Indian Institute of Technology
Kanpur
NP-TEL
National Programme
On
Technology Enhance Learning
Course Title
Advanced Characterization Techniques
Lecture-27

by…
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Hello everyone in today class on advanced characterization techniques.

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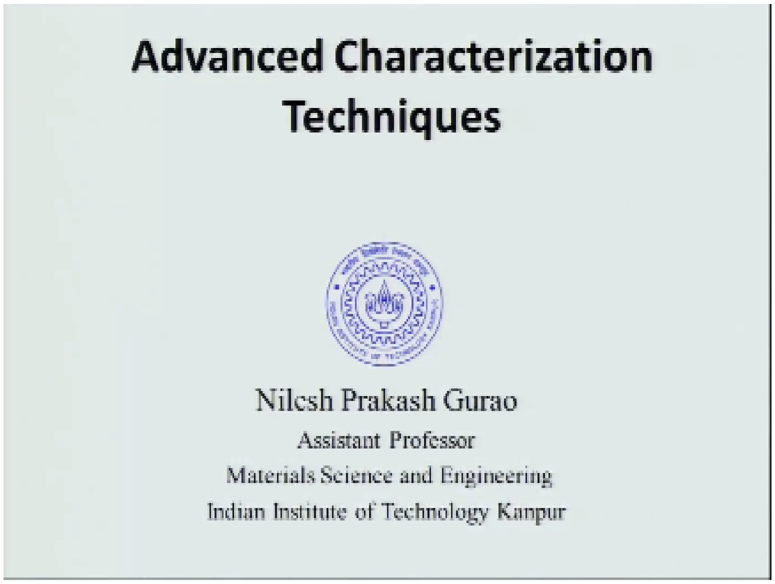

Advanced Characterization Techniques

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We are going to deal with.

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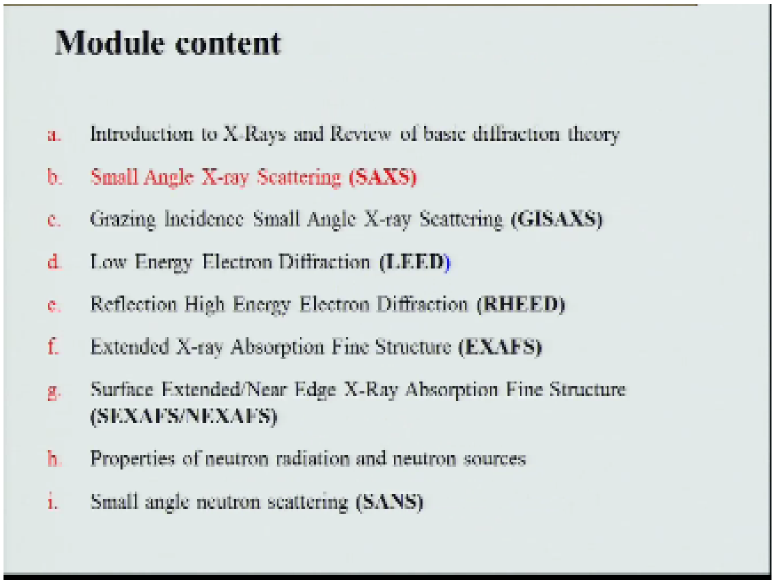

Module content

a. Introduction to X-Rays and Review of basic diffraction theory
b. Small Angle X-ray Scattering **(SAXS)**
c. Grazing Incidence Small Angle X-ray Scattering **(GISAXS)**
d. Low Energy Electron Diffraction **(LEED)**
e. Reflection High Energy Electron Diffraction **(RHEED)**
f. Extended X-ray Absorption Fine Structure **(EXAFS)**
g. Surface Extended/Near Edge X-Ray Absorption Fine Structure **(SEXAFS/NEXAFS)**
h. Properties of neutron radiation and neutron sources
i. Small angle neutron scattering **(SANS)**

Small-angle x-ray scattering in the last two classes we try to understand how does diffraction work and why we use x-rays, in today is class we are going to go back and study scattering of x-rays which we had touched upon at the beginning of the first lecture and also see how we can use scattering to get information about the structure of various class of materials.

So talking about scattering we have looked and compared scattering and diffraction we also agreed that scattering corresponds to bending of light from an object or spreading of rights light from an aperture. We know that scattering quantum mechanically as such can be defined as an interaction of the photons essentially the x-ray photons with electrons.

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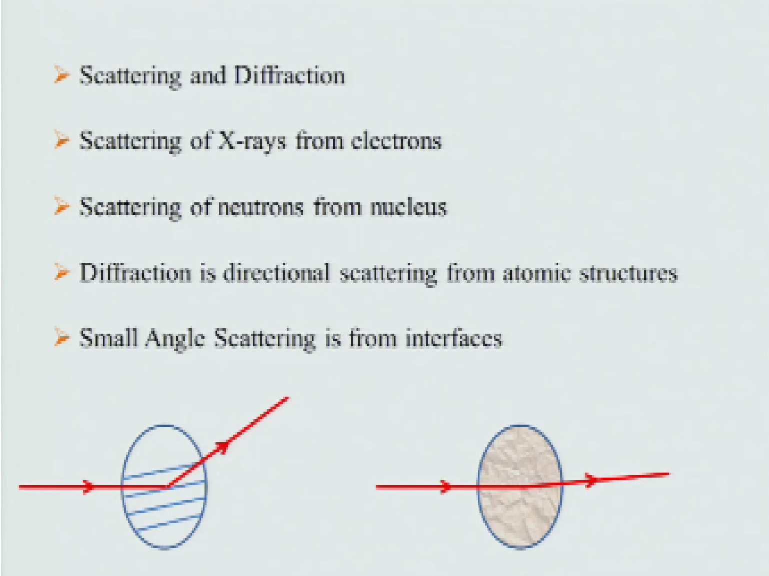

- Scattering and Diffraction
- Scattering of X-rays from electrons
- Scattering of neutrons from nucleus
- Diffraction is directional scattering from atomic structures
- Small Angle Scattering is from interfaces

At the same time scattering can also occurred for neutrons however it has to interact with the nucleus of the atoms, we know that diffraction is nothing but directional scattering and it follows the Bragg's law. However the small-angle scattering that we are going to talk about in today is lecture essentially occurs from interfaces a schematic giving depicting the difference between diffraction and that of scattering is shown in the slide.

You can see here that when the x-rays interact with the periodic arrangement of atoms we do get a diffraction, however when the x-rays interact with each and individual particles which do not form a periodic arrangement we do get scattering. A few more words about the difference between diffraction and scattering is presented in the next slide.

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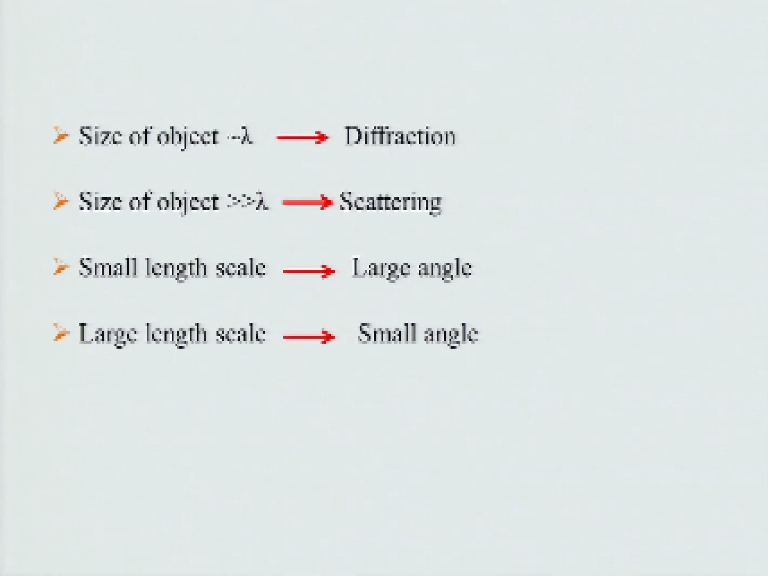

- Size of object ~λ → Diffraction
- Size of object >>λ → Scattering
- Small length scale → Large angle
- Large length scale → Small angle

We know that for diffraction to occur with the wavelength or the choice of wavelength rather has to be of the same order of that of the size the object freedom I hope you remember that for diffraction the choice of wavelength has to be such that it is less than two times the inter atomic spacing that is λ has to b< 2d, however for scattering the size of the object under consideration is much larger than the wavelength that we are using.

And therefore we can imagine that there is bending of law of the light from that particular object the size of which is much larger than the wavelength of the object. This fundamental difference between scattering and diffraction essentially ensures that the small length scales associated with diffraction leads to a larger angle considering the Braggs angle, so we have $n \lambda$ is $=2$ d sine- θ.

And the angle that we are talking about is pretty large since λ is of the same order of that of d the inter planar spacing however since scattering involves essentially large particles and the wavelength which is much smaller than the size of the particles we do get very small angles and therefore the name small-angle scattering. So the small-angle x-ray scattering was discovered by Guinner in 1937.

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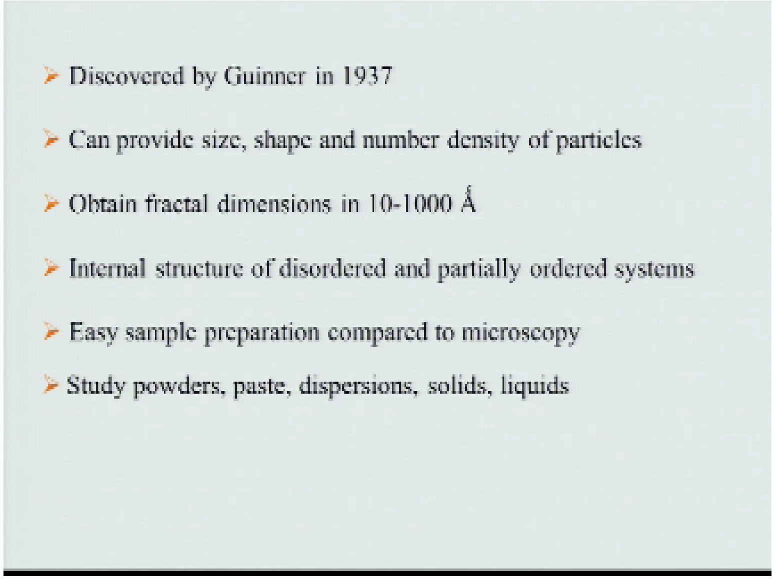

- Discovered by Guinner in 1937
- Can provide size, shape and number density of particles
- Obtain fractal dimensions in 10-1000 Å
- Internal structure of disordered and partially ordered systems
- Easy sample preparation compared to microscopy
- Study powders, paste, dispersions, solids, liquids

It has been well agreed that the small-angle x-ray scattering can provide information about the size shape and number density of particles, we can obtain fractal dimensions in a range of 10 angstroms two up two thousand and strong that is equivalent to about point 1 micron or 100 nanometers. We can also get information about internal structure of disordered and partially ordered systems.

The biggest advantage of scattering which gives us information about the size shape and over orientation of the particles compared to that of conventional microscopy say transmission electron microscopy is that the sample preparation in case of small-angle x-ray scattering is very easy, at the same time it offers us a great flexibility in terms of studying powders, based dispersion, solids as well as liquids.

I would also like to mention that we can also study thin film using small-angle x-ray scattering however this involves a lot of intricacies and this will be done in greater details in the next lecture wherein we will talk about grazing incidence small-angle x-ray scattering. So if we were to compare say scattering and microscopy with respect to the kind of information that we are getting we tend to end up getting the following points.

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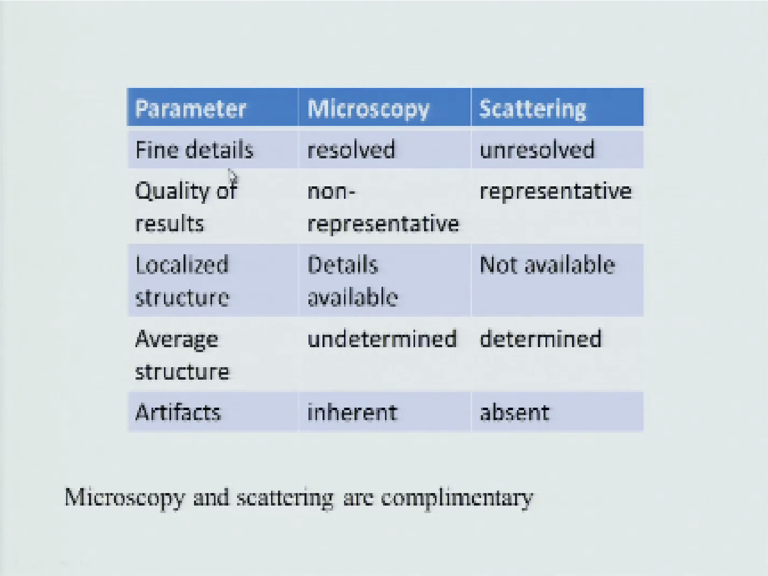

Parameter	Microscopy	Scattering
Fine details	resolved	unresolved
Quality of results	non-representative	representative
Localized structure	Details available	Not available
Average structure	undetermined	determined
Artifacts	inherent	absent

Microscopy and scattering are complimentary

We know that the finer details involved in the microstructure can be resolved in a much better way using microscopy like tem why scattering does not resolve the finer details of the microstructure. People who have done tem will have this experience that once we see some object with finer details all you got to do is just increase the magnification and get more details about that particular region or feature.

At the same time the quality of results as obtained from microscopy is not representative from one micrograph it is very difficult to draw enough conclusions; however what information we get from one scattering experiment is representative of the sample. At the same time the local I structure is available using microscopy however the localized structure is not available using scattering techniques.

We will go through the details of the scattering technique later and I hope you will be able to appreciate this difference but at the outset it is very important to realize what is the difference in scattering or small angle x-ray scattering in particular and microscopy at the outset, so another important point that microscopy offers that scattering offers over microscopy is the average structure.

So this average structure information is obtained you know much better way by scattering compared to that of a conventional microscopy, that is transmission electron microscopy, at the same time people who have used TM will tell you that TM is full of artifacts having said that a careful investigation or a careful eye is needed to get useful information from a tem micrograph.

However for scattering no such artifacts are inherent to the system however I should mention that most of the studies that deal with the scattering tend to use microscopy that is TM for complementing the observations. So I hope you appreciate that transmission electron microscopy which gives us information about this age say, the size shape and distribution of phases as well as the small-angle x-ray scattering, which also gives a similar information can be used to as complementary tools to in to decipher the micro structure of the material under consideration.

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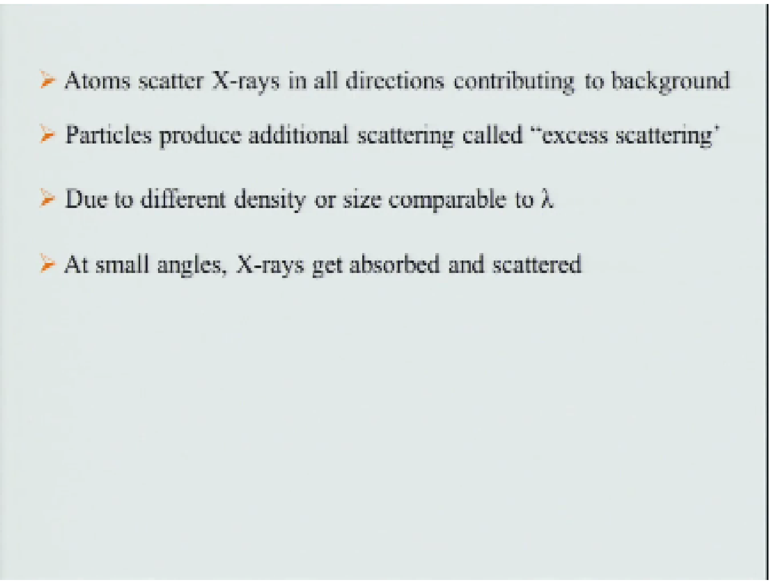

- Atoms scatter X-rays in all directions contributing to background
- Particles produce additional scattering called “excess scattering’
- Due to different density or size comparable to λ
- At small angles, X-rays get absorbed and scattered

So dealt with this in the first lecture that how scattering occurs from an electron we know that atoms which essentially are consists of a nucleus and an ensemble of electrons will also scattered x-rays and this scattering is non directional and this generally corresponds to the background. However if we have particles small particles very small particles which comprised of atoms this leads to what is known as excess scattering.

Now one can understand that this excess scattering is formed or is contributed due to the size shape and the density of the particle and that is true only when the size of the particle is not very large compared to that of the wavelength but is between, so something like 100 nanometer for a wavelength of about 1 1 angstrom. We know that at very small angles x-rays are not only going to get scattered they are also going to get absorbed.

So there is an interplay or there is to come there are two competing phenomena which are occurring at when you are when the x rays interact with miter, so one is the absorption and the other one is the scattering. Obviously since we are interested more in scattering we want that the absorption should be minimum, now how do we minimize the absorption the absorption of x-rays by a material is dependent on the density and the mass absorption coefficient as well as it is characteristic of the wave length.

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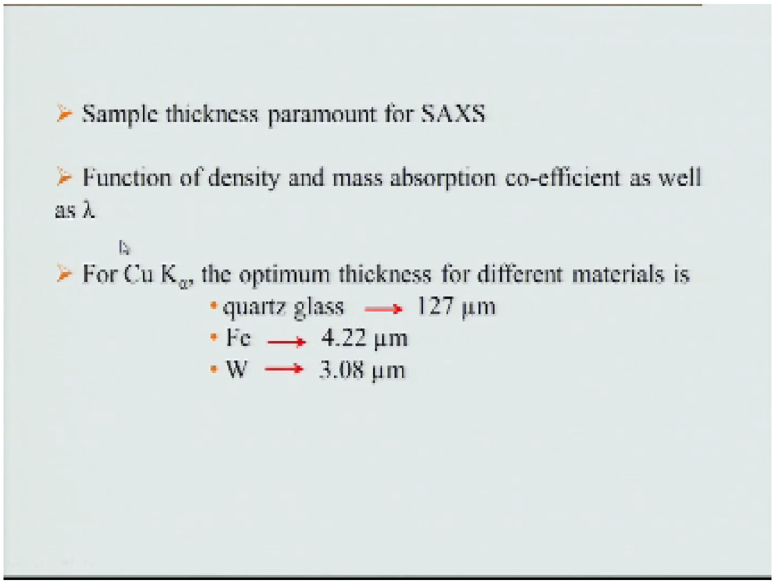

- Sample thickness paramount for SAXS
- Function of density and mass absorption co-efficient as well as λ
- For Cu K_α, the optimum thickness for different materials is
  - quartz glass → 127 µm
  - Fe → 4.22 µm
  - W → 3.08 µm

Depending on that we have just noted down here that for copper k α the optimum thickness for different materials has been noted over here, so you see for quartz glass it is 127 micron for iron it is 4.22 micron for tungsten at least 3.0 at micron. So if the sample is thicker than this most of the x-rays are going to get absorbed while the scattering signal is going to be very weak.

Therefore you can imagine that as the atomic number of the material increases we need thinner and thinner samples to obtain better signal from scattering. So let us talk more about scattering we know that we had touched upon this in the last lecture but let us see revise it again and we know that there is what is known as Compton scattering.

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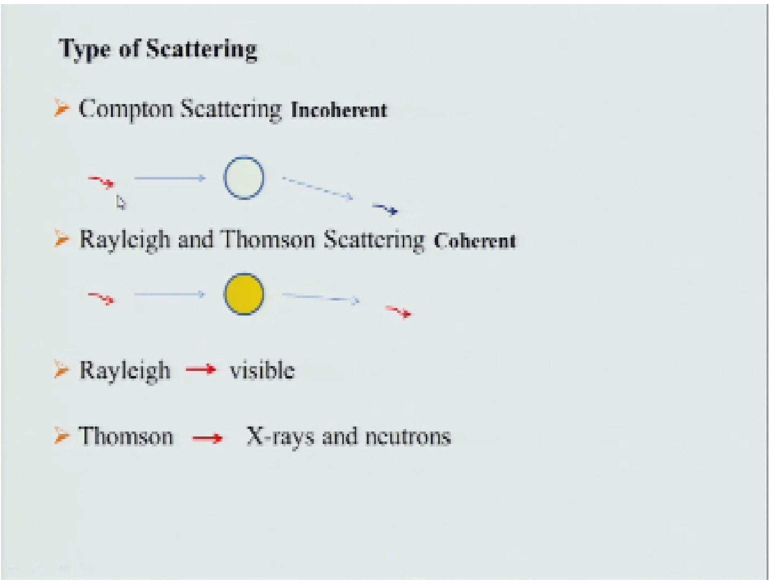

Type of Scattering

- Compton Scattering **Incoherent**
- Rayleigh and Thomson Scattering **Coherent**
- Rayleigh → visible
- Thomson → X-rays and neutrons

So we have an x-ray photon which interacts with an electron and you do get another x-ray photon which has different frequency, rather a lower frequency and therefore a lower energy than the incident x-ray photon. Therefore this entire process is incoherent that is the energy is not conserved and this corresponds to an elastic scattering. However there is also what is known as relay or Thomson scattering which essentially is elastic and coherent.

In this case the wavelength or and frequency of the incident photon remains the same after interacting with the electron, if this phenomena of interaction of the photon with the electron maintaining its frequency occurs in visible spectrum it is known as the Rayleigh scattering. However for x-rays it is known as x-rays and neutrons it is known as Thomson scattering.

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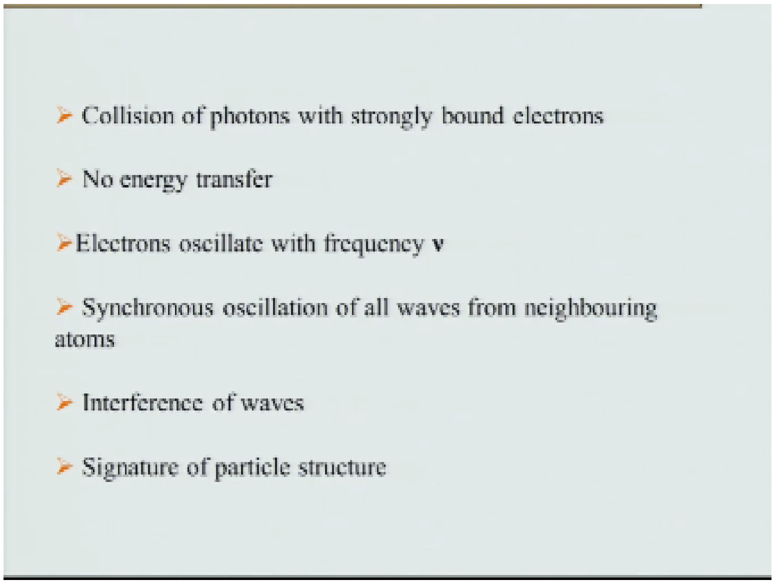

- Collision of photons with strongly bound electrons
- No energy transfer
- Electrons oscillate with frequency **ν**
- Synchronous oscillation of all waves from neighbouring atoms
- Interference of waves
- Signature of particle structure

So as such if the electron is loosely bound the scattering is incoherent however if the electrons are strongly bound, whenever the photon collides with the electron there is no energy transfer instead the electron starts to oscillate with the same frequency as that of the incident x-ray photon. Now this synchronous oscillation of all waves from the neighboring electrons and atoms leads to interference of waves and this is essentially the signature of the particle structure.

So just imagine how we start building up from an electron to an atom which is nothing but an N symbol of electrons to a particle which is nothing but a button and symbol of atoms, so the coherent oscillation of the electrons within a particle leads to scattering of the x-rays and this scattering signal is signature of the structure of the particle.

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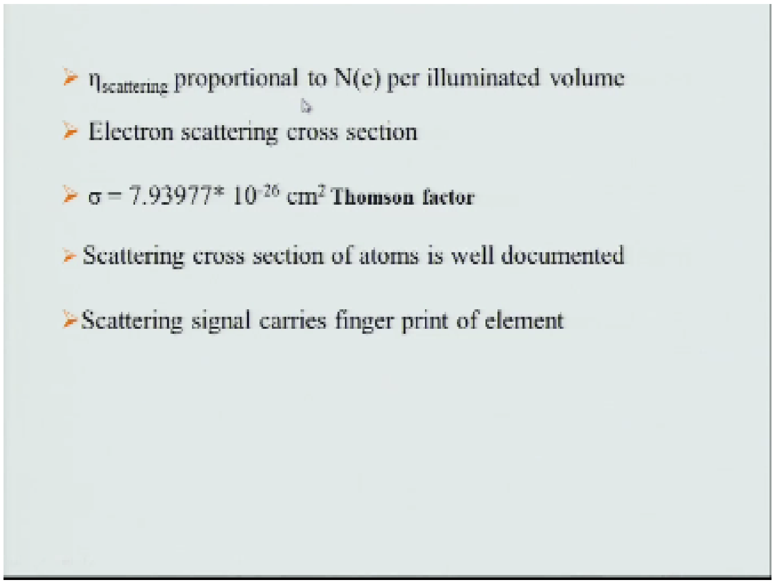

- $\eta_{scattering}$ proportional to N(e) per illuminated volume
- Electron scattering cross section
- $\sigma = 7.93977 * 10^{-26}$ cm^2 **Thomson factor**
- Scattering cross section of atoms is well documented
- Scattering signal carries finger print of element

So we can imagine that the efficiency of scattering is proportional to the number of electrons illuminated per volume, this therefore helps us to define a parameter known as electron scattering cross section. Now this is given by a σ and the value is coated over here which is 7.9 3977 into 10^{-26} centimeter square properly known as the thumbs and factor. Now scattering cross section of atoms is well documented and this catering signal essentially carries the fingerprint of element.

So I hope you can you appreciate that not only do we get information about the size and shape of the particle but also the different phases or different elements which are present in that particular particle.

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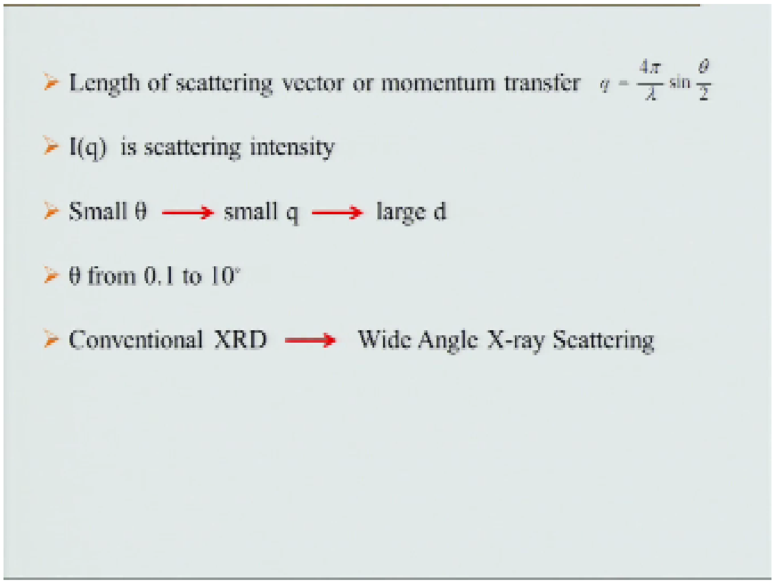

- Length of scattering vector or momentum transfer $q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$
- I(q) is scattering intensity
- Small θ $\longrightarrow$ small q $\longrightarrow$ large d
- θ from 0.1 to 10°
- Conventional XRD $\longrightarrow$ Wide Angle X-ray Scattering

So now going back and looking at the mathematical part of it we know that the length of the scattering vector or the momentum transfer that occurs between the photon and the electron can be given by parameter Q which is defined as 4 π by λ sine θ by 2 where θ is the angle of scattering. I would like to draw your attention to the definition of Q as I hope you recollect that we have a length term namely λ in the denominator.

So q is nothing but a parameter in the reciprocal space, now when we do sax we obtain the intensity of scattering as a function of Q or the scattering angle I hope you appreciate it appreciate that at small angle we get small value of Q and therefore we do get we need a large value of distance to get this signal this is because if you are very close the detector has to be very far away from the sample. So that this small angle is at a significant distance so that it can be separated out.

Unlike a smaller conventional x-ray diffraction wherein we know that the λ and D are of the same order of magnitude we get θ in the range somewhere around 20 to 100 degrees, however when we 22 say about 60 22, 22 θ in the range of 20 degrees and beyond however when we talk about the small-angle x-ray scattering we only get the angles ranging from point 1 to 10 degrees.

The conventional x-ray diffraction system our x-ray diffraction technique that we talked in the last two classes essentially is known as wide angle x-ray scattering. I hope you appreciate that now if we are able to simultaneously used small-angle x-ray scattering which gives us information about the structure of the particles and can use wide-angle x-ray scattering to get information about the diffraction.

We can get a lot of information about the structure of the material and off late there have been lot of efforts to combine these two techniques to carry out simultaneous small-angle x-ray scattering and wide-angle x-ray trained to completely characterize the material under consideration.

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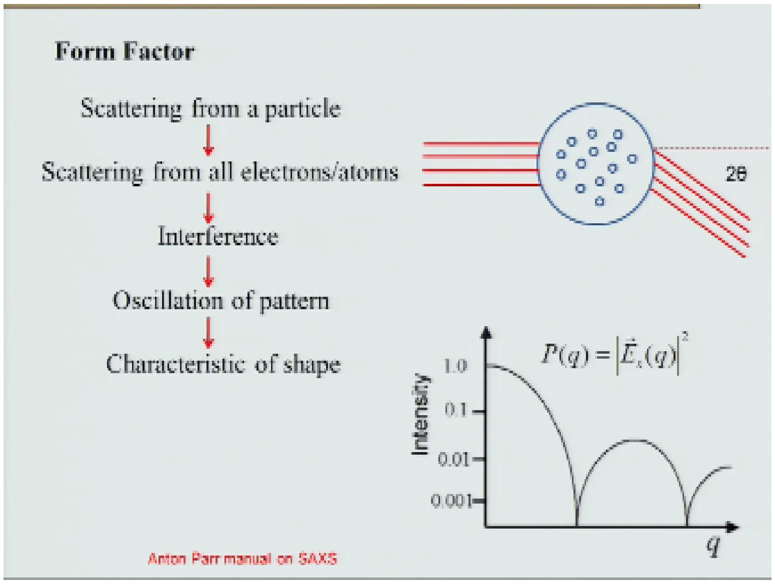

Form Factor

Scattering from a particle

↓

Scattering from all electrons/atoms

↓

Interference

↓

Oscillation of pattern

↓

Characteristic of shape

Anton Parr manual on SAXS

So as we were moving let us consider and a particle and the x-ray is getting scattered from the particle, we know that there is going to be scattering from all the electrons and therefore all the atoms. Now these views the scattered waves are going to interfere with each other and this oscillation pattern is going to have a characteristic shape. Here again I have shown you the variation of intensity as a function of Q which is nothing but the reciprocal vector.

So here we see we get such oscillations therefore you see that the x-ray signal also shows similar oscillation which are characteristic of, so talking about form factor I hope we are you all appreciate that scattering occurs from a particle which comprises of atoms and the atoms comprising of various electrons. So scattering from all electrons atoms as well as the particle essentially leads to interference of the scattered waves which leads to the oscillation re pattern which is shown over here.

And this oscillatory pattern which is obtained by plotting the intensity of the scattered wave versus the Q parameter is a characteristic of the shape of the particle under consideration.

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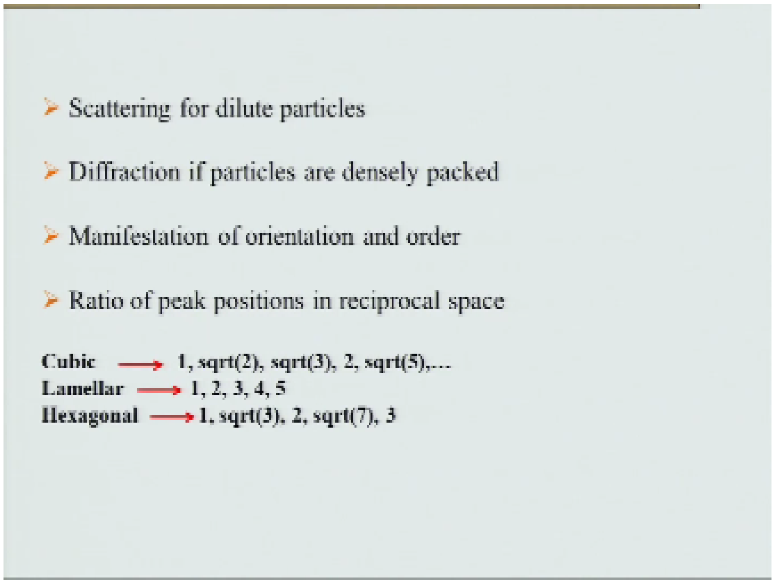

- Scattering for dilute particles
- Diffraction if particles are densely packed
- Manifestation of orientation and order
- Ratio of peak positions in reciprocal space

Cubic → **1, sqrt(2), sqrt(3), 2, sqrt(5),...**
Lamellar → **1, 2, 3, 4, 5**
Hexagonal → **1, sqrt(3), 2, sqrt(7), 3**

So if you look at scattering for dilute particles we get the scattering signal as shown in the earlier case if we are considering very dilute solutions. However there are cases where in the particles get agglomerated and there is a bit of or rather there is presence of long-range ordering in that case we get diffraction in the densely packed particles, this is this leads to manifestation of orientation and order in the pattern that is obtained after scattering.

So the risk ratio of peak positions in reciprocal space can give us an idea about the morphology of the particles, therefore if we have cubic morphology we do get the following be positive the ratio for big positions in the reciprocal space,1 √2 √ 3 2 and so on if you have laminar morphology, we get a big position ratio 1 is to 2 is to 3 is 24 while for hexagonal we have it in the ratio of 1 is 2 √3 is 2 2 and so on therefore this essentially tells us about the shape of the particle.

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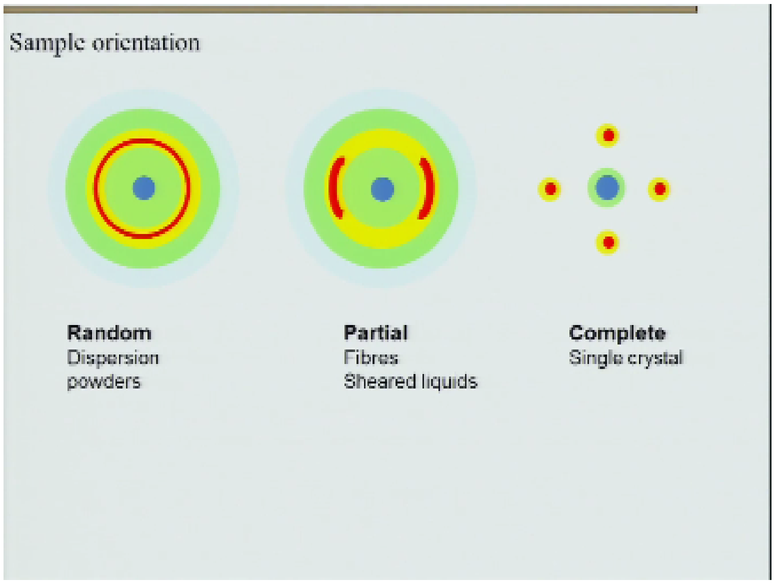

Sample orientation

Random
Dispersion
powders

Partial
Fibres
Sheared liquids

Complete
Single crystal

However when we look at the scattering signal that we get from such a morphology we do see that if there is a random dispersion of particles we do get something very similar to what we would expect in a TM diffract program or TM diffraction pattern, we do see that all the intensity is our presence we get a nice ring pattern. However when we go and see that there is partial orientation like in the case of fibers or shared liquids we get discontinuous rings like we get for highly oriented or what are known as textured materials in a transmission electron microscope.

Similarly when we go for a single crystal we do see that there is complete ordering or rather complete the ordering of the diffraction or the scattering pattern and we do get a pattern which is very similar to that of the diffraction pattern obtained from a single orientation in a transmission electron microscope. So I hope you have you appreciate the similarity between transmission electron microscopy and small-angle x-ray scattering. The beauty is in case of small-angle scattering we do get information indirectly though from the same diffraction pattern.

So we have talked about all the things that can be done and we will go about the intricacies of small-angle x-ray scattering in the couple of slides but let us first understand whether or were all small-angle x-ray scattering is useful. So small-angle x-ray scattering is very useful to study different mechanisms of phase separation.

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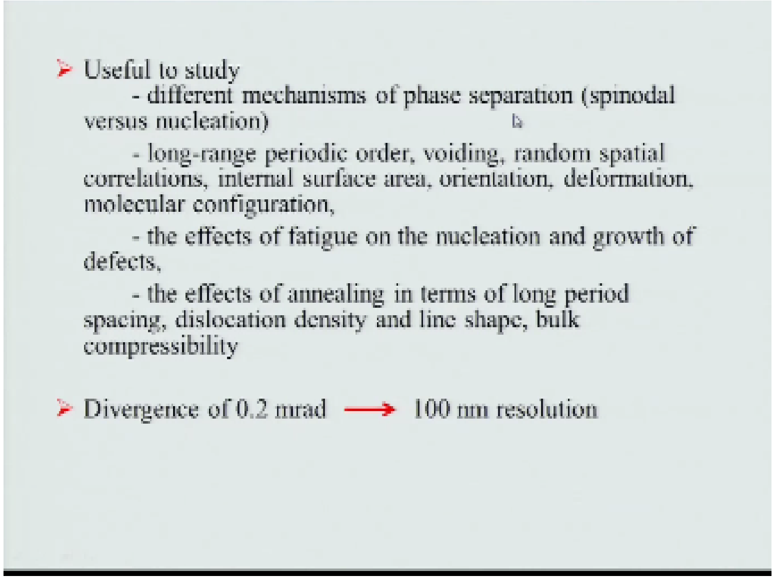

- Useful to study
  - different mechanisms of phase separation (spinodal versus nucleation)
  - long-range periodic order, voiding, random spatial correlations, internal surface area, orientation, deformation, molecular configuration,
  - the effects of fatigue on the nucleation and growth of defects,
  - the effects of annealing in terms of long period spacing, dislocation density and line shape, bulk compressibility
- Divergence of 0.2 mrad ⟶ 100 nm resolution

Namely spindle versus nucleation kind of mechanisms at the same time we can study long-range periodic order voiding random and spatial correlations, internal surface area, orientation deformation and molecular configuration, we can also study the effect of fatigue on the nucleation and growth of defects. The effects of annealing in terms of long period spacing dislocation density and line shape and bulk compressibility can also be studied.

Now this appears a wide range of things that we can cover using small-angle x-ray scattering and we would appreciate that why we can cover such a large range of experiments in small-angle x-ray scattering when we go to the instrumentation part. However I have not mentioned the tremendous use of small-angle x-ray scattering in the field of biology and for deciphering the structure of proteins which essentially works at the interface between materials and materials engineering and biology.

I am not going to touch upon those facts and in fact will focus only on material science related applications what it is to be kept in mind that small-angle x-ray scattering as revolutionized the field of biology and the biological small-angle x-ray scattering is gaining importance and day by day another important thing that I would like to mention is that what are the length scales that we are going to talk about right.

So in order to know the length scale it all depends on the kind of beam that we are getting I hope your room remember the kind of beam processing, we talked about in the last class. So there I would like to just bring it to your notice that a beam with divergence of about point 0.2mrad can give us a resolution of about 100 nanometer, which is probably is the limit of the small-angle x-ray scattering technique.

Therefore you can imagine that for all entities involving particle size up to few lengths of angstroms to about a thousand angstrom can be studied using small-angle x-ray scattering, they find tremendous use in polymer chemistry as well as polymer behavior because the length scale that is associated even with longer chains fall falls in this length scale. So let us talk about the instrumentation part, so essentially all we need is a very strong beam of x-ray.

Now the beam of x ray has to be very small in size about 50 to 80 micron and therefore I hope you remember what all we had talked about we need either a rotating anode or a micro focus x-ray tube which gives us very high brilliance and a very small beam size.

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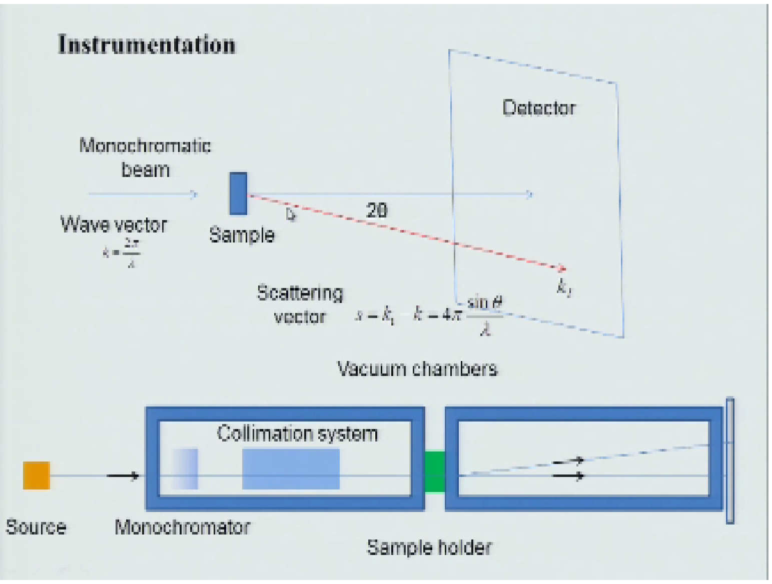

Instrumentation

Once this wave with a wave vector of 2 π by λ passes through the sample it gets scattered and we have to place a detector at a far distance the far distance is at a very large distance the large distance, I hope you remember is required because the angle associated with it is very small so in order to see an appreciable difference and to distinguish between the incident and the diffracted beam we have to keep the detector at a much larger angle.

I hope you also appreciate it appreciate that a two dimensional detector is much users much better information I would like to go back and show you this output which we had talked about I hope you appreciate that this kind of an output comprising of rings or spot patterns can be easily obtained using a area detector. Now coming to the actual assembly of small-angle x-ray scattering which is shown in this figure below we see that we have a source a monochromatic a collimation system and then a detector over here.

The point that is to be noted is that we have a sample holder right in between these two vacuum chambers so the sample holders cell can comprise of not just a sample through which the X rays pass but we can apply various external forces like deformation as well as heating on the sample and study the evolution of microstructure in C2, this is probably the biggest advantage that small-angle x-ray scattering offers in terms of studying the microstructure evolution in C2 during deformation and/or annealing.

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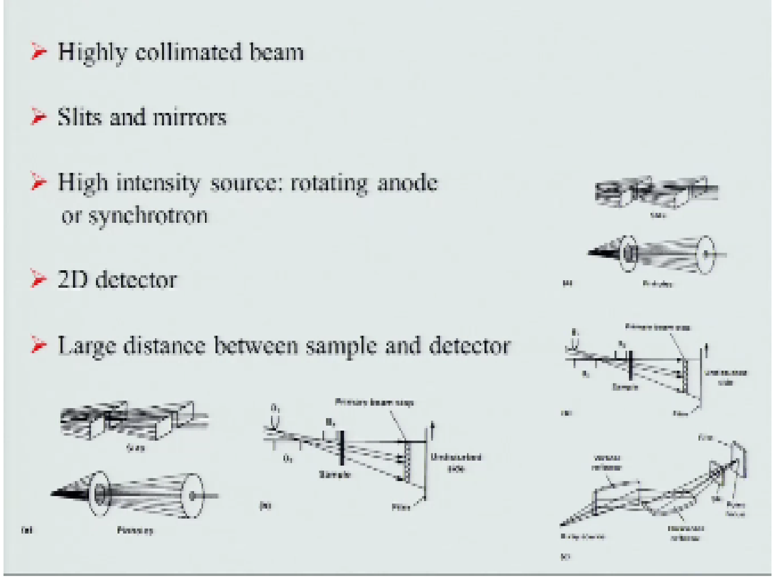
- Highly collimated beam
- Slits and mirrors
- High intensity source: rotating anode or synchrotron
- 2D detector
- Large distance between sample and detector

So I hope you appreciate that we need a highly collimated beam which can be obtained using slits and mirrors and this high intensity source consists of rotating anode or a synchrotron, till date the small-angle x-ray scattering carried out using synchrotrons is probably yielding much deeper insights into the understanding of various materials than a laboratory-scale small-angle x-ray scattering.

However a laboratory-scale small-angle x-ray scattering can provide us sufficient information, so that we can take the important samples to a synchrotron facility. So as we had already mentioned that we need to use a two dimensional detector to get of quick reading as well as the large distance between sample and detector is required. The different geometry of the optics is shown over here.

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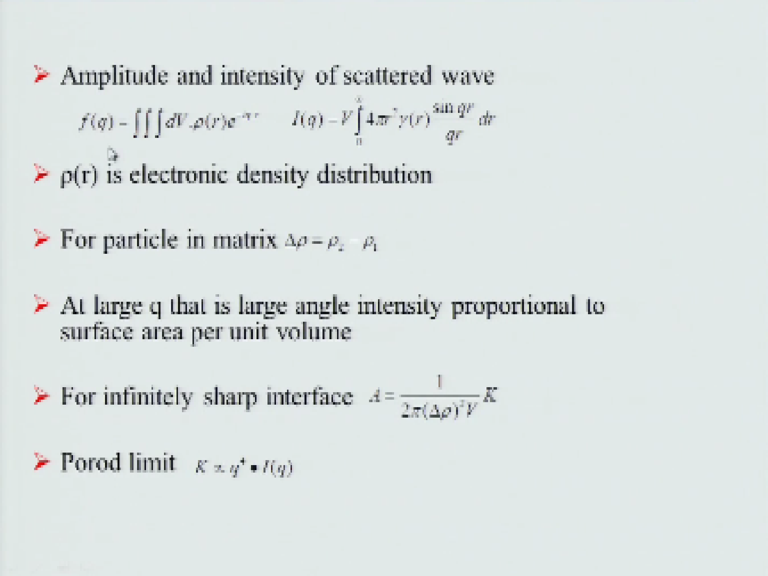

- Amplitude and intensity of scattered wave

  $f(q)=\iiint dV.\rho(r)e^{-iqr}$ $I(q)=V\int_0^\infty 4\pi r^2\gamma(r)\frac{\sin qr}{qr}dr$

- ρ(r) is electronic density distribution
- For particle in matrix $\Delta\rho=\rho_2-\rho_1$
- At large q that is large angle intensity proportional to surface area per unit volume
- For infinitely sharp interface $A=\frac{1}{2\pi(\Delta\rho)^2V}K$
- Porod limit $K\approx q^4\bullet I(q)$

So now let us talk about some little bit of physics that is associated during scattering, so we know that a scattered wave the amplitude of the scattered wave is given by F of Q is =the triple integral over the small volume and ρ R is nothing but the electronic density distribution and e power - IQR right the virtue is your scattering vector. So this defines your amplitude you know that intensity is nothing but the square of the amplitude and this is defined by the equation given over here.

So for a particle in a matrix or for that matter any two phase system the difference in the electronic density plays a very important role. Now at large a value of Q or scattering vector there is large angle intensity proportional to the surface area per unit volume. So the most important entity which will define the shape of the particle is the surface area per unit volume for infinitely sharp interfaces.

We know that the area is given by 1 over 2π ∂ ρ ^{v} by into K this K is given by the odd limit is proportional to Q ^{4} times IQ I will talk about the word limit which occurs at higher value of Q and what is known as the gunner limit which occurs at the lower value of Q, in the next few slides. So the point that we have to remember is that the intensity distribution as of as a function of Q is proportional to the RG^{2} which is nothing but the radius of gyration and I 0 is the scattered intensity not related to the shape of the particle.

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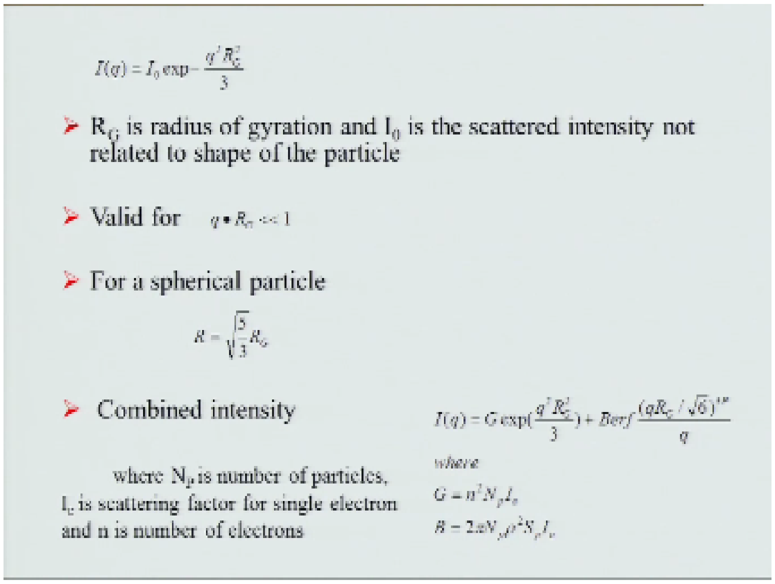

$$I(q) = I_0 \exp - \frac{q^2 R_G^2}{3}$$

- R_G is radius of gyration and I_0 is the scattered intensity not related to shape of the particle
- Valid for $q \bullet R_G << 1$
- For a spherical particle

$$R = \sqrt{\frac{5}{3}} R_G$$

- Combined intensity

$$I(q) = G \exp(\frac{q^2 R_G^2}{3}) + Berf \frac{(qR_G / \sqrt{6})^{3P}}{q}$$

where N$_p$ is number of particles, I$_e$ is scattering factor for single electron and n is number of electrons

where

$G = n^2 N_p I_e$

$B = 2\pi N_p \rho^2 S_p I_e$

So this for this phenomena or this equation is valid for all the values of Q. RG much < 1 this is what is essentially known as the jointer limit, while in the earlier case what we had talked about is at higher value of Q where the interfaces are sharp we are in the poor or limit. So I hope you appreciate that you can always combine these two regimes the whiner limit at the lower value of Q and the poor odd limit at the higher value of Q.

So this vainer and poor odd limit this essentially gives us the or defines the scattering occurring from a particular particle, so we can get the combined intensity the combined scattering intensity by superimposition of these two equations and therefore it can be defined as the combined intensity is nothing but g exponential to ^{2} r g ^{2} by 3 which comes from the governor one and + B error function q RG √6 3 $^{P/Q}$ which essentially is the contribution from the poor odd limit.

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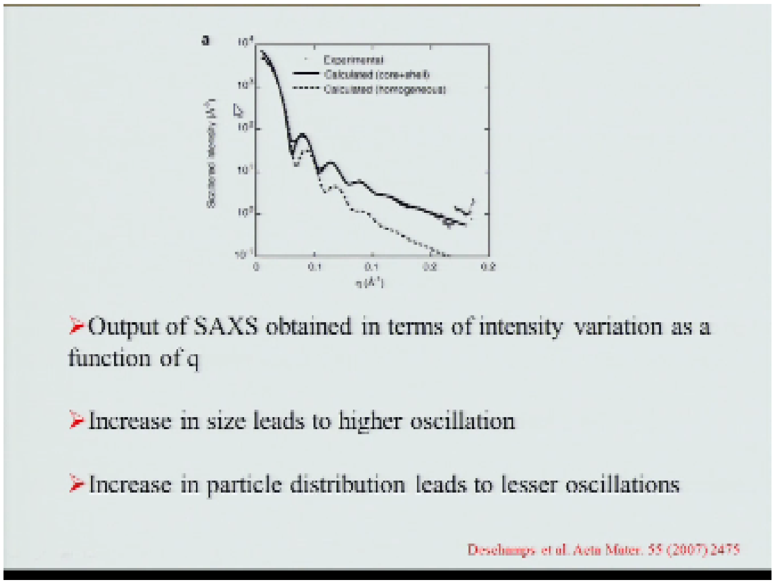

- Output of SAXS obtained in terms of intensity variation as a function of q
- Increase in size leads to higher oscillation
- Increase in particle distribution leads to lesser oscillations

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Let us not get into the complications involved in this equation and just look at the evolution of the spectrum that we get due to small-angle x-ray scattering. So the small-angle x-ray scattering gives rise to a scattered intensity versus Q diagram which comprises of this kind of a behavior and shows characteristics oscillations, I hope you appreciate that these oscillations are occurring over a range of Q as I had already mentioned that the Grinner regime essentially occurs at lower values of Q.

While the which can be looked up to here while the poor odd limit occurs at higher value of Q, so the output of obtained in terms of intensity variation as a function of Q another question that may arise to us is that we had an area detector, in case of an area detector we do see different sectors right. So how do we get this kind of a curve from an area detector this is one point that I had not touched upon in the last class.

So let us touch upon it in today is class so we had seen this is applicable for any area detector we know that.

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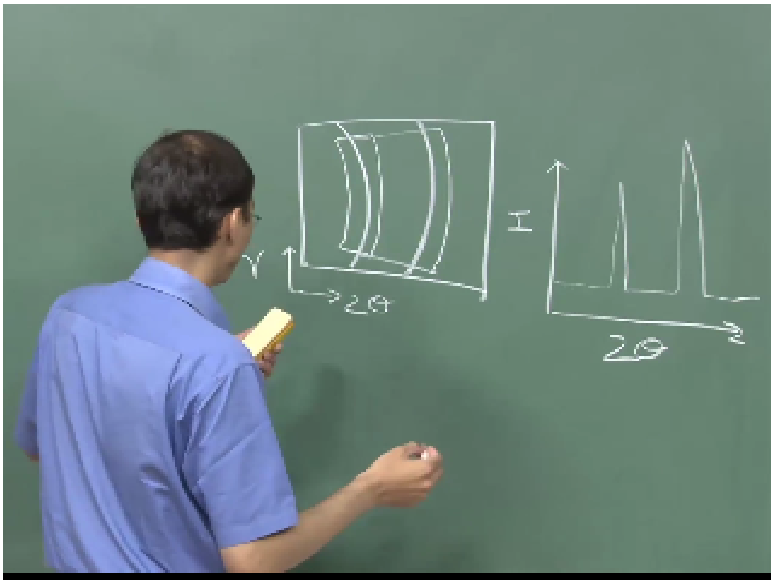

We do get diffraction rings or for that matter in this case scattering rings in order to get information what we have to do this, so I will talk this is a bit of digression but i am going to talk about the diffraction which I missed out in the last class. So you have to θ where is this is something like hi so if you want the integrated to θ intensity all we do is we just integrate it over a range of kinds rate R this will give us the integrated intensity.

Now if i want the integrated intensity of the entire pattern all I need to do is just integrate the entire region okay and once I do this if I integrate all I end up getting is this is 2θ where is this I, now each point here is at particular 2θ is essentially the integration of all the points covered over here and you will end up getting this kind of a curve. Similarly I hope i will now go and show you the kind of pattern that we had seen in small-angle x-ray scattering,

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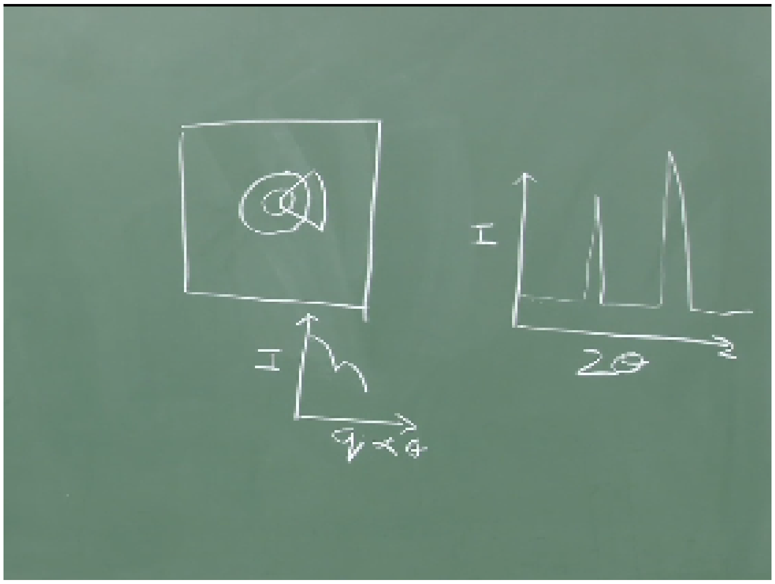

Which comprised of concentric circles right if you remember those colored graphs, so we had these concentric circles so once you integrate them okay I hope you appreciate what we end up getting is this is Q and this is I right because q is also a function of θ right q is proportional to θ right. So this is what we get by integrating, so this is the curve that we had talked about in the earlier class okay.

So now coming back to this what I would to say that there is if at all each oscillation that has shown in this curve over here let us come back to the presentation we see that each oscillation that we are getting over here corresponds or the each oscillation in the stress-strain sorry in the eye versus Q curve, essentially corresponds to the size of the particle. So the first one which corresponds to the largest size is actually the scattering which is occurring because of the from the particle the large particle.

As we had covered earlier also the cue that we are looking at okay is in the reciprocal space, so actually the particle size or the size is increasing as we move from right to left right because Q is in 1 over λ fine. So the first oscillation actually corresponds to the size of the particle okay now if there is an increase in the size this will lead to higher oscillation right. So the number of oscillations will increase so if the particle size is increasing there will be more oscillations.

Because you just think that the particle sizing is increasing the probability of oscillation or scattering occurring is going to improve and therefore with the increase in size I hope you understand that this part with increase in size is going to move towards the left right because your length this is the what you have plotted q is in reciprocal space, so this has to move the oscillation part the first oscillation minima has to move to the left at the same time the number of oscillations have to increase if the particle size is increasing.

Similarly if there is a wide distribution in the size of particles we are going to get lesser and lesser of solutions for the same reason as we discussed earlier.

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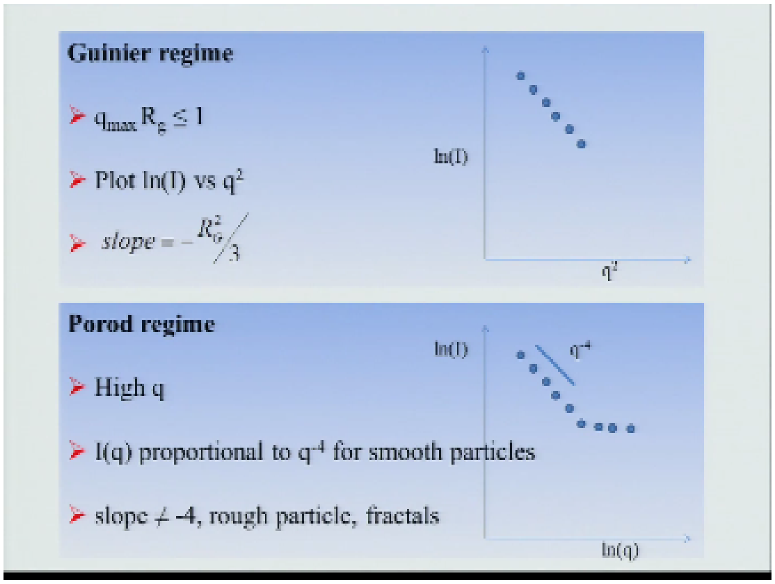

Guinier regime

- $q_{max} R_g \le 1$
- Plot ln(I) vs q^2
- $slope = -R_G^2/3$

Porod regime

- High q
- I(q) proportional to q^{-4} for smooth particles
- slope ≠ -4, rough particle, fractals

So again going back and talking about Guinier regime we saw that go in regime is valid for q RG is much lesser than one and for the maximum limit is Q Mike's into our g is less than =1 so this can be well studied by plotting LAN of the intensity versus the Q ^{2} and this fits a straight line and the slope that we get is essentially given by - r g ^{2} by 3 and you know that RG which is nothing but the radius of gyration can be actually related to the radius of the particle by this particular equation where radius of the particle is $\sqrt{\pi}/3$ times RG.

So this can essentially ensure that the size of the particle that what is the size of the particle similarly the Porod regime essentially occurs for higher value of two generally we realize that it occurs for cube greater than 1 and IQ the intensity is proportional to 1 over Q ^{4} smooth particles. So we know that you know the particle is smooth and we also know what the size of the particle is if the slope is not four or not- for we know that the particles are rough and they may have a fractal characteristic.

So having said that see how we essentially decipher the complete information about the size using this information the coiner regime this particular formula the shape using the Porod regime and size shape and what about orientation well we just have to go back and if you recollect the ratio of these Peaks which I have touched up on over here the ratio of the peak positions in the reciprocal space if they are in a particular ratio then we are going to get the shape also okay.

So you get complete information the size the shape whether it is smooth or not whether it is fractal as well as the orientation whether it is oriented in a cubic way or a lamellar way or a hexagonal. So all this information see remember this is not obtained in a direct way but in an indirect way all this information is embedded in the inner in the small-angle x-ray scattering a pattern that you obtain okay.

So but having said that all this is much easier for me to say and you to nod your heads but doing this after once you get the raw data correcting it and you know drawing valuable information from it takes a lot of time and therefore, the way we do it is using a lot of analysis. In the last lecture on x-ray diffraction also I just ended up giving you an about all the hardware part of it but the actual data analysis there can be an entire class on just how to do data analysis on x-ray diffraction itself.

Having said that I will just give you a glimpse of x-ray of data analysis for small-angle x-ray scattering wherein, we start with a small simple educated guess as into what is the size or the structure of the material under consideration, calculate the scattering function. So see this is like having a library if I have spherical particles what is the kind of scattering function that I am expecting you can do that.

Now compare your simulation with experiment I tell not only that I have particles but what this is I am having you tell that you get the simulated part and compare it with your experiments and then again go back and refine it you do this time and again go back and forth till you get a good match between your experimental and simulated results.

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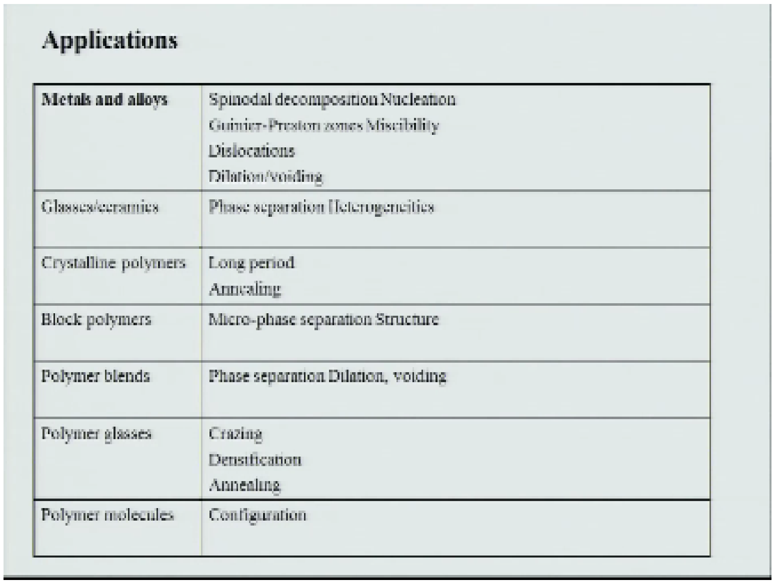

Applications

Metals and alloys	Spinodal decomposition Nucleation Guinier-Preston zones Miscibility Dislocations Dilation/voiding
Glasses/ceramics	Phase separation Heterogeneities
Crystalline polymers	Long period Annealing
Block polymers	Micro-phase separation Structure
Polymer blends	Phase separation Dilation, voiding
Polymer glasses	Crazing Densification Annealing
Polymer molecules	Configuration

Now before I go ahead and present a particular case study what I would like to show you is the various application the various processes for which you can use small-angle x-ray scattering I would like to mention that you know this course on advanced characterization techniques is not for you to go and do something on a day-to-day basis but provided you face a problem and see something interesting you should know which characterization technique you should use to solve your problem.

Therefore I will do you the application were on you know kind of you can use small-angle x-ray scattering to solve your problem. So if you are working on metals and alloys you can understudying spindle decomposition, new nucleation, GP zones miscibility dislocations dilation voiding you can use small-angle x-ray scattering for studying all these.

If you are working on glass and ceramics you can use for studying phase, separation heterogeneities long period as well as annealing in the crystalline polymers can be studied a lot of things regarding polymers can be done using small-angle x-ray scattering which correspond to micro face separation, dilatation, voiding, tracing density, annealing as well as configuration, as had earlier mentioned that in biology there is a lot of use of small-angle x-ray scattering.

However you I hope you remember you can appreciate that this signal strength or the scattering from biological molecules is very weak and therefore most of the times we need a very strong x-ray source and therefore most of the small-angle x-ray scattering to be carried out on biological samples is mostly restricted to synchrotron okay. So but on a routine basis if you get access it is worth trying to find out how what kind of information we can get using small-angle x-ray scattering.

I have therefore chosen a particular case study I will not go in much details but just present one case study and I would request that you go back and go through the case study once again to appreciate the beauty of the small-angle x-ray scattering technique.

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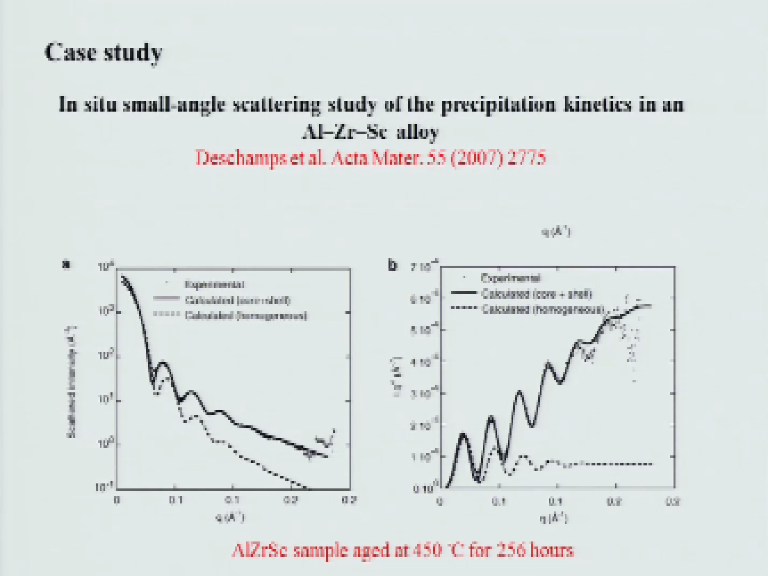

Case study

In situ small-angle scattering study of the precipitation kinetics in an Al–Zr–Sc alloy

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AlZrSc sample aged at 450 °C for 256 hours

So this is one paper by Reese amps Ethel published in active material here where they talk about in situ small-angle scattering study of precipitation kinetics in an aluminum zirconium stand annoyed. So this is very important see precipitation hardening is something that has been studied or you know plenty of years but still the actual evolution of the precipitates a during aging is not well understood particularly in something like aluminum zirconium alloy where we get a core shape structure of precipitates.

So in the first figure which is shown at the bottom you see on the left hand side we do see that the scattered intensity versus to this is the old figure that we had the scene last time around we see similar oscillations right, we can also plot the ayah intensity in 2q ^{4} versus Q and we do see there is another oscillation. So here in we have shown plotted this from I have you know borrowed this from the paper and they show that your calculated one shows a good match for the core-shell microstructure which is shown over here.

While the homogeneous one does not show, so here you see you make a test you make a calculated guess and you see that your experimental and the guest comprising of course shell micro structure consisting of two phase right which we will talk about in the next slide use your much better match. So here you start with an assumption and see whether it matches your experimental findings or not a few more information on this.

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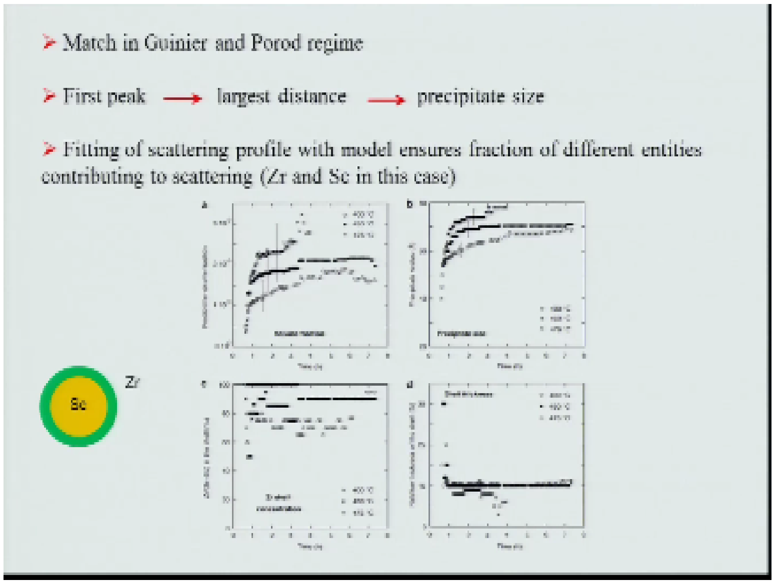

- Match in Guinier and Porod regime
- First peak → largest distance → precipitate size
- Fitting of scattering profile with model ensures fraction of different entities contributing to scattering (Zr and Sc in this case)

So you know that we get in the present case we do get a good match in the joiner as well as the poor Audrey Jane. You see that the first peak which corresponds to the largest distance which I have shown earlier corresponds to the size of the precipitate, so we can get information about the size of the precipitate similarly what calculation we are doing right to fit the peak gives us information the fitting the peak what I mean core-shell microstructure what I was talking about is that the precipitate we get a core comprising of plenty of scandium.

So it is a scandium rich code and rich periphery, so how do you get information about this core shell microstructure well while calculating this particular calculated core shell I hope you remember there was this Δρ term which you are putting so this Δρ comprises of ρ 1 and ρ 2 which is nothing but the electronic density of the faces under consideration in this case we can have scandium and zirconium.

So what all information we are getting so in the first graph over here you see we have precipitate volume fraction as a function of time, so this was done for three different temperatures we also get information about the precipitate radius again all this information is obtained from small-angle x-ray scattering we can also go back and get information about the zirconium to zirconium scandium in the shell.

So the conium plus can so the fraction of zirconium now again this information is obtained while we are doing the fitting of the scattered intensity, so we can know how does the microstructure is evolving in terms of the elemental content at the same time we also get information about relative thickness of the shell which again can be determined during our fitting and we can get information as a function of time at various temperatures.

Therefore I hope you appreciate that using a small angle scattering we can study precipitation evolution in aluminum scandium zirconium alloy as a function of time in C2. Now this is one which we get over any other characterization techniques or institute which involve in situ deformation like transfer in situ heating or and precipitation like transmission electron microscopy.

So I hope with this case study have been able to give you just a brief glimpse of what all small-angle x-ray scattering can do I hope that you go back and search for application of small-angle x-ray scattering in your area of interest. In the next class I will expose you to another technique which is a sister technique of small-angle x-ray scattering and is known as grazing incidence small-angle x-ray scattering that is it.

Acknowledgement
Ministry of Human Resources & Development

Prof. Phaguni Gupta
Co-ordinator, NPTEL IIT Kanpur

Prof. Satyaki Roy
Co Co-ordinator, NPTEL IIT Kanpur

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K.K Mishra
Jai Singh
Sweety Kanaujia
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Sweta
Preeti Sachan
Ashutosh Gairola
Dilip Katiyar
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Puneet Kumar Bajpai
Priyanka Singh

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Shivendra Kumar Tiwari
Saurabh Shukla

Direction
Sanjay Pal

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an IIT Kanpur Production