Particle Characterization

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Module No. # 11
Lecture No. # 32
Nano-particle Characterization: Properties and Techniques

Welcome to the thirty-second lecture in our Particle Characterization course. In the last few lectures, we have been examining methods of synthesizing nano-particles, as well as, dispersing them in suspension as well as in composite materials and so on.

Now, in order to for us to be able to characterize these nano processes and also to control and optimize them, it is very important that we have to be able to measure the relevant properties of these nano-particles as well as their suspensions. So, in this lecture we are going to focus on techniques that are particularly appropriate for characterizing nano-particles. As we do so, we will also look at some important properties of nano-particles, both from a functional viewpoint as well as from a material view point.

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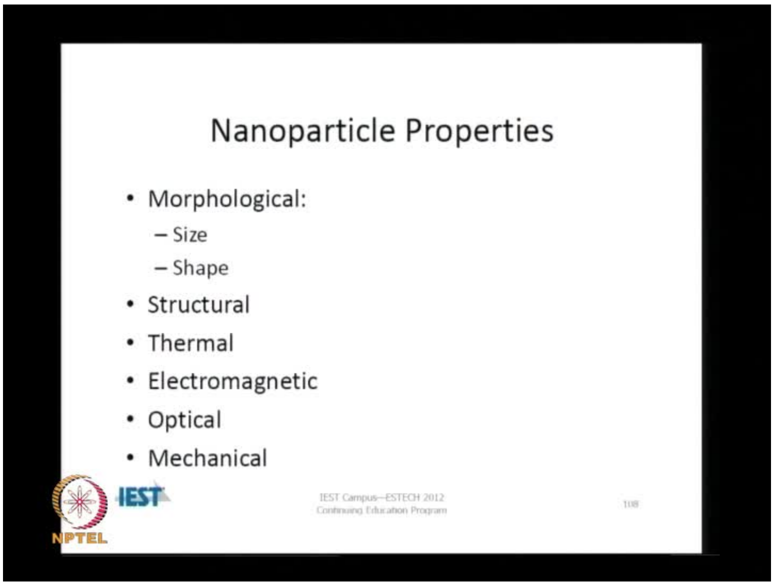

Nanoparticle Properties

- Morphological:
  - Size
  - Shape
- Structural
- Thermal
- Electromagnetic
- Optical
- Mechanical

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So, when we look at nano-particle properties, they are not too dissimilar from the properties of particles that we had listed earlier, when we started this course. There are the morphological properties - size and shape, structural properties. And then in terms of functional property enhancement, there is an emphasis on characterizing thermal properties, electromagnetic properties, optical properties and mechanical properties of nano-particles, because it is in these properties that they show particularly significant differences in the nano form compared to bulk form.

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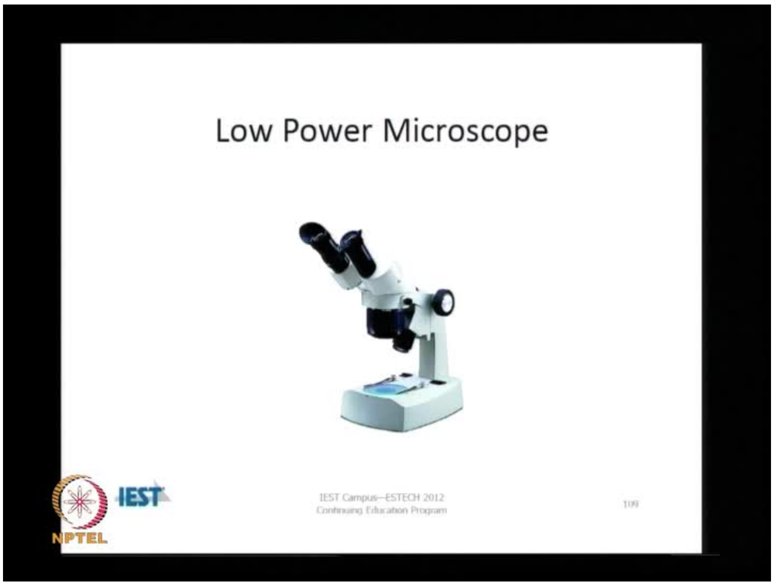

Low Power Microscope

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What are some of the tools that are used to characterize nano-particles? Well we start with the simplest of them all, which is the low power microscope, that I am sure you all used in your laboratory. You basically look through an eyepiece and look at objects with, anywhere from 10 x to a 100 x magnification, depending on the power of the microscope that you have.

It is certainly a very useful tool, and we have discussed as we have discussed earlier in this course, it is a starting point to most analysis, you really cannot jump from visual inspection to SCM or TEM because the difference is just too large. An optical microscope is an intermediate tool that is used to provide some additional magnification beyond what you can just get with your naked eyes, but at the same time, their magnification is low enough, that you can sample a fairly large surface area without wasting too much time on it. So, it is a good prescreening methodology, before you decide what more sophisticated analytical instrumentation you are going to employ.

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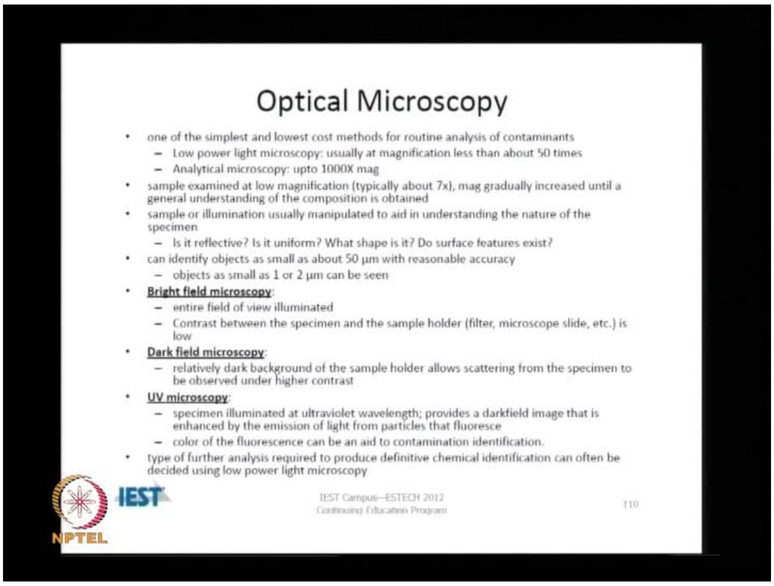

Optical Microscopy

- one of the simplest and lowest cost methods for routine analysis of contaminants
  - Low power light microscopy: usually at magnification less than about 50 times
  - Analytical microscopy: upto 1000X mag
- sample examined at low magnification (typically about 7x), mag gradually increased until a general understanding of the composition is obtained
- sample or illumination usually manipulated to aid in understanding the nature of the specimen
  - Is it reflective? Is it uniform? What shape is it? Do surface features exist?
- can identify objects as small as about 50 μm with reasonable accuracy
  - objects as small as 1 or 2 μm can be seen
- **Bright field microscopy**:
  - entire field of view illuminated
  - Contrast between the specimen and the sample holder (filter, microscope slide, etc.) is low
- **Dark field microscopy**:
  - relatively dark background of the sample holder allows scattering from the specimen to be observed under higher contrast
- **UV microscopy**:
  - specimen illuminated at ultraviolet wavelength; provides a darkfield image that is enhanced by the emission of light from particles that fluoresce
  - color of the fluorescence can be an aid to contamination identification.
- type of further analysis required to produce definitive chemical identification can often be decided using low power light microscopy

We have discussed optical microscopy earlier in our lecture, but just to recap the key points; it is a simple method, low cost, it is widely used for routine analysis, magnification less than 50 times; however, there are analytical microscopes that are available, that can provided up to 1000 x magnification. The sample is examined initially at a low magnification 5 to 7 x, and then the magnification is gradually increased, until you get a better understanding of what you are looking at.

The sample or illumination, the lighting that you provide, is manipulated to aid in the understanding. So, for example, you can assess whether the surface or particle is reflective, how uniform is it, what is its shape, what are the surface features that are predominant. With an optical microscope, you can certainly see objects as small as 50 microns or even 1 to 2 microns; however, the resolution is poor, and that is the reason why we need to go to electron microscopy.

Again, as we have discussed earlier, there is Bright field microscopy, Dark field microscopy and UV microscopy. In Bright field, you eliminate the entire field of view, and you particularly examine the contrast between the specimen and the holder. In Dark field microscopy, you use a dark background and you allow the particles to be highlighted as bright spots. In UV microscopy, you illuminate the specimen with UV wavelength and this is particularly useful in detecting particles and materials that fluoresce.

Now, the low power like microscopy is not an end to itself, for most purposes particularly in the nano regime, it is only the starting point, it allows you to decide what type of additional analysis is needed. As we have seen before, one of the first classifications you have to do is; is it a metallic or a non-metallic substance, is it an organic or inorganic substance. These types of decisions then allow you to appropriate instrumentation for doing more in-depth analysis.

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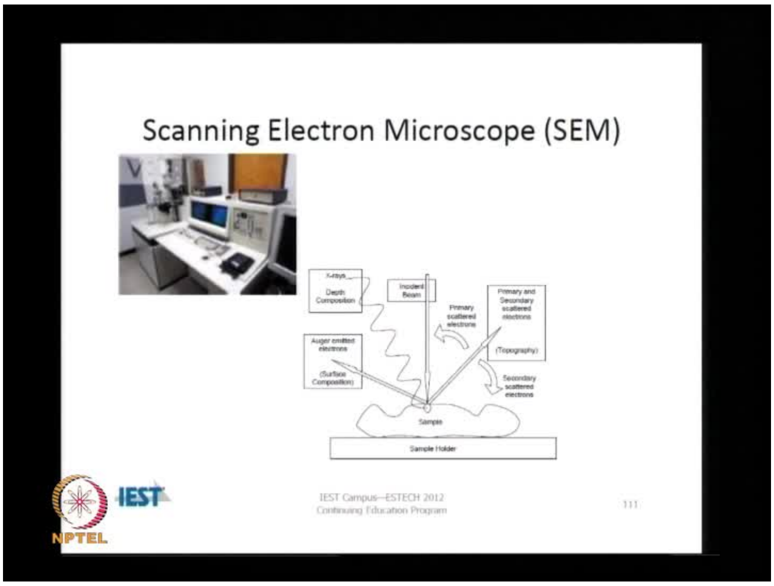

Scanning Electron Microscope (SEM)

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The Scanning Electron Microscope, as we have seen earlier, is a huge advancement over optical microscopy. Here the sample is being irradiated with an electron beam, and the electrons that are being emitted scatter electrons from the sample, that is under analysis. And by looking at these scattered electrons, by gathering them and subjecting them to appropriate analysis, we can get an idea about the topography of the surface as well as the elemental composition of the material.

As we have seen before, you can do x-ray microscopy to get analysis regarding particularly, the composition of the material and AUGER analysis, which enables you to knock off particles at various layers of the particle or surface, and therefore, enables you to do depth profiling. And by the way, in this figure you would notice that there is a mislabeling; x-rays do not provide depth analysis, they primarily provide composition analysis, AUGER electrons really provide your depth analysis.

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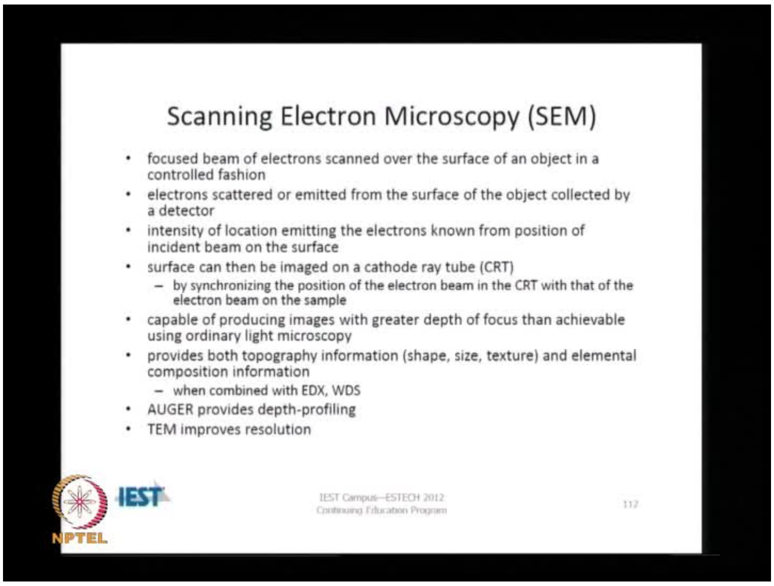

Scanning Electron Microscopy (SEM)

- focused beam of electrons scanned over the surface of an object in a controlled fashion
- electrons scattered or emitted from the surface of the object collected by a detector
- intensity of location emitting the electrons known from position of incident beam on the surface
- surface can then be imaged on a cathode ray tube (CRT)
  - by synchronizing the position of the electron beam in the CRT with that of the electron beam on the sample
- capable of producing images with greater depth of focus than achievable using ordinary light microscopy
- provides both topography information (shape, size, texture) and elemental composition information
  - when combined with EDX, WDS
- AUGER provides depth-profiling
- TEM improves resolution

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Now, looking at Scanning Electron Microscopy in a little more detail, again you take a focus beam of electrons and you run it over the surface of the object, electrons are scattered or emitted from the surface of the object, collected by a detector and the intensity of the emissions or scattering allows us to image it on a cathode ray tube, and this produces images that have very high depth of focus. The primary advantage of a Scanning Electron Microscopy is the depth of focus compared to light microscopy.

SEM can provide shape analysis, size analysis, texture and when you combine it with a energy dispersive x-ray analysis or wave length dispersive spectroscopy, it also provides elemental composition information. AUGER analyses provides depth profiling, and of course, a Tunneling Electron Microscopy, as we have seen, improves resolution by an order of magnitude compared to Scanning Electron Microscopy.

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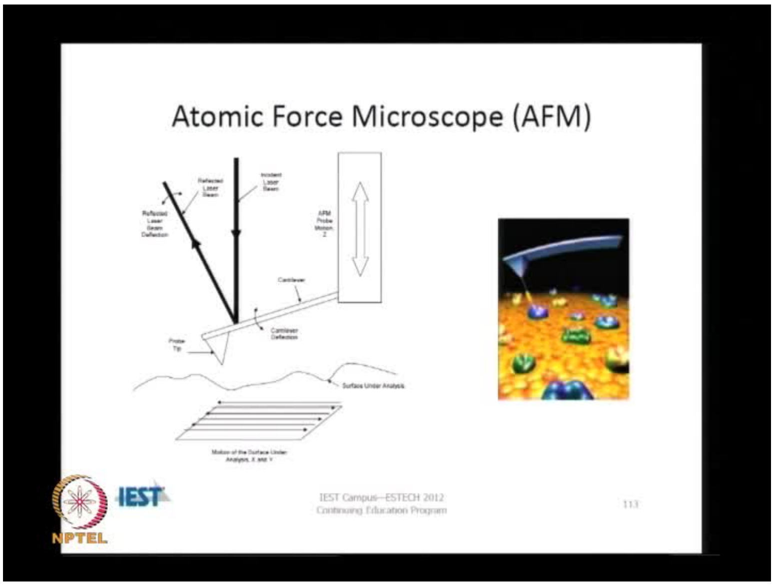

Atomic Force Microscope (AFM)

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The Atomic Force Microscope is again an instrument that we have dealt with in some detail earlier in our lecturers, in the context of particle characterization, in general. It is specially suited to analysis of nano-particles, because of its ability to manipulate as well as see matter at nano-scale or even sub nano scale.

Again, what this consist of, is a probe that rides very close to the surface with angstroms of separation between the surface and the probe. So, it is very sensitive to inter molecular forces of attraction and repulsion, and therefore, can very sensitively detect changes in the morphology or composition of the substrate, essentially by using a cantilever principle. The small deflection of the probe due to the induced force is magnified many times using a cantilever arrangement, and therefore, it enables us to identify and even quantify very small variations in surface topography in three-dimensions.

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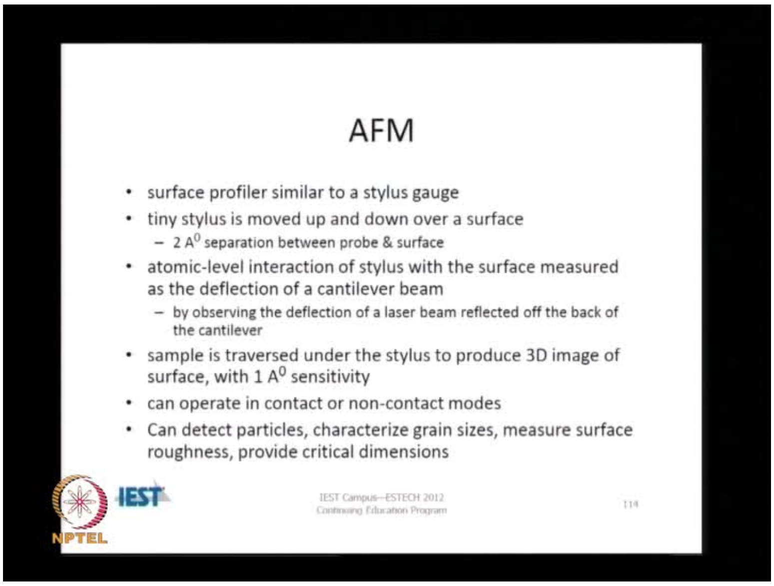

AFM

- surface profiler similar to a stylus gauge
- tiny stylus is moved up and down over a surface
  - 2 A^0 separation between probe & surface
- atomic-level interaction of stylus with the surface measured as the deflection of a cantilever beam
  - by observing the deflection of a laser beam reflected off the back of the cantilever
- sample is traversed under the stylus to produce 3D image of surface, with 1 A^0 sensitivity
- can operate in contact or non-contact modes
- Can detect particles, characterize grain sizes, measure surface roughness, provide critical dimensions

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So, an Atomic Force Microscope is essentially a surface profiler, very similar to a mechanical stylus, that is used to gauge roughness of surfaces, and in fact, it does consist of a small stylus, that is moved up and down over a surface, two angstroms of separation between the probe and the surface. This enables us to achieve an atomic level interaction with the surface, which is measured as the reflection of the cantilever beam using a laser, that is reflected of the back of the cantilever. So, essentially you traverse the sample under the stylus and obtain 3D imaging of the surface with 1 angstrom sensitivity.

As we have discussed in length, that in the class, you can operate it either in contact mode or non-contact mode, depending on how close you bring the probe to the surface. If you bring the probe within the attractive range of the intermolecular potential, then it is essentially operating in a contact mode, whereas, if you locate the probe in the repulsive region of the intermolecular potential curve, you are operating in a non-contact mode. Of course, we have also discussed the intermittent contact mode, where the probe periodically moves from the non-contact region to the contact region. And each of these modes of operations has their own particular benefits as well as disadvantages for various types of analysis. But in general, an Atomic Force Microscope can detect particles, we can characterize grain sizes, measure surface roughness and provide critical dimensions in 3D.

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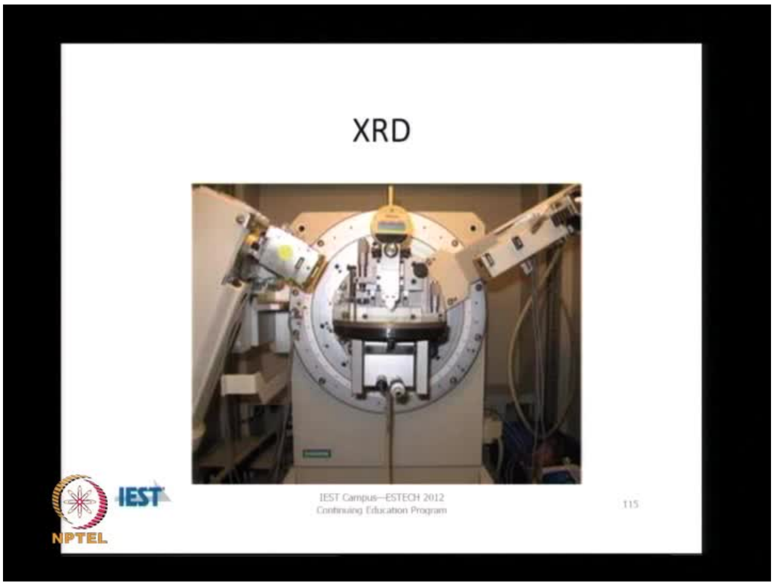

XRD

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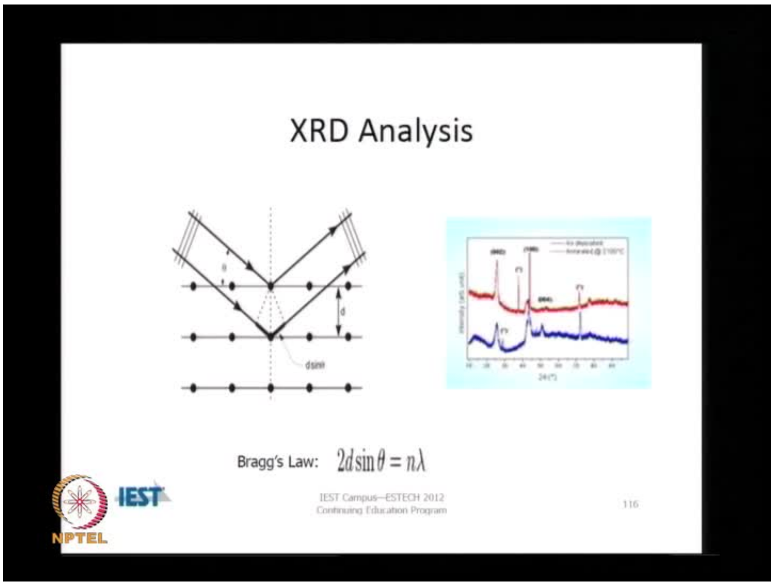

XRD Analysis

Bragg's Law: $2d\sin\theta = n\lambda$

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XRD, again we have discussed in some detail in class, it is the primary method that is used to detect the crystallographic structure of a material, and it operates by the principle of Bragg's law, which can enables us to measure inter planar distances in a crystalline structure, by looking at scattering intensity.

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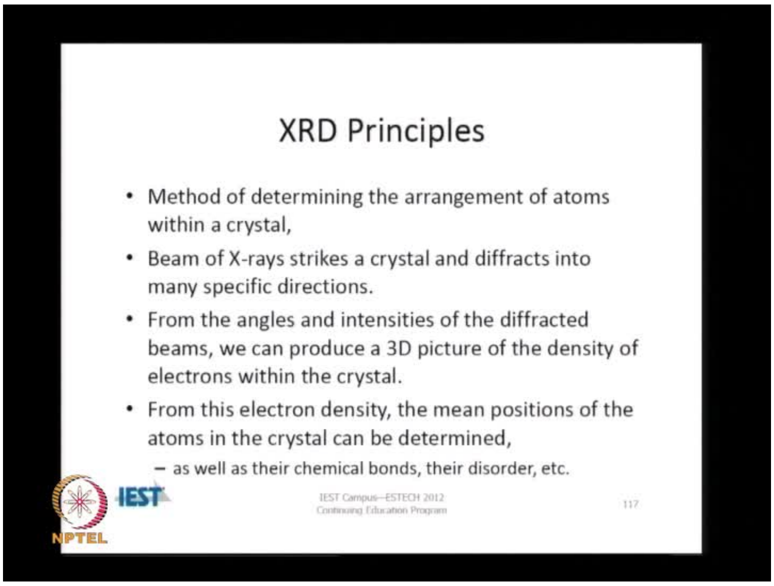

XRD Principles

- Method of determining the arrangement of atoms within a crystal,
- Beam of X-rays strikes a crystal and diffracts into many specific directions.
- From the angles and intensities of the diffracted beams, we can produce a 3D picture of the density of electrons within the crystal.
- From this electron density, the mean positions of the atoms in the crystal can be determined,
  - as well as their chemical bonds, their disorder, etc.

So in XRD, what we trying to do to is, determine the arrangement of atoms within a crystal. So, beam of x-ray strikes a crystal diffract into many directions. We measure the angles and intensities of the diffracted beams, and therefore, we produce a three-dimensional image of how the electrons are actually located within the crystal. And from that information, you can determine the mean position of the atoms in the crystal as well as the structure of the bond, the chemical bonds, the disorder in the crystal lattice and so on. So, XRD is a very powerful technique, in terms of enabling us to peek into the crystallinity of the material.

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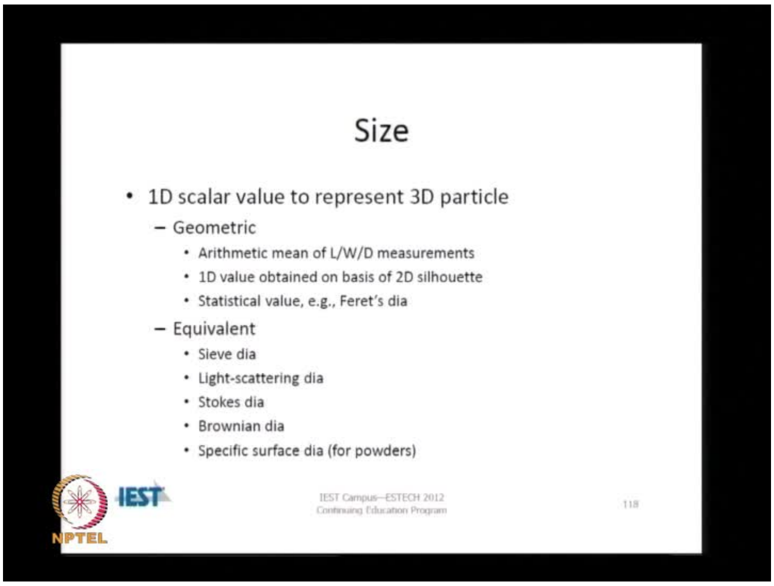

Size

- 1D scalar value to represent 3D particle
  - Geometric
    - Arithmetic mean of L/W/D measurements
    - 1D value obtained on basis of 2D silhouette
    - Statistical value, e.g., Feret's dia
  - Equivalent
    - Sieve dia
    - Light-scattering dia
    - Stokes dia
    - Brownian dia
    - Specific surface dia (for powders)

Now in terms of size analysis, we have seen several methods in this course earlier. Essentially when we talk about size, what we are trying to do is, represent even a three-dimensional particle with a dimensional scalar value. So, for example, when we represent the particle by a diameter, that is what we are doing, we are assuming that the shape of the particle is roughly spherical, and therefore, you can use essentially a single dimension to represent the size of the particle.

Size is represented in two ways, as absolute geometric values. So, for example, you can take the size of a particle in three-dimensions; call them length, width and the depth dimensions. And you can do statistical averaging of these dimensions as well. And through these geometric measurements, you can assess size. You can either do again, a single dimensional value of the size or you can obtain a two-dimensional representation of the size and so on. And you can use statistics to the level that you want; you can either relay up on a single measurements or you can measure the same particle at various angles and obtain mean values of l, w and d. We have seen some examples of statistical size analysis earlier in this course such as; Martin's diameter and Ferret's diameter and so on.

So, these are simple geometric representations of size; however, in many cases what we are interested in is, not the absolute size of the particle, but rather how it behaves in our process. The functional dimensions of the particle, in order to obtain the functional values of particle size, we typically use equivalent diameters. For example, when we use sieve analysis for size determination, the value that we are measuring is not the absolute size of the particle but the sieving diameter. It is essentially the diameter of a spherical particle, which will be sieved with the same efficiency as a real particle that we looking at. Similarly, light scattering diameter is essentially the diameter of a spherical particle, which scatters light with the same intensity as the particle under question. Stokes diameter would be the diameter of a spherical particle that settles with the same velocity as the real particle that we are looking at and so on.

And so, equivalent sizes are not absolute sizes, but they provide us with a relative measure, which can be used very effectively in controlling or running specific processes. As long as we are clear in our understanding that, particle size is never a unique value, it really depends on the method of measurement, and this is increasingly true as you approach the nano dimensions. The method of measurement itself determines the size that you measure. So, for example, if you set the particle in diffusional motion, and you measure its size based on its rate of diffusion, that is called a Brownian diameter. Is it a true representation of the geometrical size of the particle? Not really. Again, what we are measuring here is a size that represents its transport properties most closely.

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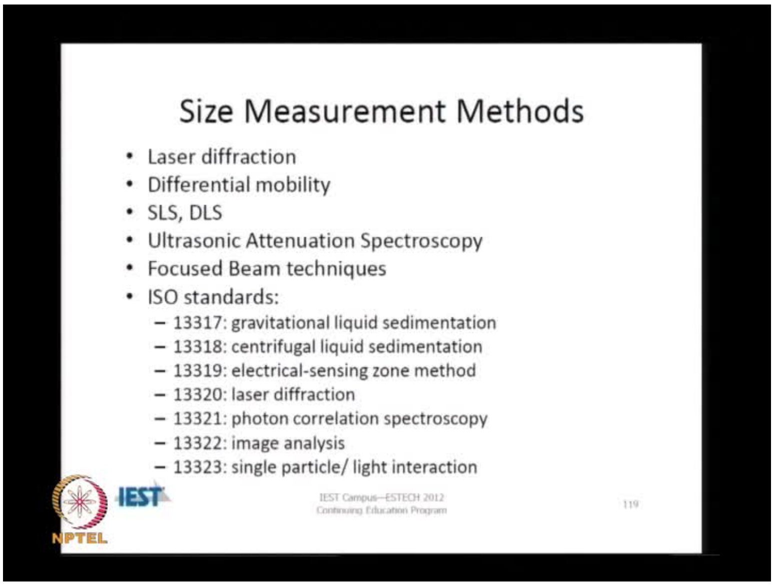

Size Measurement Methods

- Laser diffraction
- Differential mobility
- SLS, DLS
- Ultrasonic Attenuation Spectroscopy
- Focused Beam techniques
- ISO standards:
  - 13317: gravitational liquid sedimentation
  - 13318: centrifugal liquid sedimentation
  - 13319: electrical-sensing zone method
  - 13320: laser diffraction
  - 13321: photon correlation spectroscopy
  - 13322: image analysis
  - 13323: single particle/ light interaction

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There are many methods of size measurement, we have reviewed several of them in the earlier in this course; Laser Diffraction based methods, Differential Mobility based methods, Static Light Scattering and Dynamic Light Scattering based methods, Ultrasonic Attenuation Spectroscopy, Focused Beam techniques. And in fact, there are standards that have been set by the International Standards Organization, ISO, for size measurement of particles. There is standard on size measurement by gravitational liquid sedimentation, method based on centrifugal liquid sedimentation, electrical- sensing zone methods, laser diffraction methods, photon correlation spectroscopic methods, image analysis methods and single particle/ light interaction methods. So of these standards, the first two 13317 and 13318, are really not applicable to nano-particles, because they required particles to be quite large, in order to be able to characterize them based on the settling characteristics. However, standards 19 to 23 do apply to nano-particles, and we will review them in a little more detail in this lecture.

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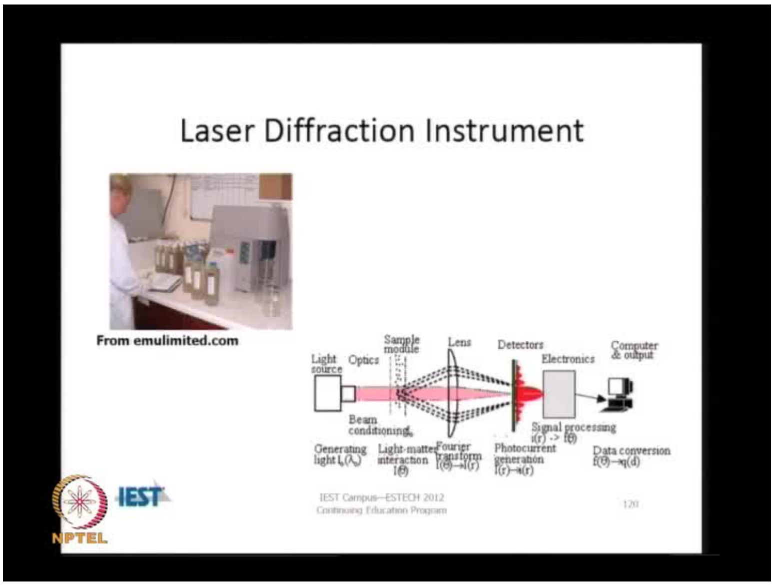

Laser Diffraction Instrument

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Now, Laser Diffraction, again we have discussed quite extensively earlier in this course, it essentially takes a light source and impinges the light onto the sample, which causes the light to be scattered. And the scattered light is then collected, through an arrangement of lenses and detectors, and the signal is analyzed. And through the use of calibration curves that relate, for example, scattering intensity to the size of a particle, you can estimate the size of the particle based up on your measurements of scattered light.

So, in principle laser diffraction is a method that works quite well for the size assessment of particle, but as we have seen earlier, when we go into the nano regime, because scattering intensities scales as particle size to the power 6, the scattering intensity is very feeble. And therefore, it is difficult to get a good signature of the particle by simply relaying on Laser Diffraction.

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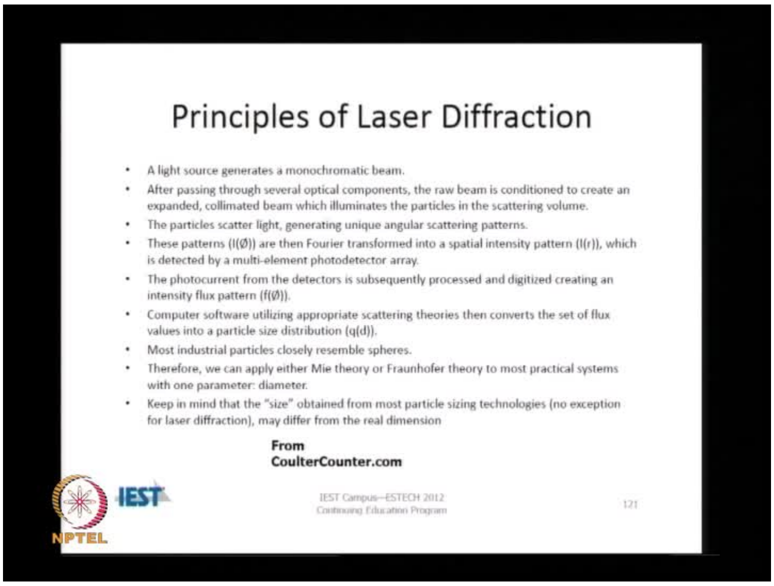

Principles of Laser Diffraction

- A light source generates a monochromatic beam.
- After passing through several optical components, the raw beam is conditioned to create an expanded, collimated beam which illuminates the particles in the scattering volume.
- The particles scatter light, generating unique angular scattering patterns.
- These patterns $(I(\varnothing))$ are then Fourier transformed into a spatial intensity pattern $(I(r))$, which is detected by a multi-element photodetector array.
- The photocurrent from the detectors is subsequently processed and digitized creating an intensity flux pattern $(f(\varnothing))$.
- Computer software utilizing appropriate scattering theories then converts the set of flux values into a particle size distribution $(q(d))$.
- Most industrial particles closely resemble spheres.
- Therefore, we can apply either Mie theory or Fraunhofer theory to most practical systems with one parameter: diameter.
- Keep in mind that the "size" obtained from most particle sizing technologies (no exception for laser diffraction), may differ from the real dimension

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The principles of Laser Diffraction are that; you have a light source, generate a monochromatic beam, then you convert to a collimated beam, you illuminate the particles, the particles scattered light in a unique fashion, every particle has a unique pattern or a fingerprint of how it scatters light. The patterns are then Fourier transformed and the photo current from the detectors is processed and digitized. And finally, use computer software to convert the measured signal into a particle size distribution.

Again, the underlying assumption here is, most particles of interest can be reasonably appropriated through spheres. Therefore, theories that are appropriate for spherical particles can be used to determine size based on scattering intensity measurements; however, the size, again the key point is that, the size obtained from most particle sizing technologies including laser diffraction, will differ from the real dimension of the particle.

Again, the definition of what is real is actually open to debate. The most real assessment of particle size is when you can actually immobilize it and look at it, for example, under a Scanning Electron Microscope or Tunneling Electron Microscope, something that has sufficiently high magnification as well as high resolution, in order for you to unequivocally determine what are its actual dimensions, and even that may only work in 2D, the three-dimensional characterization of size is not possible even with the best SCM and TEM that we have, and we have to resort to techniques like AFM to obtain sizes in three-dimensions.

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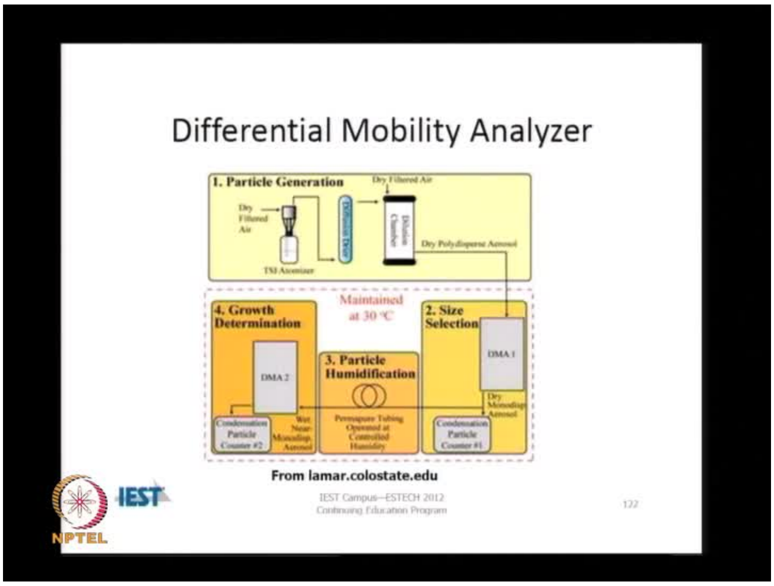

Differential Mobility Analyzer

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A Differential Mobility Analyzer really uses the transport properties of the particle in order to characterize its size. So, here you would essentially take particles, that are suspended in gas, for example, a poly dispersed aerosol, which would then go into the mobility analyzer, and here the particles will essentially be classify or separated according to size, by imposing an external field on it. And later on, as we have seen earlier, we can actually direct these particles into a condensation particle counter, which will condense material on to the particle and grow it to a sufficiently large size, where it can be analyzed with the laser particle counter.

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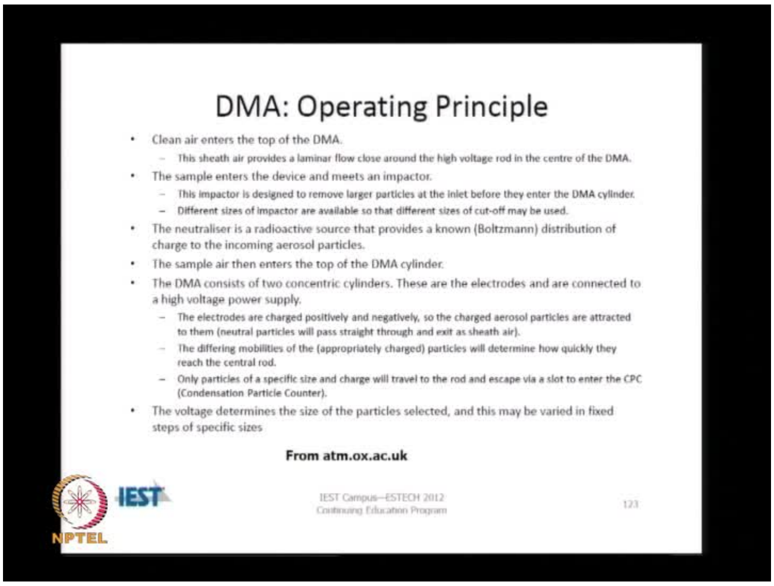

DMA: Operating Principle

- Clean air enters the top of the DMA.
  - This sheath air provides a laminar flow close around the high voltage rod in the centre of the DMA.
- The sample enters the device and meets an impactor.
  - This impactor is designed to remove larger particles at the inlet before they enter the DMA cylinder.
  - Different sizes of impactor are available so that different sizes of cut-off may be used.
- The neutraliser is a radioactive source that provides a known (Boltzmann) distribution of charge to the incoming aerosol particles.
- The sample air then enters the top of the DMA cylinder.
- The DMA consists of two concentric cylinders. These are the electrodes and are connected to a high voltage power supply.
  - The electrodes are charged positively and negatively, so the charged aerosol particles are attracted to them (neutral particles will pass straight through and exit as sheath air).
  - The differing mobilities of the (appropriately charged) particles will determine how quickly they reach the central rod.
  - Only particles of a specific size and charge will travel to the rod and escape via a slot to enter the CPC (Condensation Particle Counter).
- The voltage determines the size of the particles selected, and this may be varied in fixed steps of specific sizes

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So, the operating principle of Differential Mobility Analyzers is that, you take the sample mix it with air and introduce it into a chamber, where you actually impose an external field on it, for example, you can impose an electrical charge on these particles. When you do that, again the particles will move at different rates depending on their sizes. So, by looking at their mobility in the electrical field that is applied, you can separate the particles by size, and later on you can then analyze them under a laser particle counter to do size assessment.

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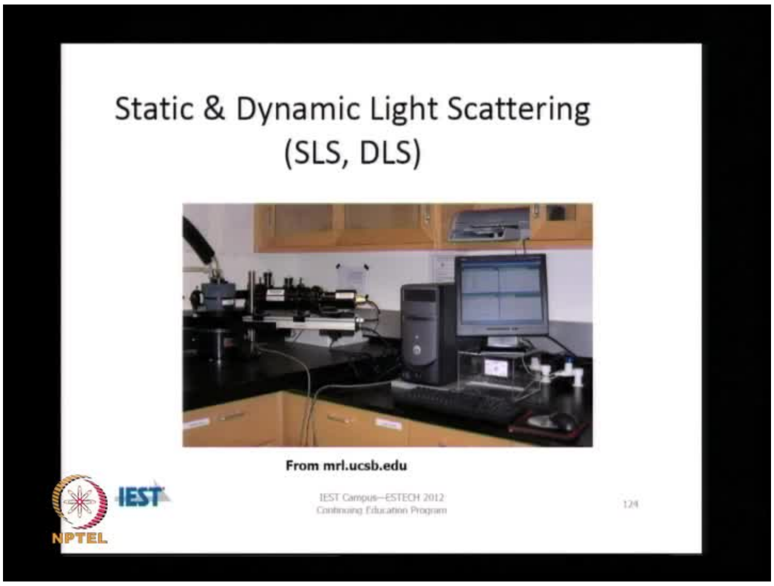

Static & Dynamic Light Scattering (SLS, DLS)

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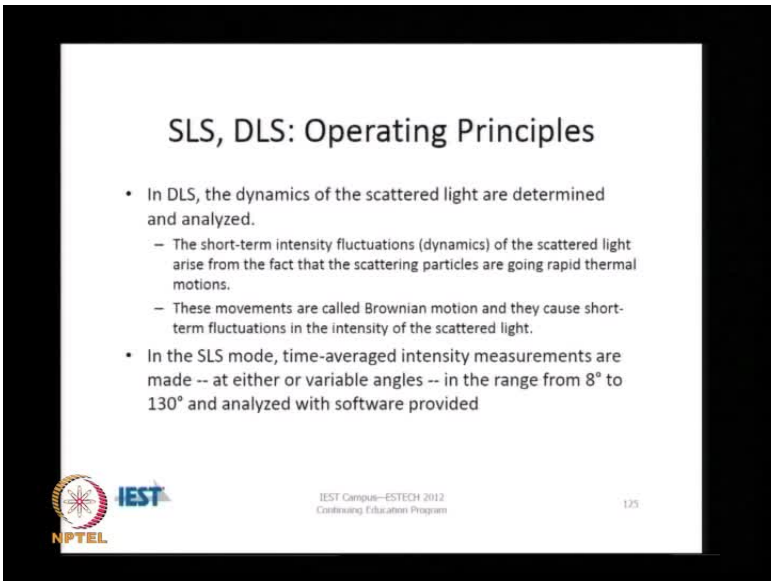

SLS, DLS: Operating Principles

- In DLS, the dynamics of the scattered light are determined and analyzed.
  - The short-term intensity fluctuations (dynamics) of the scattered light arise from the fact that the scattering particles are going rapid thermal motions.
  - These movements are called Brownian motion and they cause short-term fluctuations in the intensity of the scattered light.
- In the SLS mode, time-averaged intensity measurements are made -- at either or variable angles -- in the range from 8° to 130° and analyzed with software provided

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Now, methods such as Static and Dynamic Light Scattering, commonly known as SLS and DLS methods, essentially still rely upon light scattering as the main technique for detection. But the way that they are differentiated is that; in Dynamic Light Scattering, what we are really looking at is scattering of light by particles that are dynamic in nature, that have sufficiently high velocities, that even short term intensity fluctuations of scattered light, that arise from the fact that the particles are moving around, can be detected quite sensitively. So, you can essentially do time resolve measurements and you can locate particles at different instance of time, and the distance that these particles have travelled between one light exposure to the next, actually gives you indirectly an estimate of particle size, since that mobility is dictated by their size. So, these movements of particles are called Brownian motion. And when they are small enough, the motion is at sufficiently high velocities, that they do cause measurable fluctuations in the intensity of the scattered light.

On the other hand, in Static Light Scattering, the presumption is that; we are not looking at individual nano-particles. What we really trying to characterize are the clusters of particles, that have grown to a sufficiently large dimension that they are not very mobile, that they are essentially stationary. And therefore, you can look at them for sufficient period of time without having to worry about their moving around to a significant extent. So, from the view point of light scattering, you can assume that the particles are essentially fixed in place and apply measurement principles.

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Acoustic Attenuation Spectroscopy

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Now, Acoustic Attenuation Spectroscopy, again we have discussed in an earlier lecture in some detail, this is particularly suited to high concentration slurries. So here, instead of looking at light scattering as an indicator of particles size, you look at the scattering of an acoustic field. And you also use, in this case, a spectroscopic method, you cycle the acoustic field through various frequencies, and you look at the associated spectra, and you compare it with a mathematical model for how this acoustic field will be attenuated for a given distribution particle sizes, for a given material. And then you match the model predictions to your actual observations, to extract the prevailing particle size distribution.

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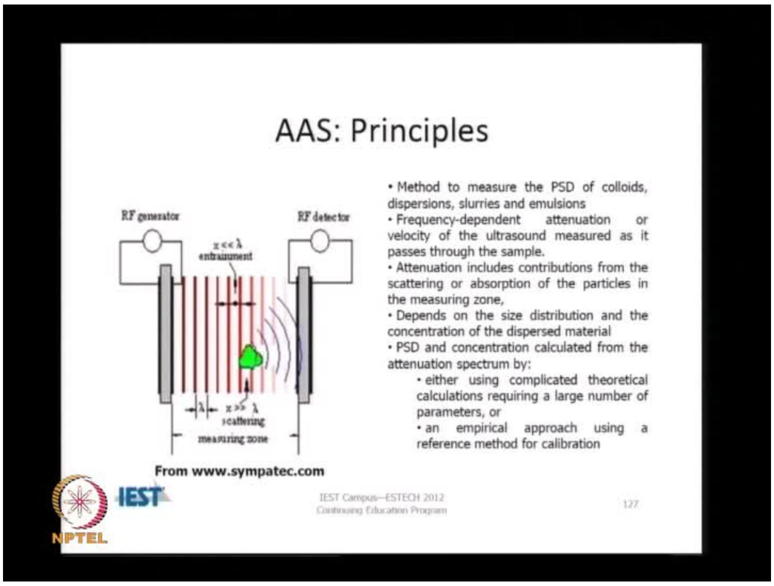

AAS: Principles

- Method to measure the PSD of colloids, dispersions, slurries and emulsions
- Frequency-dependent attenuation or velocity of the ultrasound measured as it passes through the sample.
- Attenuation includes contributions from the scattering or absorption of the particles in the measuring zone,
- Depends on the size distribution and the concentration of the dispersed material
- PSD and concentration calculated from the attenuation spectrum by:
  - either using complicated theoretical calculations requiring a large number of parameters, or
  - an empirical approach using a reference method for calibration

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So, the way the Acoustic Attenuation Spectroscopy method works, again it is primarily to measure the size distribution of collides, dispersions, slurries, emulsions, where the concentrations are expected to be fairly high. And the frequency dependent attenuation or velocity of the ultra sound is measured as it passes through the sample. And these measured signals, depends on the size distribution as well as the concentration of the dispersed material. And you then obtain the particle distribution and concentration, by either using theoretical calculations or an empirical approach. If you do not want to setup the equations and solve them, then you can also, if you have standards of known size, you can expose them to an acoustic field, measure the signal that you get, and essentially develop your own calibration curve. But, that approach only works, when you are using the same material all the time. So, if there is any change in the characteristics of the material or even if there is a substantial change in size distribution of the sample, the empirical approach would not work, and your better of going to a more theoretical analysis, which is more fundamentally based.

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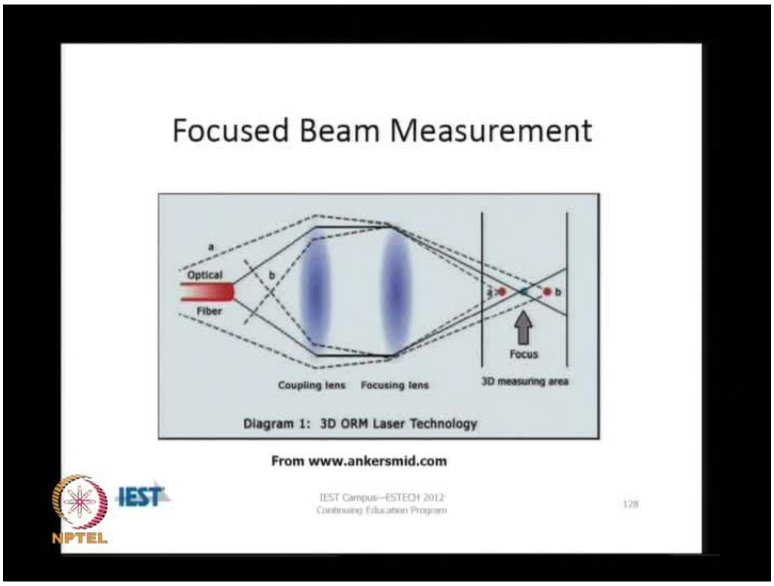

Focused Beam Measurement

Diagram 1: 3D ORM Laser Technology

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The Focused Beam Measurement technique is one that, again similar to light scattering, in the sense that, you take an energy beam and you focus it on the particle.

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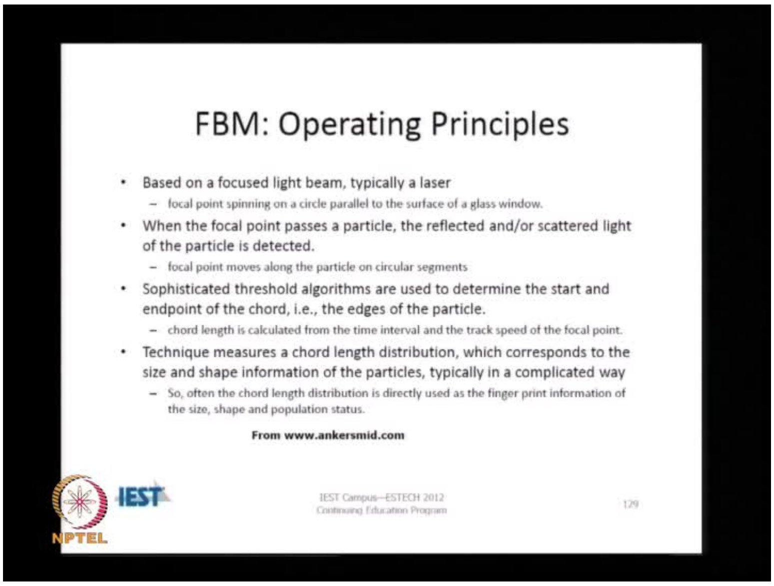

FBM: Operating Principles

- Based on a focused light beam, typically a laser
  - focal point spinning on a circle parallel to the surface of a glass window.
- When the focal point passes a particle, the reflected and/or scattered light of the particle is detected.
  - focal point moves along the particle on circular segments
- Sophisticated threshold algorithms are used to determine the start and endpoint of the chord, i.e., the edges of the particle.
  - chord length is calculated from the time interval and the track speed of the focal point.
- Technique measures a chord length distribution, which corresponds to the size and shape information of the particles, typically in a complicated way
  - So, often the chord length distribution is directly used as the finger print information of the size, shape and population status.

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Now, the beam can be any light beam, although it is a typically a laser. And here again, you try to train the focal point on the particle, and when the focal point of the light meets the particle, you measure the reflective light and/ or the scattered light.

Now, one of the advantages of this technique is; this beam is smaller than the particle dimension. So, you can actually get some resolution of the particle, in terms of the distribution of its features. So, you can actually train the beam at the specific points on the particle, and you can move the focal point along the particle and do characterization of the particle, essentially by depth, for example. The requirement, of course, is that the focal point of the beam must be smaller than the size of the particle, for this technique to be really useful. Otherwise, it becomes very similar to an SLS or DLS type of methodology.

So, the technique here measures a chord length, which does not necessarily relate to diameter. The difference between the chord and the diameter, of course, the diameter goes through the centre of the particle and joins two opposite sides; however, it is possible to take the chord length and related to size and shape of the particle, but it is a little difficult, complicated. And therefore, frequently the chord length distribution itself is used as the data that characterizes size, shape and the concentration of particles in suspension. It is again an approximation; obviously, a chord length is not necessarily a representation of particle size, but in a relative sense, it can be used to compare sizes and shapes of various particles.

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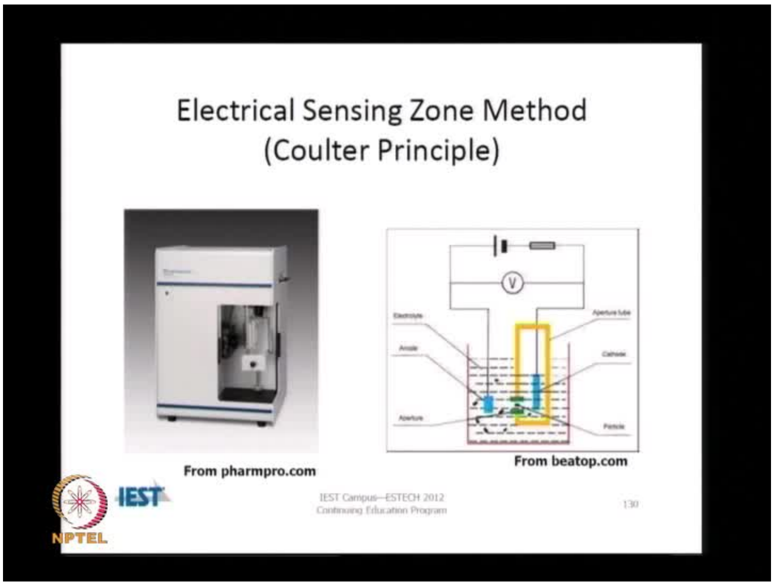

Electrical Sensing Zone Method
(Coulter Principle)

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The Electrical Sensing Zone Method, also known as the Coulter Principle, is a little different from the techniques we have discussed so far, in the sense that, here the particles are actually immersed into an electrolyte solution and the change in conductivity is measure. So, this is particularly well suited to non-conducting particles.

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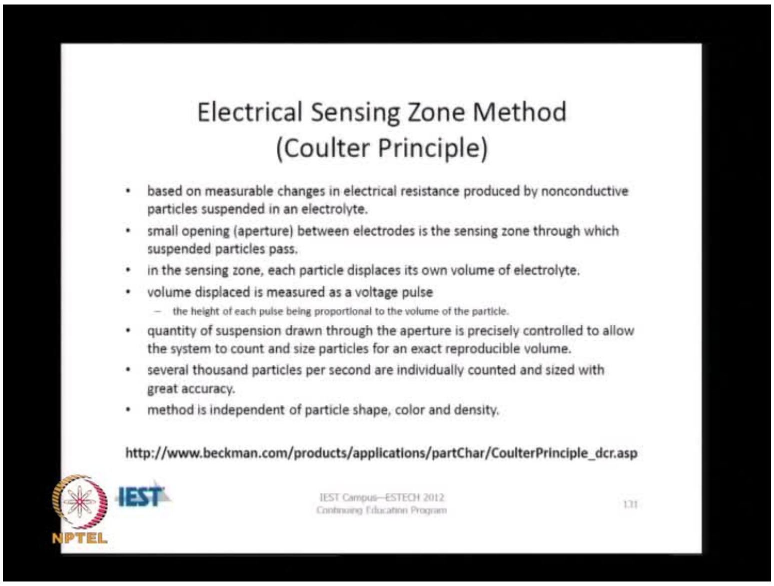

Electrical Sensing Zone Method (Coulter Principle)

- based on measurable changes in electrical resistance produced by nonconductive particles suspended in an electrolyte.
- small opening (aperture) between electrodes is the sensing zone through which suspended particles pass.
- in the sensing zone, each particle displaces its own volume of electrolyte.
- volume displaced is measured as a voltage pulse
  - the height of each pulse being proportional to the volume of the particle.
- quantity of suspension drawn through the aperture is precisely controlled to allow the system to count and size particles for an exact reproducible volume.
- several thousand particles per second are individually counted and sized with great accuracy.
- method is independent of particle shape, color and density.

http://www.beckman.com/products/applications/partChar/CoulterPrinciple_dcr.asp

So, the principle here is to measure changes in electrical resistance that is produced by non-conductive particles that are suspended in an electrolyte. So, what you have here is two electrodes and a small opening between them, which is called the sensing zone. The suspended particles pass through the sensing zone, and as it does they displace a certain volume of electrolyte. And this volume, that is displaced can actually measured as a voltage pulse. So the instrument measures not the size, but actually the volume of the particle. And from that, of course, by making assumptions regarding the shape of the particle, you can extract the diameter of the particle, for example. The quantity of the suspension drawn through this aperture must be precisely controlled, because here it is very important to use the same exact reproducible volume each time.

The advantage of this method is that; several thousand particles per second can be individually counted and sized, and the method is independent of particle shape, color or density. Of course, that is also the limitation of the method. It is very difficult, when you have a sample containing many different particles of various colors, shapes and densities. It is difficult to relay on a simple Coulter Counter measurement to assign a size to every one of these particles, because we know that some of the inter dependencies are being neglected in this measurement. But as long as you have again a very stable very consistent sample, that are always examining, and you know that distribution of a materials in the sample is not very broad, this method can be successfully used.

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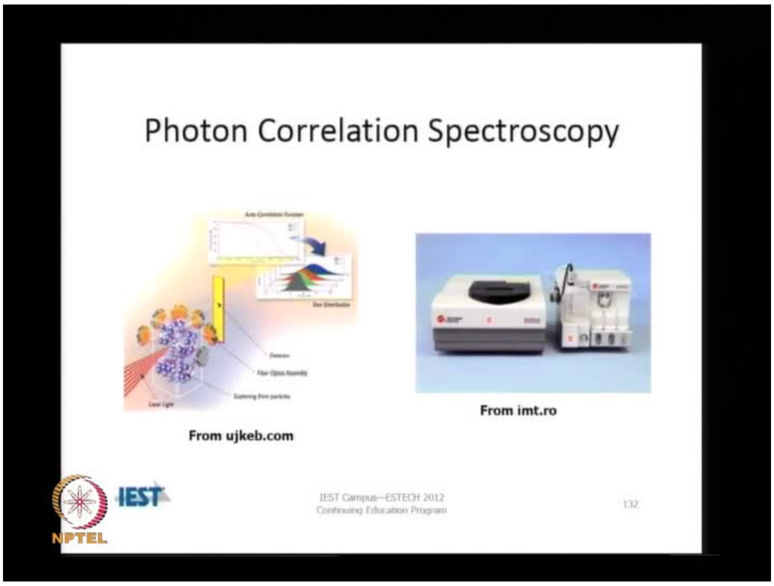

Photon Correlation Spectroscopy

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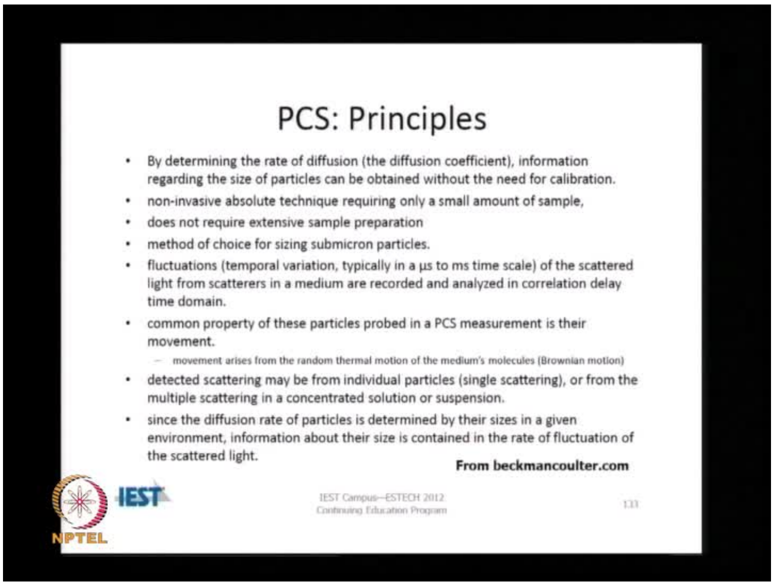

PCS: Principles

- By determining the rate of diffusion (the diffusion coefficient), information regarding the size of particles can be obtained without the need for calibration.
- non-invasive absolute technique requiring only a small amount of sample,
- does not require extensive sample preparation
- method of choice for sizing submicron particles.
- fluctuations (temporal variation, typically in a μs to ms time scale) of the scattered light from scatterers in a medium are recorded and analyzed in correlation delay time domain.
- common property of these particles probed in a PCS measurement is their movement.
  - movement arises from the random thermal motion of the medium's molecules (Brownian motion)
- detected scattering may be from individual particles (single scattering), or from the multiple scattering in a concentrated solution or suspension.
- since the diffusion rate of particles is determined by their sizes in a given environment, information about their size is contained in the rate of fluctuation of the scattered light.

From beckmancoulter.com

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Now, Photon Correlation Spectroscopy is actually only another name for DLS, the Dynamic Laser Diffraction based methodology. Here, what we are really doing is determining the rate of diffusion or the diffusion coefficient of the particles.

Some of the advantages of these techniques are that; it is non-invasive, its absolute, in the sense that, it does measure the diffusion rate of the particle, which should in principle be related to its size. So, the only assumption here is of the shape.

You are assuming a spherical particle, when you estimate the diffusivity based on the rate of transport of a particle. It does not require extensive sample preparation, and it is actually the method of choice for size analysis of sub micron particles. Again, what we are doing here is measuring the fluctuations, the time dependent variations of scattered light, and you are recording it and analyzing it, to see how far particles have moved for a certain time delay. So, the common property that the measurement focuses on is the movement. The movement of particles that arises from the random thermal motion, also known as Brownian diffusion.

Now, the detector scattering may be from individual particles or from multiple scattering in a concentrated solution or suspension. So, like all light scattering base techniques, this requires a very dilute sample. If you have a concentrated suspension, the only method of choice really is acoustic attenuation.

So, the diffusion rate of the particles is determined by their size and therefore, the size here, is being estimated based on the rate of diffusion of the particle, which is reflected in the rate of fluctuation of the scattered light.

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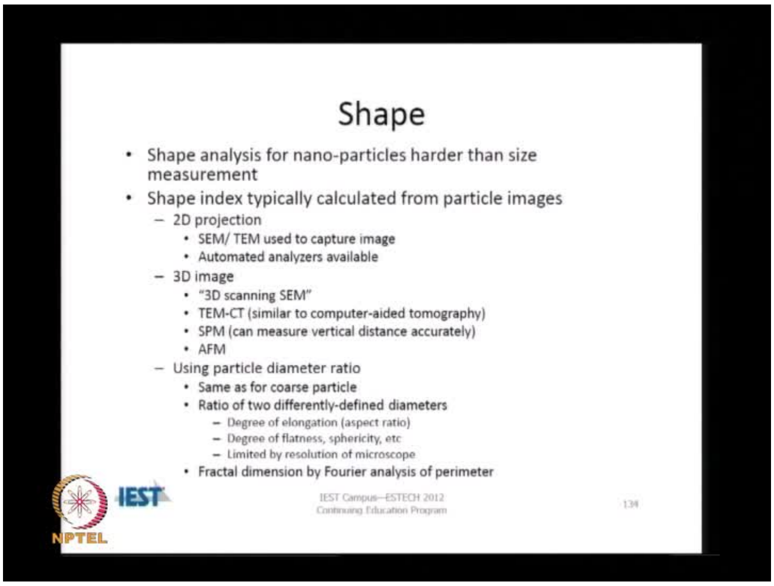

Shape

- Shape analysis for nano-particles harder than size measurement
- Shape index typically calculated from particle images
  - 2D projection
    - SEM/ TEM used to capture image
    - Automated analyzers available
  - 3D image
    - "3D scanning SEM"
    - TEM-CT (similar to computer-aided tomography)
    - SPM (can measure vertical distance accurately)
    - AFM
  - Using particle diameter ratio
    - Same as for coarse particle
    - Ratio of two differently-defined diameters
      - Degree of elongation (aspect ratio)
      - Degree of flatness, sphericity, etc
      - Limited by resolution of microscope
    - Fractal dimension by Fourier analysis of perimeter

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Now, switching over to shape analysis, shape is a qualitative measure, unlike size, which is qualitative. And therefore, shape analysis is always harder compared to size analysis. Now, shape just like size, can be obtained through projections. So, you can take a three-dimensional object projected onto three-dimensions or a 2D plane and obtain shape that way. So, for example, so you can calculate a shape index by projecting a 3D object onto a 2D plane. Here, you can obviously use SEM and TEM, because they are good at measuring two-dimensional images, and you can also automate it, both SEM and TEM are available with automated measurement capability. So, you can literally have thousands of three-dimensional particles in the nano size range, leave the sample over night, and by the time you come back to in the morning you will have a shape distribution analysis for the entire population of particles. The only limitation is you are not going to get 3D information, what you are going to get is a two-dimensional projection of the 3D particle.

On the other hand, if you really want to get 3D image, there are now instruments available to be able to do that. The SCM and TEM are now available in modified version to obtain 3D morphologies. Scanning Probe Microscopy, which we have talked about earlier, is another method that can measure vertical distances accurately, so it can add the third dimension to your measurement. And of course, the Atomic Force Microscope is well suited to measuring the third dimension as well.

Now, shape is usually assessed by taking one or two characteristic sizes, and either using the absolute sizes or by using a certain ratio. So, using the particle diameter ratio, you can assign a size, or you can take the degree of flatness, degree of elongation, is also known as aspect ratio, sphericity, these are all parameters that we have listed earlier when we are discussing shape characterization of particles. Again, when you try to assess the shape of nano-particles, some of these techniques may just not work because they require a very high degree of resolution.

So, for example, flatness may be not too difficult to assess for a micron size particle, but for a nanometer sized particle, the resolution that it calls for is probably beyond the limit of many of our commercially available instruments. So, we had been prepared to assess shape of nano-particles by methods that are somewhat different from methods that are used to assess the shape of larger particles. For example, fractal dimensions, you can actually analyze the perimeter of the particle and do Fourier analysis to extract the common features, and you can actually assign a fractal dimension to the particle by the using that technique.

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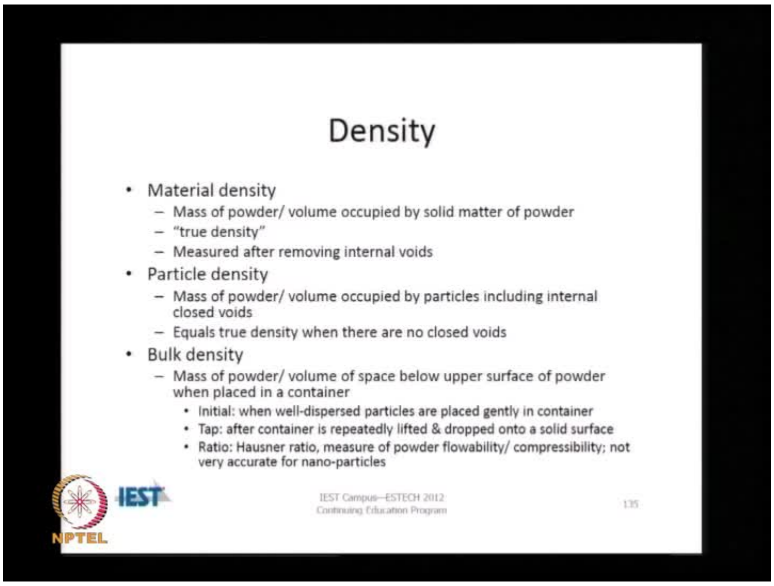

Density

- Material density
  - Mass of powder/ volume occupied by solid matter of powder
  - "true density"
  - Measured after removing internal voids
- Particle density
  - Mass of powder/ volume occupied by particles including internal closed voids
  - Equals true density when there are no closed voids
- Bulk density
  - Mass of powder/ volume of space below upper surface of powder when placed in a container
    - Initial: when well-dispersed particles are placed gently in container
    - Tap: after container is repeatedly lifted & dropped onto a solid surface
    - Ratio: Hausner ratio, measure of powder flowability/ compressibility; not very accurate for nano-particles

The method of density measurement, on the other hand, is something that is done in three different ways. You can assess Material density, you can assess Particle density or you can assess Bulk density.

Now, the difference between these definitions is; Material density is defined as the mass of the powder divided by the volume occupied by the solid powder after you remove internal voids. So, it is also known as True density. Particle density, on the other hand, is simply the mass of the powder divide by volume occupied by the particles including the internal closed voids. So, this would equal, what is known as True density only when there are no closed voids. So, in order to obtain Particle density, you really do not have to do anything, you just take the sample as is and characterize it for density. However to obtain its True density, you have to take some steps to remove voids. Now, typically that can be done either by applying pressure to compress a sample, by applying vacuum or even temperature can be used to remove voids from a material. But you certainly have to take a few steps to convert the powder into one that has no internal voids, in order to be able to measure the Material density.

Bulk density, on the other hand, is really a more reflection of how the powder settles, when you place it in a container. So, it is a particular relevance to a industry where powders are being stored or packaged or shipped.

So, this is defined as a mass of powder divided by the volume of space below the upper surface of the powder, when it is placed in a container. And here, as we have seen before, you can talk about an initial bulk density, where well dispersed particles are gently placed in a container, or a tap density, which is the density you measure after you have place the powder in the container, but then you take the container and vibrate it, or lift it and drop it many times, or hammer it, tap it. And the ratio between the tap density and the initial density is defined as Hausner ratio, and it is a good measure of powder flow ability and compressibility. Problem is again, this is a method particularly suited for large particles. The Hausner method of measuring the ratio between the tap density and the initial density, will not be very accurate for nano-particles.

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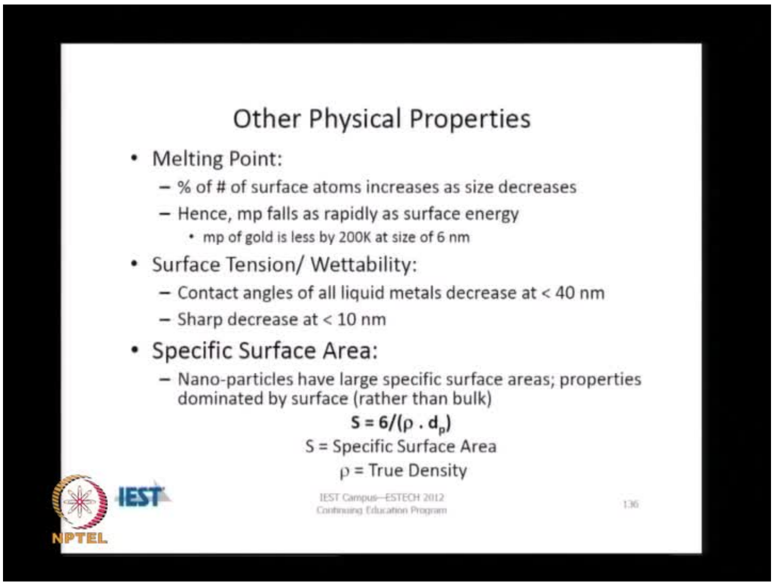

Other Physical Properties

- Melting Point:
  - % of # of surface atoms increases as size decreases
  - Hence, mp falls as rapidly as surface energy
    - mp of gold is less by 200K at size of 6 nm
- Surface Tension/ Wettability:
  - Contact angles of all liquid metals decrease at < 40 nm
  - Sharp decrease at < 10 nm
- Specific Surface Area:
  - Nano-particles have large specific surface areas; properties dominated by surface (rather than bulk)

$$S = 6/(\rho \, . \, d_p)$$

S = Specific Surface Area

ρ = True Density

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Other physical properties of nano-particles that are of interest to us are melting point. Now, it is a fact that the melting point of many metals is lower, as you reduce them to nano sizes. For example, melting point of gold is less compared to bulk gold, by 200 Kelvin, when you reduce size to 6 nano meters. So obviously, for people that are trying to work with gold, this is fantastic. So, if you can make gold particles, the nano dimensions, you can actually work with them virtually at room temperatures, you do not have to heat them to very high temperatures. So, even for simple things like making jewellery, if you can actually convert the gold to a nano form, your workability increases quite a bit. And the reason for that is that, the reason actually is the same for all the other enhancements we see for nano-particles, the percentage of atoms on the surface is much higher in a nano-particle compared to the percentage of atoms in the core of the particle.

The simple volumetric effect, you are essentially taking the same volume of material and you are packing it into a much larger surface area, when you go to nano dimensions. Increase in surface area implies that the sub surface in the core areas are reduced. So, that is a consequent we do not normally think about, we all know that nano-particles have high surface area, but what that means is that, there is less area now contained in the interior of the particle and relatively more area on the exterior of the particle. And that has several implications, including the fact that melting points are lower.

If you look at surface tension and wettability compared to larger particles, the contact angles of all liquid metals will decrease at 40 nanometers and less dimensions, and when you get to 10 nano meters there is a huge decrease in the contact angle. Now, what does that mean? A decrease in contact angle means more wettable. Right. So, again it is a reflection of the greater reactivity of a nano-particle. A nano particle is just more open to interaction with its environment. A surrounding liquid or fluid can wet a nano-particle much more effectively than it can wet a particle of larger dimensions. Of course, a specific surface area effect is one, we all know about nano-particles have large specific surface areas and their properties are dominated by the surface. That again, is a key difference between a nano-particle and a particle of larger dimensions.

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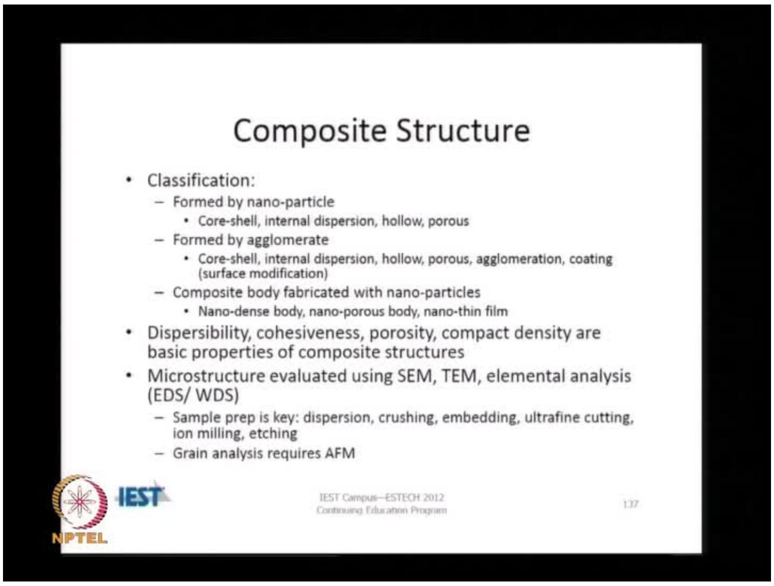

Composite Structure

- Classification:
  - Formed by nano-particle
    - Core-shell, internal dispersion, hollow, porous
  - Formed by agglomerate
    - Core-shell, internal dispersion, hollow, porous, agglomeration, coating (surface modification)
  - Composite body fabricated with nano-particles
    - Nano-dense body, nano-porous body, nano-thin film
- Dispersibility, cohesiveness, porosity, compact density are basic properties of composite structures
- Microstructure evaluated using SEM, TEM, elemental analysis (EDS/ WDS)
  - Sample prep is key: dispersion, crushing, embedding, ultrafine cutting, ion milling, etching
  - Grain analysis requires AFM

When we talk about the structure of a nano-particle, again we have to look at it in three different ways. Typically, a system involve in nano-particles, can be classified as having a nano-particle structure and agglomerate structure and a composite structure.

The nano-particle structure, simply reflects how the particle itself looks; the core, internal dispersions, the hollowness of the particle, porosity of the particle. The agglomerate structure reflects, in addition to those, the agglomeration of adjacent particles. And finally, the composite material, involves the nano material as well as the substance that it is actually dispersed in.

So, when we talk about structure in a nano-particle system, it is not unique, you have to be careful about, or you talking about the structure of the nano-particle itself, or the structure of the agglomerator, or the structure of the composite system, the three are completely different.

So, dispersibility, cohesiveness, porosity and compact density are the basic properties of the composite structures. And in order to characterize nano-particle composites, you have to be able to characterize each one of these.

The micro structure of these structures can be evaluated using techniques such as SEM, TEM combined with EDS/ WDS. Sample preparation has to be done very carefully when you approach a nano dimensions. Grain analysis requires the use of AFM, if you are talking about a nano-particle, you have grain sizes that are sub nano. AFM is the only technique that has the sensitivity and resolution to be able to measure in those dimensions.

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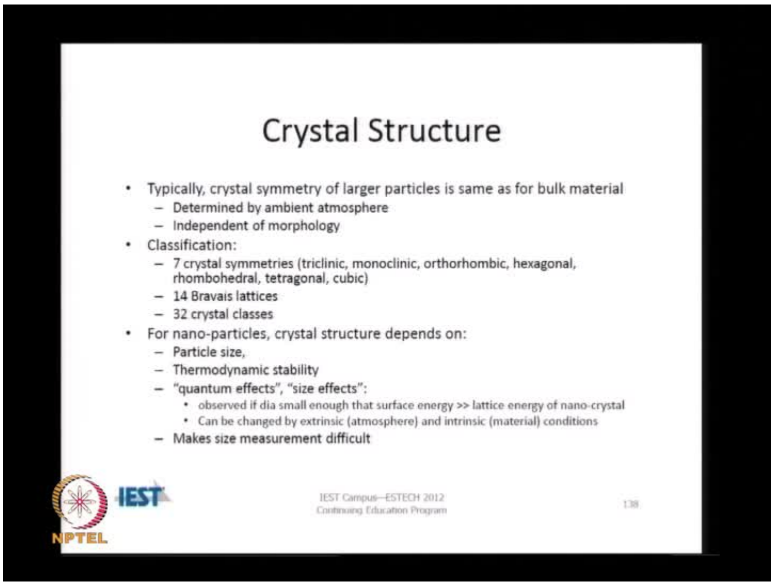

Crystal Structure

- Typically, crystal symmetry of larger particles is same as for bulk material
  - Determined by ambient atmosphere
  - Independent of morphology
- Classification:
  - 7 crystal symmetries (triclinic, monoclinic, orthorhombic, hexagonal, rhombohedral, tetragonal, cubic)
  - 14 Bravais lattices
  - 32 crystal classes
- For nano-particles, crystal structure depends on:
  - Particle size,
  - Thermodynamic stability
  - "quantum effects", "size effects":
    - observed if dia small enough that surface energy >> lattice energy of nano-crystal
    - Can be changed by extrinsic (atmosphere) and intrinsic (material) conditions
  - Makes size measurement difficult

The crystal structure, again typically the structure does not necessarily change when we go to larger particles, starting from bulk material when you go the larger particle sizes, the crystal structure remains the same. However, for nano-particles, the crystal structure can become dependent on the size of the particle, thermo dynamic effect, such as the stability of the structure, quantum effects as well as size effects. All of this is dependent not only on the internal structure of the particle, but also the exterior environment. So, with a nano-particle, you can actually, because they have such a high surface area and so much reactivity with the external ambient environment, you can even influence its crystal structure by suitably altering the external conditions.

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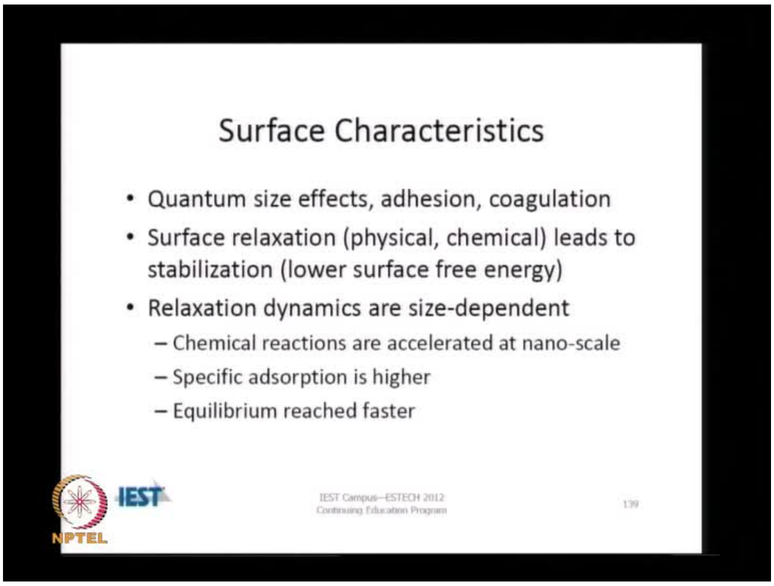

Surface Characteristics

- Quantum size effects, adhesion, coagulation
- Surface relaxation (physical, chemical) leads to stabilization (lower surface free energy)
- Relaxation dynamics are size-dependent
  - Chemical reactions are accelerated at nano-scale
  - Specific adsorption is higher
  - Equilibrium reached faster

Other surface characteristics of nano-particles are; quantum size effects, adhesion, coagulation, these we have discussed in more detail earlier, surface relaxation and stabilization. A nano-particle is in a more, in a state of equilibrium compared to larger size particles, it is closer to a state of equilibrium. And therefore, it displace lower surface free energy, now, what that means, is you have a more stable system. So, by going to nano dimensions, typically you can achieve systems that display greater physical stability as well as chemical stability compared to systems comprising of the larger particles. Chemical reactions are accelerated at nano-scale, specific adsorption is higher and equilibrium is reached faster once again, because reactivity is much greater at the nano dimension.

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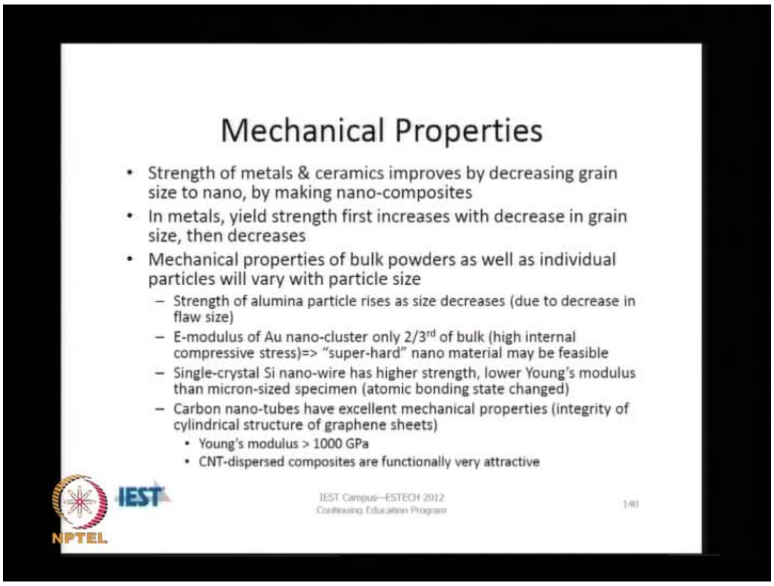

Mechanical Properties

- Strength of metals & ceramics improves by decreasing grain size to nano, by making nano-composites
- In metals, yield strength first increases with decrease in grain size, then decreases
- Mechanical properties of bulk powders as well as individual particles will vary with particle size
  - Strength of alumina particle rises as size decreases (due to decrease in flaw size)
  - E-modulus of Au nano-cluster only 2/3rd of bulk (high internal compressive stress)=> "super-hard" nano material may be feasible
  - Single-crystal Si nano-wire has higher strength, lower Young's modulus than micron-sized specimen (atomic bonding state changed)
  - Carbon nano-tubes have excellent mechanical properties (integrity of cylindrical structure of graphene sheets)
    - Young's modulus > 1000 GPa
    - CNT-dispersed composites are functionally very attractive

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Of course, many mechanical properties are also altered as you approach nano dimensions. The strength of metals and ceramics improves by decreasing the grain size to the nano size and making the nano composites. However, in metals, yield strength, interestingly first increases with decrease in grain size, but eventually it starts to decrease. Mechanical properties of bulk powders as well as individual particles vary with particle size. The strength of the alumina particle changes as size changes, E-modulus changes, Young's modulus can be changed by changing size. And the reason that carbon nano tubes have excellent mechanical properties is mainly because the cylindrical structure of graphene sheets is very stable. So, it is the stability that really gives it the strength.

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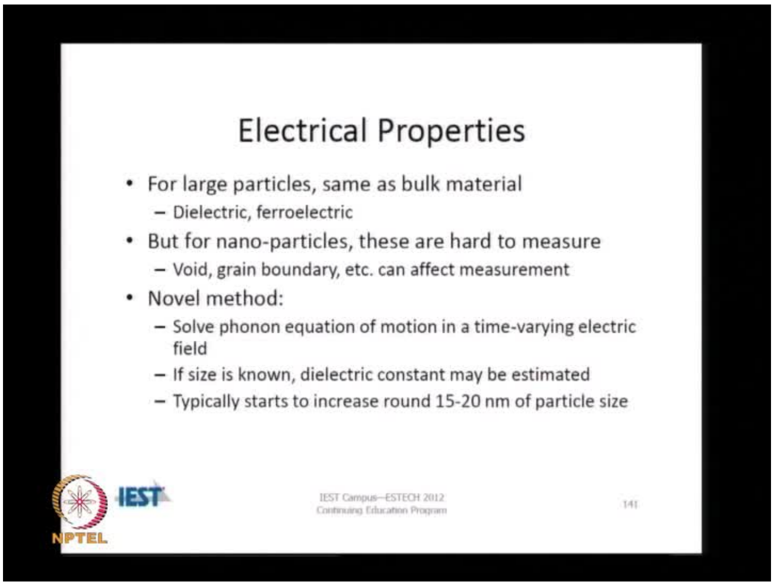

Electrical Properties

- For large particles, same as bulk material
  - Dielectric, ferroelectric
- But for nano-particles, these are hard to measure
  - Void, grain boundary, etc. can affect measurement
- Novel method:
  - Solve phonon equation of motion in a time-varying electric field
  - If size is known, dielectric constant may be estimated
  - Typically starts to increase round 15-20 nm of particle size

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Electrical properties, again for large particles they tend to be same as for bulk material, for nano-particles they are very likely to be very different, but they are also hard to measure. There is a new method, which involves the solving of the phonon equation of the motion in a time varying electric field, where essentially if you know the size you can calculate the dielectric constant, or if you know the dielectric constant you can calculate the size, that has enabled us now to start measuring the properties of nano sized particles, the electrical properties of nano sized particles. You see a significant enhancement around 50 to 20 nanometer of particle size.

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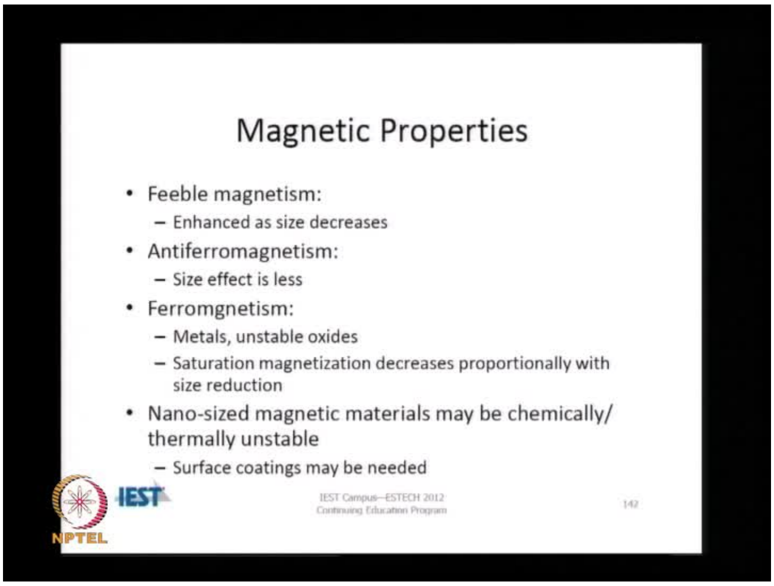

Magnetic Properties

- Feeble magnetism:
  - Enhanced as size decreases
- Antiferromagnetism:
  - Size effect is less
- Ferromgnetism:
  - Metals, unstable oxides
  - Saturation magnetization decreases proportionally with size reduction
- Nano-sized magnetic materials may be chemically/ thermally unstable
  - Surface coatings may be needed

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Again, magnetism is a property that changes with dimension. Feeble magnetism is enhanced as size decreases, over anti-ferromagnetism is not so greatly influenced by size, ferromagnetism is again affected by size reduction. And finally, nano sized magnetic materials, while they may be more magnetic in nature, I mean the magnetic intensity may be higher, they are also more unstable. So, it is difficult to make an nano sized magnetic material and hope to obtain stable properties. Typically, this is addressed by adding surface coatings that sustains the magnetic effect over a longer period of time.

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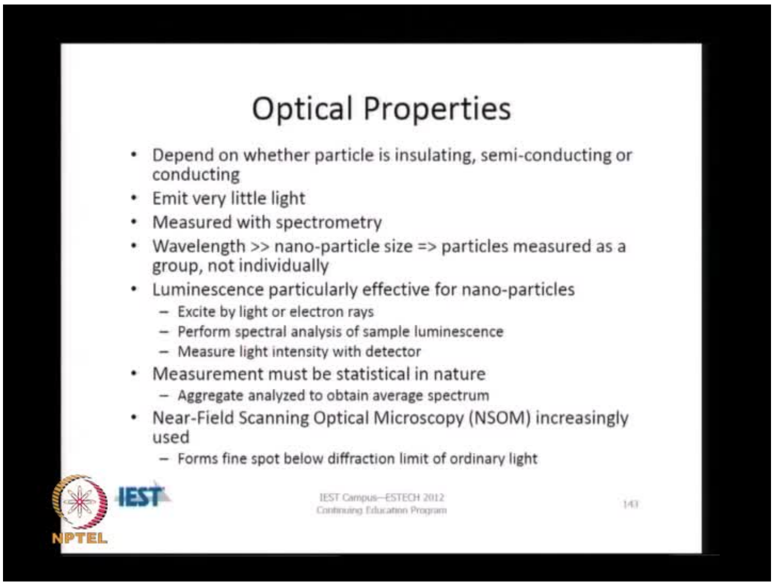

Optical Properties

- Depend on whether particle is insulating, semi-conducting or conducting
- Emit very little light
- Measured with spectrometry
- Wavelength >> nano-particle size => particles measured as a group, not individually
- Luminescence particularly effective for nano-particles
  - Excite by light or electron rays
  - Perform spectral analysis of sample luminescence
  - Measure light intensity with detector
- Measurement must be statistical in nature
  - Aggregate analyzed to obtain average spectrum
- Near-Field Scanning Optical Microscopy (NSOM) increasingly used
  - Forms fine spot below diffraction limit of ordinary light

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Optical properties, as we have seen, they certainly change with particle size. The optical behavior of nano-particles will depend on whether it is an insulating particles, semi conducting or conducting particles. Nano-particles on their own do not emit light very much, again light emission is a surface area dependent property, so as particles become smaller, the emission of light decreases just as scattering decreases.

One of the key things to remember is; if the wavelength of the incident light is larger than the particle size that you are trying to measure, you are not going to be able to measure the single particle, you are actually going to be measuring groups or clusters of particles. So, the wave length of incident light has to be matched to the size of the particle you are trying to measure, it must be kept significantly smaller than the size of the object.

Luminescence measurements are very effective for nano-particles because of their chemical reactivity. They are easily exited by light rays or electron rays. So, you can do spectral analysis of sample luminescence to obtain information about the size, shape as well as composition of nano-particles. In general, because of the small dimension of nano-particles, single measurements are not sufficient and you have to rely on statistical measurements.

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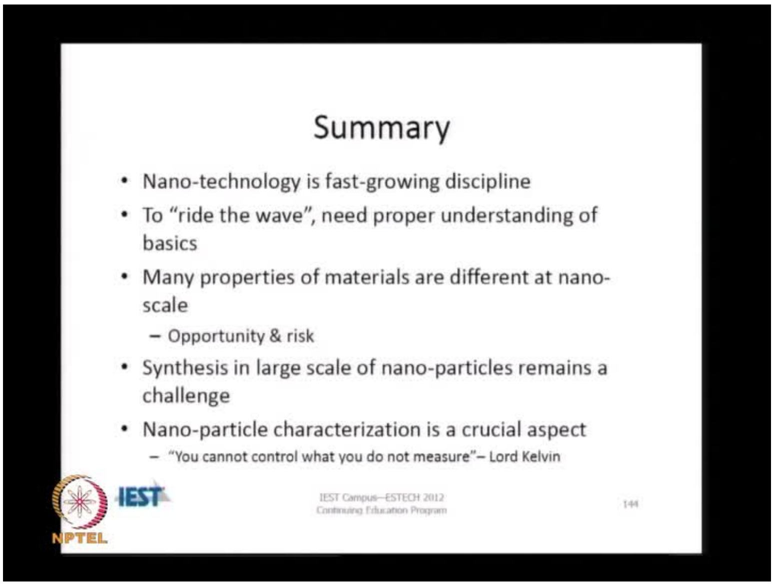

Summary

- Nano-technology is fast-growing discipline
- To "ride the wave", need proper understanding of basics
- Many properties of materials are different at nano-scale
  - Opportunity & risk
- Synthesis in large scale of nano-particles remains a challenge
- Nano-particle characterization is a crucial aspect
  - "You cannot control what you do not measure"– Lord Kelvin

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So to summarize, nano technology is a fast- growing discipline, as we all know. And if you want to really play in this field, you have to understand the basics of nano-particles. Understand that many properties of materials are different at nano scale, they certainly presence an opportunity that is also an enhanced risk factor. We have already seen some harmful consequences of nano products that being commercially made, the nano materials can penetrate skin very easily.

So, the human hygiene effects of nano-particles are still being debated. Same thing with nano fertilizer, while we are certainly seeing an enrichment of material in the soil, it is also quite possible that these nano additives are passed up the foot chain and humans mind up ingesting these nano-particles, which again lead to cancer and other problems. So, the opportunities and risks associated with nano materials have to be better understood as well.

Synthesis in large scale of nano-particles remains a challenge. The bottom-approaches specially do not lend themselves to scaling for larger quantities. So, there is a lot of opportunities here. And finally, nano particle characterization is a crucial aspect of all this, because as Lord Kelvin once said, you cannot control what you do not measure.

So, if you do not have the ability to characterize nano-particles, both qualitatively and quantitatively, you are never going to be shore what you get. The variations and product quality, quantity, all of these you have to be able to measure and address and so in order to do that, we have to be aware of various techniques of particle characterization and be able to apply them as needed. So, that concludes our discussion of particle characterization as it applies to nano technology. In the next lecture, we will discuss a little bit about nano fluids, which is another interesting application where nano-particles are being used to enhance conductivity of various fluids, and we will look at what specific characteristics of nano-particles play the most significant role in enhancing the properties of nano fluids.

Any question on what we have covered today? See you at the next lecture then.