Nanostructures and Nanomaterials: Characterization and Properties

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Lecture - 9

Introduction to Nanomaterials (C1)

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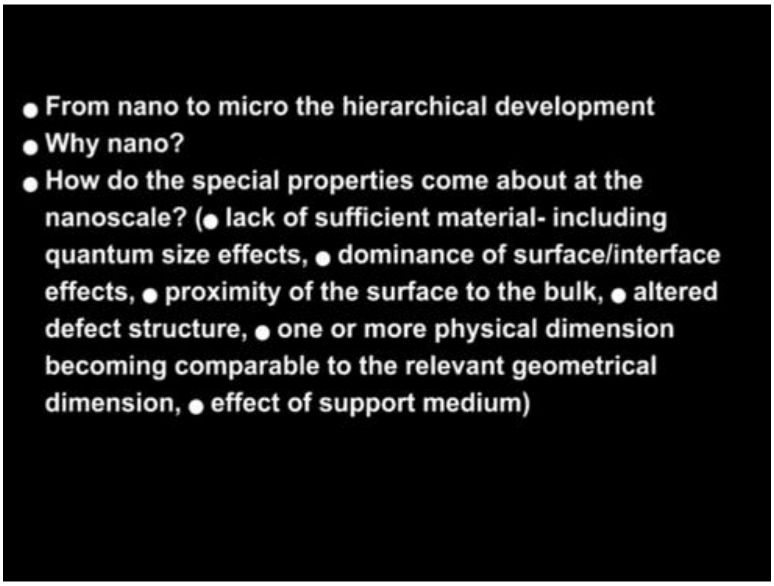

- From nano to micro the hierarchical development
- Why nano?
- How do the special properties come about at the nanoscale? (● lack of sufficient material- including quantum size effects, ● dominance of surface/interface effects, ● proximity of the surface to the bulk, ● altered defect structure, ● one or more physical dimension becoming comparable to the relevant geometrical dimension, ● effect of support medium)

We already travels across multiple lens scales, and we have seen that one has to perhaps see multiple order of lens scales before we understand how was certain property arises. How certain order has been defined with respect to the structure or even a property.

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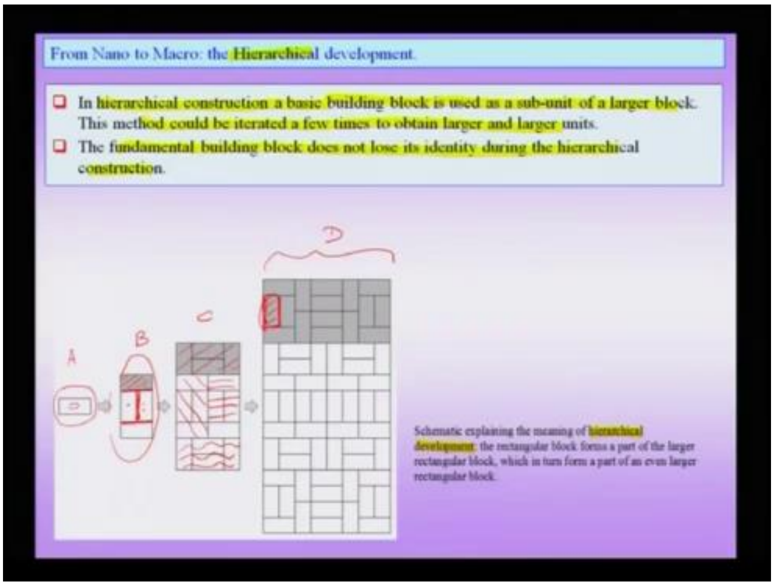

From Nano to Macro: the Hierarchical development.

- ☐ In hierarchical construction a basic building block is used as a sub-unit of a larger block. This method could be iterated a few times to obtain larger and larger units.
- ☐ The fundamental building block does not lose its identity during the hierarchical construction.

Schematic explaining the meaning of hierarchical development: the rectangular block forms a part of the larger rectangular block, which in turn form a part of an even larger rectangular block.

Now, we will take up us particular type of ordering or what we call in hierarchiral construction which is found in many materials. This hierarchiral construction actually gives rise to certain important properties in the context of nano materials. This hierarchiral construction typically stands with some building blocks which is actually in the nano scale, and therefore we have to start with the certain building blocks. We will take up to couple of schematic to a understand a how this hierarchiral development takes place before we go to specific examples where in such an architecture gives rise to some very important and very specific kind of properties.

This otherwise cannot be obtain by using monolithic material or even a certain kind of hybrid in hierarchiral construction a basic building block used as a subunit of a larger block. This method is actually iterated few times to obtain larger and larger units the important thing to note here is that the fundamental building blocks does not lose its identity during hierarchiral construction.

Therefore, if I have to get the specific property, each one of these fundamental units is important and they should not lose its identity while it make this hierarchiral construction. So, let us take us schematic example explaining the meaning of what is meant by this hierarchiral construction. So, I have for instance a large microscopic or micron size block which I can which I have seen, which can be constructed here.

This can be constructed starting with the single unit for instance this is the brick rectangular brick and I can use this rectangular brick as a sub unit in a larger unit sequence. When I make this larger construction, this rectangular brick with similar rectangular bricks gives rise to larger unit which itself is a rectangular brick of a similar aspect ratio in doing going from step a to step b. Of course, I may have some kind of inter layer that mean some kind of cement or some kind of layer separates.

Actually, one of these building blocks like the one marked in gray with a different part of the system like the one mark by this single dot or one mark by double dot. Therefore, I may use some inter layer glues or I may use some kind of inter layer which assistance can actually play an important role in this hierarchiral development. Therefore, if the block itself is a nano size dimensions, then the inter layer also which now for instance I can draw the schematically as a layer in between will also be of the nano scale dimension. Now, in stage c I take this block which I have used, which I have constructed using blocks like a and use it itself as a fundamental building blocks.

Therefore, now if look at stage c there is one unit like b here there is another unit like b here, there is another unit like b here and finally there is a unit like b here and d stage you can see here I am using four of these blocks to construct a larger unit. Finally, you can see the stage d also involves putting many of these c blocks together and therefore, I have obtaining larger and larger units, but d stage there is a building blocks somewhere which is hidden which is like the a block which I started.

Of course, as I pointed out, there could be inter layers which separate this individual building blocks with the other part of the system. Another nice example would be for instance I will explain on the board what you meant called the evolution of hierarchiral surface roughness. For instance, suppose I talk about my surface and I am talking about for instance a material like this and I am focusing on the surface.

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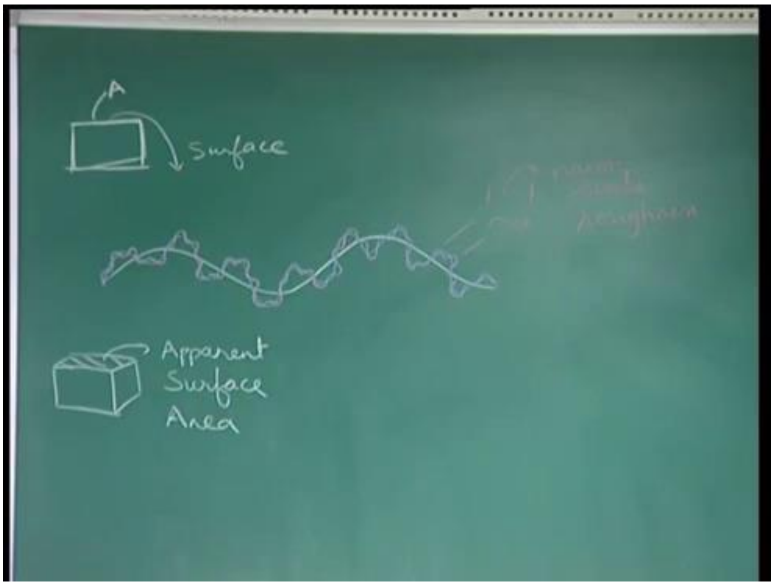

This surface could have certain wavelength length like this its roughness on this surface roughness. For instance, I could have another wavelength of surface roughness, for instance I could think of a wavelength super impose on top of this. In other words, in the presence of this blue surface line blue waviness the actual surface will be this, but I need not to end my story here, I can go one more level for instance and talk about even final surface roughness having even smaller wavelength.

Of course, I can go to final of roughness surface getting rougher and rougher. Important point to note is that say suppose take my block like this the upper end surface area would be the surface area a, but as a make my surface rougher and rougher, the actual surface area tends to increase. Therefore, for a given unit surface area, suppose I am looking three dimension, this kind of a surface the upper end surface area, which is this upper end surface area is constant. As you can see, the actual surface area keeps on increasing as increases surface by making a more and more corporate or more and more rough in the context of nano structure.

At some point of time, I would like to put a wavelength for instance rate could be a wavelength which is of this. So, I could talk about the wavelength like this, which is having nano meter, so this is a very nice way of actually increasing the surface area of this material without actually breaking the particle into finer and finer stages.

In some sense, you can see the structure is self similar that means I look at go deeper and deeper scale and I find that surface looks exactly identical at various length scale, where a self similar across all length scale I would call fractal. In typical system, you note this at least there are a few wavelength which are present when I talking about the surface roughness. Similarly, we have taken up at least two example to understand how we can have hierarchical development, of course a bulk material.

One of these in each one of these cases as we can see there is a certain enhancement in the property, which we can obtain and if my fundamental building blocks of lowest wavelength in the case of wavelength happens to be in the nano scale. Then, I can clearly see that this comes under the class of hierarchical development of nano materials. Now, let us see some example of hierarchical structure and how this hierarchical structure give us some kind of what you might call extremely beautiful properties three examples given here all three are from nature.

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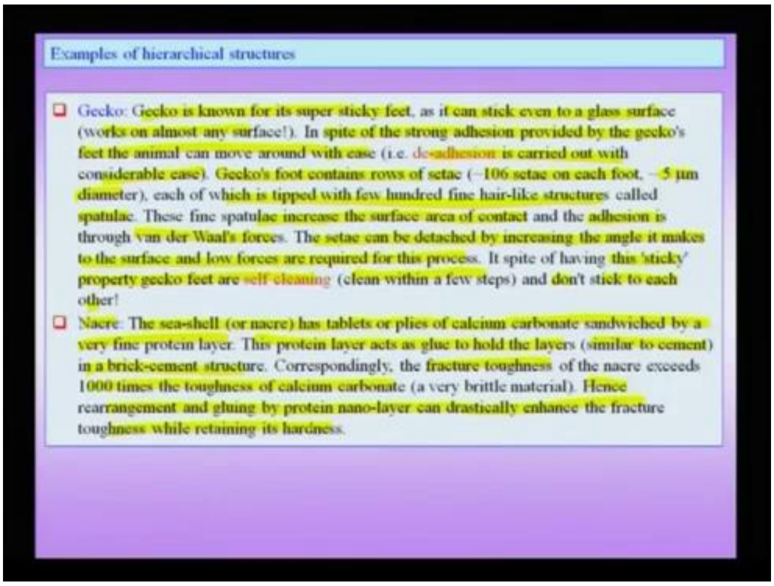

Examples of hierarchical structures

- ☐ Gecko: Gecko is known for its super sticky feet, as it can stick even to a glass surface (works on almost any surface!). In spite of the strong adhesion provided by the gecko's feet the animal can move around with ease (i.e. de-adhesion is carried out with considerable ease). Gecko's foot contains rows of setae (~106 setae on each foot, ~5 μm diameter), each of which is tipped with few hundred fine hair-like structures called spatulae. These fine spatulae increase the surface area of contact and the adhesion is through van der Waal's forces. The setae can be detached by increasing the angle it makes to the surface and low forces are required for this process. It spite of having this 'sticky' property gecko feet are self cleaning (clean within a few steps) and don't stick to each other!
- ☐ Nacre: The sea-shell (or nacre) has tablets or plies of calcium carbonate sandwiched by a very fine protein layer. This protein layer acts as glue to hold the layers (similar to cement) in a brick-cement structure. Correspondingly, the fracture toughness of the nacre exceeds 1000 times the toughness of calcium carbonate (a very brittle material). Hence rearrangement and gluing by protein nano-layer can drastically enhance the fracture toughness while retaining its hardness.

Here, nature has somehow master this art of doing hierarchical construction to obtain given set of properties, which otherwise can we thought of as contradictory to each other. Geeko is lizard kind of creature which is known for its super sticky feet, it can even stick on glass surface. In other words, it can hang upside down from glass surface and its beauty is that it is taking property works on any surface in spite strong addition provided Geeko’s feet.

The animal can move around with ease that means de adhesion is carried out with considerable ease, now if there are no substances made by man, which I have extremely sticky. In such material, the problem is that if addition is where easy and de adhesion become extremely tough that means it is usually a one way process. Then, the de-adhesion is easy, then adhesion is not that good, but here is the beautiful example where nature has the engineer feet of Geeko's. So, there you can walk around any surface and while walking around, it requires repeated adhesion and de adhesion of this surface.

This is achieved with the construable and the body weight will entirely have to be carried even it is upside down. This is done with construable efficiency, now this is done by actually having Geeko's feet which consists of setae about 106 setae on each foot. Each one of these 5 micrometer diameter, these seate are tipped with the few hundred fine hair like structure called spatula. So, here we have a hierarchical construction of the feet consisting seate, the seate consisting of spatula and spatula actually increase the surface area of contact. In other words, even though my upper end surface area remains constant, but the effective surface area increase considerably by the presence of these hair like spatula.

The adhesion is through Van der vaals and us we know the Van der walls forces are weak forces, they not like covalent bonding they are not like unique bonding. In spite the fact that now we dealing with van der vaals bond, now as the surface area is been considerably the overall bonds strength is very good the setae can be detached by increasing the angle.

It makes the surfaces and low forces are required in this process this is actually what is giving the considerable de adhesion fact that it is like the setae sits here. Now, suppose increase the angle contact it can come off, so let me show on this board, and suppose I have my higher feet sitting here detached by an angle. So, at any point of time the entire feet is not being detached, but only a row of these spatuale setae are being detached from these surfaces.

Another great beauty of this kind of what you meant called Geeko feet is the fact that when you accept something to be very sticky accepted to pick of lot of dirt, because it is normally sticking as I said any surface.

So, correspondingly, of course dirt will also stick to the surface with considerably, but this is not the case in spite of being an very sticky material Geeko’s feet have property of self cleaning. Actually, the very walking process itself acts like a cleaning process and it can clean itself with in the few steps. Another interesting property is that if setae stick to any surface it should stick to each other as well, but this not happen and the geometry and configuration such that they don’t stick to each other.

If setae were actually strict to the each other, then this would implies that the overall surface area available for the setae or the spatulae stick with the given surface would reduce, but this does not happen. Actually, you have a marvelous kind of a device which has the multiple rows, so it’s a and there are of course now efforts, what you meant called mimic the structure or what you meant called biganostic structure, which can do the job of Geeko. Perhaps, with time we get closer and closer what nature has injured quite some time already these summaries, what Geekos will does it gives good forces of adhesion.

Van der waals forces by increase area, which consists of hierarchical construction involving setae and spatulae. In spite of having these extreme ability to take, it does not stick dirt on itself too much while walking cleaning takes place this feed do not stick to each other and de adhesion is also achieved with construable. In spite of fact that you actually have a strong bonding between the surface and feet of the Geeko, so here is the one marvelous example of a hierarchical construction in nature, which is giving as unique set of property.

This cannot be achieved by using for instance monolithic kind of a material like glue, which we typically used in industry. Another beauty of nature is the example of nacre the seashell on nacre has tablets or plies of calcium carbonate sandwiched by a very fine protein layer. This protein layer acts like a glue to hold a layer similar to cement in brick cement structure this structure has the beauty that it has the high fracture toughness. It exceeds the thousand times of calcium carbonate for which actually this structure, this nacre is made hence rearrange gluing of protein nano layer can drastically enhance the fracture toughness while retaining its hardness.

So, this sea shell has the beautiful property because it essential to survival that it is got very good impact of system, because often in sea shells would be smashed against rocks.

If the sea shell would break, then it would not good for the organism life, therefore if the sea shell engineered itself or nature has engineered the sea shell in such way that it has the extremely good fracture toughness. If you look at the constituently, it is actually made of calcium carbonate, which has you know extremely brittle material, then how is this calcium carbonate giving rise to good fracture toughness.

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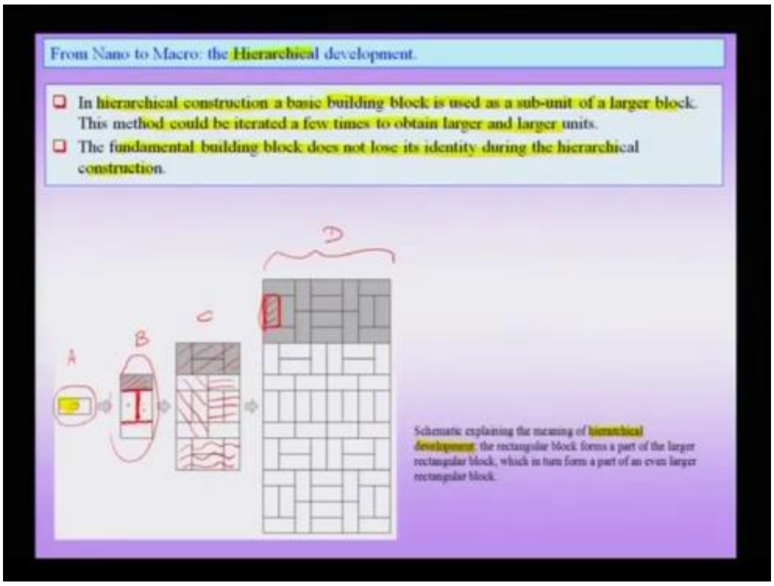

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This is done in a manner do not identical to this kind of construction, but very similar to construction, where in you have the calcium carbonate layer in any adhesion, you have this nacre layers which is intertwining these kind of calcium carbonate layers.

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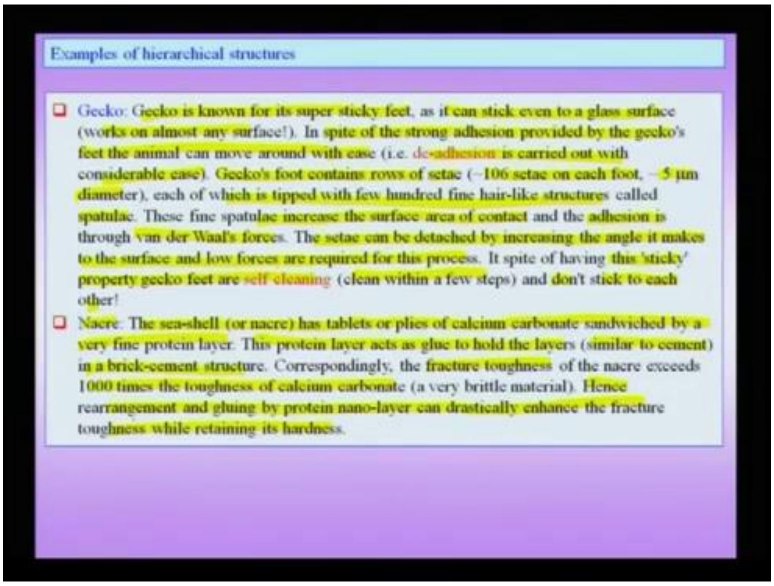

Examples of hierarchical structures

- Gecko: Gecko is known for its super sticky feet, as it can stick even to a glass surface (works on almost any surface!). In spite of the strong adhesion provided by the gecko's feet the animal can move around with ease (i.e. de-adhesion is carried out with considerable ease). Gecko's foot contains rows of setae (~106 setae on each foot, ~5 µm diameter), each of which is tipped with few hundred fine hair-like structures called spatulae. These fine spatulae increase the surface area of contact and the adhesion is through van der Waal's forces. The setae can be detached by increasing the angle it makes to the surface and low forces are required for this process. It spite of having this 'sticky' property gecko feet are self cleaning (clean within a few steps) and don't stick to each other!
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There, we have an hierarchical construction of this and the overall geometry arrangement these two layer nano protein layers along with the calcium carbonate layer give this nacre is very good fact of roughness. So, the protein layer performs two function one its acts like a glue between two bricks of two calcium carbonate, but in addition it also provides what you meant called the energy absorption ability which gives beautiful impact toughness. Without example, we considered again for an hierarchical construction giving rise to specific property in the case of lotus leaf which we already encounter that before.

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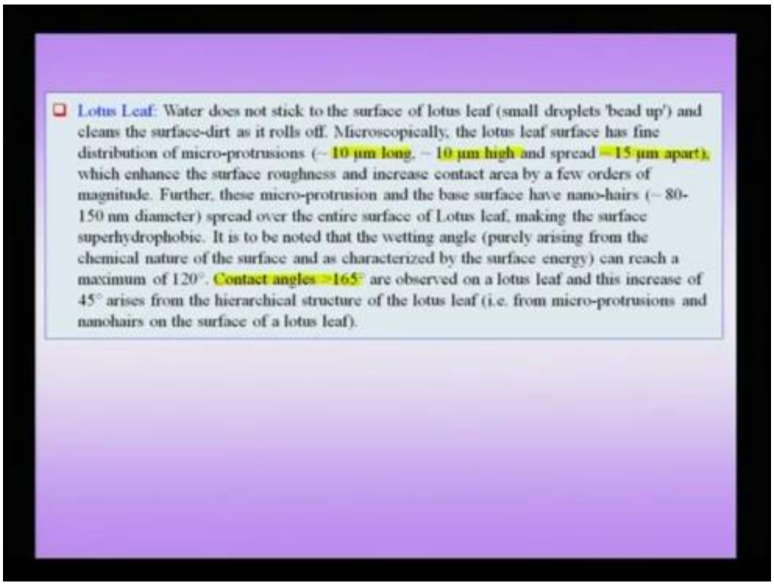

- Lotus Leaf: Water does not stick to the surface of lotus leaf (small droplets 'bead up') and cleans the surface-dirt as it rolls off. Microscopically, the lotus leaf surface has fine distribution of micro-protrusions (~ 10 µm long, ~ 10 µm high and spread ~15 µm apart), which enhance the surface roughness and increase contact area by a few orders of magnitude. Further, these micro-protrusion and the base surface have nano-hairs (~ 80-150 nm diameter) spread over the entire surface of Lotus leaf, making the surface superhydrophobic. It is to be noted that the wetting angle (purely arising from the chemical nature of the surface and as characterized by the surface energy) can reach a maximum of 120°. Contact angles >165° are observed on a lotus leaf and this increase of 45° arises from the hierarchical structure of the lotus leaf (i.e. from micro-protrusions and nanohairs on the surface of a lotus leaf).

We have already seen that the property of super hydro phobicity and super hydro phobicity as we pointed out implies and we talking about very higher contact angles greater than 165 degree. Now, this 165 degree is what you meant called the upper end macroscopic contact angle and microscopically if we look at the system things are very interesting.

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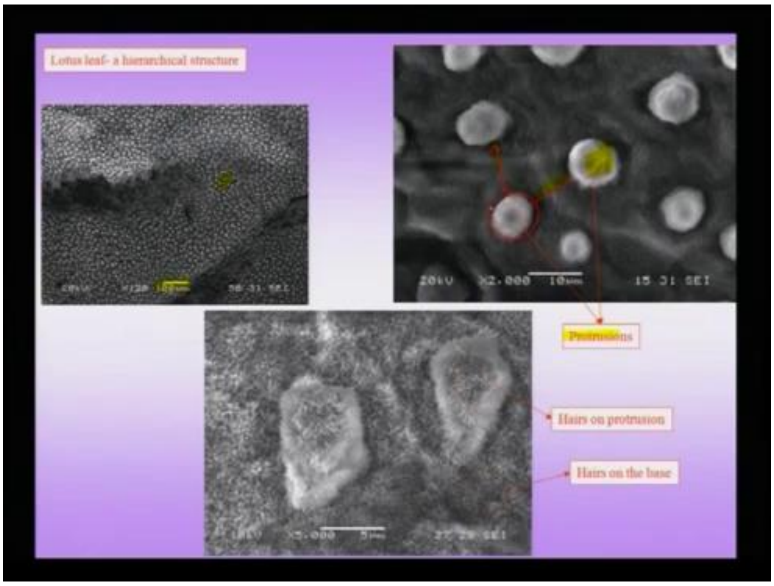

Lotus leaf- a hierarchical structure

This is happening because when hierarchical construction as shown here. So, if you look at the lotus leaf, now this is scale about 100 microns in a scanning electron microscope. You can see that three are these protrusion, we can see that these protrusion white kind of structure here.

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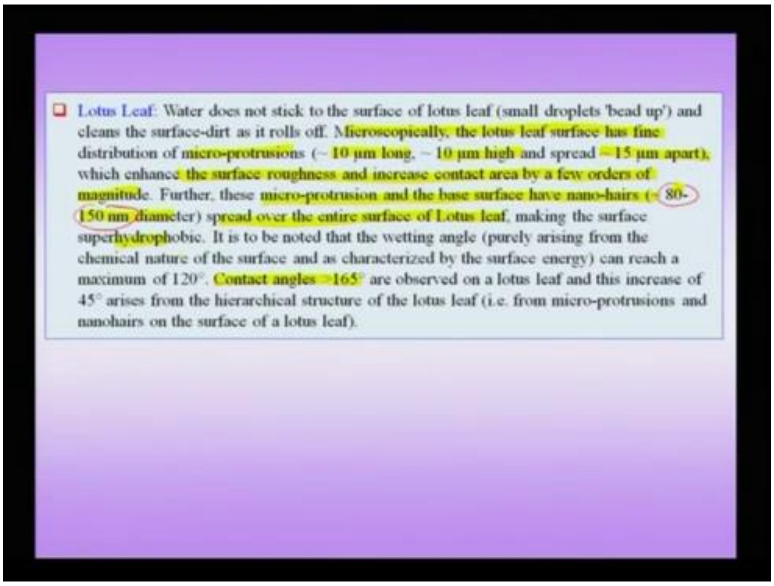

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Now, these protrusion are of course they have certain and we would like to be calling about micro protrusion and there about ten micro meter long 10 about 10 micro meter height and about 15 micro meter long as you can see in this kind of a picture. So, these are about 10 micrometer dimension and there about 15 to 15 micrometer far away from each other, so they have a very specific kind of a geometry, so these micro protrusion here. Now, it is abuse that kind of property super hydro phobicity we are talking about here is with respect to some kind of a dirty kind of a water.

Obviously, this kind of a contact angle cannot be a achieved for any kind of solution like to through on the material because lotus leaf typically as optimizers the structure. So, only what you meant called dirty water, not other kind of solvent which we might want to try on these. So, microscopically if we look at this lotus leaf, it is consist of fine distribution of micro protition, which enhances surface roughness and increase the contact area by few orders magnets, but the structure does not stop there.

Further, these micro protition and the base of the leaf itself has have nano gears and these nono hears 80 to 150 nano meter dimension. So, heart of the this whole hydro super hydro probhicity is a nano structure and this nano structure has the dimension of the order of 80 to 150 nano meters. This is spread over the entire lotus leaf that means it is present on the micro protition and also based on the leaf making the surface super hydrophobic.

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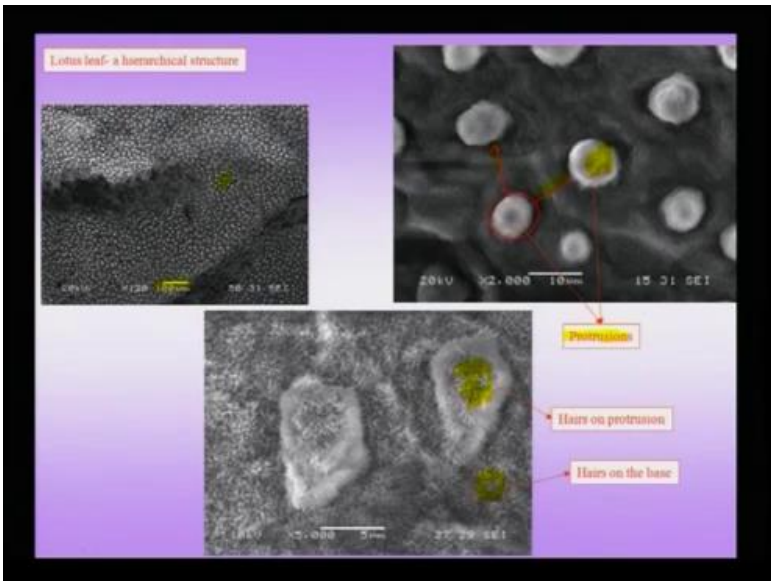

Now, as a pointed out, let me first show you where is this micro protition hair like structure, so you can see here these are the micro protitions. Then, you can see that there are hairs on the base and also hairs on the micro protitions and if you look at the water drop, it is actually being not support by on directly on the leaf lotus leaf surface, but it is supported by these nano hairs.

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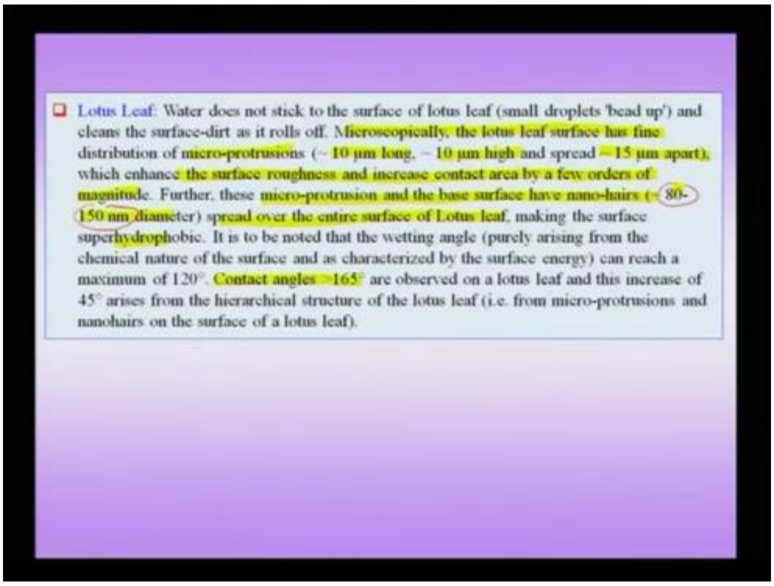

- **Lotus Leaf**: Water does not stick to the surface of lotus leaf (small droplets 'bead up') and cleans the surface-dirt as it rolls off. Microscopically, the lotus leaf surface has fine distribution of micro-protrusions (~ 10 μm long, ~ 10 μm high and spread ~15 μm apart), which enhance the surface roughness and increase contact area by a few orders of magnitude. Further, these micro-protrusion and the base surface have nano-hairs (~ 80-150 nm diameter) spread over the entire surface of Lotus leaf, making the surface superhydrophobic. It is to be noted that the wetting angle (purely arising from the chemical nature of the surface and as characterized by the surface energy) can reach a maximum of 120°. Contact angles >165° are observed on a lotus leaf and this increase of 45° arises from the hierarchical structure of the lotus leaf (i.e. from micro-protrusions and nanohairs on the surface of a lotus leaf).

This is what is actually leading to finally to fact that macroscopically we can achieve the contact angles which of even about 150 degrees. So, this kind of construction you can visualize as some kind of analog of what you might called surface roughness which we constructed. Of course, this is not a very simplistic kind of surface roughness, which was schematic analog showed here, this consists of very specific kind of the structure and these structure as you might imagine has to perform other roles apart from code. Being super hydrophobics was a leaf leaving entity and the leaf surface has to perform other roles likes photosynthesis extra.

These structure which making super hydrophobic cannot interfere with other roles of the leaf and this is what beautiful kind of a hierarchic structure consisting of micro protitions and nano hairs. So, we have consider the few examples and we have seen that hierarchy construction is found many places in nature and beauty of the hierarchic construction is that it gives rise to combinational properties.

This otherwise cannot be obtained by what you meant called monolithic construction or a single length scale construction. Now, we have ask this question implicitly of few times before, but let us know explicitly list out that why we need to go to the nano scale. This listing is important because often our research our effort should be directed in such a way so as to get the maximum benefits in terms of properties and performances.

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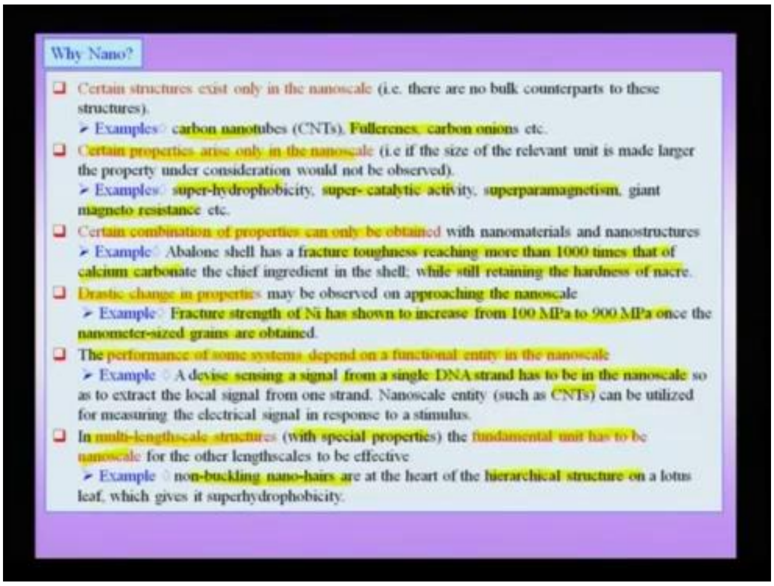

Why Nano?

- ❑ Certain structures exist only in the nanoscale (i.e. there are no bulk counterparts to these structures).
    - ➢ Examples: carbon nanotubes (CNTs), Fullerenes, carbon onions etc.
- ❑ Certain properties arise only in the nanoscale (i.e if the size of the relevant unit is made larger the property under consideration would not be observed).
    - ➢ Examples: super-hydrophobicity, super- catalytic activity, superparamagnetism, giant magneto resistance etc.
- ❑ Certain combination of properties can only be obtained with nanomaterials and nanostructures
    - ➢ Example: Abalone shell has a fracture toughness reaching more than 1000 times that of calcium carbonate the chief ingredient in the shell; while still retaining the hardness of nacre.
- ❑ Drastic change in properties may be observed on approaching the nanoscale
    - ➢ Example: Fracture strength of Ni has shown to increase from 100 MPa to 900 MPa once the nanometer-sized grains are obtained.
- ❑ The performance of some systems depend on a functional entity in the nanoscale
    - ➢ Example: A devise sensing a signal from a single DNA strand has to be in the nanoscale so as to extract the local signal from one strand. Nanoscale entity (such as CNTs) can be utilized for measuring the electrical signal in response to a stimulus.
- ❑ In multi-lengthscale structures (with special properties) the fundamental unit has to be nanoscale for the other lengthscales to be effective
    - ➢ Example: non-buckling nano-hairs are at the heart of the hierarchical structure on a lotus leaf, which gives it superhydrophobicity.

We should note that certain structure like fullerenes carbon onions etc and carbon nano tubes existing only in the nano scale. There is no bulk counterpart, therefore we have to go to the nano scale if we have to study the structure and utilize. So, clearly very strong to go to the nano scale certain property arise only in the nano scale again the dirty implies there are no bulk counterpart to these properties.

We have already talked about few of these for instance the super hydro probhicity super catalytic activity super para magnetism joint magantor system etc. You have notice that actually there is no bulk counterpart, these properties and this implies that we have to go to the nano scale and bring out these properties. The additional property could be certain combinational property can only be obtain when we go the nano scale and we already seen for instance in the abalone shell it is got good facture toughness reaching more than 100 times that of the calcium carbonate while still retaining its hardness.

Typically, we know that if the material is very tough that means it is very tough tail usually less hard, but here you have an extremely hard material, which has been engineered, which is also retaining usual hardness. So, we have all ready seen some more combinational like this, we will encounter more of such combinational as you go into a various topics in the scores, but we have to note that it may not be the individual property which is unique. The combinational could be unique as you go down to the nano scale and these combinational what gives, for instance the component its application its performance.

In actual service, there could be drastic change in properties as you approach in the nano scale, we know that for instance we already seen that when you go down green size in nano structure nano crystalline poly crystal. You actually increase the hardness of the material, but this increase in the hardness is more what you might called at macro scale or the micron scale is actually gradually increase. If you want drastic increase that means increase few orders of magnitude or at least a factor which is making a worthwhile to study these material such may start happening only in this nano scale.

For instance, fracture toughness strength of Nickel has been shown to increase from 100 MPa to 900 MPa once nano meter sized grains have been achieved, so the fracture strength can be increased. Now, it is happening only when you go down to the nano scale, similarly other property we will seen for instances absorption of gases .

We will actually make the calculation to show the how the surface area increases going to give the drastic increase in the amount of gases which can be absorbed on the surface. So, this implies that we have to here there is the property is varying, but we want to weigh, but we want to go down to the nano scale to see a considerable enhancement in properties nothing no new properties arising not that new structure forming here. That does that the amplification factor is large and this warns us to go down to nano scale, the other thing which could happen is that performances of some system depends on functional entity the nano scale.

Now, this is again new, then if I start with macro scale entities then I will able not to get the performances which I can get by going down to a nano scale entity, which is performing a very specific role. We have seen that device sensing signal from the single DNA can be extracted if you have nano structure like carbon nano tube and whose electrical output what we you are studying.

So, that means that if my if I have to extract signal from single DNA then obviously my sensor or my probe has to be on the same length scale. I cannot use the microprobe then, which will actually average out then my signal across many cellular structure. This is not my goal if I have to do this then obviously my probe also has to be have an wavelength or has to have an length scales which corresponds to length scale of the problem which I am tiring to study. So, it is clear that I have to go to nano scale if I have to for instance single cell and deliver a drug or I have to extract single signal from single DNA or I have to effect only a few cells in the tissue.

Then, we have already seen one beautiful example that in multi length scale structure and we have seen the very special property the fundamental unit has to be of a nano scale. If I do not start the fundamental unit has on the nano scale, then I may have the enhancement properties, but overall structure will not have the this kind of beautiful property which we see. So, for the case of lotus leaf or the case of the Geeko feet and the heart of this we saw in the case of lotus leaf there are non buckling nano hearts nano hears.

This is of course hierarchically built into the surface of the leaf which gives us super hydrophobhicty. So, there clear cut reasons why we want to go down to the nano scale, but we have to differentiate all these cases, because then we can get best out of our design.

So, see how actually this new things coming in the nano scale and how we can achieve those new things with minimum efforts. So, just to summarize this line certain structure exists only in nano scale certain properties arise only in the nano scale, but there is certain a another case where the properties exist in the macro scale. There is a drastic enhancement in the property you may want to have the certain specific combinational property which is may not possible by using macro scale entities in an hierarchical construction.

For instance, you may want to keep the nano and the fundamental unit few of nano scale to get that the important benefit in terms of properties or combinational properties and of course we saw based on the kind system you trying to study. If that system itself happens to be in nano scale or below you need to have your sensor your drug delivery system corresponding to that verifying scale or the nano scale.

Now, let us ask question that we have notice that there are some specific property coming about we have to ask our self how to does this properties come this on this nano scale? The broader answer of this question will be obtain when we see many more example as we go across various topics in this course, but we should understand that and differentiate the various classes of property which come about in the nano scale. Here, we specifically talking about those structure which also existing in the macro scale.

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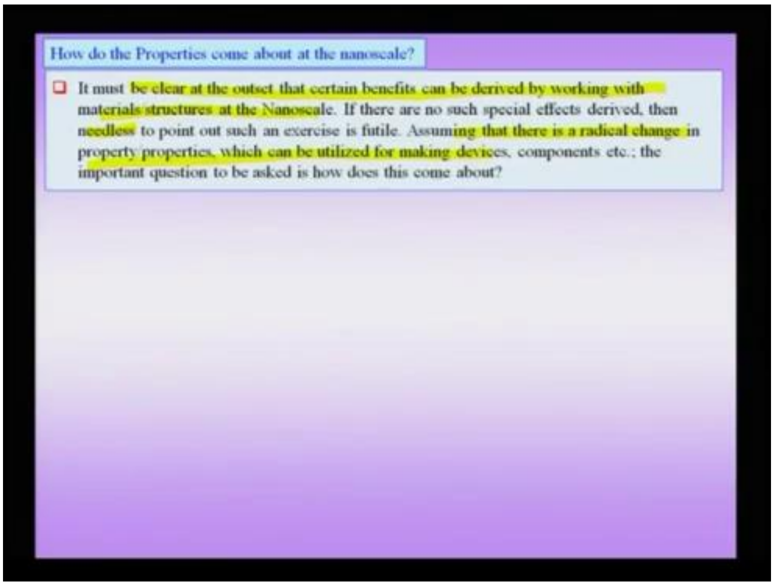

How do the Properties come about at the nanoscale?

- ☐ It must be clear at the outset that certain benefits can be derived by working with materials structures at the Nanoscale. If there are no such special effects derived, then needless to point out such an exercise is futile. Assuming that there is a radical change in property properties, which can be utilized for making devices, components etc.; the important question to be asked is how does this come about?

So, it must be clear from outside that certain benefits can be derived working with materials structure and nano scale and of course,, that makes a you know worthwhile to study this. Otherwise, this would be an point less exercise assuming that there is a radical change in this properties which can of course utilize making device and components my question is that how does this change in the properties come across. This is of course very important question because once we have our classification and the approach path in our mind mechanism in our mind then of course we can engineer our components better.

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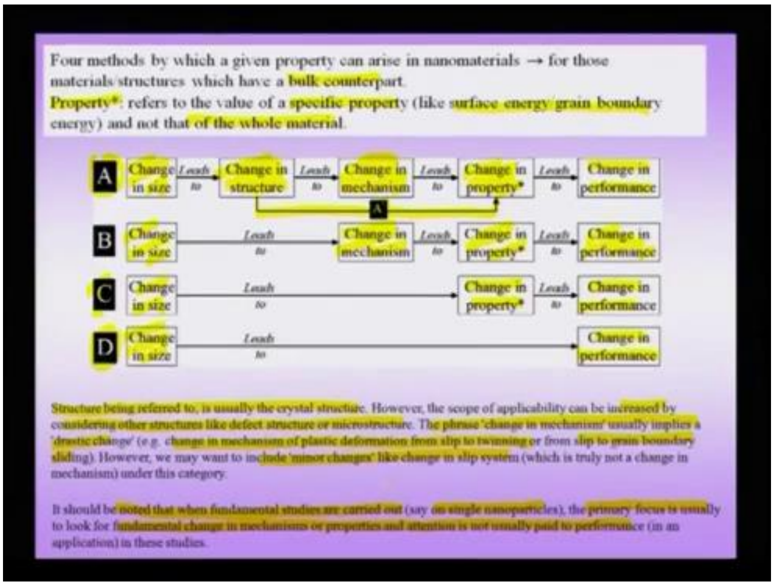

Four methods by which a given property can arise in nanomaterials → for those materials/structures which have a bulk counterpart.

Property*: refers to the value of a specific property (like surface energy/grain boundary energy) and not that of the whole material.

A Change in size Leads to Change in structure Leads to Change in mechanism Leads to Change in property* Leads to Change in performance
A
B Change in size Leads to Change in mechanism Leads to Change in property* Leads to Change in performance
C Change in size Leads to Change in property* Leads to Change in performance
D Change in size Leads to Change in performance

Structure being referred to, is usually the crystal structure. However, the scope of applicability can be increased by considering other structures like defect structure or microstructure. The phrase 'change in mechanism' usually implies a 'drastic change' (e.g. change in mechanism of plastic deformation from slip to twinning or from slip to grain boundary sliding). However, we may want to include 'minor changes' like change in slip system (which is truly not a change in mechanism) under this category.

It should be noted that when fundamental studies are carried out (say on single nanoparticles), the primary focus is usually to look for fundamental change in mechanisms or properties and attention is not usually paid to performance (in an application) in these studies.

Four methods, what you meant be we can daily need four methods and these four methods specifically referred to those cases where in there is a bulk counterpart. That means I have a case where there is a green size, in the case micron scale and keep on reducing my green scale. Then, I go to the nano scale, I could be talking about the crystallize which is even millimeter in the size and slowly reduce the crystallize size to the nano scale.

So, in other words if I am going bulk state to nano state, then how is the that the property changing and here we are not considering the cases like for instance of property of carbon nano tube which has no bulk counter parts. That means they exist only in the nano scale therefore, we are not talking about properties which arise in the very specific cases where there in there is no bulk counterpart.

This particular classification we are also dealing with property in the language that it is the specific property. That means the surface energy and green bond energy and not that of the whole material we talking about the property which is for instance surface energy per unit area again boundary energy per unit area when I am talking about overall energy of the whole system. So, in this classification we will see that there are four possible methodologies crudely speaking that you have a change in size.

That means you reducing the size and simply this may lead into the change in performances this is what you meant called the Tibullus way of understanding Tibullus case by which a new or a enhancement in performance comes about. Of course, this is a simple way to understand this, suppose I have material and I keep dividing these material into smaller and smaller pieces as we are considered, this is the surface area is going to increase and for now. Assuming that the surface energy per unit area is not changing much, then in spite of the fact that there is no change in the specific property, we see that the overall amount of gases that such a surface can absorb.

We are going to increase and therefore, will have change in performance here there is no great change in the mechanism or any one of those very interning scenario take place. This is at least what you accept from what you may called reducing bulk crystal to nano crystal or bulk system and nano size system. That means this is guarantee take place for you because now you have reduce a eleventh length scale and in spite fact that there is nothing interesting happing, you still getting change in the performance the other end of spectrum is case a.

Here, change in size leads to a change in structure and we will have come and to say about what is structure we are referring to here this can lead to the change in mechanism. This is operative in the system this can further lead into change in the property of course whenever there is change in the property. This will lead into change in the performances of the component or these specific devices or these specific materials we are considered in between the case a which is shown here and case d. There can be other scenarios like change in the size may not lead to a change in structure, but can directly lead into change in the mechanism this change in the mechanism most probably lead to the change in property.

Finally, of course this will lead to the change in performances, so this is the another path way which can lead into the change in performances case c is change in size lead to the change in the property directly. That means there is no change in the mechanism this can lead to a change in performances and so summaries this other complicated looking table or completely looking flow chart.

There are four possible scenarios with sub scenario which is also be marked as a prime, so in case a change in size leads to the change in structure which leads to a change in the mechanism which can lead to the change in property. Finally, change in performance the other end of the spectrum involves change in size directly leading change in performances without any change in the structure mechanism or property intermediate between these two is change in size. This leads to change in mechanism which is leading to the change in the property and finally, to change in performances. So, in some cases it is possible that change in size leads the change in structure, but still there is no change in mechanism.

That means I can directly jump from stage two in the classification a to a stage four which is now change in structure leading to the change in property which is leading to the change in performances without actually involving change in mechanism. So, in these case we use a word structure we use a word mechanism and of course, we already define what you mean by property. So, the structure being referred to usually the crystal structure and a how were if once to you know relaxes condition and the scope of applicability of these kind of flow chart. Then, other kind of structure like defect structure of micro structure could also be brought into the scope of this classification.

The phrase change in the mechanism usually implies a drastic change in the mechanism of for instance plastic deformation from slip to twining or from slip to green boundary sliding how were minor changes like slip change system. This is truly not a change in mechanism can also brought into this category, but while listing the change in for instance mechanism. We want to say that for instance that when you have macro scale system, it was slip dominated by plastic reformation dominated by slip and whenever for instance security nano meter green size.

It could be actually be slip dominated by green boundaries slightly or slip dominated by twin. Therefore, there is a clear cut change in the mechanism by which plastic reformation taking place at how were it could so happen that when you go reduce the green size additional kind of slip system, slip system may be activated.

This is not what we might call in principal change in the mechanism, but these may be listed some way under the category of some change in mechanism. It should also be noted when fundamental studies are carried say on single nano particles primary focuses usually to look for the fundamental change in mechanism properties and attention usually not paid to performance in these studies. This is a important point to note because sometimes you have a single particle on which the entire test is carried out.

For instance you may have nano particle which is 50 nano meter in size, any you may carry out compression studies on these particle. Therefore, what you get out of such a study could be a property like an elastic modulus or it could be stress at which dislocation nucleated in this system. Here, we are not specifically talking about the performances say nano particle like this in the making of a device or a names device. So, this is the sometime very carefully has very carefully kept in mind, there might not be a report in literature of the kind of the performance we are accepting from this kind of property and we have to at the state.

For instance, put an our thinking to understanding let how if the given least this particle have these kind of a property what kind of a performance I can gain by using these particles those often when such particles put together to form a component. There may be scenario that take effect or of course also there could also be a problem with respect to a what you meant called destructive interference in the between the particles giving rise to a loss in property which we had absorb for a very single. For instance, single nano crystal, so here we are talk summarize this line here we are talking about those properties which do not or those structure or those cases where in there in bulk counterpart.

Obviously, we are excluding those which have no bulk counter parts and the property we are referring to is a specific property we want to see how these specific property. Finally, it is giving rise to a genuine performances achieved and this classification achieved helps us mentally to workout you know. For instance, work out engineer the material so as to get required change in the property on performances.

So, let us take a few examples to see may be we will revisit this topic later on how change in crystal structure takes place when the there is reduction in size. That means we all know that there is certain bulk crystal structure which is stable at a given temperature and pressure. Here, we talking about not change in temperature or pressure to achieve this new crystal structure, but typically we talking about change in reduction size.

So, purely this is a size dependency transformation or change in crystal structure. That means that at small sizes certain other crystal structure may be becomes stable purely because of these size effects. Additionally, we may want to subject these small scale crystals and small scale structures or reduce dimension structures to pressure or change in the various temperature to see how these kind of materials behave.

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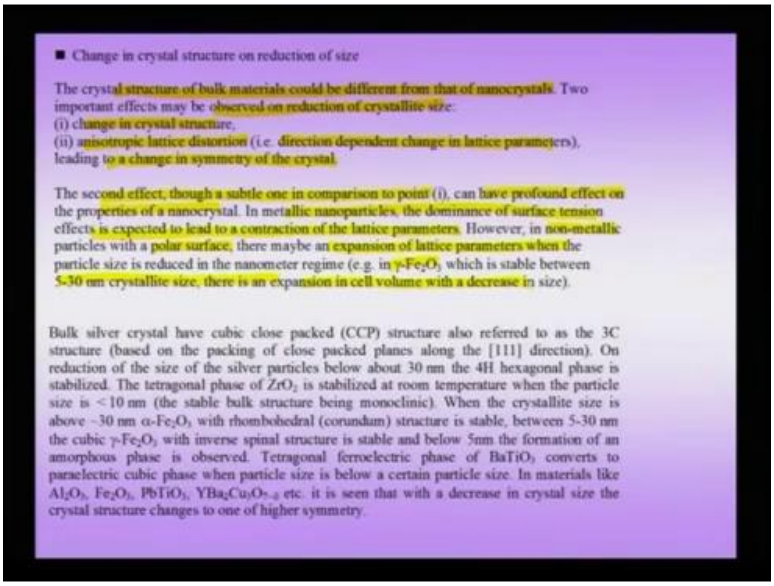

- Change in crystal structure on reduction of size

The crystal structure of bulk materials could be different from that of nanocrystals. Two important effects may be observed on reduction of crystallite size:
(i) change in crystal structure,
(ii) anisotropic lattice distortion (i.e. direction dependent change in lattice parameters), leading to a change in symmetry of the crystal.

The second effect, though a subtle one in comparison to point (i), can have profound effect on the properties of a nanocrystal. In metallic nanoparticles, the dominance of surface tension effects is expected to lead to a contraction of the lattice parameters. However, in non-metallic particles with a polar surface, there maybe an expansion of lattice parameters when the particle size is reduced in the nanometer regime (e.g. in γ-Fe_2O_3 which is stable between 5-30 nm crystallite size, there is an expansion in cell volume with a decrease in size).

Bulk silver crystal have cubic close packed (CCP) structure also referred to as the 3C structure (based on the packing of close packed planes along the [111] direction). On reduction of the size of the silver particles below about 30 nm the 4H hexagonal phase is stabilized. The tetragonal phase of ZrO_2 is stabilized at room temperature when the particle size is < 10 nm (the stable bulk structure being monoclinic). When the crystallite size is above ~30 nm α-Fe_2O_3 with rhombohedral (corundum) structure is stable, between 5-30 nm the cubic γ-Fe_2O_3 with inverse spinal structure is stable and below 5nm the formation of an amorphous phase is observed. Tetragonal ferroelectric phase of $BaTiO_3$ converts to paraelectric cubic phase when particle size is below a certain particle size. In materials like Al_2O_3, Fe_2O_3, $PbTiO_3$, $YBa_2Cu_3O_{7-\delta}$ etc. it is seen that with a decrease in crystal size the crystal structure changes to one of higher symmetry.

These crystal structure of bulk system materials very different from that of nano crystals two important effects may be observe on reduction of crystallize size one of course change in the crystal structure itself which is of course drastic change. The second possibilities is an anisotropic lattice distortion which is direction dependent change in lattice parameters leading to change in the symmetry of a crystal. So, there are two possibilities one is change in the crystal structure, second is the change in lattice parameter this change in lattice parameter. Additionally, could be an isotropic that means change along one direction lattice parameter could be different then change in the other direction the second effect, which is change in lattice parameter.

Anisotropic lattice parameter is actually certain effect as compare to one which is drastic effect. It can have propend effect of a properties of a nano crystal in metallic nano particles the dominance of surface tension effects is expected to lead to the contraction of the lattice parameter. That means that in metallic materials the surface, which is now seat of surface tension can lead to the contraction of lattice parameter. Therefore, this is the direct cause for reduction in lattice parameter in non metallic materials, the situation could be very different from metallic particles and these non metallic particles, we are referring to a those which have polar surface.

Unlike the metallic particle, there may be expansion of lattice parameters and this is been observed in the case of gamma Fe 2 O 3 and for this effect to be become a prominent effect. Typically, we have to reduce a crystallize size to nano metric lens scale this polar surface where in there is a repulsion in di poles from the surface can actually lead to the expansion in the cell volume with the decreasing size. So, there are two distinct effects when we talking about surface tension and its role in what you might called the lattice distortion and lattice contraction or lattice expansion one.

Of course, the lattice expansion could be uniform or isotropic in some other cases the lattice expansion could be an isotropic in the case of metallic particles, you could have particles have nano meter length scale dominated by surface tension effects. Here, you actually observe contraction of lattice parameter, but in specific example like gama Fe 2 O 3, which have a polar surface when you talking about 55 to 30 nano meter crystalline size. Actually, there could be a lattice expansion, which is now caused by the polar surface where in the dipoles tends to ripple each other.

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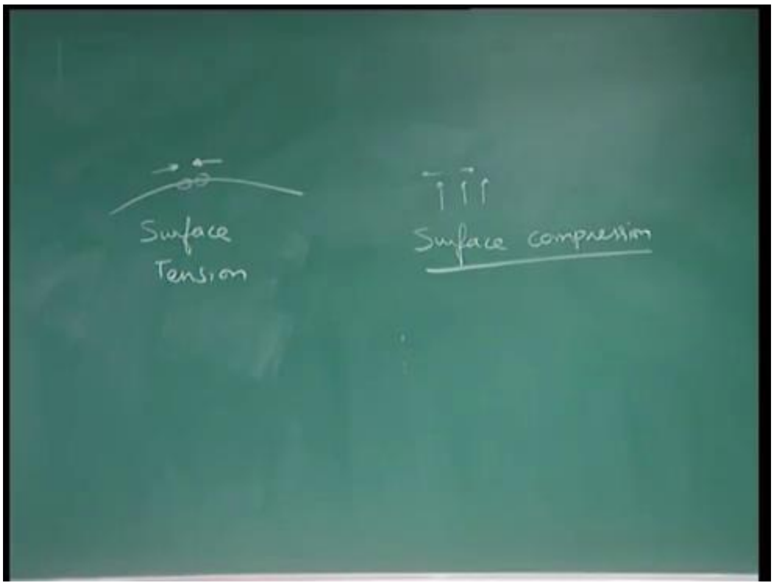

So, let me show this schematically suppose I have a metallic surface in which there are atoms and the surface itself once to contract itself to reduce a surface energy because the atom sitting in the surface have higher energy. This is the original of the surface tension this surface tension effects can leads to the lattice parameter contraction now we know nano particles. The overall the surface area or the surface to volume ratio is very large, but suppose I am talking about polar molecule with actually dipolar dipoles on the surface.

Now, these dipoles tend to repel each other and this repulsion implies that actually we are talking about effect, which is something like surface contraction. These surface compression suppose to surface tension which is extremely new effects seen, which becomes dominant in nano scale can it actually leads to perhaps lattice parameter expansion?

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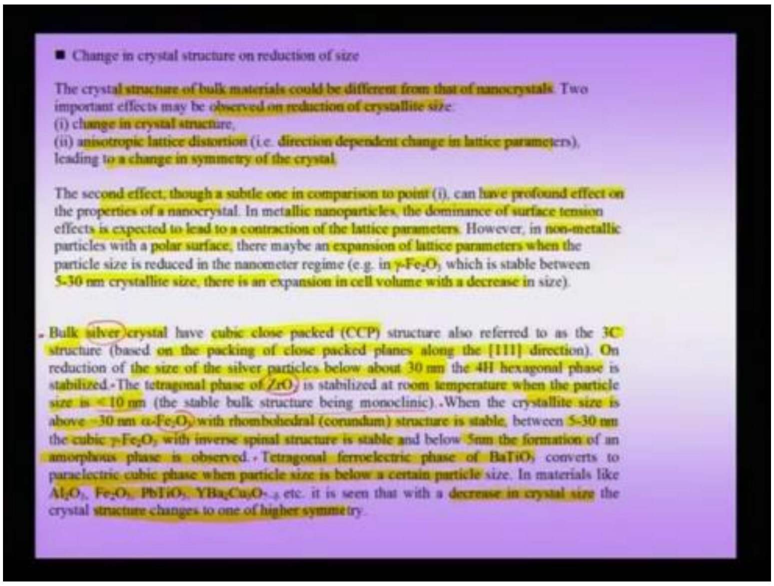

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Of course, in the case of gamma Fe 2 O 3, more studied are done to be carefully analysis these effects and the role of surface expansion in leading to a what you meant called lattice parameter change. Other examples, interesting examples are in case of change in the crystal structure is the case in the silver silver has you know cubic close pack crystal having an FCC lattice.

Typically, what you have it is got to a three c structure that means there is a what you called staking a 1 1 on planes on the one one on direction. Each one of these planes has hexagonal symmetry, but overall symmetry along the 1 1 direction is three four on the reduction of size of the silver particles below about 30 nano meter, we find that the 4 h hexagonal phase is stabilized.

So, this bulk phase is the 3 c phase which is the cubic face and when you reducing the particle size about 30 nano meters, you notice that actually hexagonal phase which is classified has four h, beacuse repeat unit is four layers long is stabilized. Similarly, if you notice that you talking about the tetragonal phase in the zerkonia is stabilized at room temperature, when the particle size is less than about 10 nano meter.

So, we are talking about the few examples here number one is bulk silver number two is the case of zerkonia where in typically you find that if you talking about bulk zerkonia, the tetragonal space is meta stable to temperature by reducing the particle size is about 10, less than 10 nano meter.

We can actually stabilize the tetragonal phase while the actually bulk stable phase is monoclinic phase. We have notice that this partial stabilize zerkonia is in the meta stable structure is in the case of bulk material itself is responsible for the transformation toughening effect. The third example is the case of the alpha Fe 2 O 3, when the crystalized size is above 30 nano meter, alpha its over 3 with rhombohedral structure is stable, but between 5 and 30 nanometer the cubic Fe 2 O 3 with inverse spinal structure is stable.

This is not the end of the story when we actually go down to the even smaller sizes like less than 5 nano meter, we find that the amorphous phase is stabilized. Of course, there are, so let us summarize the points regards to Fe 2 O 3 about 30 nano meter, it is the rhombohedral structure, which is stable between 5 and 30 nanometer. It is the cubic face which is stable with an inverse final structure and below 5 nano meters, it is excepted that amorphous phase become actually the amorphous phase is observed is the truly stabled or not is a question which is more performed question?

We are not taking to here and further studies may be required to see if actually an amorphous structure can be stable about what you meant called crystal structure. The issues involved here of course is the fact that how many unit cells do we have to put to gather before we can call the long range order has to be established.

So, their some very profound issues with regard to actually classifying an amorphous structure to be more stable than what mean called crystal structure there are report in the year 2000 and before which has showed that actually in the amorphous structure. These are theoretical reports amorphous structure is more stable than given crystal structure not any given crystal structure, but given crystal structure artificially.

Of course, the given crystal structure they are comparing with is the crystal structure which is stable in the bulk form. Therefore, from these examples, we can clearly see that there is a tendency in many materials to change in the crystal structure when the crystal size is reduced. These three examples we are considered so far is the case of silver the case of zerkonia and the case of Fe 2 O 3 and we have seen that such consideration we put for very profound question as to can an amorphous phase. We more stable than any given crystal structure this is the more profound question of course which needs to be address further.

Now, another example is the case of the tetragonal ferroelectric phase of barium titrate on the reduction of the particle size the ferroelectric phase converts to para electric cubic phase. This is the again now when I talking about ferro electric ad para electric of cousre talking about change in the crystal symmetry. More importantly, we also talking about change in the physical property, so ferro electric phase actually changes to para electric phase when the crystal size is reduced.

We will take up more such examples when we study electric behaviour and magnetic behaviour of particles where in we seen that reduction in crystal change can actually lead to the profound changes in terms of magnetic and electric behavior of particles. Other examples of which we can take up, which we studied in literature include materials like alumina Fe 2 O 3 Pb Ti O 3 barium copper oxide. Then, there with a decrease in the crystal size, the crystal structure changes to one of higher symmetry. So, this is what you meant called change in the crystal structure effect with reduction in particle size is not restricted to few example we considered here, it is found the many more systems.

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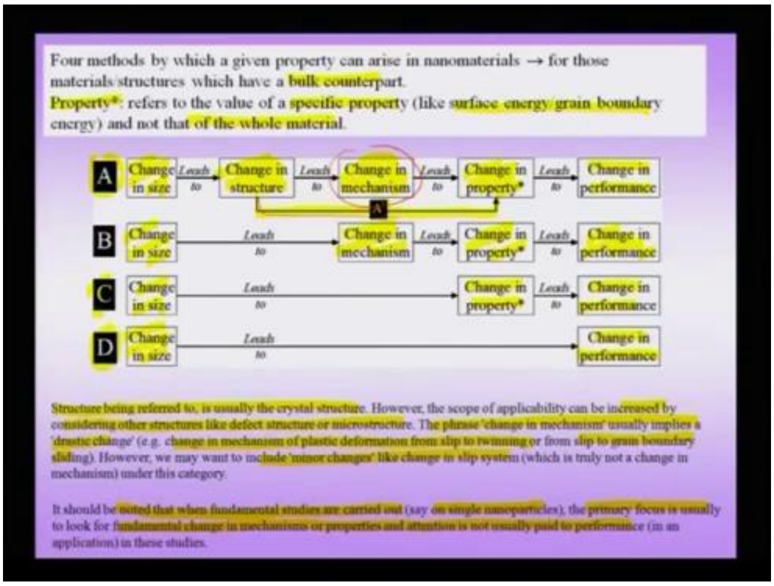

Four methods by which a given property can arise in nanomaterials → for those materials/structures which have a bulk counterpart.

Property*: refers to the value of a specific property (like surface energy/grain boundary energy) and not that of the whole material.

A Change in size Leads to Change in structure Leads to Change in mechanism Leads to Change in property* Leads to Change in performance

A'

B Change in size Leads to Change in mechanism Leads to Change in property* Leads to Change in performance

C Change in size Leads to Change in property* Leads to Change in performance

D Change in size Leads to Change in performance

Structure being referred to, is usually the crystal structure. However, the scope of applicability can be increased by considering other structures like defect structure or microstructure. The phrase 'change in mechanism' usually implies a 'drastic change' (e.g. change in mechanism of plastic deformation from slip to twinning or from slip to grain boundary sliding). However, we may want to include 'minor changes' like change in slip system (which is truly not a change in mechanism) under this category.

It should be noted that when fundamental studies are carried out (say on single nanoparticles), the primary focus is usually to look for fundamental change in mechanisms or properties and attention is not usually paid to performance (in an application) in these studies.

This change in crystal structure as you can see from the picture we are concerned that is there is the change in the crystal structure this is the accepted to a company by a change in mechanism. Definitely, if you are going by passing the mechanism route definitely change in property, therefore, it is very important note there is a change in crystal structure as you reduce the size.

Even if there is no change crystal structure, is there change in the for instance lattice parameter? Because any anisotropic lattice distortion or a change in the lattice parameter would itself contribute to change in property to the some extent or the other.

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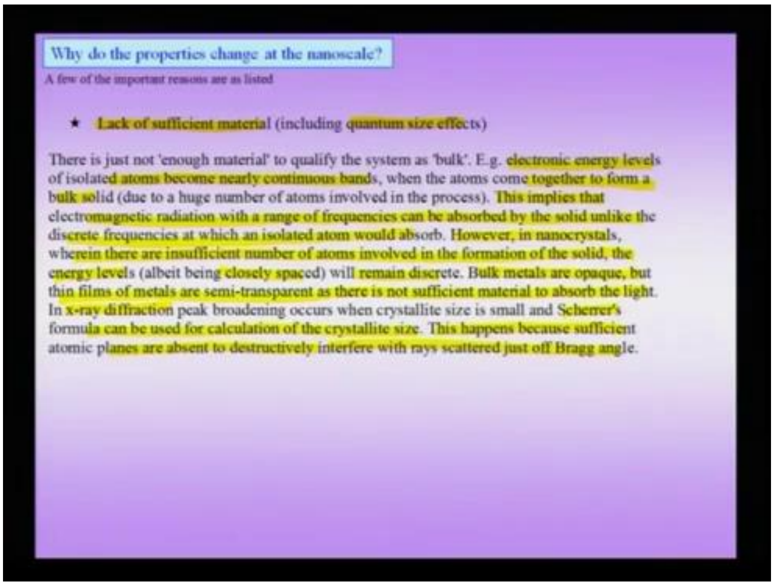

Why do the properties change at the nanoscale?

A few of the important reasons are as listed

- Lack of sufficient material (including quantum size effects)

There is just not 'enough material' to qualify the system as 'bulk'. E.g. electronic energy levels of isolated atoms become nearly continuous bands, when the atoms come together to form a bulk solid (due to a huge number of atoms involved in the process). This implies that electromagnetic radiation with a range of frequencies can be absorbed by the solid unlike the discrete frequencies at which an isolated atom would absorb. However, in nanocrystals, wherein there are insufficient number of atoms involved in the formation of the solid, the energy levels (albeit being closely spaced) will remain discrete. Bulk metals are opaque, but thin films of metals are semi-transparent as there is not sufficient material to absorb the light. In x-ray diffraction peak broadening occurs when crystallite size is small and Scherrer's formula can be used for calculation of the crystallite size. This happens because sufficient atomic planes are absent to destructively interfere with rays scattered just off Bragg angle.

So, we have already seen how properties can change as you go down to the nano scale and we are considered various methods by which can happen which have classified as ABCD, but we have ask every similar analyse question. Why do properties change in nano scale, we are listing here few of the important reason and we would note that they range from the most trivial. Perhaps, the most performed, so there reasons are sometime extremely trivial and therefore, there is what you meant called in some sense a laklashar reason you might call it.

On the other hand, there could be reason which is extremely performed, so we will start from one of what you meant called trivalent or simple kind of reason that there is actually a lack of sufficient material. We include here quantum size effects, but there is simply lack of sufficient material and therefore, the property changes to give an example. For instance, if we talk about bulk gold it is not transparent. Suppose, I make my gold foil very thin, it is become translucent, it is not that the inherit property of the gold is not to absorb because now when you through light on gold it is going to excite plasmon resonances.

Therefore, it is going to absorb light, but this there is not enough material to actually absorb all the light which is been thrown at it, therefore, in some sense this is an effect which may call lack of sufficient material. Let us take a few more example we know that electronic energy levels in isolate items become nearly continuously bands when they come to gather to form bulk solid. Typically, let me consider for instance bulk crystalline solid as there is huge number atoms involved in this whole process typically molar more, we can think of these energy levels to be so closed to be spaced that they arrive nearly continues.

We might called there a continues band kind of structure this implies the electromagnetic radiation with a range of frequency can be observed in the solid unlike the discrete frequencies which an isolated atom would absorb. So, these range of frequency has been observed this a pure effect because of the fact that there is continuous band and band can complete many kind of excitation. However, in nano crystals wherein insufficient numbers of atoms involved in the formational solid the energy levels could of course be close, this phase will remain discrete.

So, there is an insufficient number atoms to actually make what this band continues and therefore the absorption similarly, will tend to be discrete as compared to the case of what you meant called bulk solid which as nearly continues energy levels. We will take of more of these examples later on when we talk about electronic properties, but it is important note that this is of course, quantum size effects, but there is simplistic reason behind what is happening. We are already concerned this example that the bulk metals are big, but thin films are semi transparent as there is not sufficient material to absorb the light.

Of course, we are not taking about absorption of light we are talking about certain other kind of radiation this would equally a true if the that radiation can pass through less amount of items that it needs to encounter. Now, suppose a very related kind of phenomena we talk about which is x ray diffraction in x ray diffraction. We know that for instance I have a poly crystaline material if I reduce my green size to micron level and further I can use x ray diffraction to actually measure the crystallize size. This is because when you reduce the crystallize size the peeks in an x ray broad because peek broadening come from other effects like for instance strain come from stacking folds.

It can come from what meant a called instrumental broadening etc, but for now I have restricting myself to the peek broadening which is coming from x ray what you meant called the crystallize size. We typically use a schrrers formula for calculation of crystalized size and we know of course that the schrrers formula itself has a certain brazine which is sufficiently what you meant called can give crystalize size.

Now, this effect of broadening is happing because there is not enough amount of sufficient number of atomic planes to destructively interfere with the incoming bean. In other words, outside the bragg angle whatever distractive interference should take place there is not enough number of planes in the material to give us that destructive interference.

Therefore, we actually observe the peek broadening so this peek broadening in some senses is an effect which is purely coming from lack of sufficient amount of material or in the case of x ray diffraction lack of sufficient amount of crystallographic planes. So, when we go to nano scale you will observe that the peek broadening is more as I keep on reducing the crystallize size and this is the an effect, which is in some sense very simple effect coming from lack of sufficient material.

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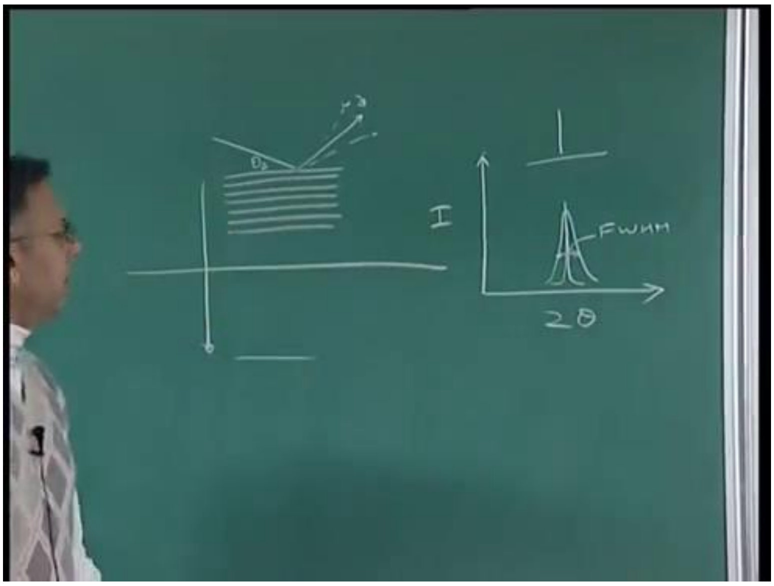

So, just to draw this schematically I know that suppose I have my atomic planes coming here I know that if I am sending beam at that Bragg angle, then I know that this beam will be diffractive. That means at this angle there will be coherent force scattering and at any angle which is away from this angle. For instance, the angle like this or angle like this there will be destructive interference, but for these destructive interference for this beam the plane which is out of phase which is topmost plane.

Actually, it lies deep within the crystal, the closer you get to this Bragg angle further down will be that plane which destructively interferes with this beam to get redact of that beam. Suppose, I truncate my crystal here that implies that not only this beam will continue to exist, but there will be range of beams surround it. These will continue to exist in the rewards 2 theta was intensively plot instead of obtaining sharp peak or more ideally delta peak, I would actually absorb abundantly. So, these broadening which is given by the full width half maximum comes from the fact that there is sufficient material to destructively interfere.

Therefore, cancel all the race which are of Bragg angle, which have broad angle therefore I can see that there are sufficient no of phenomena or certain kind of phenomenon, which can simply explain by the fact that there is insufficient material. Therefore you are getting certain a what you meant called different properties in nano scale and this should not be confuse with those more profound properties which we will come across. Those more profound effects which will take up soon, the second kind of properties which we have which is again to be accepted.

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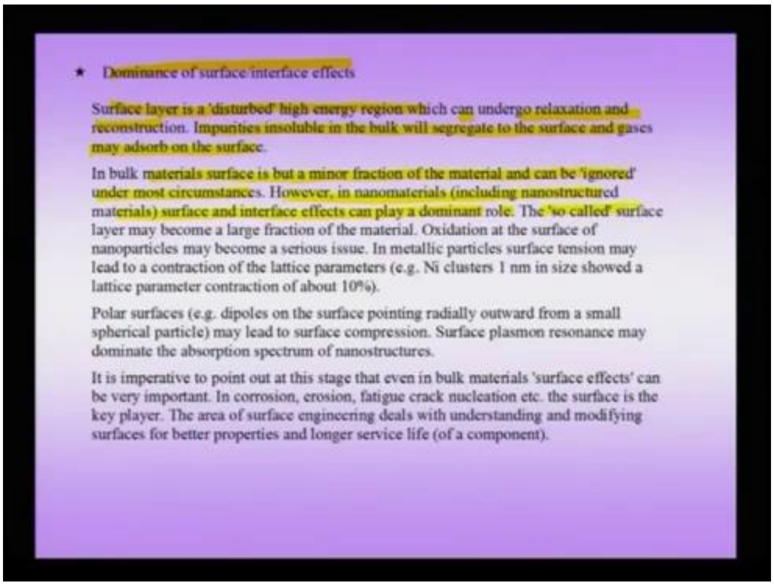

★ Dominance of surface/interface effects

Surface layer is a 'disturbed' high energy region which can undergo relaxation and reconstruction. Impurities insoluble in the bulk will segregate to the surface and gases may adsorb on the surface.

In bulk materials surface is but a minor fraction of the material and can be 'ignored' under most circumstances. However, in nanomaterials (including nanostructured materials) surface and interface effects can play a dominant role. The 'so called' surface layer may become a large fraction of the material. Oxidation at the surface of nanoparticles may become a serious issue. In metallic particles surface tension may lead to a contraction of the lattice parameters (e.g. Ni clusters 1 nm in size showed a lattice parameter contraction of about 10%).

Polar surfaces (e.g. dipoles on the surface pointing radially outward from a small spherical particle) may lead to surface compression. Surface plasmon resonance may dominate the absorption spectrum of nanostructures.

It is imperative to point out at this stage that even in bulk materials 'surface effects' can be very important. In corrosion, erosion, fatigue crack nucleation etc. the surface is the key player. The area of surface engineering deals with understanding and modifying surfaces for better properties and longer service life (of a component).

We have already seen some examples of these is dominance of surface and interface effects we know that surface layer is disturb layer which is higher energy region. This can undergo relaxation and reconstruction, so the surface layer because it is an high energy region to reduce this energy it may contribute relation because of lack of bonding in the perpendicular direction. Also, in some cases like silicon actually undergo a process known as the reconstruction.

That means the surface crystallography could be very different from the bulk crystallography impurities insoluble in the bulk will segregate to the surface and gases may also absorb on the surface. Therefore, maintaining the surface pure in most cases actually a difficult task in bulk materials the surfaces is, but a minor fraction of the material and can be ignored.

Under the most circumstances it is not that in bulk material the surface is very different from or may not be very different from nano materials or nano crystals. The point is that it can be ignored safely without causing much difference to a result fear calculating how were in nano materials including nano structures materials surface. Interface effects can a play a very important and dominant role these, so called surface actually may be become large fraction of the material because the surface is when we talking about the surface. We are not restricted of the cells to it just the mono layer on the surface, but sometimes what we defining as the surface could be few atomic dimensions into the crystal.

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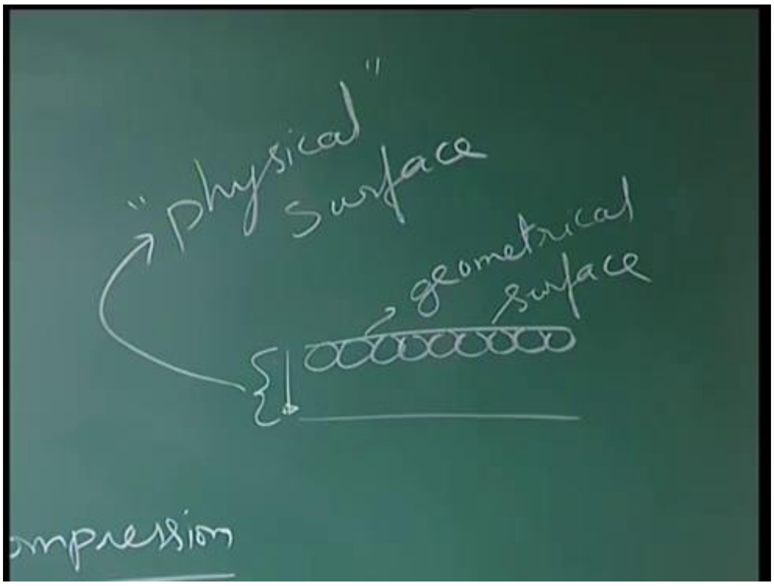

So, when you defining the surface of geometrically the surface implies the outer most layer, but suppose I am taking about relaxation and reconstruction I may want to go little deeper and actually talk about few atomic layers. And these physical surface has we pointed out can actually undergo things a effects like reconstruction and relaxation.

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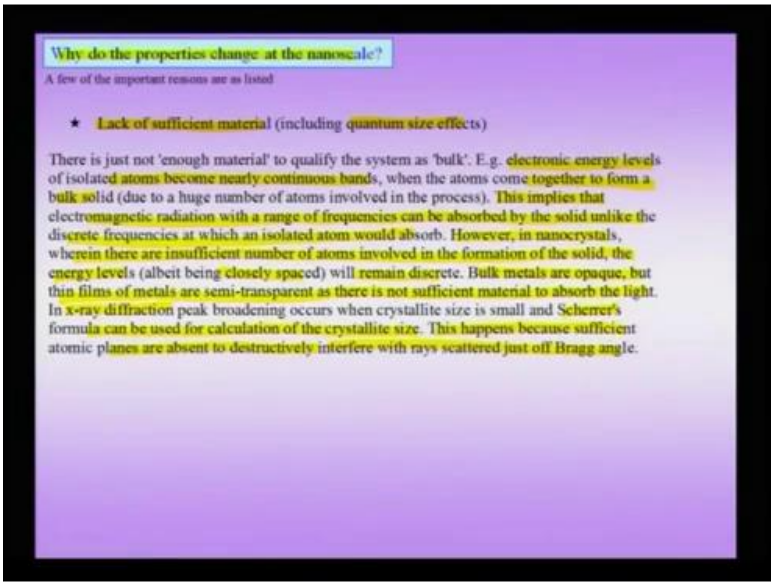

Why do the properties change at the nanoscale?

A few of the important reasons are as listed

- ★ Lack of sufficient material (including quantum size effects)

There is just not 'enough material' to qualify the system as 'bulk'. E.g. electronic energy levels of isolated atoms become nearly continuous bands, when the atoms come together to form a bulk solid (due to a huge number of atoms involved in the process). This implies that electromagnetic radiation with a range of frequencies can be absorbed by the solid unlike the discrete frequencies at which an isolated atom would absorb. However, in nanocrystals, wherein there are insufficient number of atoms involved in the formation of the solid, the energy levels (albeit being closely spaced) will remain discrete. Bulk metals are opaque, but thin films of metals are semi-transparent as there is not sufficient material to absorb the light. In x-ray diffraction peak broadening occurs when crystallite size is small and Scherrer's formula can be used for calculation of the crystallite size. This happens because sufficient atomic planes are absent to destructively interfere with rays scattered just off Bragg angle.

This surface because of is high energy is a recite oxidation and nano particles this may become very serious issue. So, surface can be a region of segregation surface can be region of absorption of gases, but further it may also oxidase therefore, there are certain there are more than one reason why this surface actually can change its composition. Therefore, cannot be treated like the bulk in terms of its various chemical effects and we already seen that how surface tension and an example shown here nickel cluster one nano meter in size can show a lattice parameter construction about 10 feet.

This is a huge fraction lattice parameter this is again coming from surface tensioning effects we also seen the case of polar surfaces. We considered surface compression effects can come into play and in cases where there is lot surface plasmon resonance may dominate the absorption spectrum in nano structures. So, when we talk about plasmon resonances in normal material of course, you can say that the surface plasmon resonance do not play much of role.

In case of nano material that may you can actually dominating the absorption spectrum, therefore it can see that the surface is special reason it exist in most materials. Of course, structure of surface itself could be altered as that go down to nano scale, but more importantly volume fraction of the surface. Now, I am talking about the physical surface is actually going to increase as go onto nano scale and this is going to alter the properties in a drastic way. It is again re entering the obvious thing that is that the bulk material surface effect can be very important and example of this is corrosion erosion fatigue crack nucleation etc.

In all these phenomena, we can clearly see that surface is the key factor for instance fatigue of a specimen which has been machine to a smoother finish would be very different from the fatigue of specimen which is pretty rough. If there is a way of surprising or reducing what you meant called the steps and inclusion and protrusion is produce during fergue testing. Then, the surface life or fatigue life of the component can be increased the area of surface engineering deals with understanding and modifying surfaces for better properties and longer surface life and surface engineering.

As you can clearly see its going to play a much more important role when you taking about the nano materials and nano structures and I am using what surface as we shall see during the many example we considered. We should not restrict our self only to external surface which is of course very important because it is that reason which is actually coming into contact with the outer part of the system. The outer world where which is now pointed as we say pointed out could be having gases, it could be having oxidizing atmosphere which could be the region from where certain impurities actually defuse into the system, but we should also take into account interfaces.

We shall we have already concern about the examples and return to the examples where in we see that surface and interface effects are very dominant effects. These effects which is present in all bulk materials can actually get accentuated in the case of nano materials and surface assumes a very important role. Nevertheless, this effect of dominant of surface and interface effects is what is what may called as accepted this is not something, which is what you meant called absolutely new or something, which is something new cannot explained in terms of simplistic argument.

So, we considered two reasons as to why property change the nano scale and both of them can what you meant can what you meant one minute argue come from simplistic argument one. It is of course lack of sufficient material this second of course this by dominant or dominance of surface and interface effects in the case of bulk nano structure material. The overall surface area does not increase its only the interface area which is the green boundary area which may increase as you reduce the green size of a poly crystal to the nano metrics range. Therefore, I have to have integrate approach where I am talking about the surfaces and interfaces when I am dealing with nano materials and nano structures.

The third is again one of those effects which we may call an obvious effect, which is coming from the proximity of the surface to the bulk. So, this comes again in the class of those reasons which as one might sake one can actually easily anticipate easily predict and easily, perhaps even calculate when it comes to how a nano materials is different in since properties from bulk materials.

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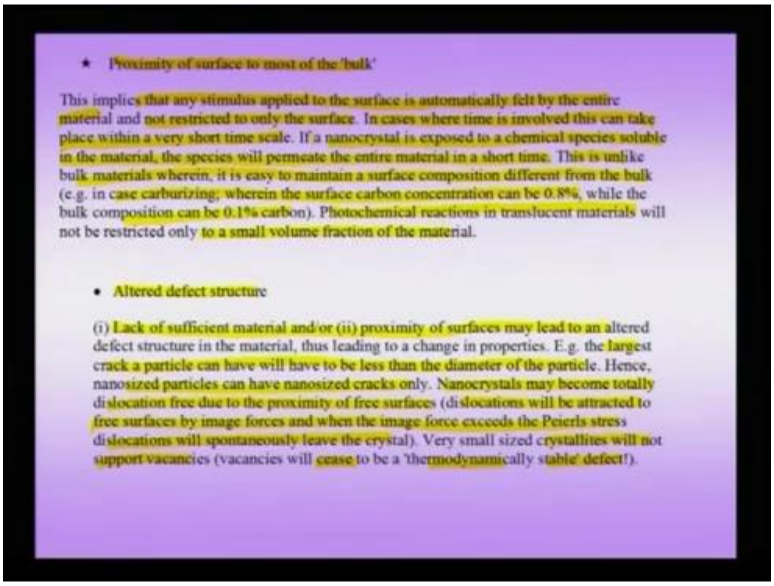

- **Proximity of surface to most of the 'bulk'**

This implies that any stimulus applied to the surface is automatically felt by the entire material and not restricted to only the surface. In cases where time is involved this can take place within a very short time scale. If a nanocrystal is exposed to a chemical species soluble in the material, the species will permeate the entire material in a short time. This is unlike bulk materials wherein, it is easy to maintain a surface composition different from the bulk (e.g. in case carburizing; wherein the surface carbon concentration can be 0.8%, while the bulk composition can be 0.1% carbon). Photochemical reactions in translucent materials will not be restricted only to a small volume fraction of the material.

- **Altered defect structure**

(i) Lack of sufficient material and/or (ii) proximity of surfaces may lead to an altered defect structure in the material, thus leading to a change in properties. E.g. the largest crack a particle can have will have to be less than the diameter of the particle. Hence, nanosized particles can have nanosized cracks only. Nanocrystals may become totally dislocation free due to the proximity of free surfaces (dislocations will be attracted to free surfaces by image forces and when the image force exceeds the Peierls stress dislocations will spontaneously leave the crystal). Very small sized crystallites will not support vacancies (vacancies will cease to be a 'thermodynamically stable' defect!).

This proximity of surface to the bulk implies the at any stimulus applied on the surface is automatically felt by the entire material, so this is very special case and this is not restricted to this surface.

Suppose, I am talking about photochemical reactions in translucent materials, this will not obviously restricted only to the surface, but the entire volume of the material could be effected by these photochemical reactions this is one example. For instance to tell you that in nano materials the reason called surface and the reason called the interior may be very closely and intimately and interconnected which makes difficult for us. For instance to avoid certain effects which will take up here and in cases where time is involved, this can take place then enough word for instance very short time scale. In another words, if I stimulus in the surface which could be chemical specious it could be for instance some kind of oxidizing atmosphere.

Then, entire bulk of the material or the entire volume of the material will feel this stimulus of within a short time scale if a nano crystal exposed to a chemical species like a soluble in the material. The species will permeate the entire material in a short period of time this is unlike bulk materials, where in it is easy to maintain a surface composition different from the bulk composition and we have seen such an example before that in the case of case carburizing.

The surface carbon concentration can be as 0.8 percentage while the bulk composition can be 0.1 percentage, so to summarize this aspect that in nanomaterial the entire material could be will within what might called an handshake or proximity to this surface. Therefore, now I cannot say that I will imply certain stimulus or certain chemical specious on the surface and expect only the surface to affected in case of bulk material. Typically, you would call few millimeters even as the surface, but in the case of nano material which itself is totally may be 100 nano meters in size the entire bulk could be affected when you try to impose a chemical specious.

If this specious soluble in the material it will completely diffuse into material and you will have an what you meant called the middle of the material feeling the excess composition which you are imposed. We are talking photo chemical reaction entire material will be effected and therefore, it is now difficult for me to actually isolate my bulk from the surface. Therefore, I have to read the whole system as one system in many cases many of the effect as we have seen actually arises from the proximity of the surface to the bulk one subset of these is also worthwhile to be considered is the case of altered defect structure.

This we shall see come from lack of sufficient material or proximity of surfaces that means we are talking about alter defect structure coming from some of the effect. We have now just seen which is proximity of the surfaces as in the slide or the case of lack of sufficient material. So, these effects we have seen now can actually lead altered defect structure in the material and as you can see if the defect structure is altered. Then, automatically you are going to have an alter set of properties which is going reflect in terms of performance of the material or the component, which is material used to construct.

The example could be largest crack a particle can will have has to be less than the diameter of the particle if the crack extends throughout the particle, of course particle will break into two. Therefore, two particles instead of one therefore, the largest crack that the material nano particle can sustained would also be a nano dimension. Therefore, nano sized particles can only have nano sized cracks only we will notice that nano crystals may become totally dislocation free due to the proximity of free surfaces we will take up this topic later on in little more detail.

Here, dislocations will be attracted to free surfaces by this images forces and when this image force exceeds what is known as the inherent laities friction of the material which is otherwise called pearls stress dislocation will spontaneously leave the crystal. Very small sized crystallites may even not support vacancies that means vacancies will cease to be a thermodynamically stable defect in nano crystal. So, this may also happen and we will have little more to say about this topic of alter defect structure in one another coming lecture.

The important point is that because of lack of sufficient material or because of approximately surfaces you actually will have a alter defect structure. One of these for instance lack of sufficient material would lead to what you meant called reduce configuration stabilization of a vacancy. Therefore, nano crystal or nano crystal will become completely vacancy free and proximity of free surface could implies that the image force experience by dislocation may also exceed the pulse stress and system may become spontaneously dislocation free.

So, these interesting effect or arising because of what we just now talk approximately of the bulk and lack of sufficient material. So, there are these three and effects which are finally, giving rise to what you meant called an alter defect structure and when we define micro structure we said that micro structure sensitive property are going to be sensitive to the defect structure. My defect structure is part of the definition of microstructure in our scheme of things and therefore you notice that those property would drastically change.

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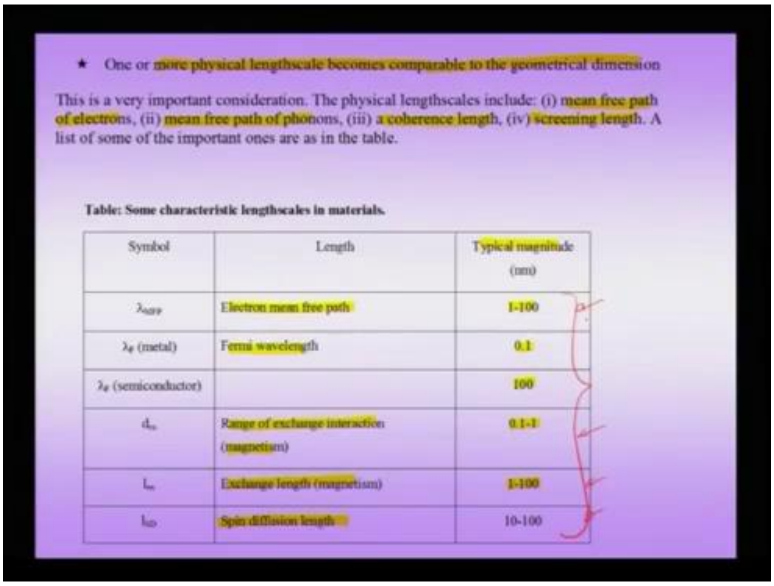

- One or more physical lengthscale becomes comparable to the geometrical dimension

This is a very important consideration. The physical lengthscales include: (i) mean free path of electrons, (ii) mean free path of phonons, (iii) a coherence length, (iv) screening length. A list of some of the important ones are as in the table.

Table: Some characteristic lengthscales in materials.

Symbol	Length	Typical magnitude (nm)
λ_{MFP}	Electron mean free path	1-100
λ_F (metal)	Fermi wavelength	0.1
λ_F (semiconductor)		100
d_{ex}	Range of exchange interaction (magnetism)	0.1-1
l_{ex}	Exchange length (magnetism)	1-100
l_{SD}	Spin diffusion length	10-100

When you alter the defect structure, but there are other reasons and this is the alternate way of looking at same problem. In some sense, some of these can thought of a profound effects that where in one or more of physical length scale becomes comparable to the geometrical dimension of the system. So, suppose I have crystalized size, then one of the physical parameter which governs physics the problem may actually become the length scale of that physical entity may actually become comparable to the length scale of the physical system we are considering.

This could be an nano crystal, for instance there are we will talk about these various quantities in relevant chapter, but some example could be that the crystallize size could be comparable to the mean free path of electrons. It could become equal to the mean free path of phonons, it could be a coherence length in the material, which matches the length scale of material which is now comparable to the size of the material.

There can be many more property, it could be a screening length in the material which is now comparable to the size of the material. There can be many more properties which we can list which all contribute, finally to the profound effect which comes in nano materials because as you can see that if you have already seen such example. Let me take this same example again is the case of spin diffusion length becoming equal to the length scale of the material.

Before I take of that example, so let me see that in the stable, there are quantities electron mean free path the Fermi wavelength the range of exchange interaction. For instance, this is now relate to the magnetism and this a very important quantity and we can also talk about exchange length in the magnetism. There is a typical length scale associated with these physical properties, for instance the electron means free path typically vary from 1 and 100 nano meters the Fermi wavelength is the much smaller number numerically in semiconductor. The Fermi wavelength could be larger and in the case of exchange interaction, again it can range from 0.1 to 1 nano meters.

In the case of exchange length and magnetism, it can have a wide range from 1 to 100 nano meters, so when my particle or crystalize size starts approach any of these dimension. Of course, if I am taking about magnetic material, I would worry about some of these effects here when I am talking about the conductivity I would worry about the electron mean free path. Then, I would see that my properties are going to drastically change when I go to the nano scale at the heart as you can see here more profound effects here because the fact that the now I am not nearly saying the material becoming the smaller.

It is not the gradually effect which is going to change, but it could drastically change when I hit these magical numbers of these physical quantity below which my length scale has is going to lead to drastic change in properties. So, since we consider this one examples as we reiterate that example is the case of spin diffusion length.

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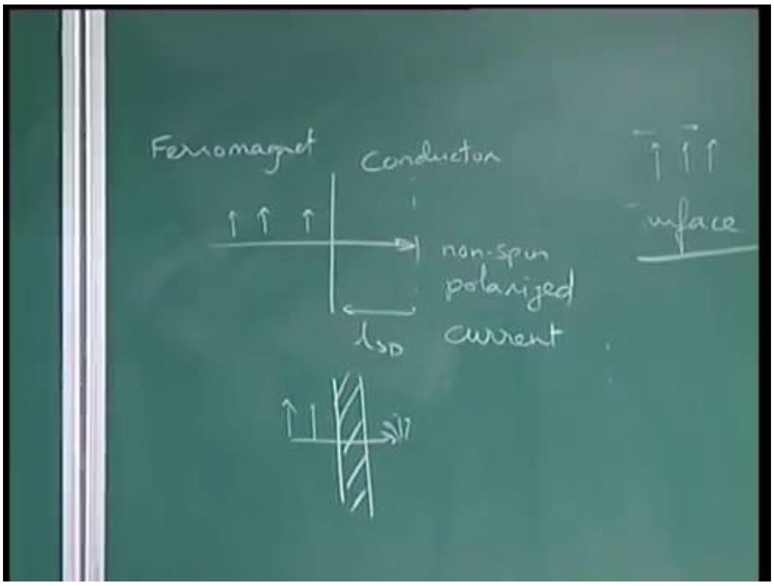

So, suppose I take a conductor on the right hand side this is the normal conductor and these is now ferromagnetic and I pass current from left to right, so what would happen is that the current which comes would spin polarize into the material. So, I have a spin polarize current defuse entering this material, but because now this is not a magnetic material the spin memory of this spin polarize current would die down after a few scattering events.

Therefore, after some time, this would not be a spin polarize current, so you have after certain distance which is now my spin diffusion length. I would have a, so it is very clear that all my spin memory dies away after a certain stage, I would have an normal current just found in normal conductor.

This is because the scattering event which should take place in the normal conductor, but suppose now my length of the whole conductor which I am talking about this very small and which is what we consider as the sandwich layer in the system. Then, the spin memory will not completely died, of course there will be the certain randomization. So, I will show the spin memory may be slightly randomize, but still there will be the spin polarization and the system. The current will continue to be spin polarize even after passes through this conducting layer, therefore you can see that here even through in some sense this also lack of sufficient material you might say.

There is a fundamental physical length scale involved here which is my spin diffusion length with which I can co relate now my what you might called the physical parameter can be co related with length scale in the size length scale of the system. Therefore, you can see that profound effect start to appear when you actually go down below the size length scale and we will consists some of these in the upcoming topics. So, just to summarize the set of important question that why do the properties change the nano scale it could be because of lath of lack of sufficient material.

It could be because of dominant surface and interface effects, it could be because of proximity of surface to most of the bulk it could be because of some more these effects giving rise to alter defect structure. Finally, of course if one or more physical length scale becomes comparable to the geometrical dimension of the system, then I would accept that certain drastic new properties will arise in the system. We have been actually listing some important reasons why the property could change, but one other extraneous kind of reason also is worthwhile considering here.

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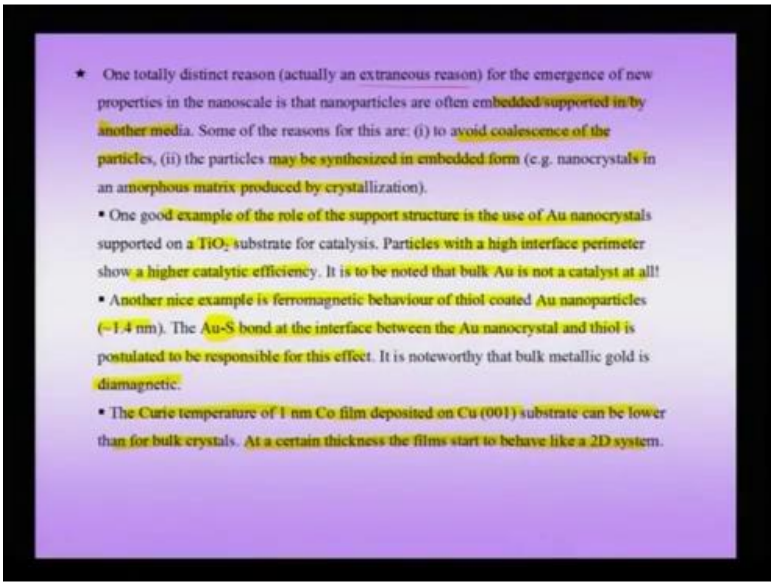

★ One totally distinct reason (actually an extraneous reason) for the emergence of new properties in the nanoscale is that nanoparticles are often embedded/supported in/by another media. Some of the reasons for this are: (i) to avoid coalescence of the particles, (ii) the particles may be synthesized in embedded form (e.g. nanocrystals in an amorphous matrix produced by crystallization).

- One good example of the role of the support structure is the use of Au nanocrystals supported on a TiO_2 substrate for catalysis. Particles with a high interface perimeter show a higher catalytic efficiency. It is to be noted that bulk Au is not a catalyst at all!
- Another nice example is ferromagnetic behaviour of thiol coated Au nanoparticles (~1.4 nm). The Au-S bond at the interface between the Au nanocrystal and thiol is postulated to be responsible for this effect. It is noteworthy that bulk metallic gold is diamagnetic.
- The Curie temperature of 1 nm Co film deposited on Cu (001) substrate can be lower than for bulk crystals. At a certain thickness the films start to behave like a 2D system.

Through truly speaking, this is not same class of reason which we are now talked about this is because when we actually for instance synthesis manufacture. Some of these nano particles or nano crystal or nano phase materials they may not be free standing. They are often embedded or supported by some another media, so even through for some other instance I want to use gold nano particles of catalytic application.

I cannot have free standing gold nano particles because this will be carried away by the medium and I would like to embedded them on the surface or actually supported on the surface or second media of which is of straight. This is accentual for its being continued be part of the system and act like effective catalytic, now some of the reasons why we other reasons why we want to do it just to avoid the coalescence of the particles. Suppose, I put together gold nano particles, they will coalescence, actually they will may grow with time.

Actually, and not lead to a green size become the larger than the nano crystals with which we started the second reason of course is that the particles may be synthesized in embedded form. For instance, when I talking about nano crystals in an amorphous matrix it may be produced by crystallization of the amorphous matrix. Therefore, it is by design or by default embedded in an amorphous matrix, so it is not an free standing nano particles and therefore, I cannot avoid taking into account the effect of the matrix or effect of the supporting of the medium. Sometimes, we shall see as we already seen that the effect of the supporting medium actually could be positive.

One good example of the support structure we have seen is the case gold nano crystal supported on its substrate which could be for instance titanium substrate for catalysis particles with a high interface perimeter show higher catalytic efficiency. It is to be noted that bulk gold is not a catalytic at all, so we have seen this example before that gold in the nano scale can become can shown catalytic activity. In fact, it can be a very good specific catalyst for a certain kind of reaction, but the role of the substrate of supporting medium cannot be ignored. Here, it is seen that those particles which have larger perimeter of support for instance suppose I had two gold particle one like this.

The other one this has the larger perimeter would support and this shows higher catalytic activity as compared to this which has lower perimeter of contact which has little shown lower catalytic activity. Therefore, clearly gold is become a catalytic at the nano scale, but the role of the interface in the support structure is also playing a very profound role in the whole property.

Another nice example is ferromagnetic behaviour of the oil coated gold nano particles and we have talking about the gold nano particles is of the size about 1.4 four nano meter the gold sulfur bond at the interface between the gold nano crystal.

Then, thiol is postulated to be responsible for this effect, so you don't accept gold to be Ferro magnetic neither is thoil Ferro magnetic. Then, how is that this combination golden thiol is becoming ferro magnetic, so it has been postulated the gold surfer bond is actually at the interfaces is responsible for that. Therefore, you can see that the interface itself which is of course coming from the way gold is dispersion the thoil is playing a very important role in the emergence of totally new property.

Here, gold is normally diamagnetic and this embedding is coming a ferro magnetic behaviour. So, absolutely new property can emerge there can b enhancement in the property in the case of catalytic activity. One more example we would like considered here the curie temperature of 1 nano meter cobalt film deposited on copper 0 0 1 substrate can be lower than that for bulk crystals. at a certain thickness the films start to behave like a 2 d system.

So, in this case again cobalt film is influenced by the copper substrate and if of course I am talking about epitaxial film epitaxial would further influences the way that the magnetism is going to be present in this material. Nnevertheless, in all the system you can see that you are having support medium, because it is difficult to produce one nano meter cobalt film as a free standing film. It will tend to war and it will not be a flat film even and it may be difficult to study this properties free standing film.

Typically, therefore, it is on a substrate or on a support medium and this support medium could actually be influenced the property of the system as the whole. This may have to be taken into the account when you talking the properties of material or the properties of the nano scale system. And as you can see not truly property of nano crystal itself, but property coming in some sense from an extraneous reason.