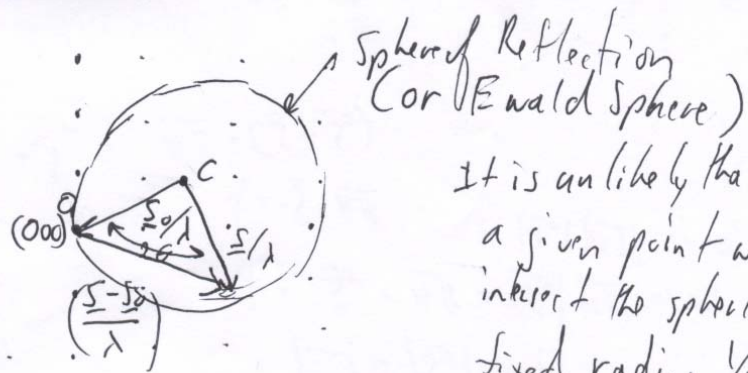
1)
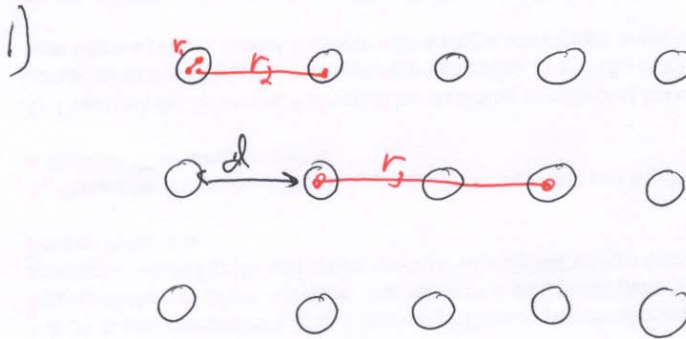
Consider only one d-spacing

1) Probability of a rod in phase of the atoms is one at $r=0$ then 0 at $r >$ the atom size but $r < d$ and high at $r=d$ etc.
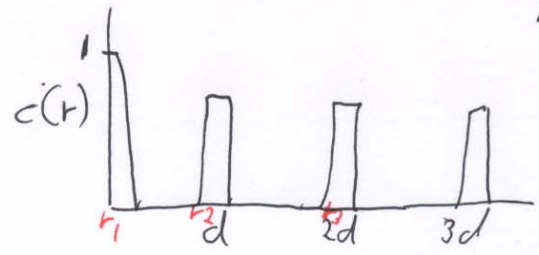
This correlation function can be represented by a single sin wave of wavelength d
So the resulting FT is single valued

$q = \frac{2\pi}{d}$

$I(q)$

q

4)

Sphere of Reflection
(or Ewald Sphere)

It is unlikely that a given point will intersect the sphere of fixed radius $\frac{1}{\lambda}$ in a fixed orientation relative to the lattice

5) By rotation of the crystal to all possible orientations the sphere of reflection traces out a larger sphere of radius $\frac{2}{\lambda}$ called the limiting sphere.

Limiting Sphere
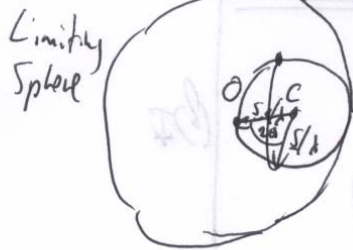
For the intersection of the Ewald sphere with a reciprocal lattice point rotation of the lattice will trace out a circle on the surface of the Ewald sphere creating a Debye-Scherrer ring on the film which is part of the surface.

3

061101 Quiz 6 XRD

This week we began consideration of the calculation of the diffracted intensity based on an inverse space vector $\mathbf{H} = h\mathbf{b}_1 + k\,\mathbf{b}_2 + l\,\mathbf{b}_3$ and real space atomic positions $\mathbf{U} = u\,\mathbf{a}_1 + v\,\mathbf{a}_2 + w\,\mathbf{a}_3$. The reciprocal space vector $\mathbf{H}$, is connected to the Bragg angle 2θ through Bragg's law and equations for the d_{hkl}-spacing. The real space atomic position, $\mathbf{U}$, is connected to the crystallographic structure and orientation relative to the incident x-ray.

1) Give an expression that describes the structure factor, F_{hkl}, for a crystal with N atoms at positions u_i, v_i, w_i. (This involves a sum of complex exponentials.)

2) For an FCC structure show that this expression yields 4f for hkl unmixed and 0 for hkl mixed.

3) The Thompson function describes diffraction from a single free electron. What is a single free electron and why is the diffraction from a single free electron important to the calculation of diffraction from a block of copper using partially polarized x-rays such as in the diffractometer used in the lab?

4) The multiplicity factor, p, for {111} is 8 while for {110} is 12. What is the multiplicity factor and why does it differ for these two types of planes (show how values of 8 and 12 can be obtained)?

5) For the brass key run in the lab this week we use Vergard's law to determine the zinc/copper content. Would you expect orientation of the crystals in this processed sample to effect the results? What if the key contained a coating of chrome and we wanted to determine the amount of chrome in the key?

1) $F_{hkl} = \sum_{i=0}^{N-1} f \exp(-i2\pi(hu_i + kv_i + lw_i))$

2) For FCC there are 4 atoms per unit cell: [0 0 0]; [1/2 1/2 0]; [1/2 0 1/2]; [0 1/2 1/2], yielding,
$F_{hkl} = f(1 + \exp(-i\pi(h+k)) + \exp(-i\pi(h+l)) + \exp(-i\pi(k+l)))$
if h, k, l are unmixed (all even or all odd) then the argument to the exponentials will be all even since the sum of two odds is even and the sum of two evens is even. Given that $\exp(-in\pi) = (-1)^n$, even powers will result in $F_{hkl} = f(1+1+1+1) = 4f$. For mixed Miller indicies, one argument will always be even (two odds or two even) and the other two will be odd (sum of one odd and one even). Then the structure factor is $F_{hkl} = f(1+1-1-1) = 0$ so these peaks will not be observed.

3) A single free electron is an isolated electron in free space, i.e not bound to an atom and dilute so there is no interference with other electrons. This is the building block for construction of the diffracted x-ray intensity from any material. We consider the scattering from an electron, then interference in the atom, atomic form factor, then interference between atoms, crystallographic structure factor and finally how the crystals are put together in the sample, i.e. the block of copper. For unpolarized x-rays the Thompson factor yields the Lorentz polarization factor (1 + $\cos^2 2\theta$). For partially polarized x-rays we need to consider the degree of polarization, $\cos^2 2\alpha$ for a crystallographic monochromator for instance. Then the Lorentz factor becomes (1 + $\cos^2 2\alpha$ $\cos^2 2\theta$).

4) The multiplicity factor, p, reflects the number of indistinguishable planes in a unit cell. This number is different for different planes so a plane with many indistinguishable types in a unit cell will have a relatively higher diffracted intensity compared to planes with fewer indistinguishable types. For {111} the normal to these planes point to the corners of the unit cell so there are 8 indistinguishable (111) planes in a cubic unit cell. For {110} the normal to these planes point to the edges of the unit cell so there are 12 of these planes in a cubic unit cell.

5) Orientation will effect the relative intensity of diffraction lines, but since Vergrad's Law does not use the relative intensity but the d-spacing, it is not sensitive to orientation as long as the diffraction peak can be observed. Determination of the amount of chrome will involve comparison of peak intensity similar to the Moly/Copper measurement and will certainly depend on orientation of the crystals in the processed key.

1) Scattering from any object in small angle can be described in terms of an average size, the radius of gyration, Rg, through the Guinier function,

$$I(q) = Nn_e^2 \exp(-q^2 R_g^2/3). = K \exp\left(X^2/2\sigma^2\right)$$

where $X = q$ and $s^2 = 3/(2R_g^2)$. What kind of function is Guinier's law?

2) The Fourier transform of an exponential is an exponential in the paired Fourier parameter, i.e. "r" in this case. Explain in real space why the kind of function you mentioned in part 1 can explain the pairwise correlation function for any object in the small-angle regime. (You may want to compare a protein in a crystal to a protein in solution in this answer.)

3) Atoms of a given type are indistinguishable while objects on the colloidal/nanoscales have a distribution in size and shape. How can this effect the difference between scattering in the XRD range of angle and scattering at small-angles. (Give an example of an object on the colloidal or nanoscale).

4) The diffusion of atoms is extremely rapid with the mean free path (average translation) of about 0.1 mm or one million times their size, while colloids move slowly with mean free paths on the order of their size at best. Explain how this effects the difference between XRD and small-angle scattering.

5) In lab we measured small-angle scattering from lamellar crystals in polymers. Explain how the polymer chain and the polymer unit cell build up this stacked lamellar structure. (Draw sketches to show how the unit cell and chains fit into the lamellar crystals and explain why the lamellae tend to stack.)

ANSWERS: 061108 Quiz 7 XRD

1) This is a Gaussian function with a mean of q = 0 that describes a bell-shaped curve or normal distribution about q = 0 for a random distribution.

2) The protein in a crystal is fixed in orientation relative to other proteins in the crystal. When a solution is made of this crystal, the protein is free to rotate and translate rapidly so that a SAXS pattern will observe a smeared structure. Further, the calculation of the pairwise correlation function involves taking a random starting point in a particle (which is already randomized by rotation and translation) and measuring the probability that a point in an arbitrary direction from this starting point is also in the particle. This serves to further smear out the structure. Any structure, regardless of shape will display a radius of gyration. The radius of gyration is the moment of inertia using electron density as a weighting factor.

3) It is not possible to organize colloidal structures into a real crystal with long range order. It is also difficult to impossible to arrange nano-scale structures in a real crystal. This is due to imperfections in structure and due to the lack of a real thermodynamic equilibrium for large objects. For example, sand on the beach has similar grain sizes but will never form a crystal structure with long range order. This means that only a few structure factor peaks will be possible (usually only one) in small angle scattering and that the diffractions peaks will be extremely broad due to disorder and irregularity of the structural units.

4)   Colloids can't really form crystals from a kinetic perspective even if they had perfect structure. They can't probe enough arrangements due to slow motion to find an energy minimum on any reasonable time scale. This means that the structure factor will be dominated by defects and disorder despite some tendency to form crystals.

5)
http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/Chapter2html/Chapter2.html
http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/Phillips-review-90.pdf
http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/Phillips1994.pdf

061117 Quiz 8 XRD

This week we covered polymer crystal structure and determination of the degree of crystallinity using x-ray diffraction.

1) Starting with an expression for the difference in Gibbs free energy between a lamellar crystal and the melt (including bulk and surface terms) derive the Hoffmann-Lauritzen expression for the lamellar thickness, $t = 2\sigma T_0/(\Delta H_f (T_0-T))$. List the assumptions you need to make. (You will need to associated ΔS_f with T_0 and ΔH_f by setting the free energy to 0 at the equilibrium melting point, T_0.)

2) Polymer crystals can display various polymorphs (different crystalline structures). List one polymer that displays polymorphs and explain the conditions under which polymorphs might be formed.

3) List three differences between polymer diffraction patterns and a metal powder pattern in 2D.

4) How is the degree of crystallinity determined from a polymer diffraction pattern?

5) Other than sperulites, what other types of crystalline forms are observed in polymers (list at least two others).

ANSWERS: 061117 Quiz 8 XRD

1) First an expression for the Gibbs free energy difference between a lamellar crystal of volume V and surface area 2A and the melt at equilibrium temperature T is written:

$\Delta G_f = 0 = V(\Delta H_f - T \Delta S_f) - 2 \sigma A = tA(\Delta H_f - T \Delta S_f) - 2 \sigma A$

so

$t = 2 \sigma/(\Delta H_f - T \Delta S_f)$ (1)

also, at T_0 the crystal is of infinite thickness so it has no surface and,

$\Delta G_f = 0 = V(\Delta H_f - T_0 \Delta S_f) = tA(\Delta H_f - T_0 \Delta S_f)$

so

$\Delta S_f = \Delta H_f/ T_0$ (2)

and substituting this in equation (1),

$t = 2 \sigma/(\Delta H_f(1 - T/T_0)) = 2 \sigma T_0/(\Delta H_f(T_0 - T))$.

2) Polypropylene or Nylon, The polymorphs form under different conditions of pressure and shear

3) Broad Peaks; High degree of orientation of patterns;   Presence of amorphous Halo.

4) Plot Iq^2 vs q and determine the area under the crystalline peaks C and under the amorphous halo (A). The fraction crystallinity is C/(C+A) and the degree of crystallinity is 100*C/(C+A).

5)   Lozenge-shaped single crystals, stacked single crystals, axialites, shish kebabs, fibrils and fibers.

061201 Quiz 9   XRD

1) Give the two examples of static and dynamic elastic scattering discussed in class and describe the correlation function associated with each.

2) What two kinds of spectroscopy (inelastic scattering) were discussed that use x-rays as the incident radiation. Give the difference between these two techniques.

3) Why is a large magnetic field needed for NMR spectroscopy? Explain the terms deshielding and shielding of nuclei. What is a FID.

4) What is the difference between bright field and dark field imaging in a TEM?

5) Give 3 differences between an electron beam and an x-ray beam that effect diffraction.

ANSWERS   061201 Quiz 9   XRD

1) The examples given in class were x-ray diffraction and dynamic light scattering. The correlation function for x-ray diffraction is the pairwise correlation function of electron density in space and for dynamic light scattering it is the time correlation function for fluctuations in intensity.

2) XAS orXAFS and ESCA or XPS. X-ray absorption spectroscopy involves a plot of absorption versus wavelength or frequency showing various absorption edges and the lambda cubed decay in absorption with wavelength. XAFS can be used to determine ionization states of metals. X-ray photoelectron spectroscopy involves measurement of the number of photoelectrons ejected from the surface by incident x-rays at various energies. This is used to characterize the chemical composition of the surface.

3) The large magnetic field "holds" the nuclear spin magnetic moments so that they can absorb radio frequency radiation. Deshielding indicates the partial removal of electrons from around a nucleus by neighboring chemical groups such as a halide or aromatic group. Shielding indicates the addition of electrons around a nucleus by neighboring chemical groups such as a metal. FID is the free induction decay which is the observed signal in a pulsed NMR experiment.

4) Bright field image is the normal TEM image made from the full incident beam. Dark field image is an image constructed from one diffraction spot.

5) Electrons have much lower wavelength, electrons are absorbed at a much higher rate and they can generate secondary electrons and can charge a sample so as to build up a repulsion between the incident radiation and the sample. The electron beam is focused and much smaller than the x-ray beam so that it can be aimed at a single small grain. There are other differences.