# Nanostructures and Nanomaterials: Characterization and Properties
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## Lecture - 13
## Surface Effects and Physical Properties
## Surface Effects and Physical Properties of Nanomaterials (C2)

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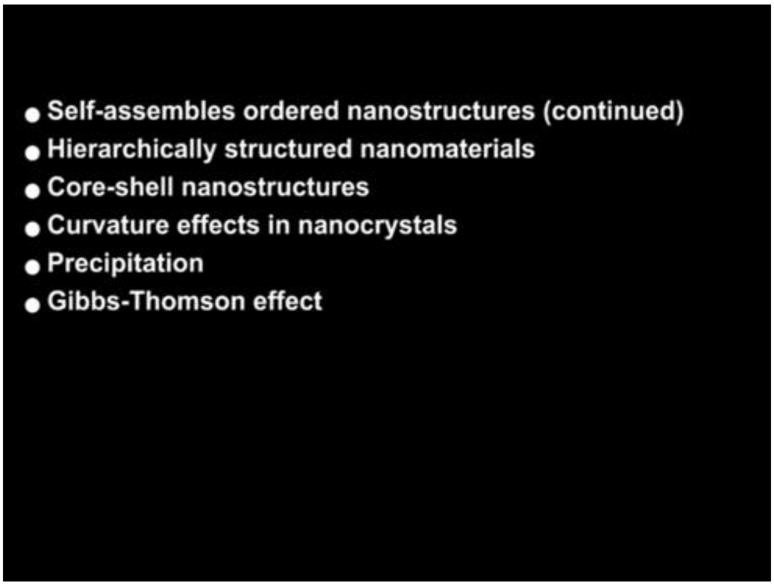

- Self-assembles ordered nanostructures (continued)
- Hierarchically structured nanomaterials
- Core-shell nanostructures
- Curvature effects in nanocrystals
- Precipitation
- Gibbs-Thomson effect

Lets us continue with the discussion of self assembled ordered nanostructures with assembling particles with multiple sizes of phases.

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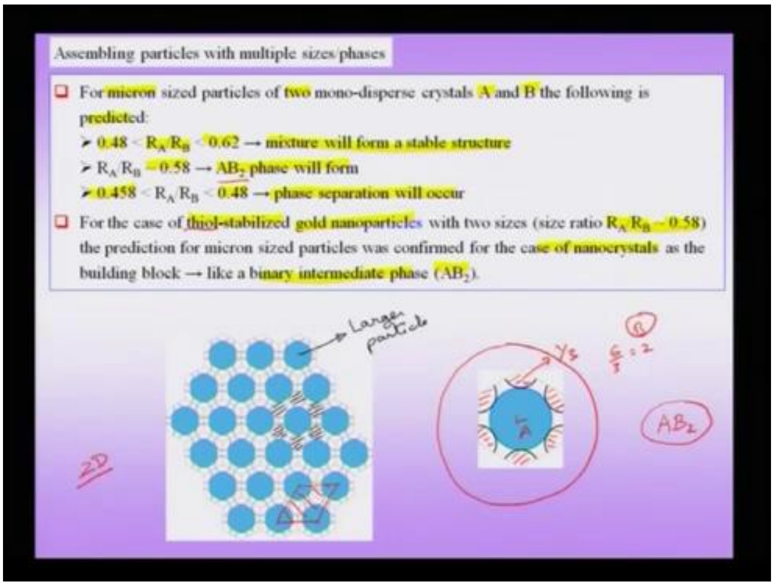

Assembling particles with multiple sizes/phases

- For micron sized particles of two mono-disperse crystals A and B the following is predicted:
  - $0.48 < R_A/R_B < 0.62$ → mixture will form a stable structure
  - $R_A/R_B \sim 0.58$ → $AB_2$ phase will form
  - $0.458 < R_A/R_B < 0.48$ → phase separation will occur
- For the case of thiol-stabilized gold nanoparticles with two sizes (size ratio $R_A/R_B \sim 0.58$) the prediction for micron sized particles was confirmed for the case of nanocrystals as the building block → like a binary intermediate phase ($AB_2$).

It has been shown that for micron size particles 2 size spheres, which are labeled A and B. The following was predicted it was seen that for a size ratio between R A by R B in the range of 0.48 to 0.62, the mixture will form a stable structure. Out of this, if the size is particularly close to 0.58, then you will form an A B 2 phase, and we are noting here that these sizes we are talking about is in the range of microns and not yet in the nano scale. And it was also predicted that if the size range is between 0.458 and 0.48 then or the size ratio range is in between 0.458 and 0.48 phase separation will occur.

So, it is important to test that, if can we form binary mixtures of the type AB 2 with spheres in the nanoscale? For that people have tried gold particles, which have been thiol stabilized and soon we will see why we need to stabilize these molecules thiol. And if the size ratio was taken to be close to 0.58, then the prediction which was seen for micron size particles was confirm for the case of nano crystals as well. That is even for the nano crystals if the size ratio is close to 0.58.

Then, we can actually form a stable AB 2 kind of an phase, which can be thought of as an binary intermediated phase. The arrangement of the two particles in this phase is as shown in the figure below. The larger particle is the one which is shown in the blue color, so this is the larger particle. And now these particles are in the nano scale regime, and this smaller particle is the one which is shown with this sphere here, and I will shade these smaller particles as follows.

So, surrounding each one of those larger particles, you have 6 smaller particles, and surrounding each one of the smaller particles you actually have 3 larger particles. Therefore, I can actually draw an unit cell for this structure, which is now a 2 dimensional crystal with a stoichiometry AB 2, this is my unit cell. But to calculate this stoichiometry to be AB 2 it is better that I consider a hexagonal kind of a cell, which is shown on the right hand side here. Here you have the larger particle, and these are parts of this smaller particle 6 of which are surrounding the larger particle.

And now I can calculate this stoichiometry because now one-third of each of the particles is contributing to this call. There are 6 of them, so that makes it two of those for each, that means two of B for each one of the A particles, which is the larger particles, thus giving the stoichiometry AB 2. And of course, in this schematic diagram the thiol molecules have not been shown, but it is essential that if I am using gold nano particles, then it should be stabilized with thiol otherwise these particles may center. And therefore, I will not get A structure which is described as in the schematic below. So, this is now a 2 dimensional crystal with the unit cell as shown here, which is now in the nano scale regime. Now, the question arises, we have micron says size crystals which can form with stoichiometry AB 2.

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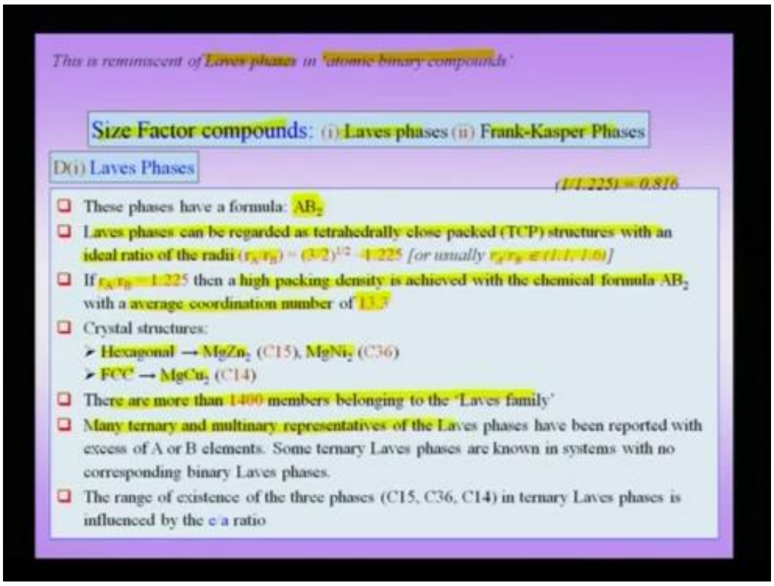

*This is reminiscent of Laves phases in 'atomic binary compounds'*

Size Factor compounds: (i) Laves phases (ii) Frank-Kasper Phases

D(i) Laves Phases

*$(1/1.225) = 0.816$*

- These phases have a formula: $AB_2$
- Laves phases can be regarded as tetrahedrally close packed (TCP) structures with an ideal ratio of the radii $(r_A/r_B) = (3/2)^{1/2} = 1.225$ *[or usually $r_A/r_B \in (1.1, 1.6)$]*
- If $r_A/r_B = 1.225$ then a high packing density is achieved with the chemical formula $AB_2$ with a average coordination number of 13.3
- Crystal structures:
  - Hexagonal → $MgZn_2$ (C15), $MgNi_2$ (C36)
  - FCC → $MgCu_2$ (C14)
- There are more than 1400 members belonging to the 'Laves family'
- Many ternary and multinary representatives of the Laves phases have been reported with excess of A or B elements. Some ternary Laves phases are known in systems with no corresponding binary Laves phases.
- The range of existence of the three phases (C15, C36, C14) in ternary Laves phases is influenced by the e/a ratio

There are nanoscale crystals which can form with this stoichiometry AB 2, but are the analogs of this in the normal atomic crystals and obviously there are. And the normal atomic crystals are called they laves phases, which are atomic binary compounds. And if you look at the largest scheme of size factor compounds, there are 2 kinds of size factor compounds one is the laves phases, another is the frank Kasper phases. And if you look at the laves phases, they form with this stoichiometry AB 2, which is this stoichiometry we are, we are talking about.

In the case of micron sized or the nano sized particles forming the prostates, but here the clear at difference is that these A and B are atoms in the case of the laves phases. And there are well known examples of such kind of laves phases like MgZn 2 and MgNi 2, both of which have hexagonal crystal structure or belong to the hexagonal lattice. MgCu 2 which is a cubic close or has a FCC lattice that is underline lattice.

And therefore, we also have analogs of these kinds of AB 2 binary compounds, which are basically size factor compounds, that means size is the determining factor for the formation of these compounds. Unlike for instance, some of the humerothery compounds where in e by a ratio stabilizes the compounds. These laves phases are regarded as tetrahedrally close packed structures with an ideal radius ratio R A by R B turning out to be root of 3 by 2 which is 1.225.

Obviously this 1.225 the inverse of which is 0.186 is clearly a different number compared to the 0.58 which we have seen for the case of the larger phase spheres which form an AB 2 stiochiometry whatever the less these are stabilized for this size ratios close to 1.225 and typically they form not just at 1.225, but for a radius ratio in the range of about 1.1 to 1 6. And if the R A by R B is 1.225, then a high packing density is achieved with the chemical formulae A by 2 with an average coordination number which is 13.3.

Of course, you might say that the maximum coordination possible in the case for instance FCC or HCP H is 12, but that is for a mono disperse sizes, but mono disperse that means you have particles of the same sizes spheres of the same size, but when you consider two sizes, then you can have an higher coordination number which can be 13.3 in the case of the R A by R B being about 1.225.

There are about more than 1400 members belonging to this laves family that means, it is very abundant and well known kind of a structure which is, can be thought of as an analog of the nano crystal which we just saw which forms an AB 2 kind of phase. Of course, these phases are 3 dimensional crystals, these laves phases. Unlike the 2 dimensional crystal which was shown to be forming with an AB 2 in the size ratio giving 0.58.

So, this is the important difference and many of the ternary and multinary representatives of the laves is also been reported with excess of A or B elements, some ternary laves phase are known in systems with no corresponding binary laves phases. So, there are some important members in the ternary class as well when it comes to laves phases. Therefore, to summarize this part, when I take nano crystals of two sizes, and then I can form a stable structure, I may even see phase separation or you may form a very well defined ordered structure with two which might call as a super lattice structure with an AB 2 standard stoichiometry. This AB 2 kind of stoichiometry can be observed when R A by R B is in the range about 0.58.

Now, we have considered a few types of these self assemble structures, for instance we talked about the nano crystalline solid, we also talked about. And this was one example of nano crystallined solid, where silver nano crystal was used to form a crystal using the FCC lattice.

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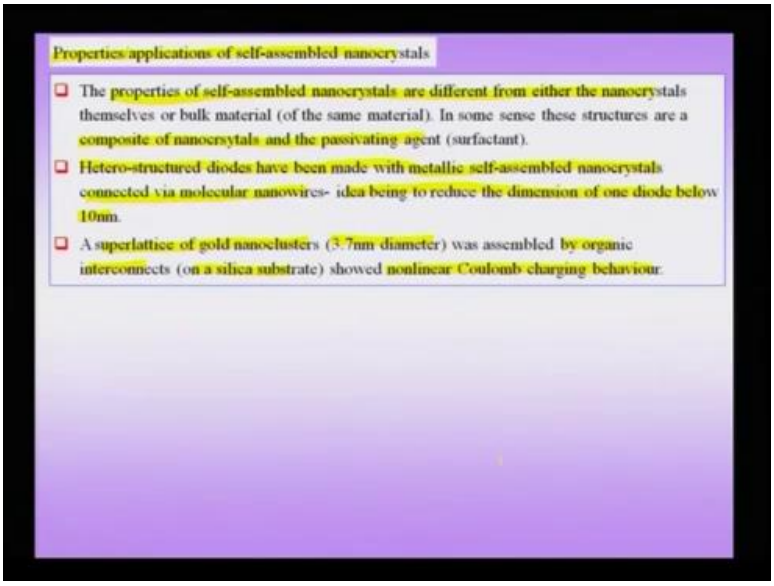

Properties/applications of self-assembled nanocrystals

- The properties of self-assembled nanocrystals are different from either the nanocrystals themselves or bulk material (of the same material). In some sense these structures are a composite of nanocrsytals and the passivating agent (surfactant).
- Hetero-structured diodes have been made with metallic self-assembled nanocrystals connected via molecular nanowires- idea being to reduce the dimension of one diode below 10nm.
- A superlattice of gold nanoclusters (3.7nm diameter) was assembled by organic interconnects (on a silica substrate) showed nonlinear Coulomb charging behaviour.

And now we have seen a binary nano crystal or nano crystalline solid. But many properties and application have also been envisage for these self assembled nano crystals. The properties of self assembled nano crystals are different for either the nano, either the nano crystals or the bulk material. In some sense because we are now making these nano crystals with some passivating agent in many cases, as we saw in the case of gold we have to use a passivating agent.

And therefore, the property is some kind of an outcome of the, as a composite of the nano crystal and the passivating agent. So, it is not amerely a property of the nano particle which is going on to form the crystal it is not merely a property of their passivating molecule. But in some kind of an average or some kind of an additional property which can come because of this kind of a composite.

For instance some application have been envisage for these kind of self assembled nano structures, like hetero structured diodes have been made with metallic self assembled nano crystals connected by a molecular nanowires. The idea here being to reduce a dimension at diode below about 10 nanometers. So, this is one of the important application which has been envisaged for metallic self assembled nanocrystal connected by a nanowires. Super lattice of gold nanocyrstals about 3.7 nanometer in diameter was assembled by organic interconnects on the silica substrate, and this showed non-linear coulomb charging behavior.

We will be talking about more about this coulomb charging behavior and coulomb blockade later on when we talk about electrical properties of nano materials. But this is one of the interesting applications wherein we have a gold nano clusters, which have been assembled by a organic interconnects and which shows some kind of a non-linear coulomb charging behavior. Like we have ordered crystals, we can also have ordered pores and these pores can exist in multiple length scales.

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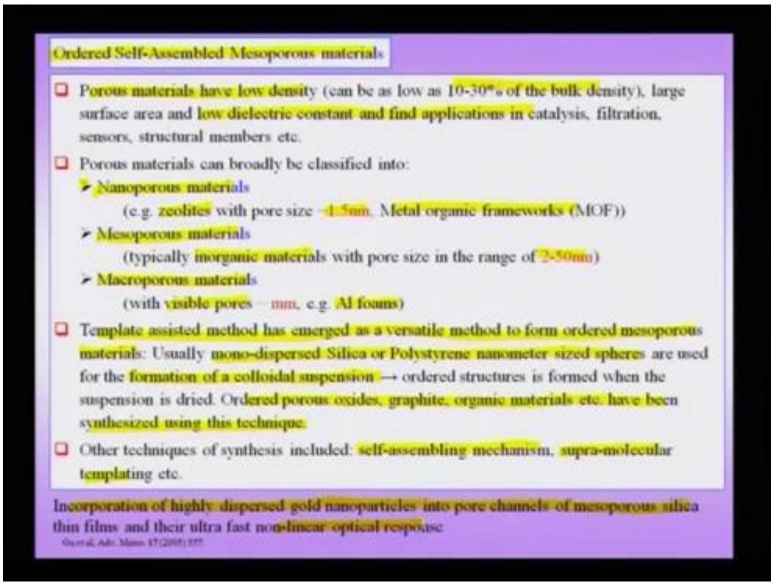

Ordered Self-Assembled Mesoporous materials

- Porous materials have low density (can be as low as 10-30% of the bulk density), large surface area and low dielectric constant and find applications in catalysis, filtration, sensors, structural members etc.
- Porous materials can broadly be classified into:
  - Nanoporous materials
    (e.g. zeolites with pore size ~1.5nm, Metal organic frameworks (MOF))
  - Mesoporous materials
    (typically inorganic materials with pore size in the range of 2-50nm)
  - Macroporous materials
    (with visible pores ~ mm, e.g. Al foams)
- Template assisted method has emerged as a versatile method to form ordered mesoporous materials: Usually mono-dispersed Silica or Polystyrene nanometer sized spheres are used for the formation of a colloidal suspension → ordered structures is formed when the suspension is dried. Ordered porous oxides, graphite, organic materials etc. have been synthesized using this technique.
- Other techniques of synthesis included: self-assembling mechanism, supra-molecular templating etc.

Incorporation of highly dispersed gold nanoparticles into pore channels of mesoporous silica thin films and their ultra fast non-linear optical response

They can be in fact macroscopic which are visible to the naked eye, they can be mesoporous in which we are talking about the pore size in the range of about 25 nanometers. And we can have nanoporous materials where they pore size is extremely small. So, we can, in other words we are now going to describe ordered self assembled mesoporous materials.

And though we using the word mesoporous we are going to take a picture at the largest picture wherein we are also going to briefly talk about these other kind of porous material like the nanoporous and the macro porous materials. Porous materials have A low density because now we do not have a homogeneous monolithic material, but we have porous part of the structure. And therefore, there is could be a reduction in the density and the density of the porous material could be about 10 to 30 percent smaller than the bulk density.

Such materials obviously have large surface area or some of which is in internal of course, and some of which is external. And therefore, this surface area, and low electric, low dielectric constants gives a lot of applications specially in catalysis, filtration, sensors, structural members, etcetera. When you are talking about structural members for instance, this lower density also implies that now we can either be a constable weight saving. And there are could be other structural members, which are taking the maximum load and this structural member for instance can be used for space filling.

Additionally if you look at these porous materials, you can fill the pores with the secondary material, which can form an integrated component in the functional of the whole component. For instance now I can fill the pores if they are small enough with some kind of a grease material. Now, this secondary material would function additionally to the main material in giving some kind of a lubrication while in service.

Now, as we said these porous materials can exists in 3 length scales, the nanoporous materials and nice examples of these zeolites and metal organic frame works and here the pore itself can be consider part of the crystal structure. That is why the pore size is extremely small it is of the order of 1.5 nanometers.

So, these are pores within in some sense the crystal structure itself. In mesoporous materials, which are typicalyl inorganic in nature, the pore size is much larger, and these have to be specially made using some artificial methods like we shall see like tinplating methods. Macro porous materials like we just we said given example, which are the pores are visible to the naked eye, and one example would be aluminium foam are also finding wide spread application nowadays. And we shall not discuss these macro porous materials in detail here.

Now, how do we, how can I make these mesoporous materials? A template assisted method has emerged the most versatile and common method to form ordered mesoporous materials, and here typically we take mono dispersed silica or polystyrene nano diameter sized spheres. And typically this means that we are using a single size sphere. And we form a colloidal suspension ordered structure are formed when actually the suspension is dried.

Therefore, I take a mono dispersed silicon or polystyrene that means, fix size spheres and in a colloidal suspension I allow the suspension, the particles to order when actually dry the substance. And using this method ordered porous oxides, graphite, organic materials, etcetera have been synthesized. There are other techniques also which have been used by people to assemble or self assemble mesoporous material, and these include supra molecular templating and self assembling can some etcetera.

Now, as I was mentioning that, you may leave the porous material as a pore and use it like for instance in filtration or catalysis, where you have a lot of surface area, internal surface area especially, which can be used advantageously in mechanism like catalysis wherein you really need lot of surface area. But additionally as I pointed out that you can actually fill these pores with the another material, and this material could actually be an active component in the properties.

And one example which I am just randomly taking from literature is, in which people are in cooperate in a high dispersed gold nano particles into the pore channels of mesoporous silica thin films, and they are studied the optical response behavior which is formed to be non-linear. Therefore, now when I make a mesoporous solid or even a nanoporous solid, I need not work just with the porous material, which I could do of course I can directly use it of direct application, but I can use it as a medium for actually putting in a second member.

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Eight units surround the pore in the metal-organic framework called MOF-5. Each unit contains four $ZnO_4$ tetrahedra and is connected to its neighboring unit by a dicarboxylic acid group.

One nice example is in the case of the metal organic frame work, wherein actually one nice example of metal organic frame work is the what is call the MOF 5, wherein you have, for instance I will just drawn a schematic of this MOF 5 on the board.

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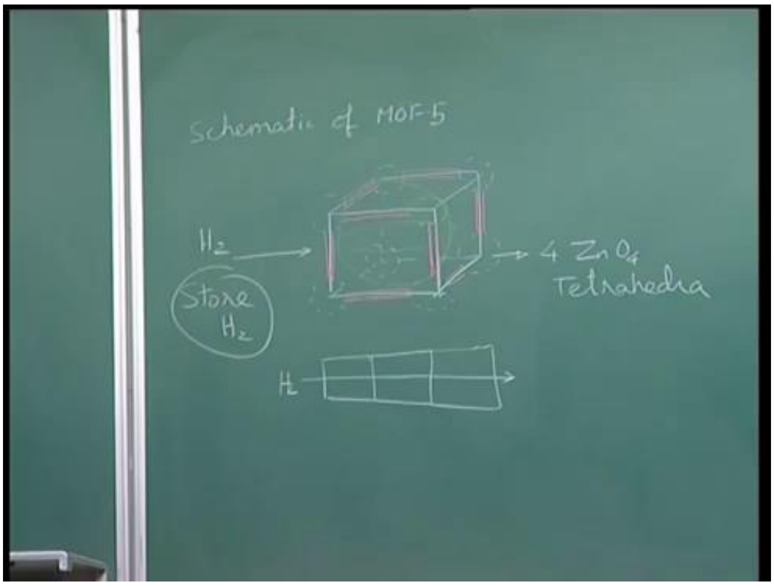

So, you have these ZnO 4 tetrahedral, and each one of these ZnO 4 tetrahedral which is of course, there are four of them in each one of these corners as schematically shown in by dotted lines. And each one of these is connected to the neighboring four tetrahedral by dicarboxylic acid group, which is schematically shown by these double red lines, these double red lines.

And now this structure implies that these sort of dense regions of matter are separated from each other by this dicarboxy acid group, and there is lot of volume within the unit cell. And in fact you can schematically sometime draw this volume to be a sphere which is a large sphere which exist inside this units cell. So, this is a large volume which resides in the unit cell. And this volume can actually be used not, to not only transport molecules small molecules like hydrogen, but also store hydrogen.

These interaction of hydrogen with this MOF 5 is more like a precipitate option that means, there is no strong covalent or other kind of bonding. This implies that if I really have to store, put hydrogen and store hydrogen, then I have to work at low temperatures, wherein the hydrogen does not de absorb because of entropic effects. Therefore, because of these free pores, and you can visualize that these free pores are connected to each other. That means now I have unit cells which are beside each other and there is this interconnectivity of these pores.

And therefore, hydrogen can be transported across these unit cells by at any phase center, phase centers. And in the end of course, this volume inside this unit cell itself can be used to actually store hydrogen precipitate and be at slightly lower temperature, so that now the precipitate option forces are not broken by thermal effects. So we can clearly see that these mesoporous materials they, as you, as synthesized condition itself they offer certain benefits, wherein you have a high surface to volume ratio which can be used for ketolysis, or these pores can actually be used for filtration.

That means now certain only certain molecules will be allowed through the pores depending on the pores size, and another molecules will be kept out because of this filtration process. But additionally you can actually use this as an active medium, like we saw it the case of MOF 5 for storage of hydrogen.

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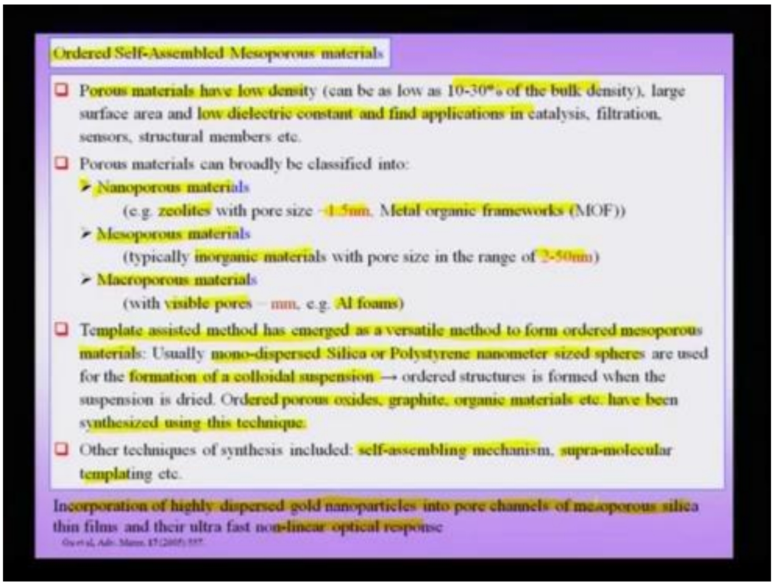

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Gu et al, Adv. Mater. 17(2005) 557

And even if you are, and we definitely saw another felt that suppose if I put in additional particles like the case of the gold nano particles in the channels of mesoporous silica, then I can have important effects like non-linear optical response. So, ordered self assemble mesoporous materials, which includes, now I am talking about nanoporous materials additionally, definitely are finding very important applications and their important class of materials in their own right.

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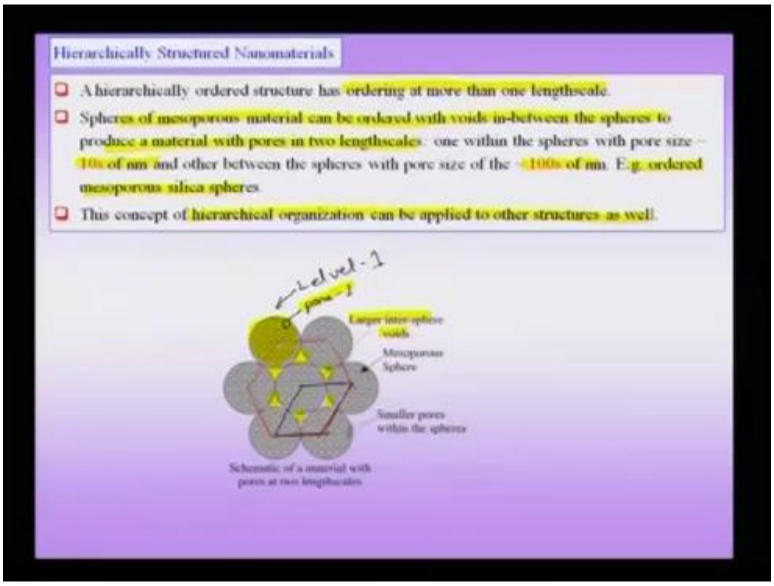

Hierarchically Structured Nanomaterials

- A hierarchically ordered structure has ordering at more than one lengthscale.
- Spheres of mesoporous material can be ordered with voids in-between the spheres to produce a material with pores in two lengthscales: one within the spheres with pore size ~10s of nm and other between the spheres with pore size of the ~100s of nm. E.g. ordered mesoporous silica spheres.
- This concept of hierarchical organization can be applied to other structures as well.

Schematic of a material with pores at two lengthscales

Additionally we can have hierarchically structured nano materials. In an early example we had seen that, how when used, when you see the structure of lotus leaf, it is hierarchically ordered, and this hierarchical construction can actually give rise to the important property which is super hydrophobicity. We had also seen certain kind of hierarchical constructions, like in the abnoncial which gives it extreme impact toughness.

So, hierarchical structures are abound in nature, and these hierarchical structures, we had even schematically drawn earlier that, how we can actually make a hierarchical structure. Now, in the present case, and we had noted that this hierarchical ordered structure has ordering in more than one length scale. And this subunit which is formed at one level can actually be use to construct a higher level structure, which itself forms a subunit for a even a higher level structure.

Now similarly, similar concepts can be applied for the case of porous materials, wherein spheres of mesoporous material can be ordered with voids between the spheres to produce a materials with pores in 2 length scales. That means let me now think of this as porous at 2 length scales, let us see one of these spheres which is drawn below here. So, in this sphere you can clearly see that, there are ordered pores and these pores are small pores.

Now, I can take each one of these particles and arrange them in, for instance this example shown here in the form of an hexagonal unit, and as we know in this hexagonal unit actually your unit cell will be this rhombus. Now, when I do this 2 order assembly in a first level 1 being the particle itself, and level 2 being these assemble, assembly into this hexagonal kind of array. Then, I see that there are pores here, so I can call this pore 1, which is at the smaller length scale, but additionally you also form these larger voids between the particles.

Therefore, you can clearly see this an example of a case where there are 2 length scales of pores, one length scale of the order of 10s of nanometers, which would, which would be the smaller pore, which is shown here, and between the pores which could be hundreds of nanometers. Therefore, and sub structures have formed, examples of this would be the mesoporous silica spheres. And this concept of hierarchical organization can actually applied to others structures as well.

This to summarize here, we can, we have already seen that how we can use hierarchical construction to make materials, wherein you take a subunit this subunit forms a part of a larger unit, and that unit itself forms a part of a, becomes a subunit for a even larger length scale construction.

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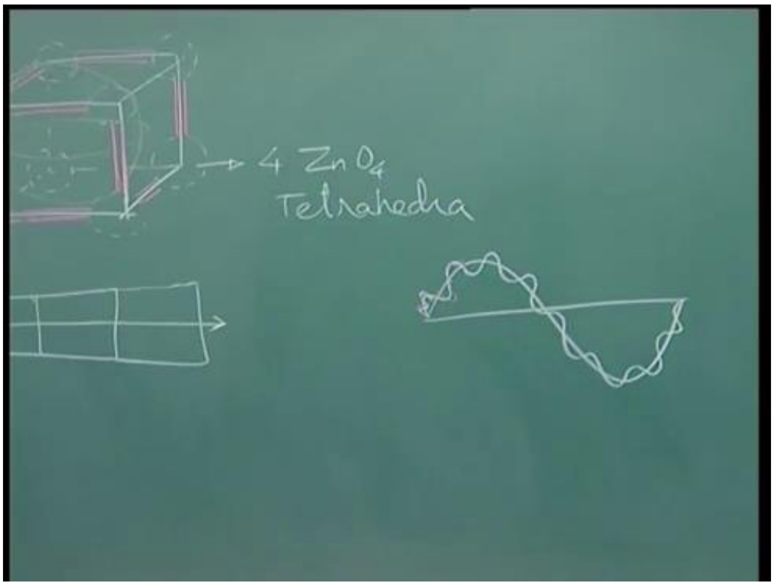

And even we had even considered a very nice schematic example at its stage, wherein we can think of, for instance… Suppose I have an ordering at this length scale, which is shown by say for instance a sine way, then I can have a smaller length scale associated or which is over layered on top of this.

And finally, you could also visualized even smaller length scale on top of this, so let me draw that it in red color, so you could have for instance this smaller length scale on top of this. So, these are for instance can be thought of as roughness at one length scale, the second length scale, and of course, they could be higher and higher length scales. Therefore, this can be thought of is hierarchical construction, and in this case this could be for a for example, be a example of surface roughness.

Similarly, we said that they can be hierarchical structure of materials not only a surfaces, but also materials and finally, here we see that there can be hierarchical construction of pores in materials, wherein I can in cooperate more than one length scale of pores. Of course, finally intended for some of an application which would make this construction useful.

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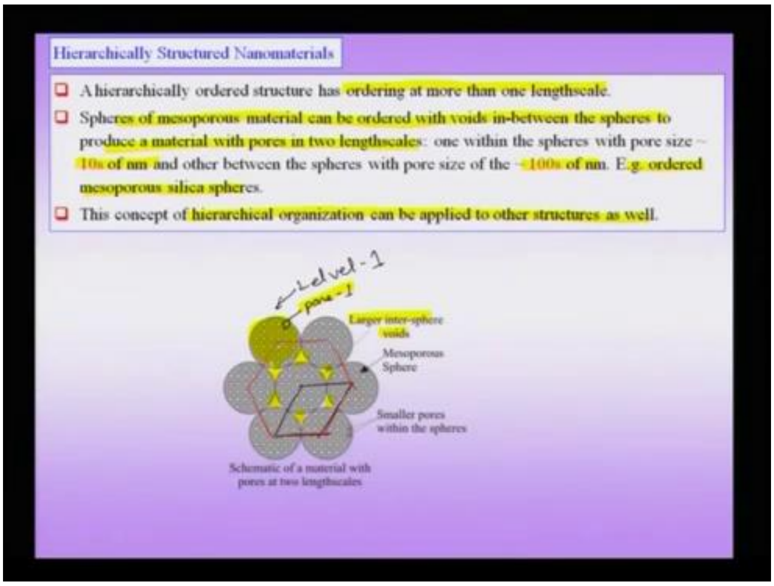

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- This concept of hierarchical organization can be applied to other structures as well.

Schematic of a material with pores at two lengthscales

So, in this particular example, we saw here, we are actually using silica nano spheres which have pores, and these pores reside within silica and nano spheres with themselves are ordered to give pores at two length scales, the smaller pores and the larger pores. Therefore, this is a nice example, where we have, we can not only have, we have an example of hierarchically structured porous materials. The next class of materials we take up briefly here, and we will describe some important properties of these materials later is the example of what you might call the core shell nano structures.

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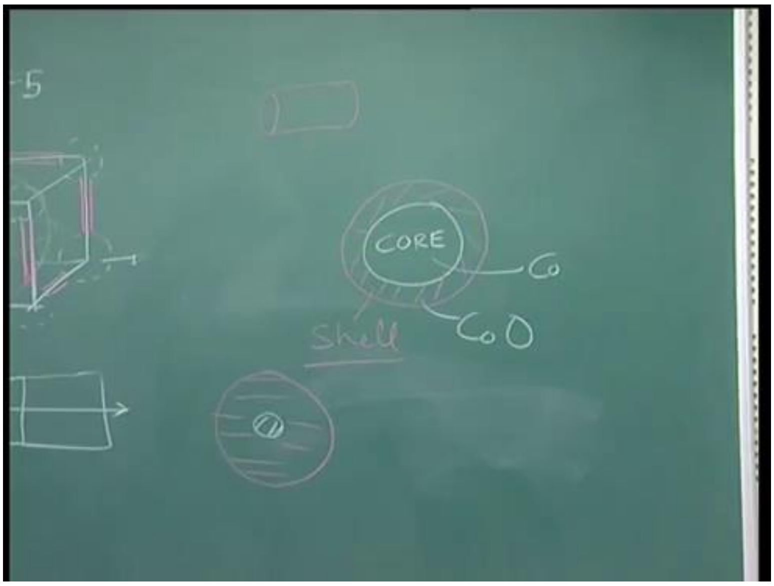

A typical core shell nano structure consists of a material which is inside this, which I call the core and around this I have a layer which I call the shell. One typical example would be where this for instance could be cobalt particle and this could be a cobalt oxide. That means it is a natural oxide which forms on top of the core, which we expect if you leave a cobalt particle outside in air.

It is not necessary of course, that this shell need be very thin, you can actually visualize cases where you can have thin cores and large shells around these cores, this also possible. And it is also not necessary that these cores need to be spherical, you can actually visualize cylindrical cores also, another shapes of course, around which you can have actually a shell which would typically follow the contour of the particle shape.

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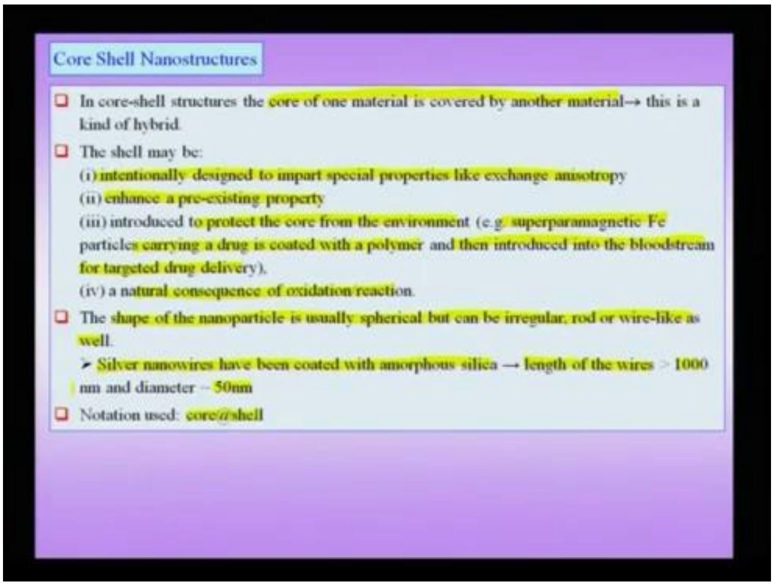

Core Shell Nanostructures

- ❑ In core-shell structures the core of one material is covered by another material→ this is a kind of hybrid.
- ❑ The shell may be:
  (i) intentionally designed to impart special properties like exchange anisotropy
  (ii) enhance a pre-existing property
  (iii) introduced to protect the core from the environment (e.g. superparamagnetic Fe particles carrying a drug is coated with a polymer and then introduced into the bloodstream for targeted drug delivery).
  (iv) a natural consequence of oxidation/reaction.
- ❑ The shape of the nanoparticle is usually spherical but can be irregular, rod or wire-like as well.
  - ➢ Silver nanowires have been coated with amorphous silica → length of the wires $>$ 1000 nm and diameter $\sim$ 50nm
- ❑ Notation used: core@shell

In core shell structures, the core of one material is covered with a shell of another material, and this can be thought of as an hybrid. Therefore, this is now like a composite that the nanoscale, wherein or a hybrid in nanoscale, wherein there are two materials involve. The shell of course, may be intentionally designed to impact special properties, like exchange anisotropy.

This exchange anisotropy is an important magnetic property, which we will deal in detail when we talk about magnetic properties of nano particles and nano crystals. But essentially we want to say that it has intentionally mean designed. It can enhance a pre-existing property, for instance it may not impart special new properties to the particle, but may actually perform the role of enhancing a pre-existing property. It may be introduced to protect the core form the environment, like suppose you are talking about super paramagnetic iron particles, which are used for drug delivery. It is typically coated with a polymer and then introduce in the blood stream, so that it actually has bio compatibility with the blood.

So, iron particles if, where iron particles are introduced, they will be reactive and they could be actually not have the bio compactable, and not only that the system actually remove these particles from before the drug delivery is done. And therefore, this shell actually performs an important role in the intended application which is targeted drug delivery, in which case it protects it from the environment which happens to be either blood of a person if you are talking about targeted drug delivery.

This could actually arise from an unintentional process, like it could be a natural consequence of oxidization or reaction, as we saw in the case of cobalt oxide over cobalt if you leave the cobalt particle outside. But nevertheless once this combination of the, shell over the core has been achieved. Typically it is intended for a certain purpose though it is unintentionally appearing.

But typically we expect that certain additional beneficial properties are coming from this core shell structure, which makes it useful to actually synthesize this core shell kind of a structure. Even in the case of thiol nano, gold nano particles, we had seen that we actually coated with thiol particles, so that we passivate the gold surface, so that we avoid centering at room temperature even. And the thiol particle can be thought of a, as a shell around the gold core, but we will see more examples of these kind of core shell particles, wherein intentionally the shell has been designed to, as we saw just now, to impart certain special properties.

The shape of the nano particle is usually spherical, but can be irregular rod like, wire like, or any other shape which is important in a certain application. Silver, one example of an alternate geometry rather than this sphere, is the silver nano wires have been coated with amorphous silica, and these nano wires have a more than 1000 nano meters in length, and have a diameter of about 50 nanometers.

So, that means, they are nano wires with an aspect ratio of about 20, and these have a shell of amorphous silica over silver, which is a silver conducting material. Typically the convention or the notation used to describe these core shell particles is written as core at shell, though I might actually prefer the opposite notation, which is shell at core because shell actually resides on the core. But typically in literature, you note the notation that people use the notation that, it is core at shell. That means the shell is the one which is, the one which is outside, which is shown in the notation here.

Just to summarize this slide, we have seen that there are hierarchical constructions possible, there are hybrids possible, and there is one special class of hybrids which is call the core shell nano structures, where in the core of one material is covered with a shell of another material, when I say other material, which we noted that it could actually be just the oxide of the same material itself.

And we have noted that, there are four reasons why we may actually have a shell around a core, one could for instance we saw the least of the trivial is that, it is a natural consequence of oxidational reaction when you leave the nano particles outside. But more usually, it is intentionally designed to import special properties, like for instance we said it could have actually something like an exchange anisotropy in magnetic particles.

You could actually enhance a pre-existing property and we will take up examples of florescence etcetera, when we want to actually enhance a preexisting property. That means the shell itself, core itself has this property, but by putting a shell around it, this property is enhanced. And we more often than not, actually introduce the shell to protect the core from the environment. And one nice example of this we saw was, wherein we are using the nano particle, like an iron super paramagnetic iron which is use for targeted drug delivery.

And in this case what happens, why we need super paramagnetic iron is because the magnetic field is actually use for transporting the particles to near the region where the affected region, or the region which is been damaged, and we want to transport the drug to that region. And therefore, we are using super paramagnetic iron. And we will of course, later on see what is super paramagnetic iron, why how this is super paramagnetic property come in iron? This we will see later, but nevertheless we want to passivate this molecule and typical a polymer is used to protect this iron nanoparticles from the blood stream.

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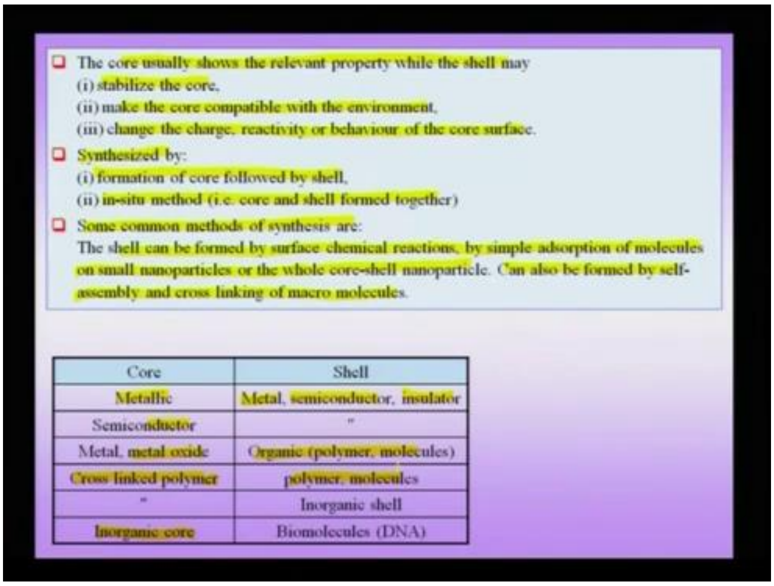

- ☐ The core usually shows the relevant property while the shell may
  (i) stabilize the core,
  (ii) make the core compatible with the environment,
  (iii) change the charge, reactivity or behaviour of the core surface.
- ☐ Synthesized by:
  (i) formation of core followed by shell,
  (ii) in-situ method (i.e. core and shell formed together)
- ☐ Some common methods of synthesis are:
  The shell can be formed by surface chemical reactions, by simple adsorption of molecules on small nanoparticles or the whole core-shell nanoparticle. Can also be formed by self-assembly and cross linking of macro molecules.

| Core | Shell |
|---|---|
| Metallic | Metal, semiconductor, insulator |
| Semiconductor | " |
| Metal, metal oxide | Organic (polymer, molecules) |
| Cross linked polymer | polymer, molecules |
| " | Inorganic shell |
| Inorganic core | Biomolecules (DNA) |

So, the core usually shows the relevant property, while the shell may actually stabilize the core as we had seen before, make the core compatible with the environment or change the charge reactivity or behavior of the core surface. So, there are important functions that, the shell performs and that is why this core shell composite actually gives some beneficial effects. And the synthesis of typically of these core shell nanostructures is done either by formational core for followed by the shell means, you first synthesis the core, then you have a shell synthesize around it, or you can actually use an in situ method where in the core and shell actually are manufactured or formed together.

Some common methods of synthesis we are listing here without actually going into the detail, the shell can be a formed by a surface chemical reaction by simple absorption of molecules, or small nano particles, or the whole core shell nanoparticle. They can also be formed by self assembly and cross linking of macro molecules. That mean there is method, we can use more than one method actually to put a core around the, shell around the core.

And this could be a simple reaction, adsorption of molecules, or they can be a some kind of cross linking or assembly process, wherein you put the shell around the core. Here there are listed below some examples of shells around cores, and typically the core is a, can be a metallic, a semiconducting core, it can be metal oxide, it can be a cross linked polymer, or even an inorganic core. And the shell would consist of, for instance could be a different metal or nonmetal, it could be a semiconductor on a metal or it could be a insulator on a metal.

Similarly, on a semiconducting core, you could actually put a metal semiconductor or an insulator, and on a metal or a metal oxide you could actually put a organic which is could be a polymer or a serious of molecules around it. And if you have a polymeric core, then you could actually put, which is typically done is you use to typically polymeric molecules around the polymeric cores. Typically there are fewer examples of metallic or semiconducting shells around polymeric cores. And you can actually put bio molecules around like this for DNA around inorganic cores.

So, there are wide variety of choices when it comes to the core and shell that means, I have now a process by which totally I am modifying. Thus my particle and the modification either of this leads to stability or actually make the core more compatible with an environmental, or actually modify something on the surface of the core. Such that I can no tailer my properties of the core. And additionally we saw, could, we actually introduce newer properties which did not existantly core. And now since have a gamet of possibilities, of not only the core kind of core particle that I can choose, but also the shell particle.

Therefore, there lot of interesting properties an exploration which are going on wherein, the explore wide variety of cores and shells to impart very special properties. We will take up some examples of these core shell and the properties which arising them, and we especially talk about for this optical properties and magnetic properties. Next we take up the important topic of curvature effects in nano materials. Now when you talking about a bulk material, we typically assume that a bulk material is in infinite.

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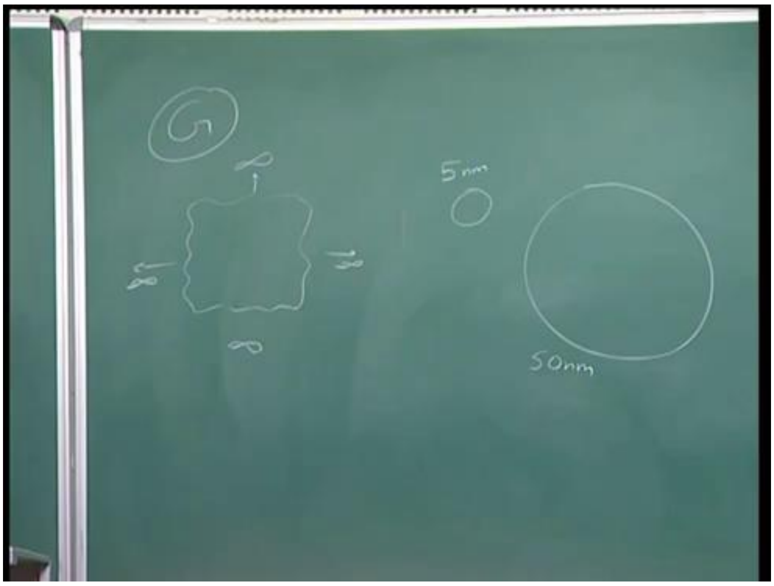

In another words, I can schematically draw a bulk material like having no boundaries, and this is infinite in all directions. And typically when I use for instance a property like Gibbs free energy G, then I am talking about a Gibbs free energy of an infinite material wherein, there is no geometry, there is no description of any kind of a shape in the property. But it is obvious, then I am talking about nano particles and nano materials, then there is a certain geometry, like just now talked about spherical nano particles.

Now, we can have a spherical nano particle of small size, we can have a spherical nano particle of a larger size. It is obvious that the property is which are related to surface are going to be different for these two kinds of nano particles. From this group we can find nano particle and this could be for instance, some much larger particle like a 50 nanometer particle. Unlike a bulk material which we describe with The parameter like G whenever I am talking about a real material in which case I have to deal with the concept of the surface.

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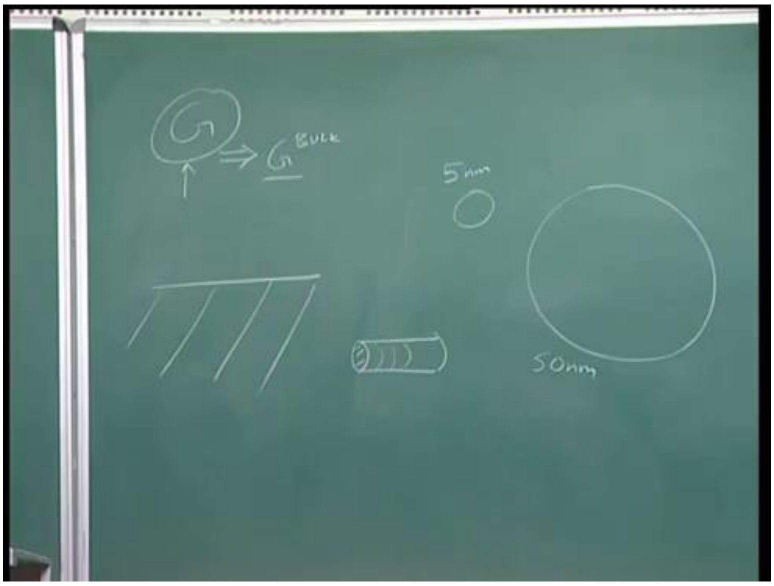

That means I have something which is the termination for the bulk. And typically if you want to consider, what you might call a semi infinite space then you can have a flat inter phase between the material and the air or vacuum. Unlike this kind of a flat inter phase it is clear that, these particles actually have a curved inter phase. And now suppose I am talking about a cylindrical particle, then you can clearly see that you have one phase which is curve the cylindrical style, while the other surface is flat.

So, it is in some sense a combination of a semi infinite bulk material and spherical nano particle. Now, in these kinds of materials it is obvious that the surface effects are going to come into play and therefore, I cannot use a value like G which is typically meant to say that it is G bulk. Important effects and properties come into play when I am actually using a nano material, nano particle because of the surface or inter phase effects.

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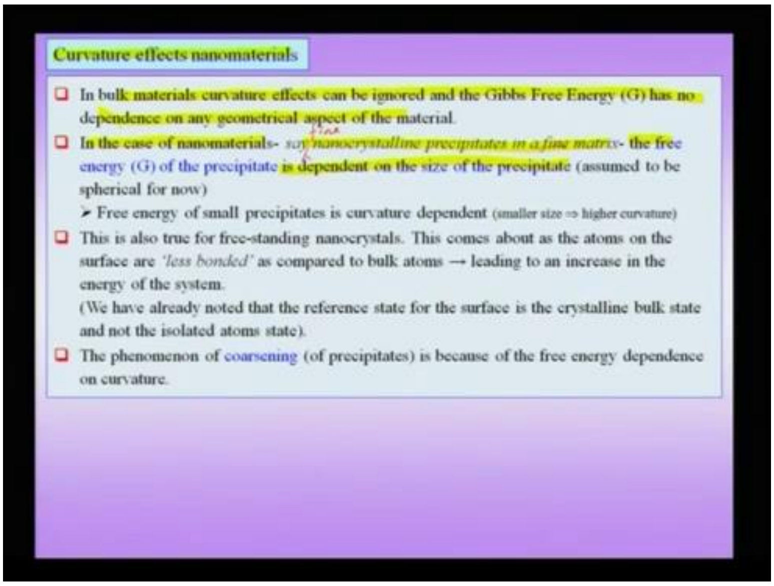

**Curvature effects nanomaterials**

- In bulk materials curvature effects can be ignored and the Gibbs Free Energy (G) has no dependence on any geometrical aspect of the material.
- In the case of nanomaterials- *say* fine *nanocrystalline precipitates in a fine matrix*- the free energy (G) of the precipitate is dependent on the size of the precipitate (assumed to be spherical for now)
  - ➢ Free energy of small precipitates is curvature dependent (smaller size ⇒ higher curvature)
- This is also true for free-standing nanocrystals. This comes about as the atoms on the surface are *'less bonded'* as compared to bulk atoms → leading to an increase in the energy of the system.
  (We have already noted that the reference state for the surface is the crystalline bulk state and not the isolated atoms state).
- The phenomenon of coarsening (of precipitates) is because of the free energy dependence on curvature.

Therefore, in bulk materials curvature effects can be ignored, and the Gibbs free energy has no dependence on any geometrical aspect of the material. So, we are talking about a bulk material, I really do not concern any geometry, or a surface, or an inter phase, and I just assume that there is a single parameter G which describes my Gibbs free energy. In the case of nano materials, and typically I am here talking about nano particles, or nano crystalline materials where, the green size in the scale of nano.

Then, we are actually dealing with certain inter phases, like it could be a green boundary or a free surface. And for example, now I will talk about a particular example, which will we use to exemplify the importance of curvature and nano materials is that, in the case of nano crystalline precipitates or in a matrix. Actually I am talking about fine nano crystalline precipitates in a matrix, and so this requires a little correction.

So, this is fine nanocrystalline precipitates in a matrix. The free energy or the precipitate is now not a single number, but is dependent on the size of the precipitate and the, and now for instance, I am assuming that the precipitate is spherical. Though actually we will see in real systems the precipitate could be disc shape, it could be an oblate spheroid, it could be even be a prolate spheroid.

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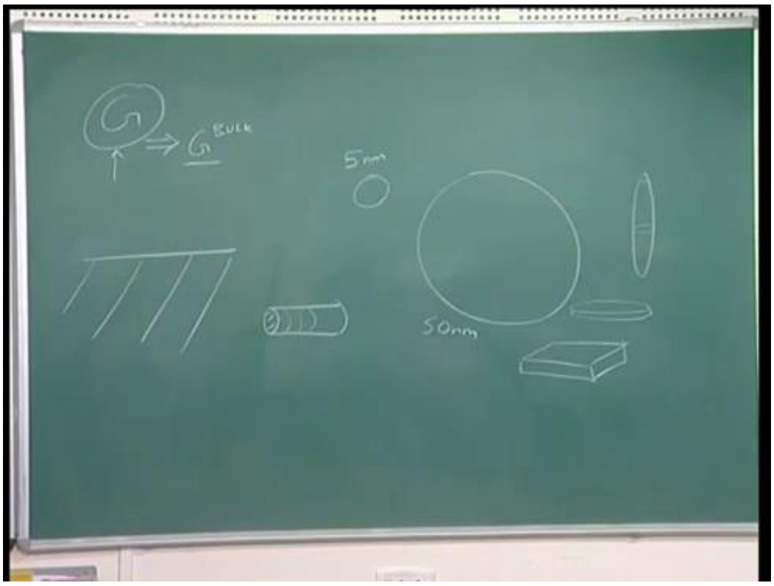

In other words, suppose I need not, the precipitate need not be of this kind of a shape, it can be a squashed, it can be a long prolate spheroid. That means, it is like a spheroid like this, which has a circular cross section, but it is elongated which is, which sometimes is called a needle shaped. It could typically be the form of even of a disc or it could be in the shape form of a plate.

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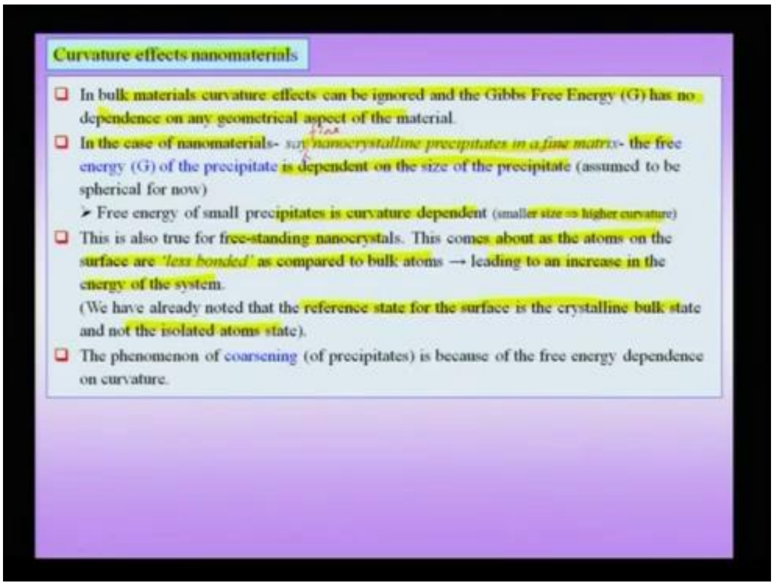

**Curvature effects nanomaterials**

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  (We have already noted that the reference state for the surface is the crystalline bulk state and not the isolated atoms state).
- The phenomenon of coarsening (of precipitates) is because of the free energy dependence on curvature.

So, there are various geometries of this precipitates possible, but for now I will assume that the precipitate is spherical and this free energy of this precipitate is now going to be curvature dependent. In other words, if I am talking about a spherical particle, I am assuming that it is size dependent. Therefore, Gibbs free energy is not a constant number now anymore and it is depend on the size, and smaller the size of the spherical precipitate higher is going to be my curvature. And as we shall see soon that therefore, the energy of the system is going to be higher.

Now, this is what we consider for precipitate is also going to be true for free standing nanocrystals, and the reason is not difficult to understand, why this free energy of this nanoparticles has to a nanocrystals has to be a higher than that of the bulk material? This is because the atoms on the surface are less bonded as compared to the bulk atoms, this leads to an increase in the energy of the system.

Now, of course, that I am talking about an increased energy or lowering of energy, we have to, we have already noted that before that, the reference state for the surface is the crystalline state and not the isolated atoms state. So, I am saying it is higher energy, I am assuming that I am comparing my free energy of this particle with the free energy of a bulk crystalline solid and not with the unbonded state wherein, the atoms are far apart.

Now, why should curvature actually determine your bondedness? We will have drawn schematic to understand this, so let us take a flat surface like this, we ((Refer Time: 38:40)) highly curved surface, like for instance the particle drawn here.

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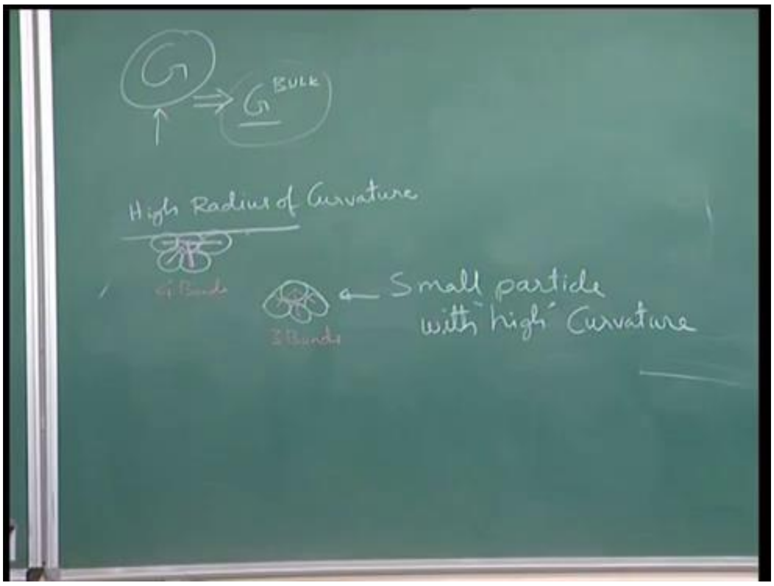

So, in a flat surface for instance the atom sitting on the surface might have neighbors like this, so each one of them is going to be bonded say 1, 2, 3, 4. So, there are four bonded atoms around this. Now, suppose I consider a highly curved surface, in which case I have particle like this, then I can see that or an a atom on the surface me actually be bonded only to three atoms.

So, this is of code of crewed schematic, which I am drawing for you to for illustrate the point, but if had a flat surface, which is like more like a low curvature system, then I would typically find that my bonding is better and is four bonds we can see here meanwhile in this case there are three bonds. That means, that there is one bond lower here, and that means that this crystals in this is a higher state of energy with the respect to the system which is having a lower curvature or high radius of curvature.

So, this can be thought of as a system with high radius of curvature, and this is a small particle. And high curvature automatically implies that it is called a small radius of curvature. Now, having this kind of an effect that means, a curvature effect has important consequences on the properties of materials, and one of these properties we will take up in a little more detail now, which is the phenomenon of coarsening for instance of precipitates.

Now, this, there are two important aspects when you are talking about coarsening, one is the reduction in the overall energy which is the global effect, and additionally there are also bother about some very local effect, which is coming from the curvature. And both these effects we will try to understand and how this Gibbs free energy is going to determine, what you might call the solubility of a solute and the equilibrium concentration around the particle.

So, just to summarize this slide, curvature plays a very important role in a nano materials, a nano crystals, a nano particles. Unlike the case of the bulk materials where, I can describe the system by a quantity which is a Gibbs free energy, which is not geometry or size dependent. When you come to smaller and smaller particles because of this effect of actually unsatisfied bonds, or a there is an excess energy up and above the bulk energy.

And therefore, these particles are in some sense more unstable as compared to the bulk material, and they are, and we have already seen consequences that, they are very reactive. And we will take a one specific example of these kinds of curvature effects in a phenomenon known as coarsening of precipitates. Now, when does coarsening take place? Of course, of first things of an, as an example now I will take the aluminium copper system, or aluminium 4 percent copper system which is shown here.

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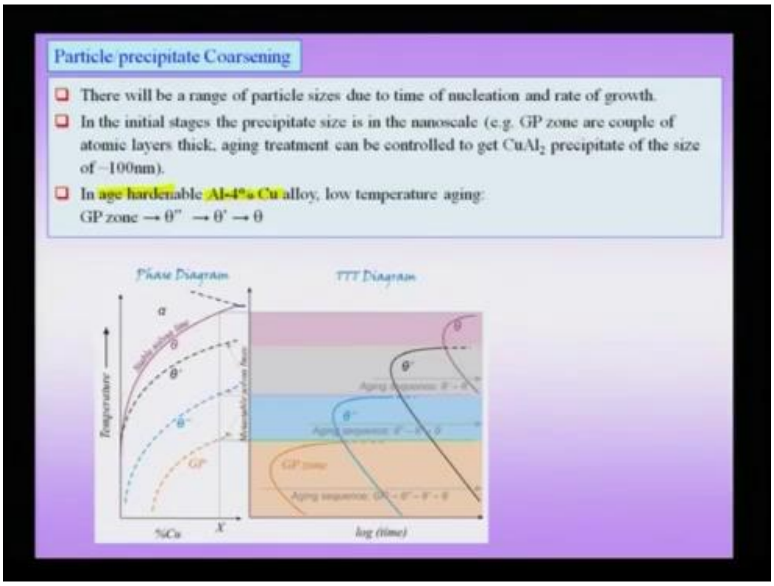

Particle precipitate Coarsening

- There will be a range of particle sizes due to time of nucleation and rate of growth.
- In the initial stages the precipitate size is in the nanoscale (e.g. GP zone are couple of atomic layers thick, aging treatment can be controlled to get $CuAl_2$ precipitate of the size of ~100nm).
- In age hardenable Al-4% Cu alloy, low temperature aging:
  GP zone → θ" → θ' → θ

And this is a typical system known for what is called an age hardening system. And in this age hardening system we follow four steps to actually give rise to a fine dispersion of precipitates. And this fine dispersion of precipitates could be actually in a nano scale.

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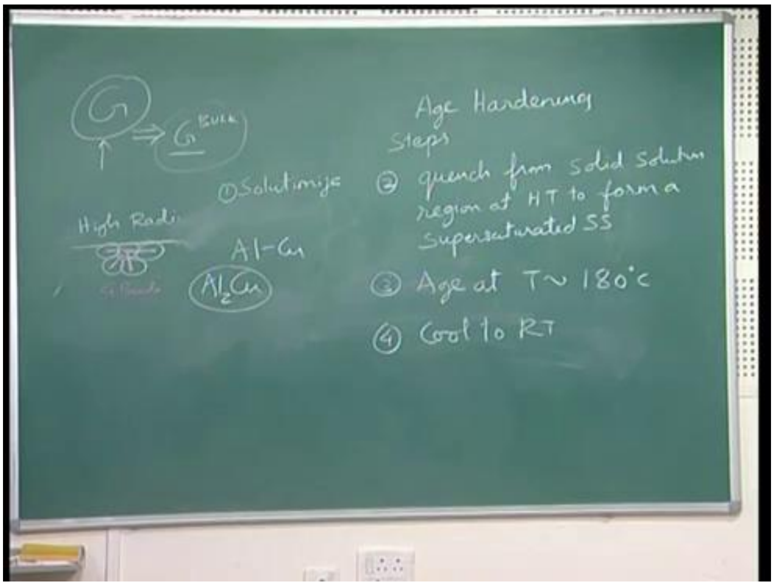

Age Hardening
Steps
① Solutionize
② quench from solid solution region at HT to form a supersaturated SS
③ Age at T ~ 180°C
④ Cool to RT

So, the four steps we follow are, and this is actually not the first step, if as solutionize at high temperature. It is for solutionize at high temperatures, followed by quenching from high temperatures, then we age then we cooled to room temperature. Now, when, actually take this alloy which already consist of stable precipitates, and stable precipitates in a aluminium copper system actually happens to be Al 2 Cu precipitate.

Now, we take it to high temperature, it should dissolve the precipitates, and we take it to the region in the phase diagram where you have a solid solution that means, uniform solids solution. Then, we quench from high temperature to room temperature to actually obtain a super saturated solid solution. That means now all the copper is in the solid solution form in the aluminium matrix. Then we actually heat it again to a higher temperature, which is about 180 degree celsius, even actually if the solution is left at room temperature over a period of long periods of time, this precipitates will tend to form.

And therefore, precipitation does takes place even at room temperature, but to accelerate the process we can actually heat it to high temperatures about degrees. And therefore, it will actually have a precipitation process, the choice of 180 degrees we will explain very soon why that is required. And finally, we cool to room temperature to obtain a fine dispersion of precipitates. As we shall later, this fine dispersion of precipitates actually required to strengthen this material, if you take an aluminium copper solid solution.

It is actually already stronger then the pure aluminium because of solid solution strengthening, but this strengthening alone is not enough because aluminium is a beautiful material because of it is corrosion resistants, it is light weight etcetera. And therefore, we would want to make lot of structural applications with aluminium. But because of it is lack of strength being an FCC crystal or a, what you might call a cubic close pack crystal, it is not very strong and we want to strengthen it.

And this age hardening process can actually increase the strength from about 100 MPA to about 400 or 500 MPA. And therefore, we want to have a fine dispersion of precipitates, which will now impede my dislocation motion which will give in, give me my strengthening effect. So, the important thing in the whole process is to get a fine dispersion of precipitates.

So, in the initial stages as we shall see that whatever was a super saturated solid solution will actually precipitate, and this precipitation process is not a state forward process that actually the equilibrium precipitate theta, which is a tetragonal phase is not directly obtain from the, because of the reason that if a theta precipitate comes out, then the activation barrier for such a process is higher. And therefore, a serious of meta stable precipitates are obtain.

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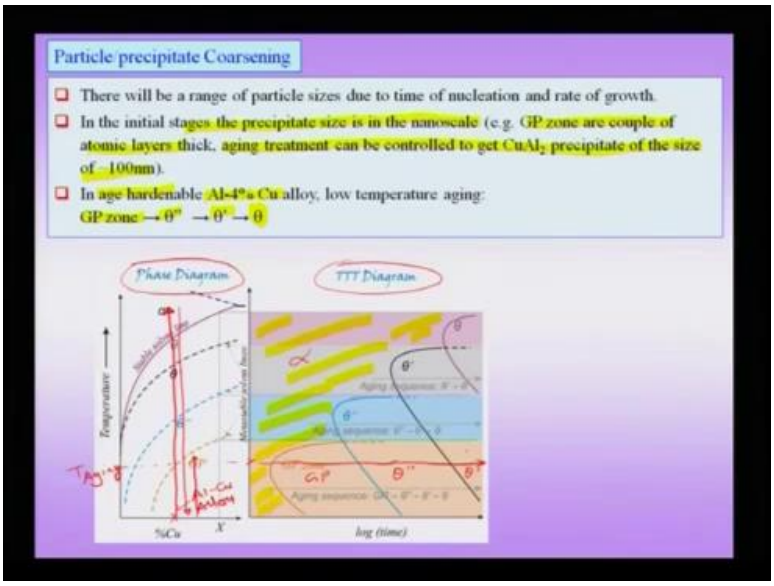

Particle/precipitate Coarsening

- ❑ There will be a range of particle sizes due to time of nucleation and rate of growth.
- ❑ In the initial stages the precipitate size is in the nanoscale (e.g. GP zone are couple of atomic layers thick, aging treatment can be controlled to get $CuAl_2$ precipitate of the size of ~100nm).
- ❑ In age hardenable Al-4% Cu alloy, low temperature aging: GP zone $\rightarrow \theta'' \rightarrow \theta' \rightarrow \theta$

And therefore, these series involves actually the precipitational of GP zone is first, followed by theta double prime precipitate which is a meta stable phase. The theta prime phase which is another meta stable phase, and finally the theta phase, which is a stable phase.

Now, which is actually found in the equilibrium phase diagram. Now, suppose I took, I did a slow cooling and did not use the process which I have described here, then what happens is that you will actually obtain very coarse theta precipitates, which will not be effective in the impeding the motion of dislocation, which means the strength obtain will be lower. But by now, by actually doing this process and getting a fine dispersion of precipitates, we can actually obtain a higher hardest, hardness.

In the initial stages, the precipitate size is in the nanoscale for instance, GP zones are couple of atomic layers thick, and aging can be control to get Cu Al 2 precipitates in the size of about 100 nanometers. That mean, these precipitates are already in the nano scale and they are, can be called, this whole system can be called in some sense and nano crystal and material. But remembering that, it is not the grain size we are talking about which is in the nano scale, it is actually the precipitate size which is in the nano scale.

Now, the region we actually heat to, to get this uniform solid solution is above the aluminium 4 percent copper alloy somewhere here, let me draw some schematically, so this is now my aluminium copper alloy. I heated to this alpha region which will give me an solid solution, then I quench it to room temperature as step 2 and then after quenching I actually age it at some temperature, which is in this region. This is my, and the reason for aging at low temperature is.

Now, if I age it low temperatures the left hand side is my phase diagram, and in the right hand side I have got my TTT diagram, which is the time temperature transformation diagram. And I have separate C curves for the transformation of this phase from the alpha phase, which is on the left hand side of this diagram to the various phases. So, this whole left region, now let me shade this left region, this is now my alpha phase field in this TTT diagram, and on the right hand side are various other phases.

And now suppose I age at low temperatures, now this temperature I am aging is, this temperature, then I can see that I can actually go through a sequence of precipitates which is now first the GP zone, then you got the theta double prime precipitate. The theta prime precipitate an if I wait long enough, I will actually get my equilibrium theta precipitate. But typically I do not wait that long and I actually try to control my precipitation process, so that I can have some of these coherent precipitates which has a fine scale a distributed in my matrix.

Now, using this kind of a process, I am actually trying to make a fine scale of precipitates, but what happens if I wait long enough, what happens? Initially of course, we have seen that you have a precipitation that means, that you are going to obtain nucleus of a phase and this nucleus will grow and I will show that schematically on the board.

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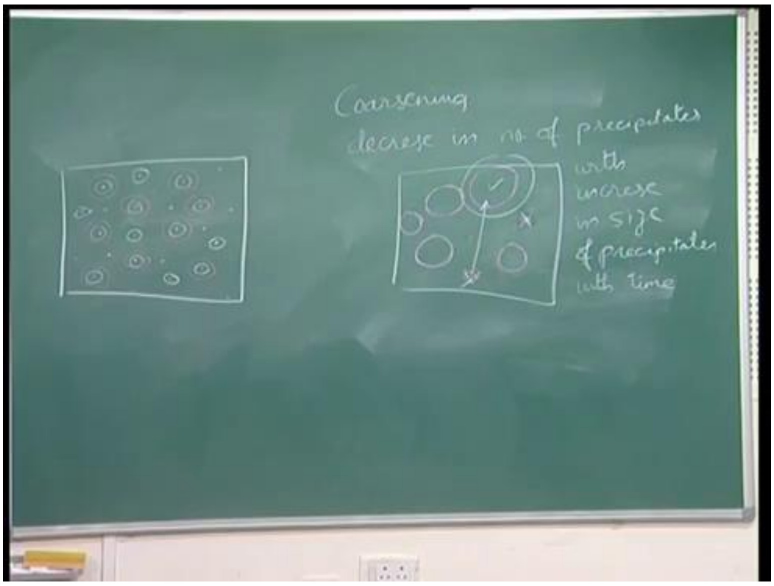

So, I initial precipitation, you have a uniform solid solution here. And initially at some point T, there will be some nucleus which will form. And typically the size of these nuclei itself is nano scale. Then at a later time you will notice that these would have grown to some size these nuclei, and at the same time new nuclei would have appeared at various other places. If I wait further longer, then I would notice that these would have grown to even larger size, while these nuclei which appeared later would have grown a little longer, and additionally there will be nuclei which would have appeared at a time which is T 3.

This process will continue till all the solute has come out in the form of the precipitate, but will the system freeze at stage? No, after all the precipitates have come out, now let me draw a schematic of that stage when all, almost all the solute is already in the form of precipitate. That means, now my system has come down to a equilibrium state, micro structure level equilibrium wherein, now I got precipitates in the system. And of course, the all these precipitates need not be of same size some could be smaller, some could be larger, and some could be of medium size.

Now, at this stage, the concentrations are such that the matrix is in approximately given by the phase diagram, and there are certain distributions of phases. This system does not freeze here. And reason the system does not freeze here goes back to two reasons, one is that because there is an inter phase between now my matrix and the precipitate, and this is now this inter phase is going to be an high energy region as we have just noted.

So, instead of having so many precipitates of these sizes, suppose I put larger and larger precipitates that means, my interphase area to volume ratio would actually decrease, and that means that by the system is will go downhill in energy. In other words, if I do not put small many precipitates, I put large precipitates few number then this system will actually go downhill in energy.

And this implies that the system wants to go from a higher energy state which is the state with many small particles or many small precipitates to a case where there are a few number of large precipitates. This is of course, the process known as coarsening. Now, the question arises, why would such a process or how would such a process take place? It obviously implies that if all the precipitates of course, increase in size, then there is no mass consideration right.

This implies that some of that smaller precipitates will have to vanish, decrease in size and vanish and the larger ones will have to grow right. But these particles are not actually touching each other, so mass transport from one particle to another say, this smaller particle to this larger particle will actually have to be mediated by the matrix. Why would such an mass transport actually take place is, what is important to understand in the word the global criteria is decrease in Gibbs free energy or decrease in energy.

And therefore, the we want to put fewer number of larger particles, which will actually lead to a reduction in energy that is obvious, but there has to be a local reason and this local reason is what is given by curvature effects. And that is what we will try to understand how curvature effects in this especially in this nano scale precipitates will actually give rise to effects of coarsening which is what we trying to consider now. During the aging process many things are actually parallely happening, and it is important to know what are those things which happen before we understand the phenomenon of coarsening.

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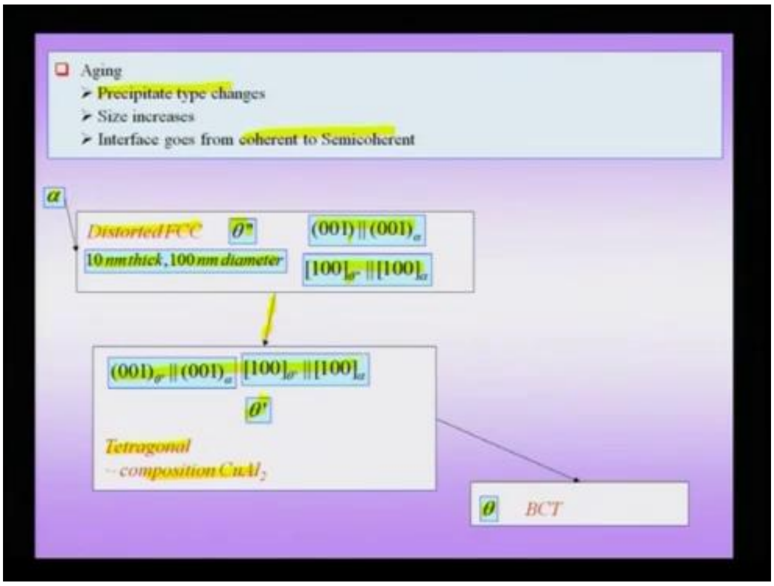

- Aging
  - Precipitate type changes
  - Size increases
  - Interface goes from coherent to Semicoherent

$\alpha$

Distorted FCC $\theta''$ $(001)\,\|\,(001)_\alpha$

$10\,nm$ thick, $100\,nm$ diameter $[100]_{\theta''}\,\|\,[100]_\alpha$

$(001)_{\theta'}\,\|\,(001)_\alpha$ $[100]_{\theta'}\,\|\,[100]_\alpha$

$\theta'$

Tetragonal

~ composition $CuAl_2$

$\theta$ BCT

The precipitate type itself changes that means, there is not a single type of precipitate which exist as we have seen. Then initially you have the GP zones, which goes to theta double prime which finally, goes to theta prime to theta, which is the equilibrium phase. The size of these precipitates will increase with time, suppose have the theta prime precipitate which will grow with time.

And then of course, finally, it as we saw it will transform to, the theta prime will transport theta double prime to theta, when you actually heat the C curve in the time transformation diagram. And additional thing which actually happens parallel, is their initially the interphase between the precipitate, like form since the theta double prime and the matrix tends to a coherent, and with time it becomes semi coherent.

And finally, certain phases may become main coherent and other may remain coherent and therefore, the interphase tendency is to go from coherency to semi coherency to in coherency as with time. The sequence of precipitates which we have seen is that, initially we have an uniform solid solution, on aging you get theta double prime phase which is a distorted FCC phase. And typically this is in the form of disc, which is about, or a plate which is about 10 nanometer thick and about 100 nano meter in diameter.

Though these are actually nano scale precipitates, and these precipitates form with the certain orientation relationship with the matric. And in this case of the alpha theta double prime, it happens to be the 0, 0, 1, plane in the theta double prime is parallel to the 0, 0, 1, plane of the matrix alpha. And the 1, 0, 0, direction in theta double prime phase is parallel to the 1, 0, 0, direction in the alpha matrix. If you wait further long enough while aging, then you will actually get a theta prime phase, which is a tetragonal phase with the composition approximately equal to Cu Al 2. And even this theta prime phase has as at orientation relationship with respect to the matrix.

And when this theta double prime phase forms, certain interphase are coherent while certain others are incoherent, semi coherent and tetragonal C is to go from there to incoherency as a precipitate size increases. Finally, of course, you form the body centered tetragonal phase is theta which is the equilibrium phase, which is found in the phase diagram.

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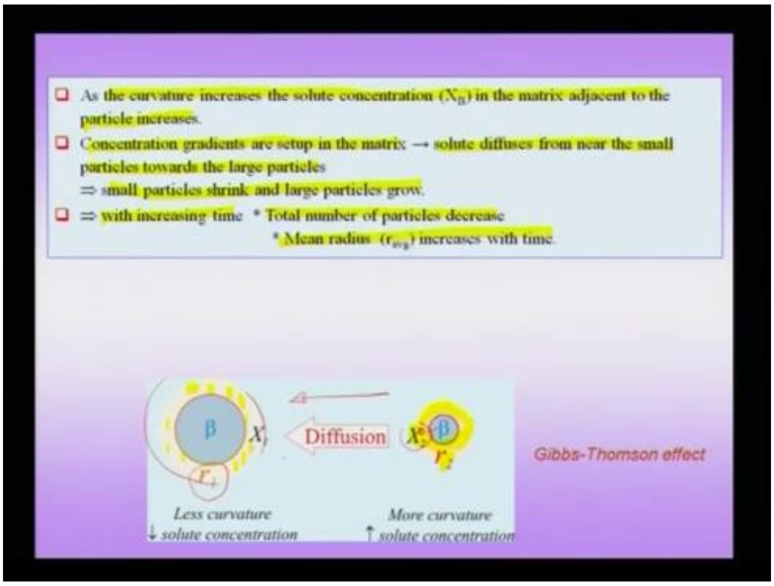

- As the curvature increases the solute concentration ($X_B$) in the matrix adjacent to the particle increases.
- Concentration gradients are setup in the matrix → solute diffuses from near the small particles towards the large particles
  ⇒ small particles shrink and large particles grow.
- ⇒ with increasing time * Total number of particles decrease
  * Mean radius ($r_{avg}$) increases with time.

Now, there we said that, we need to understand the local reason, why coarsening takes place? To understand this, let us assume that there is an uniform distribution of precipitates with an average concentration of solute, and the solute in this case happening to be copper, in the example of aluminium copper system which is present in the matrix. In the setting of this average composition, let me consider two precipitate particles or precipitate crystals, one, smaller one with the radius R 2 and a larger one with a radius R 1. And you to want to understand that how such a small precipitates, which is the beta phase can actually dissolve, and the larger precipitate which is R which is the radius R 1 can grow to a larger size.

And if this I understand this mechanism I can hypothise how as in a assembly of various sizes, how smaller precipitate will tend to manage, how larger precipitates will tend to increase in size, and therefore, overall reducing my inter phase area and therefore, reducing my energy of the system. Now, the composition of the solute, which is an equilibrium with the precipitate is now not independent number, but actually is a function of the curvature.

As the curvature increases the solute concentration in the matrix adjacent to the particle actually increases that means, if I have a smaller particle there, and the concentration of the solute is x 2, this is higher around the smaller particle as compared to particle x 1 where in the concentration is lower. This sets of concentration gradients in the matrix and that implies, the solid will diffuse from near the small particles towards the large particles.

So, I have a higher concentrational solid around this smaller particle, I have a lower concentration solute around this larger particle, and this implies that I am going to have a diffusion of solute from the smaller precipitate to larger precipitate. Now, if the, and of course, we have not at explain that how I am getting at this x 2 value and the x 1 value which will see in the next slide, but we trying to understand the overview first.

Now, if x 2 is depleted by diffusion because now the solid has left this part of the material and actually gone to this part the copper, which implies that now the value around the beta this R 2 particle is actually smaller. That means the particle is now going to dissolve, such that the equilibrium concentration of solid is obtain that mean, some of the copper will actually come out from the R 2 particle which implies that, the R 2 particle will tend to shrink.

Now, when the solute reaches the particle and reaches x 1 close to the R 1 particle, then this matrix around it is richer in the solute and it is rested actually can take that solute, and actually grow in size. Therefore, the larger particle will tend to grow. And on an average you will notice that, smaller particle shrink and larger particles grow, and this phenomena is known as coarsening.

And therefore, with increasing time at for in, for now we will hold at constant temperature, that total number of particles decrease, and the mean radius increases with time. So, this is what we have observe in the case of coarsening. So, the key link now which we need to understand why is that x 2 is larger than x 1.

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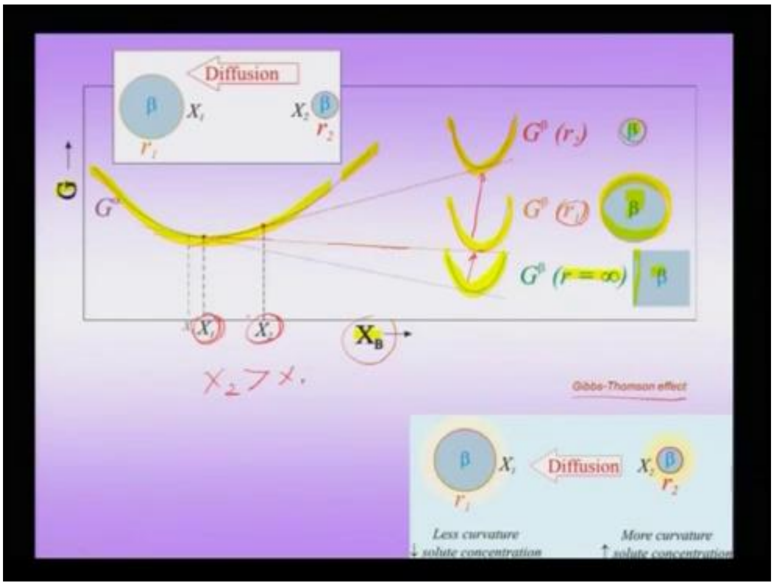

To understand that let us now plot Gibbs free energy composition plot. And now this Gibbs free energy composition part is a special kind of a plot wherein, now the Gibbs free energy for the precipitate is shown here, the beta phase on right hand side which is shown by these three curves, while there is only one curve for the alpha phase which is shown here.

In other words, these tell you now that the Gibbs free energy of the precipitate is not a constant number or a not a single curve, but is actually dependent on the curvature of the particle. And now suppose I assume a flat inter phase which means R is equal to infinity, then I have a lower Gibbs free energy. As I make the particle curvature increase the particle curvature, or in other word decrease the radius of curvature, then the Gibbs free energy actually tends to increase.

So, this goes up from the particle which is flat and finally, if you make the particle size even smaller, then you would notice that the Gibbs free energy further increases. And obviously the Gibbs free energy is a function of the concentration of the solute. So, you get these Gibbs free energy composition curves. Now, the Gibbs free energy of the entire system can actually or can be found by what is known as the common tangent construction.

Therefore, now I can draw common tangents with respect to, suppose I had a large precipitate like the beta phase. Then I can draw a common tangent, which is shown by this line here between this and this. And you would notice that the concentration of the solute which is x 1 for the radius R 1, which is an equilibrium with the precipitate of this size R 1 is x 1. That means if you have a R 1 size precipitate by that common tangent construction I would notice that the common tangent intersects my alpha curve here. And that implies the concentration of solute around this precipitate is x 1.

Now, suppose I have a smaller particle, then you would notice that it is a smaller particle with radius R 2. Now, if I make a common tangent construction for this smaller particle, then I would notice that the solute in equilibrium with this precipitate is x intersects at a point x 2, and you can clearly see that x 2 is larger than x 1. This is what we started off by saying in the previous case that, there is a larger concentration of solute around the smaller precipitate particle as compare to a larger precipitate particle.

Therefore, now I can clearly understand, why there is an enrichment of solute around the smaller particle, and this effect is actually called Gibbs Thomson effect, which is a result of the curvature effect on the Gibbs free energy. Just to summarize the slide we can clearly see that, now we do not have a single curve representing the Gibbs free energy of a precipitate.

There are multiple curves and these curves depends on the curvature of the particle or in another words the radius of curvature of the particle. As a curvature increases the radius of curvature decreases, then the Gibbs free energy increases, which implies that if have a common tangent construction with the alpha phase which is now going to give me the Gibbs free energy of the system. Then I see, I can notice that the solute which is in equilibrium with the larger particle, has lower a concentration around the larger particle as compared to the smaller particle, which is an as a higher concentration in equilibrium around it.

And this implies automatically that there is going to be a concentration gradient which is going to be setup. And therefore, there will be diffusion of solute from the smaller particle to the larger particle, which finally, of course results in the smaller particle reducing in size, the larger particle increasing in size. Finally, as a global picture, you would notice that the average particle size increases with time.