Nanostructures and Nanomaterials
Characterization and Properties
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Lecture No - 11

Surface Effects and Physical Properties of Nanomaterials

We have already seen the importance of surface and role in altering the properties of materials especially at the nano scale.

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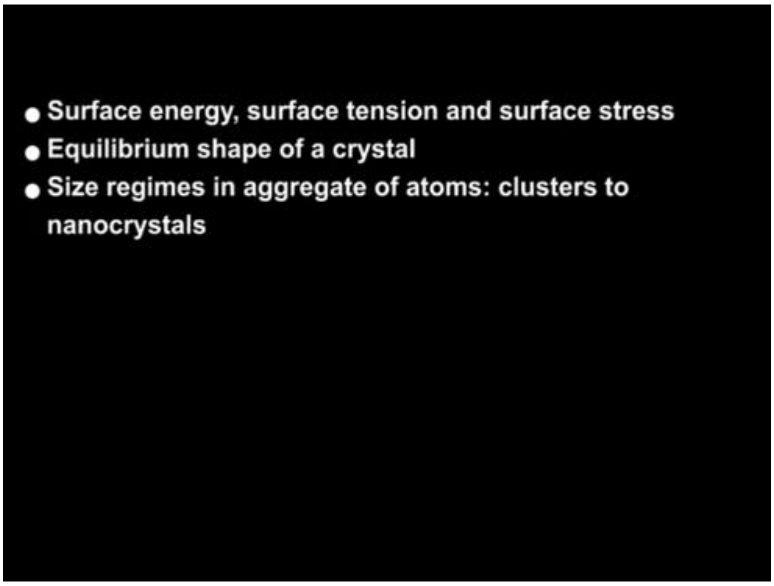

- Surface energy, surface tension and surface stress
- Equilibrium shape of a crystal
- Size regimes in aggregate of atoms: clusters to nanocrystals

Now, we will take up a formal definition of what is surface energy, what is surface stress. How should we differentiate between these concepts when it comes to liquids we say we when the concepts when you ((Refer Time: 00:47)) especially crystalline solids.

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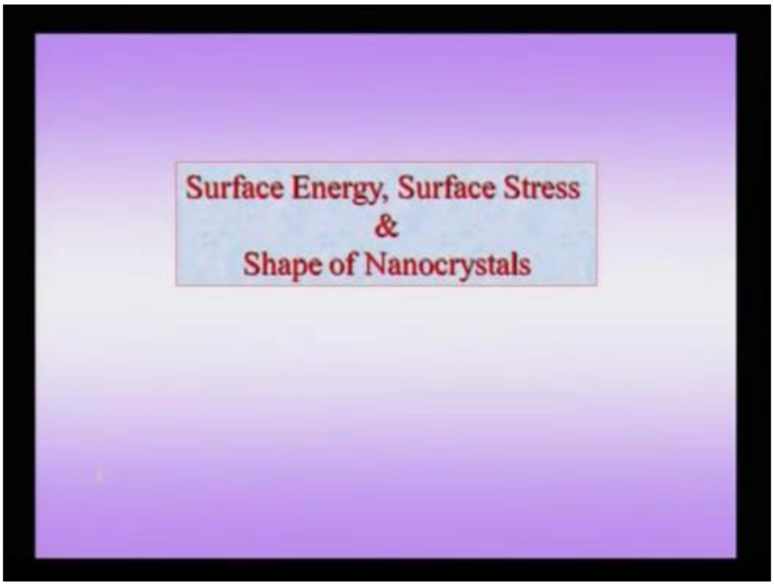

Surface Energy, Surface Stress
&
Shape of Nanocrystals

Further, how can I go about classifying what are known as clusters, which are small, which are large and then nano crystals. How the shape and other aspects come out naturally when we are talking about clusters and nano crystals.

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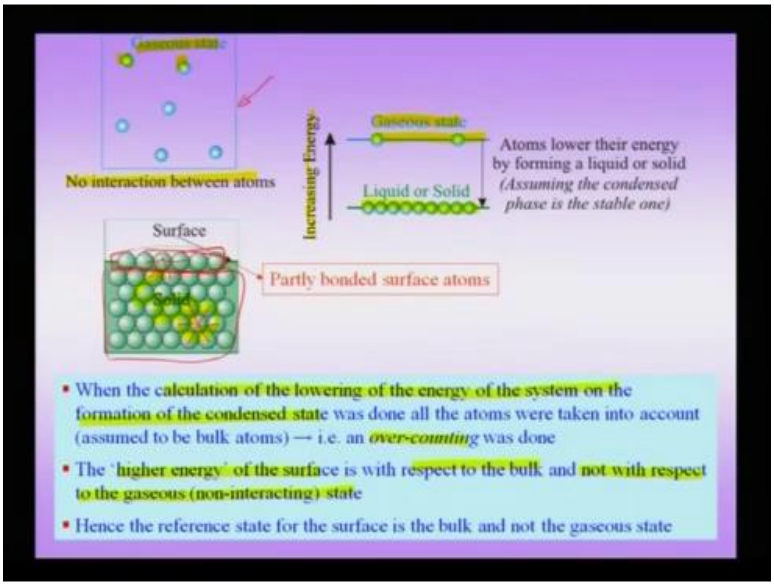

- When the calculation of the lowering of the energy of the system on the formation of the condensed state was done all the atoms were taken into account (assumed to be bulk atoms) → i.e. an *over-counting* was done
- The 'higher energy' of the surface is with respect to the bulk and not with respect to the gaseous (non-interacting) state
- Hence the reference state for the surface is the bulk and not the gaseous state

Now, I may want to assemble a solid or a liquid starting with a gaseous state. In the gaseous state atoms are far apart of course, they need not be atoms these entities could also be a molecules, but for simplicity here we consider atoms. We assume that in the gaseous state since the atoms are far apart there is essentially no interaction. Of course, there will be collisions as these atoms move about, but the kind of interaction we are talking is an attractive or repulsive interaction which continuously exists between a set of atoms.

When you want to assemble a solid or liquid, what we do is that we take the gaseous state and put it together in the form of a solid or liquid which has been drawn schematically here. If it is of course, a solid as you can see on the example here, it will be an ordered state, where you can see that there is a certain periodicity and order.

Of course, I could always assemble an amorphous solid also, but for simplicity we will consider a crystalline solid to start with. In the solid or liquid state the atoms are typically very close to each other and this formation of the liquid and assuming now that I am below my melting point or below the freezing point respectively for the liquid and the solid.

Then the system would like to lower it is Gibbs free energy by being in a state which is the state of the liquid or the solid. Therefore, below the melting or boiling points I have an increasing energy and therefore, the gaseous state represents a state of high energy in the solid or liquid state represents a state of low energy. Now, when we assemble a solid for instance from the gaseous state and now this is first what you might call a conceptual experiment we are doing. Then we see that of course, the atoms are come close to each other in the solid state.

More importantly this central atom for instance is bonded to its neighbors. In this process of bonding the energy of the system is lower and I am specifically referring to the Gibb's free energy assuming we are working at constant temperature and pressure. Now, but the atom on the surfaces as you can clearly see for suppose I take an atom here is only bonded partially compared to it is full potential. Therefore, these represents a state of higher energy.

Now, when we do a calculation for lowering of energy of the system on the formation of a condense state we assume that all the atoms are fully bonded. You can see that in this process we have done an over counting because now we assumed all the atoms are fully bonded while the atoms on the surface are only partially bonded. Therefore, atoms in the surface represent an higher energy with respect to the bulk. More importantly to keep in mind the reference state now is the bulk. For instance in this example the crystalline state and this higher energy state is not with respect to the gaseous or the non interacting state.

Therefore, when I say my surface is in a higher energy what I really imply it is got an higher energy with respect to the bulk atom not with respect to the gaseous state from which of course, I started my thought experiment. This is a very important point of an not emphasized on, but it is important to keep it in mind because now when I say the surface is in a higher energy state, I should not think that it is in higher energy state with respect to the gaseous state.

I am assuming that I am below the freezing point now. It is purely a coincidence of the fact that I did an over counting that I have even have to talk about something known as an surface energy. Suppose, I have to do an accurate calculation. In other words I only count those atoms in the bulk when I try lower find how much energy they are lowering and separately treat my surface atoms and find how many, how much of energy they were lowered.

Then I do not even have to consider a concept like a surface energy, but typically this is not how it is done. It is done by assuming that all atoms have bonded well and then I do a correction with respect to the fully bonded state which I call the surface energy tau. Hence the reference state for the surface energy is the bulk and not the gaseous state.

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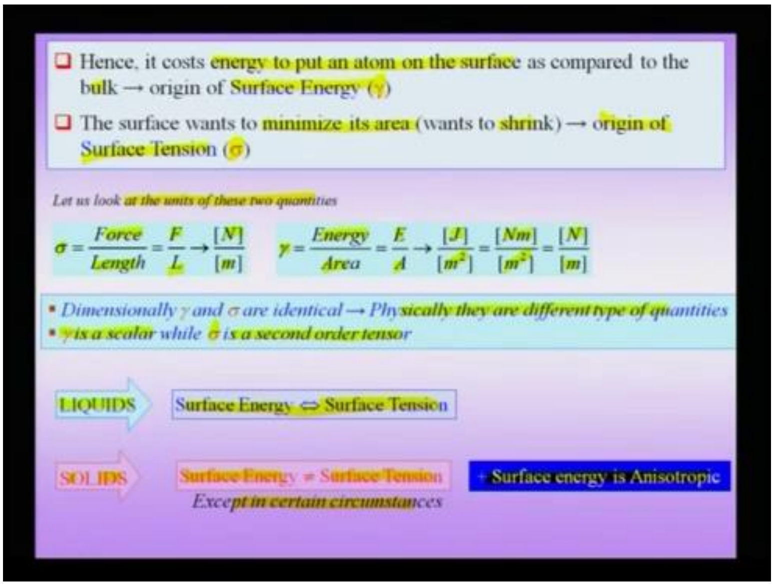

- ☐ Hence, it costs energy to put an atom on the surface as compared to the bulk → origin of Surface Energy (γ)
- ☐ The surface wants to minimize its area (wants to shrink) → origin of Surface Tension (σ)

Let us look at the units of these two quantities

$$\sigma = \frac{Force}{Length} = \frac{F}{L} \rightarrow \frac{[N]}{[m]} \qquad \gamma = \frac{Energy}{Area} = \frac{E}{A} \rightarrow \frac{[J]}{[m^2]} = \frac{[Nm]}{[m^2]} = \frac{[N]}{[m]}$$

- *Dimensionally γ and σ are identical → Physically they are different type of quantities*
- *γ is a scalar while σ is a second order tensor*

LIQUIDS → Surface Energy ⇔ Surface Tension

SOLIDS → Surface Energy ≠ Surface Tension

Except in certain circumstances

+ Surface energy is Anisotropic

Now, this automatically implies that it cause energy to put an atom on the surface and when I am saying put an atom, I put I take a bulk atom and move it to the surface then it is going to cause me energy as compared to the bulk. This is the origin of the surface energy which is typically given as symbol gamma. Now, the surface since the atoms on the surface have an higher energy, the system wants to minimize the surface area the atom want to go closer to each other or in fact into the solid.

This minimum tendency for minimization of area or the tendency to shrink is the origin of what is known as surface tension. We shall see now there is an important quotient to be kept in mind, that often surface energy and surface tension are sometimes inter changeably used, but this is not to be done. Now, the origin or the what you might call the seed for this kind of a misconception or a equivalence comes in the fact, that suppose I track my dimension the surface stressor surface tension. It is force per unit length then it is f by l and it the units turn out to be Newton per meter. The units of gamma by surface energy is energy per unit area which is e by a.

Energy being in joules area being in meter square and joules is Newton meter by meter square. Therefore, units of gamma is Newton per meter is exactly identical to the units of surface tension. Just because they are dimensionally identical, we should not think they are identical quantities physically these represent very different type of quantities, gamma is a scalar that means surface energy as we know is a scalar, while surface tension is a second order tensor.

Further we will see very soon that how these 2 quantities are different or how we should differentiate liquids and solids these are with respect to these quantities. What additional quantities and parameters do I need to consider when I am talking about solids and liquids. More importantly what is the true origin of this surface tension so these are things we will consider next just to summarize this slide we have two important quantities when we deal with surfaces.

One is surface energy other is surface tension dimensionally they are very similar or there are identitical, but we should note that they are physically very different kind of quantities gamma is a scalar and surface tension is a second ordered tensor. Liquids in liquids when I am talking surface energy and surface tension are equivalent concepts and sometimes they can be inter changeably used, but in the case of solids it is important to note that surface energy is not equivalent to surface tension.

Of course, in very under very special circumstance they may become equivalent, but for now we will assume that surface energy and surface tension represent different concepts when it comes to solids. Additionally surface energy is could be anisotropic when it comes to solids. So, this is something which is not present in liquids. Liquids we assume that the surface energy is isotropic that means it is not direction dependent. Therefore, I need to differentiate between liquid and solid surfaces, when it comes to these quantities like surface energy and surface tension and let us do that next.

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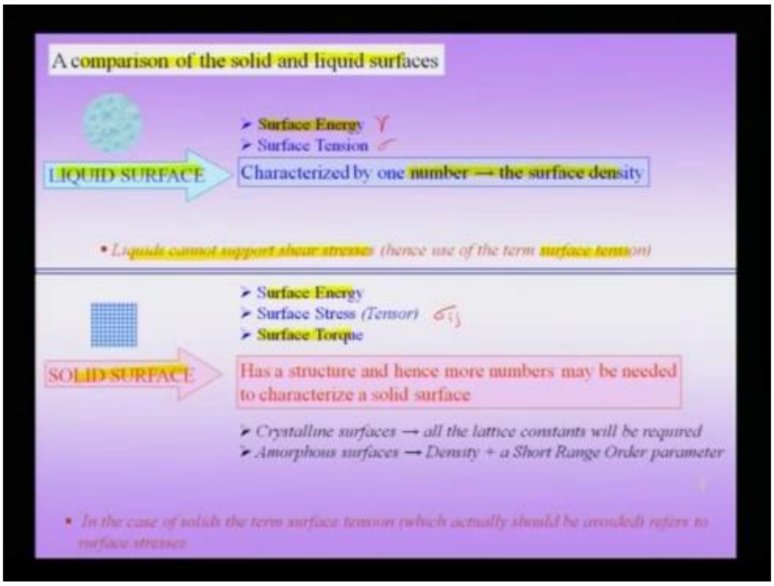

A comparison of the solid and liquid surfaces

LIQUID SURFACE

- Surface Energy γ
- Surface Tension σ

Characterized by one number → the surface density

- *Liquids cannot support shear stresses (hence use of the term surface tension)*

SOLID SURFACE

- Surface Energy
- Surface Stress *(Tensor)* σ_{ij}
- Surface Torque

Has a structure and hence more numbers may be needed to characterize a solid surface

- *Crystalline surfaces → all the lattice constants will be required*
- *Amorphous surfaces → Density + a Short Range Order parameter*

- *In the case of solids the term surface tension (which actually should be avoided) refers to surface stresses*

So, we have a comparison of these solid and liquid surfaces. Now, when I want to characterize a liquid surface. I have a few parameters which I need to specify. I need to specify the true quantities we just now dealt with. The surface energy which we have given a symbol gamma. The surface tension which I had given a symbol sigma and essential you are characterizing the surface structure itself. The liquids surface structure is characterized by 1 number which is the surface density.

In other words number of atoms per unit area which it is on the surface. So, essentially it is very easy for me to characterize a liquid surface because surface energy and surface tension represent equivalent concepts and I just need 1 parameter which is my surface density to characterize my surface. This ease is coming from the fact that liquid surfaces cannot support shear stresses.

Suppose, I apply shear on a surface then the material will flow and therefore, liquids cannot support shear stresses. So, therefore, we have a term like surface tension. Now, I want to compare this liquid surface with the surface of a solid. Then I would note that I could talk about something known as a surface energy and instead of talking about the term surface tension I may have to talk about the true quantity, which is surface stress which is a second ordered tensor.

In 2 dimensions it has got 4 numbers or 4 values which need to be specified. Additionally a surface is also associated with surface torque. The origin of surface torque is related to the fact that the surface energy could be an isotropic. That means that it depends on crystallographic plane. Suppose. I am talking about crystalline surface the energy is going to depend on that and therefore, suppose I am talking about 2 kinds of surfaces.

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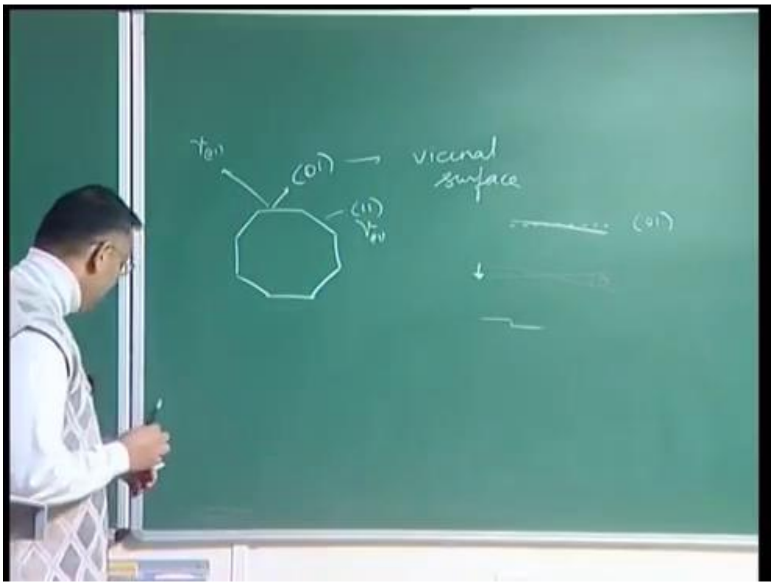

In 2 dimensions let me call this the 1 one kind of a surface. We saw we this 0 1 kind of a surface. The energy of this is expected to be different from the energy of this surface. Therefore, if an additionally these are of course, 2 important surfaces which are called low index plane surfaces, but I could also have a surface which is close to the gamma 0 1 surface or this is normally 0 1 surface, which I can call a vicinal surface.

Now, suppose this is my 0 1 surface. I could think visualize this surface which is inclined to this 0 1 surface at a small angle. So, I am considering an angel which is small. So, let me redraw this so this is my 0 1 surface and I am talking about a small angle with respect to this 0 1 surface which I call a vicinal surface. Now, since these low index planes are expected to higher density and they are also typically specified lower energy. While these kind of high index planes would have higher energy, the tendency for this plane to rotate into this orientation. Of course, it really does not rotate and typically you would find at this actually break up into steps and terraces, but that is a detail we will not consider now.

For now I will note that this tendency for rotation to a low index direction or a low energy direction is the origin of what you might call the surface torque. Therefore, when I am trying to characterize a solid surface, I need to specify a more quantities as compared and I have to go into a little more detail as compared to liquid surfaces.

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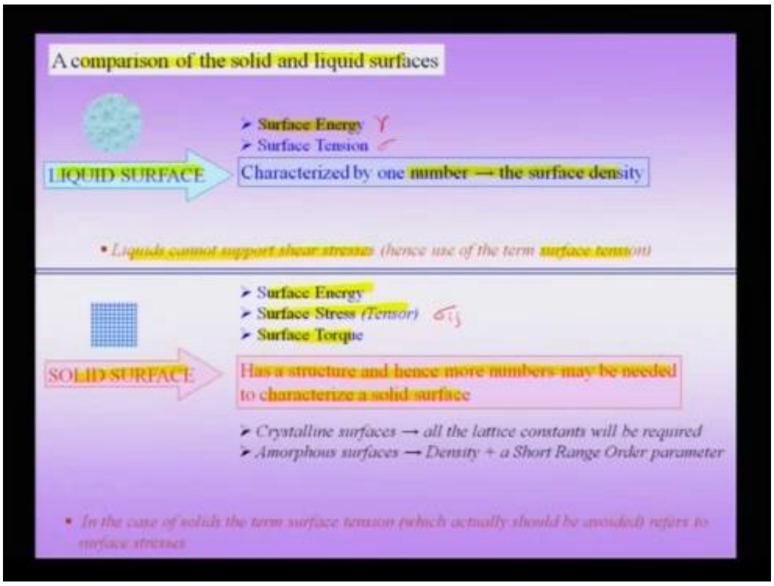

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Now, the first of which we noted was that this surface energy and surface stress are not equivalent concepts any more in a solid. These solid surface also associated with a surface torque.

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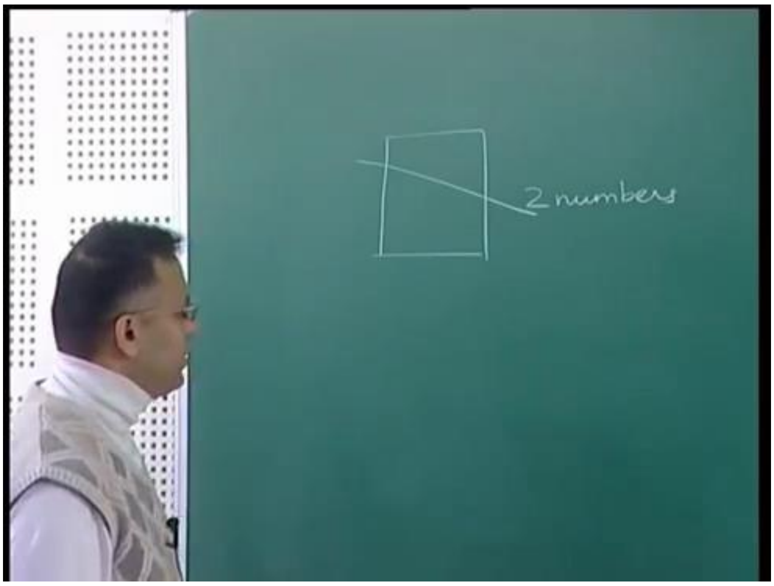

We clearly know that the surface, the crystalline, the surface of the crystalline material has structure and has more numbers need to be specified to characterize a solid surface. Macroscopically suppose I want to construct a surface from an infinite material then I need to perform a cut this cut itself will require 5 numbers to specify. So, for now I will simplify the problem, then say suppose I want to make a surface. Then I need a certain orientation at which I need to make this cut and this orientation can be given by 2 numbers or 2 independent miller indices in 3 dimensions.

Additionally I need to note where is this cut inside a crystallographic cell. Therefore, when I make a cut like this for instance a sodium chloride crystal, then I would notice that I would actually produce a polar surface and depending on where I make the cut the cut, I may have a set of negative charges sitting on the surface or negatively charged ion sitting on the surface or a set of positively ion sitting on the surface. Therefore, when I am making a surface. In a solid I need to specify more numbers then I need to specify for the case of a liquid surface.

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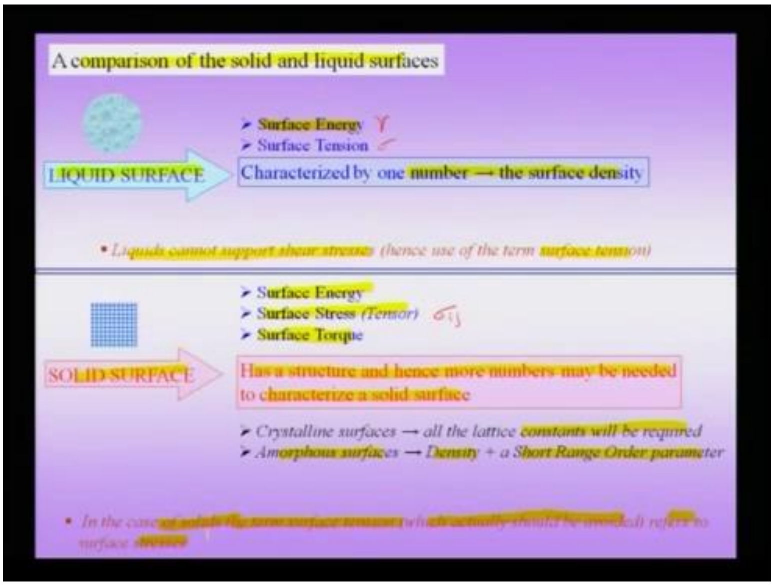

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In a crystalline surface I need to know all the lattice constants in amorphous. If I am not talking about the crystalline substance I am talking about amorphous surface then I need to know the density and a short range ordered parameter. So, in a sense a solid surface is very much unlike a liquid surface and that is when I am just even trying to create the surface for instance that is what a parameter.

I was mentioning when you try to make a cut, but additionally after the surface has been created it will be associated with quantities like surface stress and surface torque. As we are noted before a surface in a crystalline solid may undergo relaxation and reconstruction. Therefore, there are possibilities which do not exist in the case of liquid surfaces. There in the case of solids that term surface tension which is an actual should be avoided the first 2 surface stresses.

Now, we will see what is the connection between the term surface stress and the term surface tension. The surface energy can be understood gamma which we have been dealing with can be understood as the reversible work required to create a unit area of surface.

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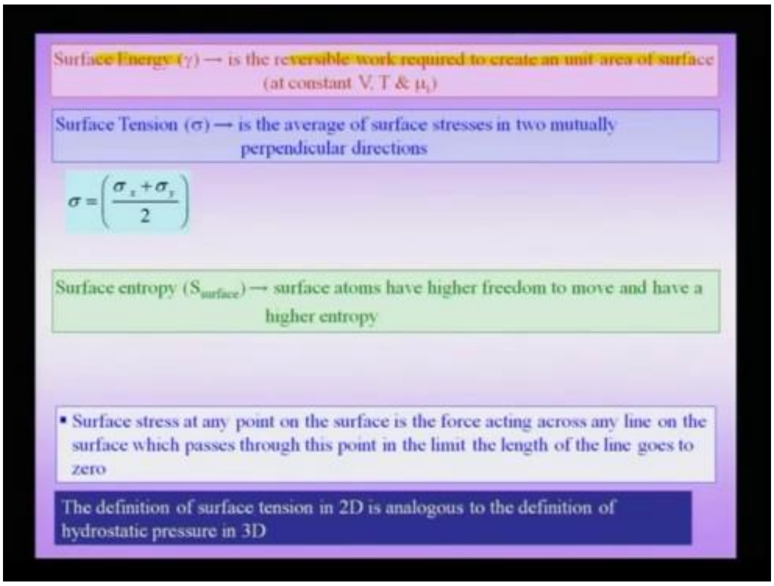

Surface Energy (γ) → is the reversible work required to create an unit area of surface (at constant V, T & μ_i)

Surface Tension (σ) → is the average of surface stresses in two mutually perpendicular directions

$$\sigma = \left(\frac{\sigma_x + \sigma_y}{2}\right)$$

Surface entropy ($S_{surface}$) → surface atoms have higher freedom to move and have a higher entropy

- Surface stress at any point on the surface is the force acting across any line on the surface which passes through this point in the limit the length of the line goes to zero

The definition of surface tension in 2D is analogous to the definition of hydrostatic pressure in 3D

So this can be understood for instance by using a soap filling for instance between 2 sliders. So, I can take 2 sliders and create a soap fill.

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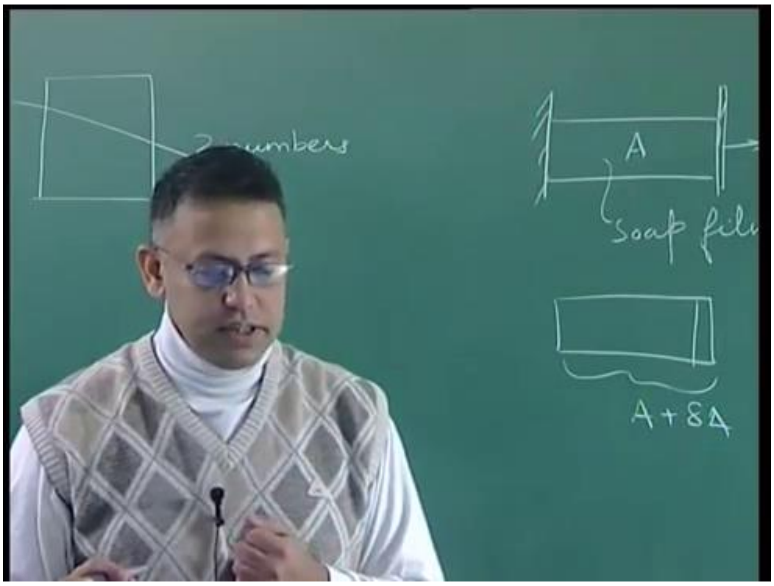

Assuming this one of the sliders is fixed and this is a soap fill. I can pull this surface, pull this slider here to this another slider, which I can pull. Then see how much work I need to do to create a unit additional area. Suppose, I am starting with this area and after pulling I may create an area which is now this new area is a plus delta a. Then I would need to track how much work is required to create an additional unit area of surface and of course, I will be working at constant volume temperature and chemical potential with respect to all the species.

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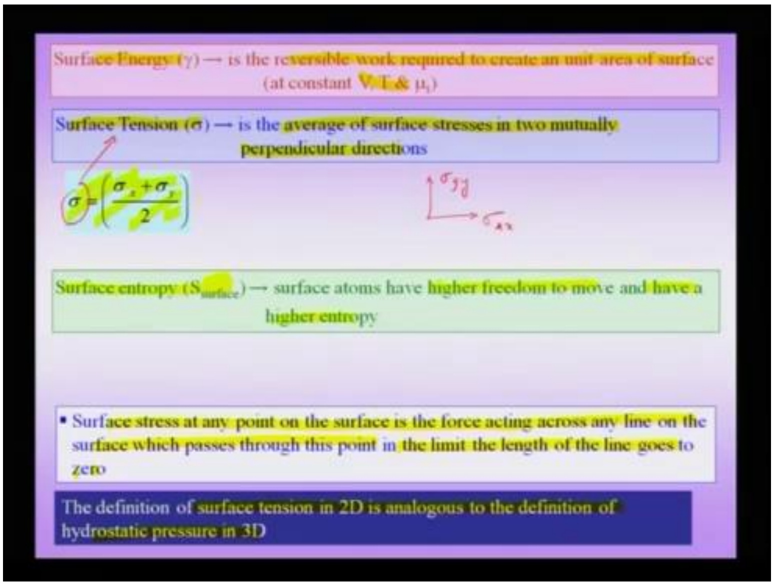

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So, this an alternate way of looking at what is meant by surface energy. Now, I would like to connect my term surface tension in the case of solid with the term surface stress. Surface tension is the average of the surface stresses in 2 perpendicular directions, that means that I take my sigma x x component and I take my sigma y y component and average term that is the term sigma which I have been referring to a surface tension.

So, in some sense you can think of surface tension as the 2 d analogous term the definition of the hydrostatic pressure in 3 dimensions. So, in 3 dimensions we have the concept of hydrostatic pressure and we know that if you apply hydrostatic stresses on any volume of body, then this body cannot undergo plastic deformation. It can only undergo volume changes. So, we have a 2 dimensional analog of that which is now my surface tension, which is the average of the 2 orthogonal stresses.

An additional factor comes into play when I am talking about a surface which is the concept of surface entropy. Now, I am talking about surface energy. I could just be talking about the just the internal surface energy or I could be talking about the enthalpy of the surface or I could be talking about the Gibb's free energy the surface.

Now, when I am talking about Gibb's free energy of the surface I need to involve the concept of surface entropy and as the surface atoms have higher degree of freedom to move. Hence they have a higher entropy. Though they may have a higher energy which is standing to might call these stabilizers surface or put as surface at the lower stability level then the bulk, but entropically a surface is more stable as compared to the bulk atom. The competition of the 2 which going to decide at what temperature I am going to have a stable surface with respect to a bulk.

Surface stress at any point on the surface is a force acting across any line on the surface which passes thought this point. In the limit that the length or the line goes to 0. So, this is the way of determining surface stresses, but as we have seen that surface stress can be thought of as the 2 dimensional analog of the hydrostatic pressure which is a term used in 3 dimensions.

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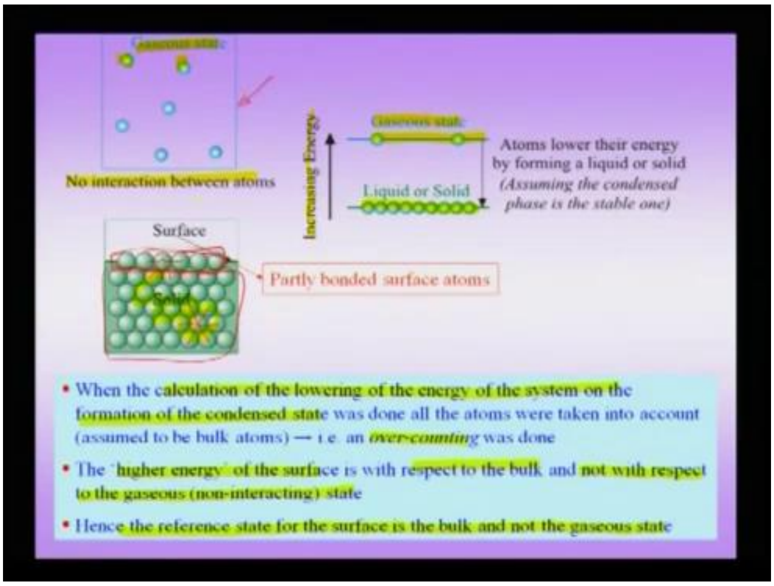

Atoms lower their energy by forming a liquid or solid *(Assuming the condensed phase is the stable one)*

- When the calculation of the lowering of the energy of the system on the formation of the condensed state was done all the atoms were taken into account (assumed to be bulk atoms) → i.e. an *over-counting* was done
- The 'higher energy' of the surface is with respect to the bulk and not with respect to the gaseous (non-interacting) state
- Hence the reference state for the surface is the bulk and not the gaseous state

So, let me summaries some of the concepts so far. Surface energy is not an energy in itself, it is an energy which comes because of over counting and when I am talking about surface energy, I am actually talking about the reference state being the fully bonded state of the bulk crystalline state. Of course, it need not be crystalline state, it can be an amorphous state or liquid, but for simplicity we consider a bulk crystalline state.

When we are talking about quantity associated with the surface I need to talk about quantities like surface energy, surface tension which are dimensionally identical.

Additionally I need to involve concepts like surface torque and surface stress. Surface tension itself can be thought of as an average the 2 orthogonal stresses, the sigma x plus sigma y by 2 and therefore, it is a 2 d analog of the hydrostatic pressure.

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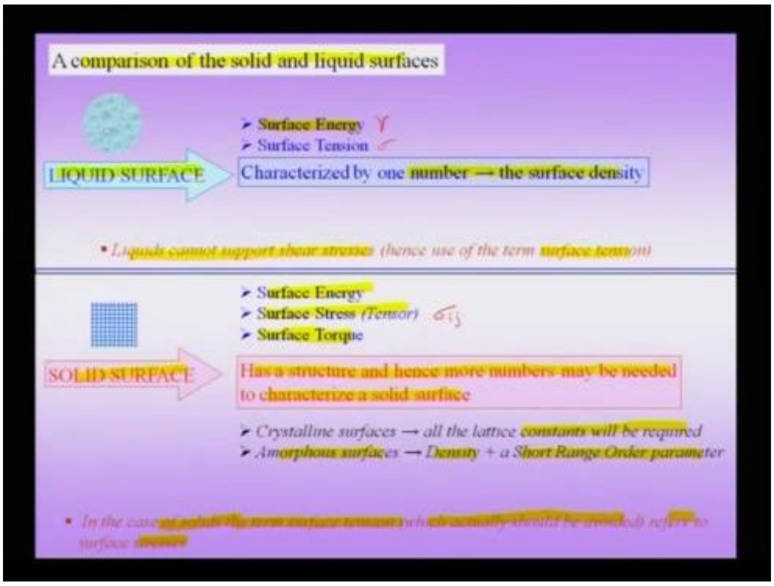

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When I am talking about solid surfaces I can no longer call the surface energy and surface stress to be represent equal and concepts. Additionally solid surfaces have a surface torque and when I am talking about solid surfaces, I may note that the surface might have undergone relaxation or reconstruction. Therefore, the crystallography of the surface, could be very different from the crystallography of the bulk. Some of these points I will just summarize which we already noted.

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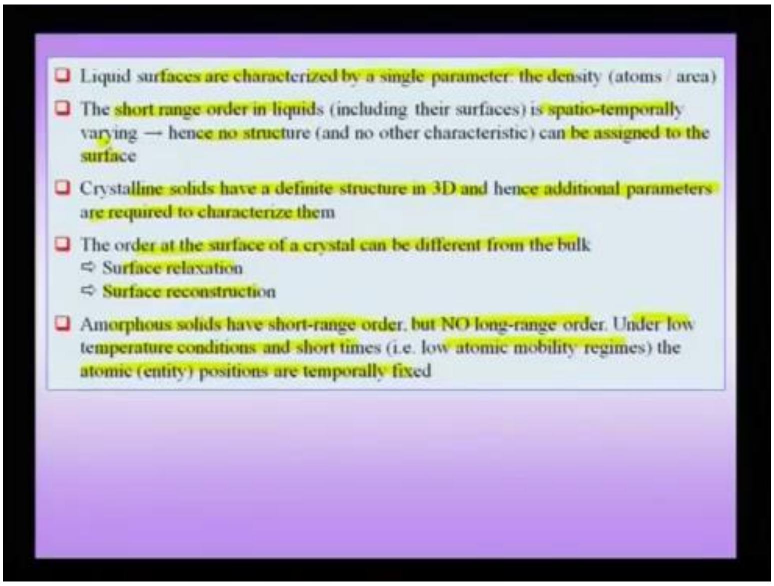

- ❑ Liquid surfaces are characterized by a single parameter: the density (atoms / area)
- ❑ The short range order in liquids (including their surfaces) is spatio-temporally varying → hence no structure (and no other characteristic) can be assigned to the surface
- ❑ Crystalline solids have a definite structure in 3D and hence additional parameters are required to characterize them
- ❑ The order at the surface of a crystal can be different from the bulk
  - ⇨ Surface relaxation
  - ⇨ Surface reconstruction
- ❑ Amorphous solids have short-range order, but NO long-range order. Under low temperature conditions and short times (i.e. low atomic mobility regimes) the atomic (entity) positions are temporally fixed

That liquid surfaces are characterize by a single number which is surface density. The short range order in liquids is patio temporally varying. Hence no structure can be assigned to the surface. So, if at all we are going to assign any kind of structure to the surface in a liquid it is going to be a frozen snap shot of what is happening for a period of time.

Crystalline solids have a definite 3 d and hence structure in 3 d and hence additional parameters are required to characterize them. The order at the surface of a crystal can be very different from the bulk and this is arising from surface relaxation and surface reconstruction. Even in absence of these quantities you would expect that the surface is going to be somewhat different from just the bulk termination.

Amorphous solids have short range order, but no long range order under low temperature conditions and short times that means we are talking about low atomic mobility regimes. The atomic entity positions are temporally fixed. So, I may have short range order on amorphous surface, but no long range order. Under a typically under at low temperatures I will assume that this short range order persist over long times.

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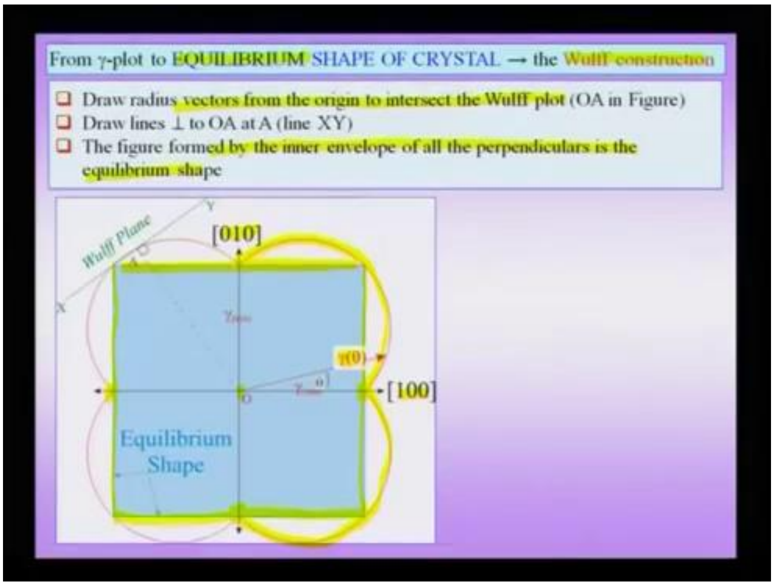

From γ-plot to EQUILIBRIUM SHAPE OF CRYSTAL → the Wulff construction

- ☐ Draw radius vectors from the origin to intersect the Wulff plot (OA in Figure)
- ☐ Draw lines ⊥ to OA at A (line XY)
- ☐ The figure formed by the inner envelope of all the perpendiculars is the equilibrium shape

Now, we have already noted that crystals tend to have a certain festal shape and how can we obtain the shape of a crystal is the next question. This question is very very closely related to the fact that we are considering surface energy. So we have already pointed out that, surface energy depends on the direction that means it is an anisotropic quantity. For instance suppose I am talking about a 3 d crystal then my 0 1 0 surface may have a different energy as compared to 1 1 1 surface, which is expect to have a different energy compared to a 1 1 2 surface. Which will again be different from every other surface which I can think of in a crystal.

Depending on a crystallography or the symmetry, obviously suppose I am talking about a cubic crystal, then the 0 1 0 surface energy is will be identical to the 1 0 0 surface energy, which will be identical to the 0 0 1 plain surface energy. So this is coming from the crystal symmetric. Now, if I grow a crystal, then typically it ends up in a certain polyhedral shape which is called the growth shape of a crystal. Suppose, I now un heal this crystal for wrong times, then the system will tend to go it is into its low lowest energy shape state, which is an equilibrant shapes state.

In which case the crystal will put out those faces which gives the system over all low energy state. How do we determine this low energy state of the crystal. In other words how do I determine the equilibrium shape of a crystal. This is done by a construction known as the wulff construction. To reiterate the wulff construction is going to give us the long time stable state of the crystal and not the growth shape of the crystal because crystals may grow in shapes which are slightly depend on the kinetics and kinetics have an attachment et cetera.

Those phases which grow very fast will exhaust themselves unlike that we going to talk about equilibrium shape it is actually in each sharp which gives us a the low energy state. The way it is done is that we start with the variation of the surface energy with respect to theta. So, we have a polar plot of the surface energy with respect to theta. You can see that suppose I am considering a fore fold direction cubic crystal, then this gamma plot will also have a fore fold symmetry.

Another important point to note is that, this gamma plot would have certain casts here as you can see, which represent low energy surface orientations. Then we draw a radius vector from the origin to intersect the wulff plot like for instance, o a in the plot. Now, take my o origin and I draw a tangent and allow it to intersect. Now, the figure formed by the inner envelope upon all the perpendiculars is the equilibrium shape. So, you can see if I keep on drawing inner perpendiculars, then I get a shape which is now for instance given by this blue box.

This is my equilibrium shape of the crystal of course, this is a schematic here and various crystals would have different kind of equilibrium shapes which may have 1 1 1 surfaces 1 0 0 surfaces, but typically these are low index surfaces which are thrown out by a crystal. A point to be noted is that, those low energy orientations obviously are the orientation are the more preferred ones and typically will show up in the, what it might call the wulff construction.

So, essential message from this is that because of anisotropy surface energy crystals would tend to have polyhedral shapes. In the case of nano crystals because it is surface dominance system, the system would or the crystal will tend to go towards it is equilibrium polyhedral shape in much shorter time scales as compared to bulk crystal. Of course, we know that most of the bulk crystals we deal with typically could be polycrystalline material. Which means that we are not actually going to get a single kind of wulff construction which we are talking about here.

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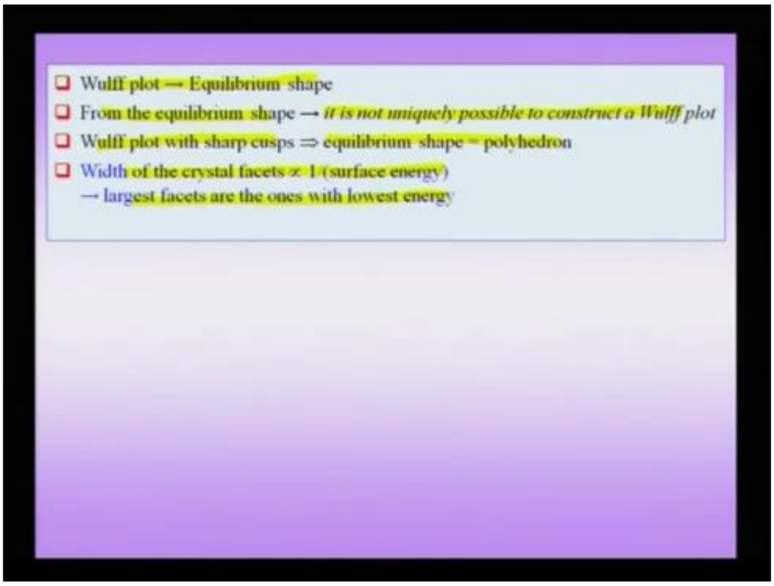

- ☐ Wulff plot → Equilibrium shape
- ☐ From the equilibrium shape → *it is not uniquely possible to construct a Wulff plot*
- ☐ Wulff plot with sharp cusps ⇒ equilibrium shape = polyhedron
- ☐ Width of the crystal facets ∝ 1/(surface energy)
  → largest facets are the ones with lowest energy

So, wulff plot gives us the equilibrium shape from the equilibrium shape it is of course, not equal uniquely possible to going the reverse direction make a wulff plot. Wulff plots with sharp cusps represent the equilibrium shape which typically a polyhedral. If of course, the anisotropy is small then you may not get a nicely fasted nicely fasted crystal as you can see here with very low number of planes representing the outer surface.

The width of the crystal facets is was proportional as the 1 by the surface energy that means that the largest facets are the ones with the lowest energy. They were the crystals obviously would put out those surfaces which have the lowest energy.

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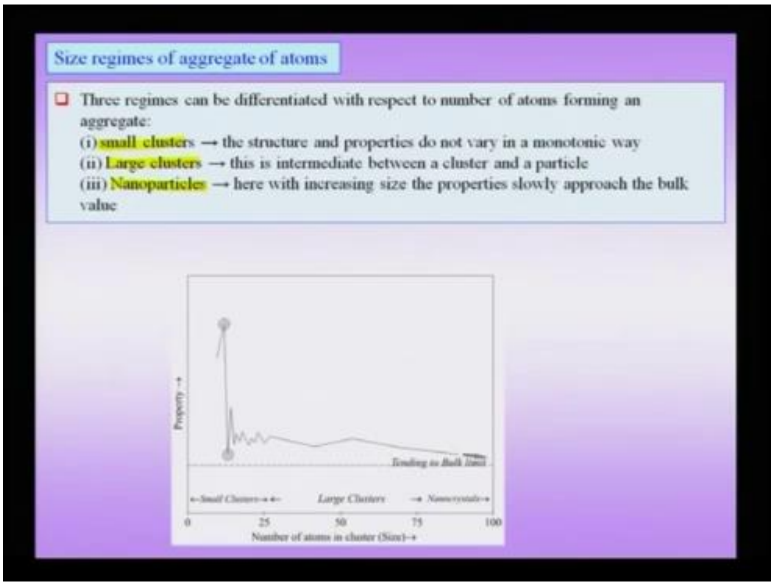

Size regimes of aggregate of atoms

- Three regimes can be differentiated with respect to number of atoms forming an aggregate:
  (i) small clusters → the structure and properties do not vary in a monotonic way
  (ii) Large clusters → this is intermediate between a cluster and a particle
  (iii) Nanoparticles → here with increasing size the properties slowly approach the bulk value

Now we move on to an equivalent, but in some sense this thing concepts. That how do I classify my nano crystals or clusters based on certain kind of a property. Now, we seen that we can go to the nano scale from 2 possibilities. One I make a bottom of approach that means they start with a few atoms or a few molecules and try to make larger and larger clusters. At some point of time if these cluster of atoms or molecules arranged themselves in a, what it might call crystalline order, then I can be actually talking about a nano crystal.

So, we will introduce 3 terms here with respect to properties. One I will call these small cluster regime. One will be the large cluster regime and of course, I will go into a region which is a called the nano particle regime and in as we shall see now, that one of the special class of interesting nano particles are the nano crystals or the crystalline nano particles. For now we will assume that this nano particle is a single crystal that means it is does not have further grains into it.

In reality of course, when I am making top down approach, you might notice that some of the particles could actually be poly crystalline. Now, why do I want to differentiate these 3 classes and how is it how is it meaningful in understanding their properties is what we will address next. Later on we will also take up an alternate way of classifying some of these because in a literature often you would find, not only classifications of the kind. Just now I mention, but there are other size regimes which are define like people define molecules, people define micro clusters, small particles and micro crystals.

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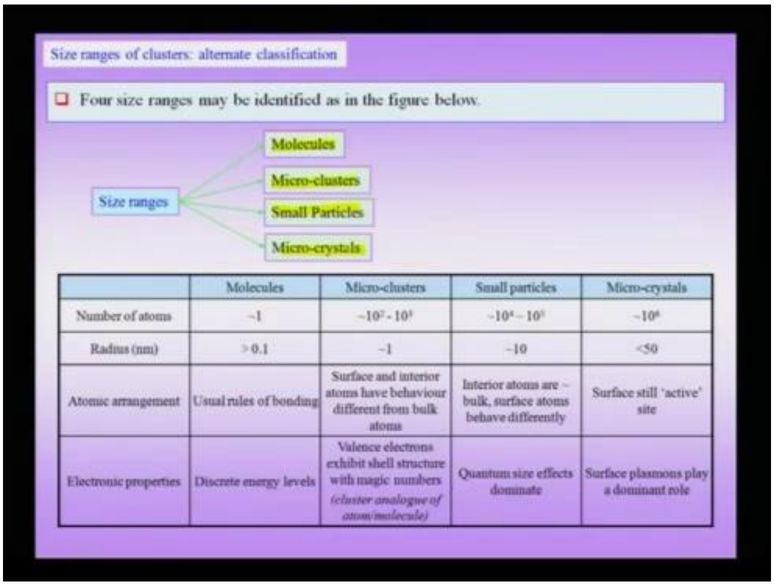

Size ranges of clusters: alternate classification

- ❑ Four size ranges may be identified as in the figure below.

Size ranges

- Molecules
- Micro-clusters
- Small Particles
- Micro-crystals

	Molecules	Micro-clusters	Small particles	Micro-crystals
Number of atoms	~1	~10^2 - 10^3	~10^4 – 10^5	~10^6
Radius (nm)	>0.1	~1	~10	<50
Atomic arrangement	Usual rules of bonding	Surface and interior atoms have behaviour different from bulk atoms	Interior atoms are ~ bulk, surface atoms behave differently	Surface still 'active' site
Electronic properties	Discrete energy levels	Valence electrons exhibit shell structure with magic numbers *(cluster analogue of atom/molecule)*	Quantum size effects dominate	Surface plasmons play a dominant role

Some of the regimes and what it might call the property regimes at the definitions would tend to overlap, but depending on the literature reading and with respect to certain specific properties. One of these 2 may be used by an author to as few to describe what you might call a cluster of atoms.

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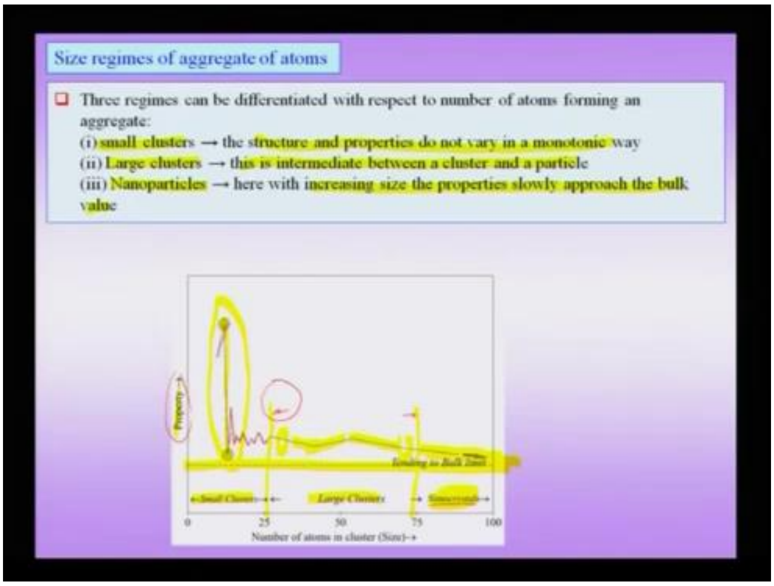

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  (i) small clusters → the structure and properties do not vary in a monotonic way
  (ii) Large clusters → this is intermediate between a cluster and a particle
  (iii) Nanoparticles → here with increasing size the properties slowly approach the bulk value

Now, how can I differentiate my 3 regimes. The small cluster regime, the large cluster regime, the nano particle regime and why do I want to do that is what we are considering. In the small cluster regime which could now be in these sub nano meter regime. The structure and properties do not vary in the monotonic way and we shall soon see that in this regime we will have certain numbers called the magic numbers. When you are talking about clusters.

The important point denotes suppose I am changing a property here which could be a property related like magnetization. It could be some of their property I am talking about and there is the dotted lines here which talks about the bulk value of this property. That means if I take a bulk material and a measure it magnetization, it will have a certain value.

Now, the 3 regimes which are approximate of course, drawn here are these 3 regimes. The regimes of this small clusters the regime with the large clusters and the regime with the nano crystals. In this small crystal regime if we notice that just by a mere addition of 1 atom a property could actually change very drastically. Now, this could be for instance a stable configuration, this could be an unstable configuration.

Hence the property could change very very drastically by mere addition of 1 atom or the removal of an atom. So, if you track the property, in the small cluster regime you will see that actually it is going under going large fluctuations. The nature of the fluctuations and the range of the fluctuations obviously depend on the property and when we get down to some other properties you will have to see that, how actually these properties could vary.

Whether the initial thing here is that I cannot talk about an average property in this case, I have to take each cluster. For instance a cluster of twelve atoms a cluster of nine atoms separately and study the properties and of course, this as you can visualize would be a challenging task. I need to first of all separate of these clusters of the same size then make on the properties. Any presence of any other size clusters would contaminate my results.

In the case of the large clusters which is basically intermediate between the cluster and the particle or the nano crystal. There is still fluctuation in the properties and here we are talking about a size regime for instance in the nanometer size regime. There are still fluctuations, but these fluctuations are much more gradual and typically if you add for instance a few atoms or 1 or 2 atoms, you do not expect that these properties is going to change in a very drastic way, as it would happen in the case of the nano small cluster regime.

So, here also there is some fluctuations in the properties. Here also you would notice that there are some possibilities of certain sharp minimum and maximum but, the overall trend line is not fluctuating that large when you actually add a few of the atoms or molecules to the cluster. On the other hand we expect that somewhere all this fluctuations have to die down and I have to approach the bulk value of my property.

Wherein now I do not have to no longer deal with individual clusters like a 30 atom cluster or 32 atom cluster separately, but I can talk about an average property which of course, is not changed with size and that is my bulk limit, but somewhere in the large nano crystal regime I would expect that this limit is obtained.

This is of course, easy to understand because this is now my what it might call the more monotonic kind of a variation in properties. So, here I am not observing fluctuations, the system slowly tending towards the bulk limit in a monotonic fraction. How many atoms actually constitute a small cluster. How many atoms would I put together to form a large cluster or a nano crystal of course, depends on, the kind of property I am studying and the kind of system I am considering.

So, for instance suppose I am talking about as we considering the magnetic property Ferro magnetic property. I am talking about make an atoms this variation could be different visa vi. For instance suppose I am talking about some totally different property, like for instance see corrosion resistant’s are oxidation or adsorption of as foreign molecule. These are some other particle like iron particle.

The intermediate regime is a regime where I would presume that the crystalline order not yet been established. In small clusters there not even sufficient number of atoms to even talk about. For instance a long range crystalline order because when I am talking about a crystal I am assuming that at least there are few tens of unit cells or few hundreds of unit cells in each dimension.

This long range order which I call a crystalline order has been established, but in the case of small clusters it is meaningless to talk about it. In the case of nano particles which is now also as we can consider an example of nano particles a crystalline state. There it is clear that I have enough number of unit cells to classify that is the nano crystal. In the large cluster regime this is some sort of a grey area, where I perhaps do not have enough number of atoms or unit cells to classify that as a nano crystal.

These large clusters may be crystalline in the some sense that they may not represent just polyhedral shell, but in this toward this end they may actually have a few unit cells, but along the way you would notice that, the structure might change from that of some kind of a cluster behavior. That have no kind of a unit cell formation to a regime where you actually have a crystalline structure.

Here though we are not especially talking about the structure, we are actually talking about the property, but it is very clear that this property would be a sensitive function of these structure. Therefore, it is meaningful for us to correlate the structure with the property we are talking specifically. So, to summarize this slide, there are 3 regimes which we can talk about which is the small cluster regime the large cluster regime and the nano particle regime.

The specific examples of nano particles we are talking about here are nano crystals. To something to qualify as a crystals we need should have sufficient number of unit cells so that a long range order has been establish. In the small cluster regime which is in some sense a very interesting regime. Mere addition of 1 particle or 1 atom or 1 molecule can actually lead to a drastic change in the properties. These fluctuations with respect to size would die down on in the large cluster regime, where in the oscillations become smaller. Of course, in the bulk in nano crystal regime it becomes monotonic.

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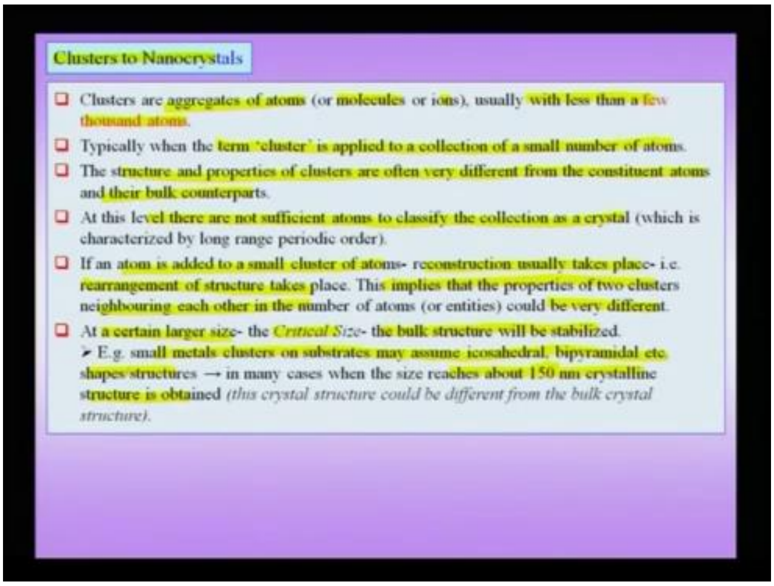

Clusters to Nanocrystals

- ☐ Clusters are aggregates of atoms (or molecules or ions), usually with less than a few thousand atoms.
- ☐ Typically when the term 'cluster' is applied to a collection of a small number of atoms.
- ☐ The structure and properties of clusters are often very different from the constituent atoms and their bulk counterparts.
- ☐ At this level there are not sufficient atoms to classify the collection as a crystal (which is characterized by long range periodic order).
- ☐ If an atom is added to a small cluster of atoms- reconstruction usually takes place- i.e. rearrangement of structure takes place. This implies that the properties of two clusters neighbouring each other in the number of atoms (or entities) could be very different.
- ☐ At a certain larger size- the *Critical Size*- the bulk structure will be stabilized.
  - ➢ E.g. small metals clusters on substrates may assume icosahedral, bipyramidal etc shapes/structures → in many cases when the size reaches about 150 nm crystalline structure is obtained *(this crystal structure could be different from the bulk crystal structure).*

So, let us now talk about going from clusters to nano crystals a little further. Clusters are aggregates of atoms of course, they could be aggregates of molecules or ions also. Usually less than a few thousand atoms. So, when I am talking about clusters typically I am dealing with a less and about few thousand atoms. Typically when the term clusters are applied to collection of small number of atoms. So, we do not use the term cluster for large collection for instance in the case of a nano crystal.

The structure and properties of clusters are often very different from the constituent atoms and their bulk counter parts. So, this is something to be kept in mind. For instance suppose I could be talking about a material which is anti ferromagnetic in the bulk, but which could turn ferromagnetic in this small cluster regime. Therefore, there is a drastic change in properties which are possible when I go to the cluster regime as compared to the bulk counterpart.

If the cluster is made up of molecules the individual molecules themselves could have a certain kind of a property, but the property of the cluster would be very different from the property of the individual molecule of the constituent atoms. At this level of the cluster there is not sufficient atoms to classify as a crystal as we saw because which is there are insufficient atoms to establish this long range periodic order.

If an atom is added to a small cluster of atoms reconstruction usually takes place I mean reconstruction with respect to the structure, which is a real rearrangement of the atoms.

We are seen that this implies that the properties of 2 clusters which are close which are close to each other in terms a number of atoms could be very different. This is what makes the study of these clusters very exciting.

At a certain largest size the critical size the bulk structure will be established. When we mean a bulk structure we have already seen we are referring to the bulk structure not only in terms the tangible kind of a definition, but here we are actually referring to in terms of the property based definitions. Small metal clusters for example, on substrate may assume icosahedral bipyramidal etcetera kind of shapes.

Obviously these icosahedral bipyramidal shapes do not represent crystals. In many cases the size reaches about 150 nanometer the crystalline structure is obtained. That means that now in the small cluster regime there are certain polyhedral shapes which are not crystalline they are just clusters. When you reach about 150 nanometers you obtain the large bulk crystalline limit and in between the 2 you could actually be stabilizing for instance different kind of crystal structure, which are not the bulk crystal structure.

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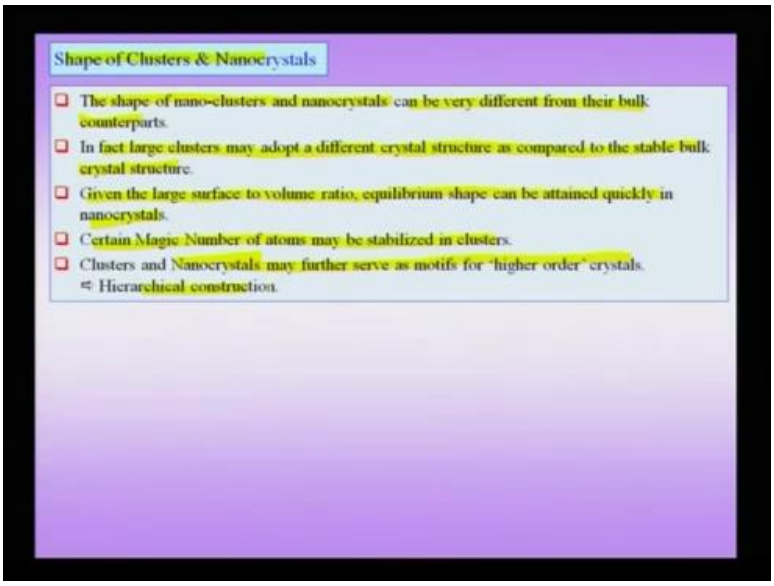

Shape of Clusters & Nanocrystals

- ❑ The shape of nano-clusters and nanocrystals can be very different from their bulk counterparts.
- ❑ In fact large clusters may adopt a different crystal structure as compared to the stable bulk crystal structure.
- ❑ Given the large surface to volume ratio, equilibrium shape can be attained quickly in nanocrystals.
- ❑ Certain Magic Number of atoms may be stabilized in clusters.
- ❑ Clusters and Nanocrystals may further serve as motifs for 'higher order' crystals.
  ⇐ Hierarchical construction.

So, let us summaries some of the aspects we have seen with respect to clusters and nano crystals. The shape of nano clusters and also nano crystals can be very different from their bulk counter parts. Now, we are talking about the shape of the external polyhedral which forms in the equilibrated shape, which we have seen that how we can obtain from a wulff construction, but a wulff construction typically applies to large crystalline macroscopic tangible bulk kind of a crystal to rather than to these small clusters.

Therefore, I may have a wulff construction for the nano crystal or the bulk crystal and I may have this clusters and these 2 shapes typically are very different. Large crystals may adopt large clusters and of course, small clusters may adopt a crystal structure, sorry now we are talking about large clusters because in the case of small clusters, we cannot even talk about the crystal structure.

The large clusters may adopt a different crystal structure as compared to the stable bulk crystal structure. So, this we have noted already and we will also see examples of phase transformations later on, wherein when we reduce the crystal size we see that new phases are stabilized. We already seen couple of those examples in the case of e 2 or 3 etcetera. During the large surface to volume ratio the equilibrated shape can be attained quickly in nano crystals and also in large clusters.

So, if I have a shape which is in I am synthesizing a solid when or its produced by a certain method and it is not the equilibrium shape it can reach the equilibrium shape very very quickly. Now, we will see next that is certain magic number of atoms where we stabilized in clusters and we will also see what is the origin of these magic number of atoms. In another words when I am talking about a cluster the cluster instead of behaving like a collection of individual atoms tends to start to behave like something like a super atom.

That means the entire cluster itself can be visualized as an entity in itself. It can be thought of a super atom and not only that, these nano crystals themselves may serve as motives in higher order hierarchical construction of crystals. We will take up some examples wherein of course, in many cases you have what is call self assembly. Wherein I start with a nano crystal and then make use this as a motive in making a larger unit crystal.

Wherein of course, I am not worried about the ordering of atoms within this nano crystal, but I am talking about ordering the nano crystal themselves in a periodic fashion to give raise to a, what you might call a crystal of a higher order. So, I can have a hierarchical construction of crystals and this is a very interesting concept which we will explore further.

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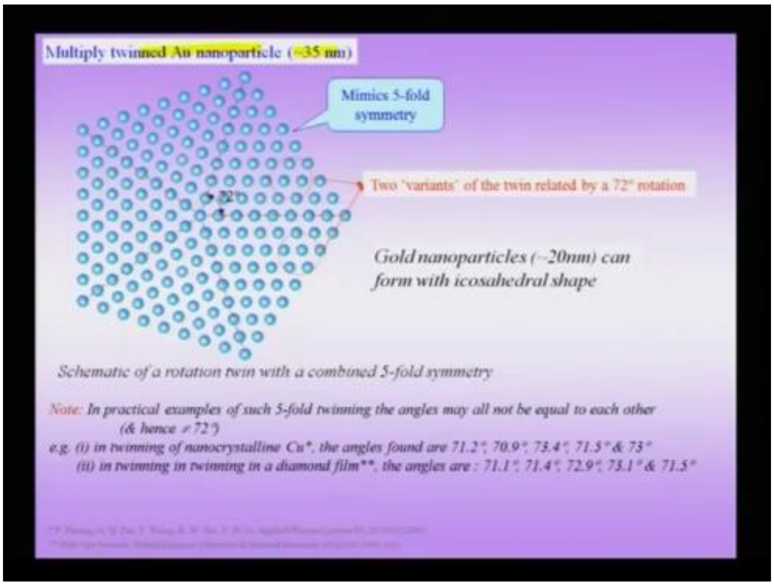

Multiply twinned Au nanoparticle (~35 nm)

Mimics 5-fold symmetry

Two 'variants' of the twin related by a 72° rotation

Gold nanoparticles (~20nm) can form with icosahedral shape

Schematic of a rotation twin with a combined 5-fold symmetry

Note: *In practical examples of such 5-fold twinning the angles may all not be equal to each other (& hence ≠ 72°)*

e.g. (i) in twinning of nanocrystalline Cu, the angles found are 71.2°, 70.9°, 73.4°, 71.5° & 73°*

*(ii) in twinning in twinning in a diamond film**, the angles are : 71.1°, 71.4°, 72.9°, 73.1° & 71.5°*

One interesting example we talked about shapes of crystals and when I am talking about a shape of a crystal. We are typically assuming that is arising naturally from some kind of a polyhedral arrangement, but if you look at some of the examples. Like for instance I am here showing a multiply twinned gold nano particle, schematic of that which is about thirty 5 nano meters. We have talk about it this kind of a structure with respect to what you might call a rotational twin.

So, we had given this is an example of a rotational twin. Suppose, I have twinning occurring in the in a bulk crystal. So, typically some of these twin boundaries would exist go in for instance in a copper crystal would extend from 1 grim boundary to another. So, let me draw that schematically here. Suppose, I am talking about a copper poly crystal. So, I have a grim structure like this and I may notice that within a single grim you may have one twin boundary and of course, another twin boundary extending from 1 grim boundary to another.

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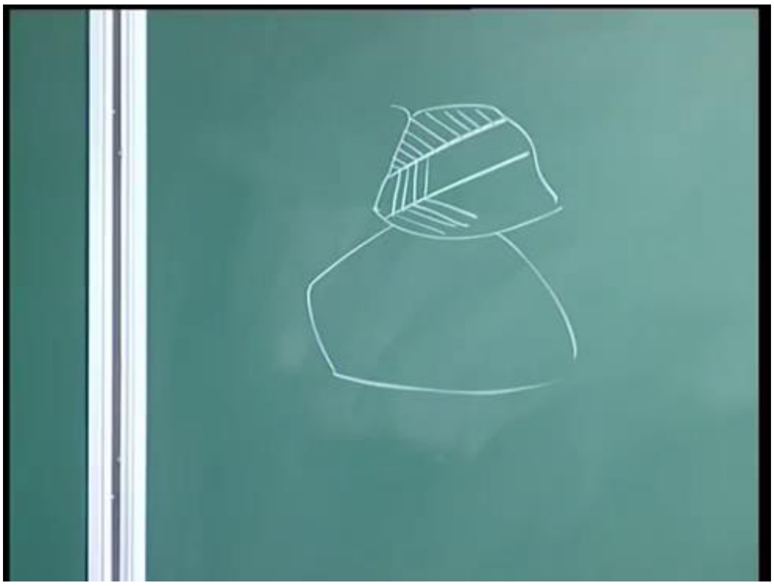

So, suppose I have crystallography planes here these crystallography plane would be reflected here like this and this other twin would actually restore my orientation. So, this is of course, twinning in a polycrystalline material, but many a times this kind of twinning would lead to internal stresses in the material. In the case of a nano particle because the way what these arise and the fact that they are not embedded in a matrix.

Actually the stresses could not be large and could actually stabilize a nano particle which is having for instance in this case fivefold rotational twin. Now, of course, that we had noted in that context of this rotational twins.

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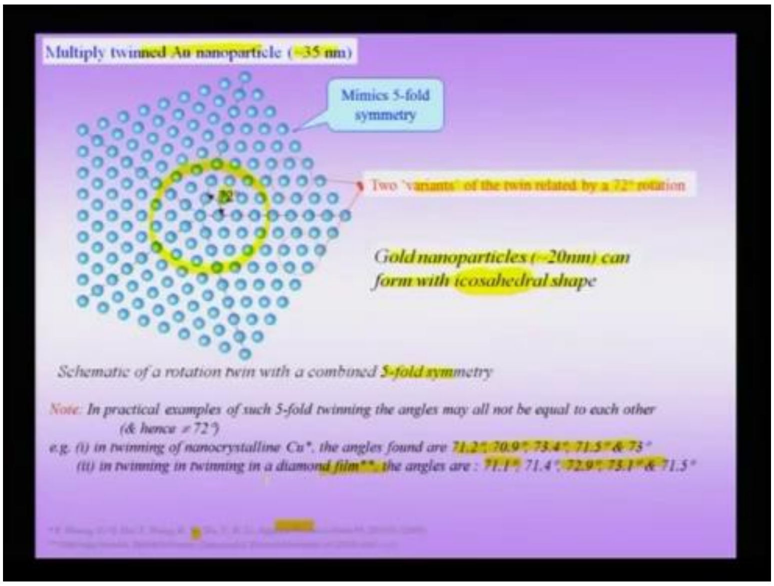

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That if I have had to put the selected area diffraction aperture here, I would mimic a system of higher symmetric. In fact I would think as if there is some fivefold symmetry and I think from this kind of a twin particle. The 2 variants in an ideal circumstance in such a crystal could be related to a 72 degree rotation, 72 degree of course, is an ideal kind of a rotation I am talking about.

If you refer to some other publication you would note is that, the actual angles in what could be close to 72 degree, but they may not be exactly 72 degree. For instance they could be 71.2 etcetera. So, they are close to 72 degrees giving this some sort of a close to a fivefold rotation. In twinning of a diamond film for instance the angles have been formed to be again close to about 72 degrees, but the interesting thing here is that, in systems wherein I am talking about twin as a defect in a perfect crystalline order.

They could be much more easily stabilized in the case of nano particles. In fact in many nano particles we will see that the deformation mo de will switch from that of, what you might call a dislocation plasticity to a twinning kind of a plasy much more easily.

This is some good feature that we have in nano particles and nano crystals. That certain defects are much more easily formed and some of these defects may actually may not be formed in their bulk counter parts. Additionally of course, you may have gold nano particles about twenty nanometer which can form with an icosahedral shape. So, we know that icosahedral symmetry is not comparable with translation, but still you find nano particles which can these kind of a shape which is otherwise not seen for bulk crystals.

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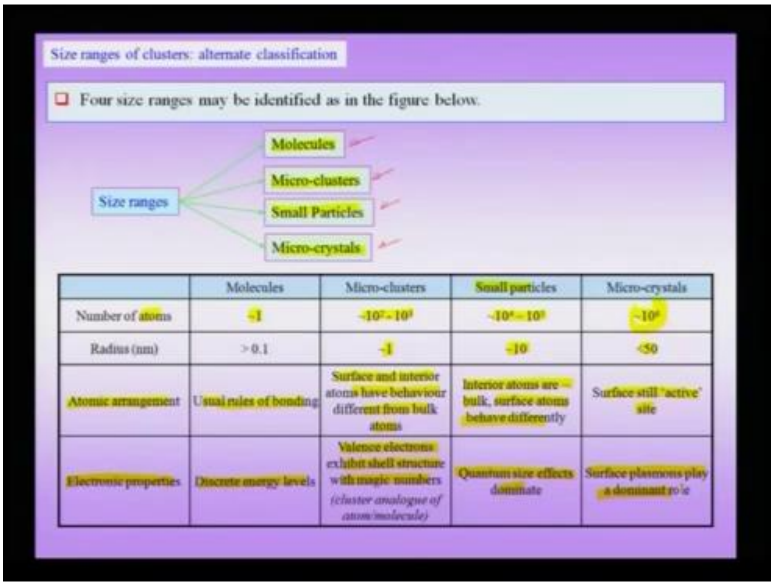

Size ranges of clusters: alternate classification

- Four size ranges may be identified as in the figure below.

Size ranges
- Molecules
- Micro-clusters
- Small Particles
- Micro-crystals

	Molecules	Micro-clusters	Small particles	Micro-crystals
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Atomic arrangement	Usual rules of bonding	Surface and interior atoms have behaviour different from bulk atoms	Interior atoms are ~ bulk, surface atoms behave differently	Surface still 'active' site
Electronic properties	Discrete energy levels	Valence electrons exhibit shell structure with magic numbers *(cluster analogue of atom/molecule)*	Quantum size effects dominate	Surface plasmons play a dominant role

So, with respect to crystal structure with respect to properties with respect defect structure within the material, we might note that the nano particles and nano crystals and nano clusters could be very very different from their bulk counter parts. This is something which is very very important for us to note. We had stated initially when we consider their classification of nano clusters visa or small clusters visa vi, large cluster visa vi nano particles or nano crystals. That they are alternate classifications used in literature.

We had even noted when we try to make the assembly called a cluster that we may not start with an atom. You could actually start with an ion or you could even start with a molecule and therefore, it is for us good to revise another classification which are typically found on literature. One of them is shown here, wherein a slightly different terminology as compared to what we have just considered is introduced.

In some sense the micro crystal which is mentioned here is very very similar to our nano crystal in some sense, but the size regimes could be overlapping with these, but may not be identical with what we are classifying here. So, we could be starting with molecules and here we are talking about individual molecules, like c o 2 it could be o 2 et cetera. The n we go to the regime known as the micro clusters regime. Then we have the small particle regime and you might notice that the micro cluster regime is similar to, what you might a small cluster regime.

The small particle regime can again be somewhat coincidence with the large cluster regime and micro crystals as you can see a much larger wherein you have about 10 power 6 number of entities. So, we said atoms here, but we should again note once again that it constituent entities need not be atoms, they could be ion or molecules. So, for molecules it is about 1, for micro crystals it is about 10 power 2 to 10 power 3 entities.

For small particles it is about 10 power 4 to 10 power 5 and larger than 10 power 6 can be thought as micro crystals the radius in nanometers for micro clusters about 1 nanometer or it could be sub 1 nanometer. Small particles are about 10 nanometers and micro crystals are larger than 50 nanometers. When I am talking about bonding characteristics or the atomic arrangement molecules of course, you have their usual rule of bonding.

In other words they could be covalently bonded or the bonding could be polar covalent etcetera. In micro crystal micro clusters the surface and interior atoms have behavior very different from bulk atoms. Now, I am comparing the surface atoms sitting in a micro cluster. The interior atom in a micro cluster with what you might call a bulk atom in a bulk crystal. I am talking about a bulk crystal I am considering something having more than about 10 power 6 may be 10 power 8 10 power 10 kind of an atom.

So, even larger number of atoms so here we surface is different from the surface which we can think of a bulk material. The interior atoms are also going to be different compared to that what we see in the case of a bulk crystal or a bulk particle. In small particle regime their interior atoms is similar to bulk. That means they are already grown so large, that their overall, what you might call environment and configuration is somewhat similar to the bulk interior atom, but definitely not identical.

The surface atom still behave very differently because still suppose I am considering a small particle still I cannot ignore the curvature effects. So, not during these course of these lectures we will see that how surface effects can alter the equilibrium between a matrix and a small particle. This is the origin of what you might call the Gibb's Thomson effect, but essentially the surface atoms still are very very different from the surface atoms in a bulk crystal.

Wherein of course, curvature effects can be ignored. In micro crystal surface is still an active site, but this can be approximated to the surface of a bulk crystal. When I am talking about the electronic properties for instance and of course, I can on in the list of properties which I am going to consider, but for just now, I am going to just talk about this in as an example electronic properties the energy levels are discrete.

Of course, for a molecule may know how a molecules and energy levels are there are similar to an atomic energy level. In the case of micro clusters the valence electrons exhibit shell structure with magic number. So, we will return to this concept very soon wherein I am talking about certain magic numbers and certain kind of a stable electronic configuration, but ever the less here too I do not expect any kind of a continuous band formation.

Still the energy levels are discrete. In small particles till quantum size effects are going to dominate and in the microcrystal level, you would expect that, you can now talk about more like continuous bands which you talk for a bulk crystal. Therefore, you could talk about conduction properties for instance which is very similar to that of a bulk crystals, but here too you would expect the surface plasmon’s are playing a dominant role. Similarly, other surface effects coming from electrons on the surface is expected to play a dominate role in determining the properties of the material.