Nanoelectronics: Devices and Materials
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Lecture - 31
Introduction to Nanomaterials

Hello I am S A Shivashankar from the Centre of Nanoscience and Engineering at the Indian Institute of Science and

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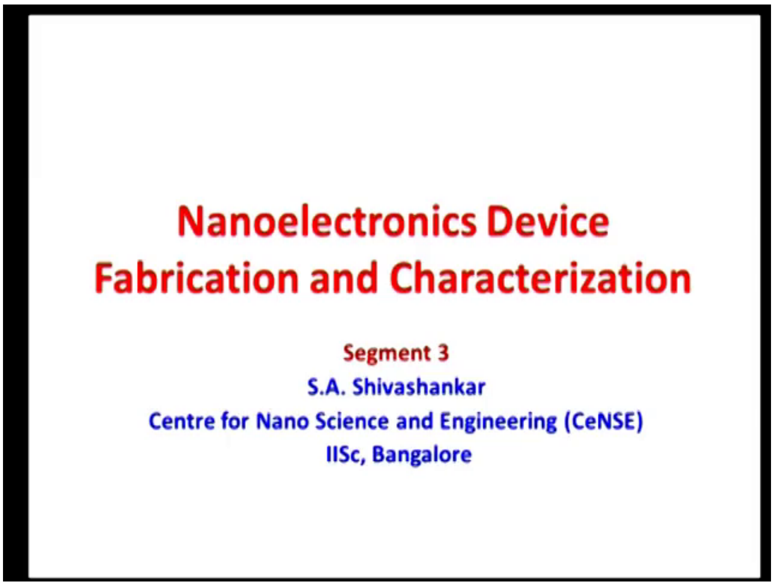

I will begin today with the segment 3 of the course Nano electronic Device Fabrication and Characterization about which you have already heard from Professor Ramakanth Bhat and Professor K N Bhat in earlier segments and those segments have dealt with device fabrication, scaling of devices basically silicon devices using essentially principles of scaling that are now well understood and even though scaling has taken devices now through the level of Nanometre length scales that are the feature sizes of silicon circuits today in VLSI, they still do not make use of properties of materials at the Nanoscale.

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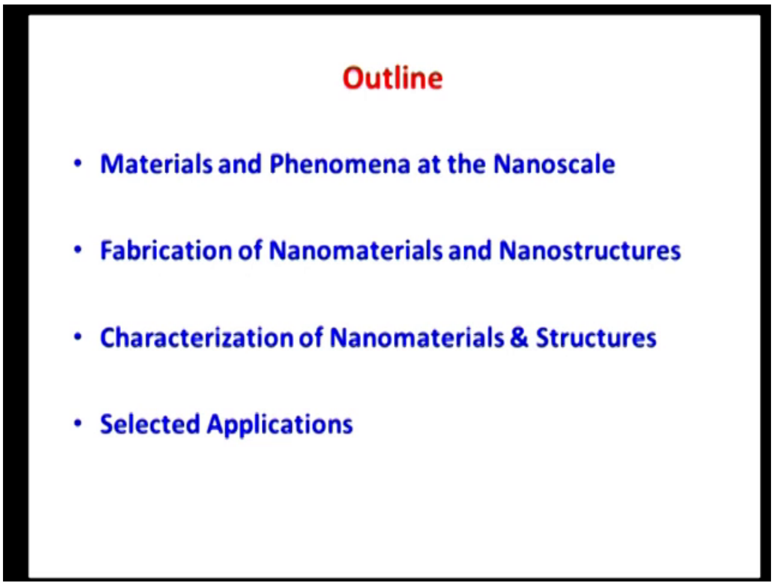

So, what I proposed to do in this segment of the course is to deal with material and phenomena at the Nanoscale, fabrication of such nanomaterials or nanostructures, characterization of these nanomaterials and structures and maybe some devices and some selected applications. Therefore this segment of the course actually deals with materials and their properties at the nanometre scale which I shall define shortly.

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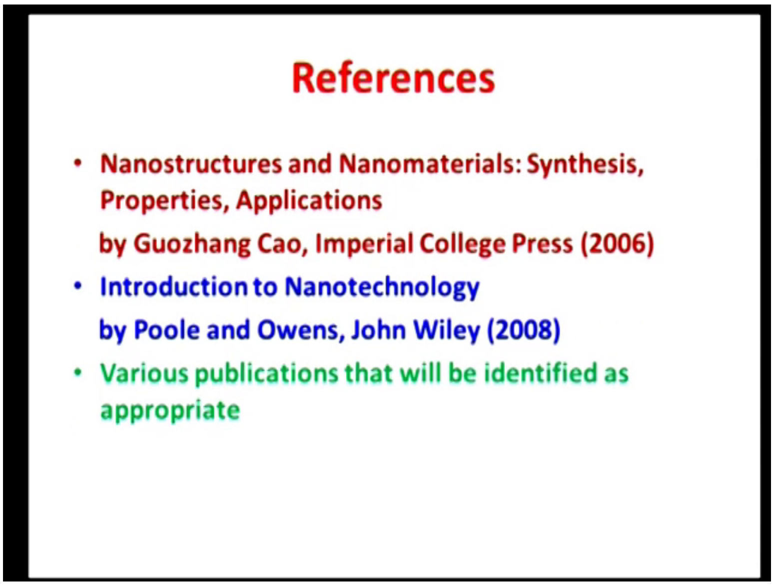

I think it is appropriate now to say that you know a certain number of references are useful, numerous books have been published on nanomaterials, nanostructures and devices and so, forth. But I have just listed 2 of them here because they are generally well known and they have undergone a couple of additions, one is the book by Guozhang Cao and the other one is the book by Professor Poole and Owens and as we go along I will also refer to various publications in different lectures that are relevant to the material of discussion on hand.

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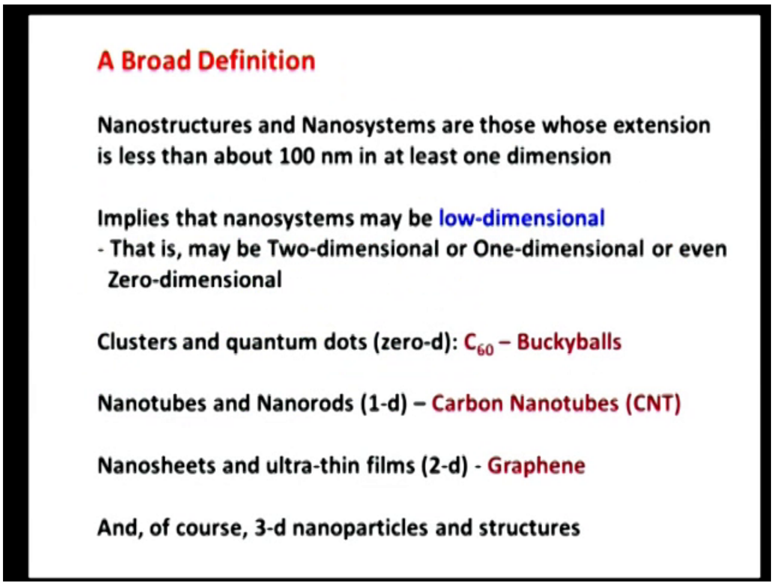

What is nano materials, nano structures and nano systems, a broad definition is in order nanostructure or nano systems are those who whose extension is less than about 100 nano meters in at least 1 dimension, what it immediately implies is that nano systems maybe low dimensional, that is they may have less than 3 dimensions with which we normally familiar. So, there may be 2 dimensional materials 1 dimensional or even 0 dimensional and there are already pretty familiar examples on these things and very interestingly all these examples that I have sighted here are made of elemental carbon.

So, quantum dots or 0 dimensional systems are exemplified by C60 or Buckyballs, Nanotubes and Nanorods are exemplified by Carbon Nanotubes which are now very well known and the most recent one is the 2 dimensional system namely the graphene sheet which is a single layer of carbon atoms that is of the graphite structure and of course, 3 dimensional particles and structures also in the nanometric size.

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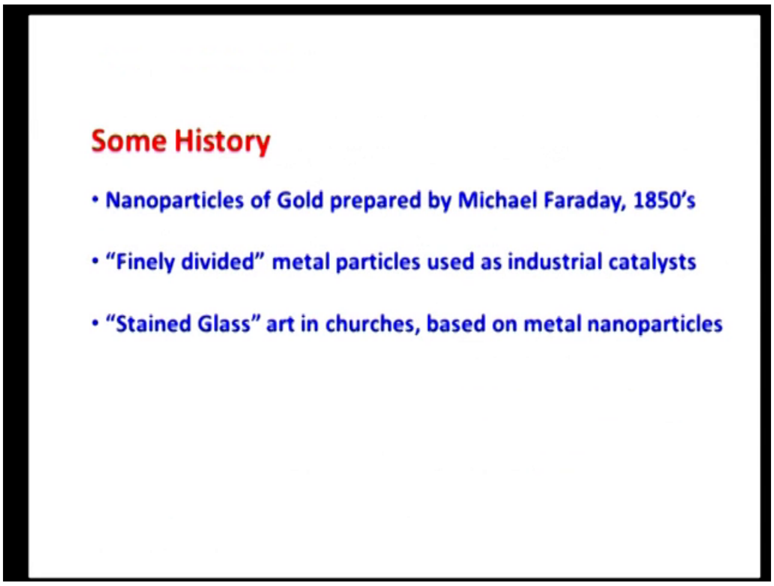

Now, some history is in order while nanotechnology, nanomaterials, nanoscience and so, on are very much in work today and a field of great deal of investigation. It is useful to remember that nanoparticles were prepared nanoparticles of gold prepared in the 1850's by Sir Michael Faraday by a technique that is pretty much similar to what people use today and in industry catalyst made of fine the divided particles in those days of course, the terminology if nanoparticles and nanosystems was not there, people called them finely divided particles. Finely, divided metal particles were used as industrial catalyst and certainly a spectacular use of nanotechnology of those days are stained glass art in churches (Refer Time: 04:40) in Europe which make use of metal nanoparticles. Therefore, all these 3 are examples of nanotechnology of those days, not necessarily a nanoscience.

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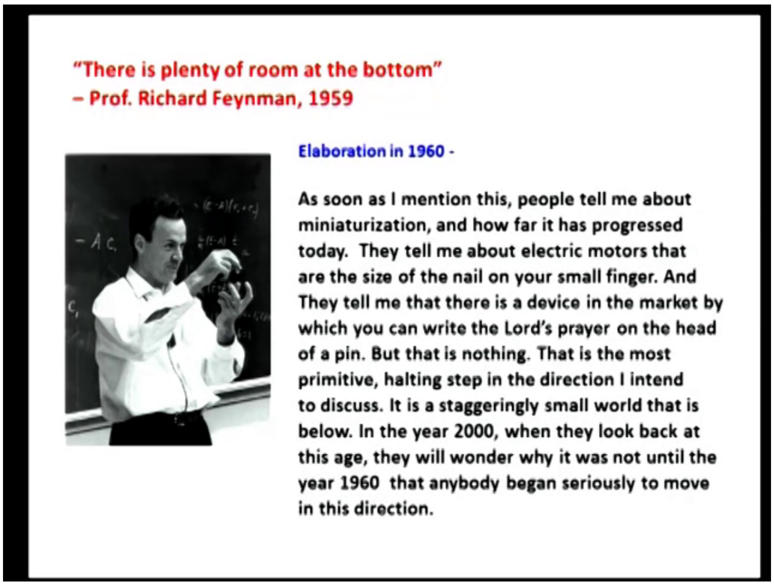

Now, you probably I heard of a famous statement by Nobel laureate Professor Richard Feynman. He said in 1959 in a talk at the American physical society that there is plenty of room at the bottom, what he meant was that while macroscopic material was very interesting and under great investigation in those days in the period of solid state physics development, what he meant was that as one reduced dimensions of objects to the extremely small sizes beyond the visible region.

Beyond the limits of what I can see then phenomena that occurred there were very interesting and what he actually anticipated in those days was scaling down of devices to such a degree that very very different phenomena would become possible and I want to read here what he said was that you know it is staggeringly small world that is below in the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction. He anticipated that the world underneath, to speak was really going to be very very interesting and in fact defining.

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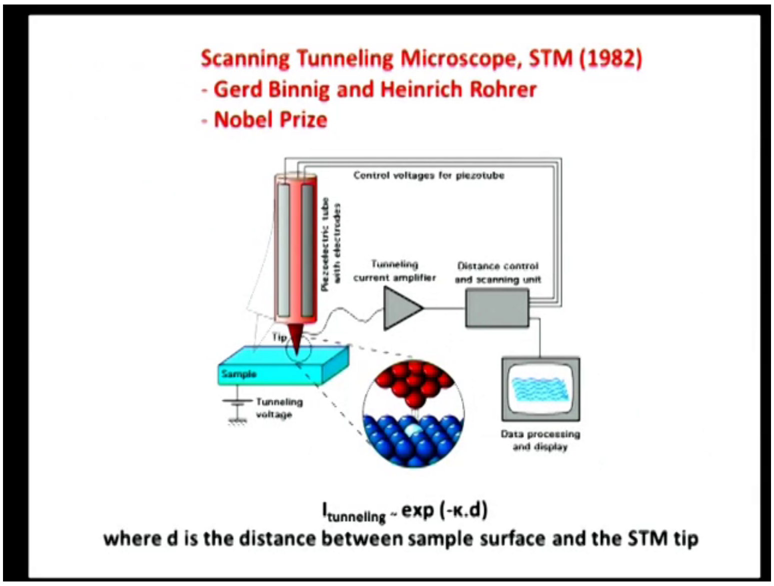

It is possible to say that the actual era of nanoscience and technology that we are in began in some way with the invention of this scanning tunneling microscope in about 1982 for which a Nobel Prize was awarded, where actually a quantum phenomenon was used as a way to look at materials on a very fine scale. In as Scanning Tunneling Microscope a very fine tip made of a metal comes very close to a surface which it is investigating also of a metal in other words both are electrical conductors and when even though they not in touch because of the phenomenon of quantum tunneling a current flows between the sample and the tip, this call a tunneling tip and this enables a close examination or taking a picture of the surface of the sample.

This was actually made possible by the invention of (Refer Time: 07:34)) electric materials ceramic (Refer Time: 07:36) electronic materials actually in the bulk which made possible controlled motion on a nanometric scale. Actually a ceramic technology of microscopic dimensions enabled the invention of a device that would resolve objects into nanometric size

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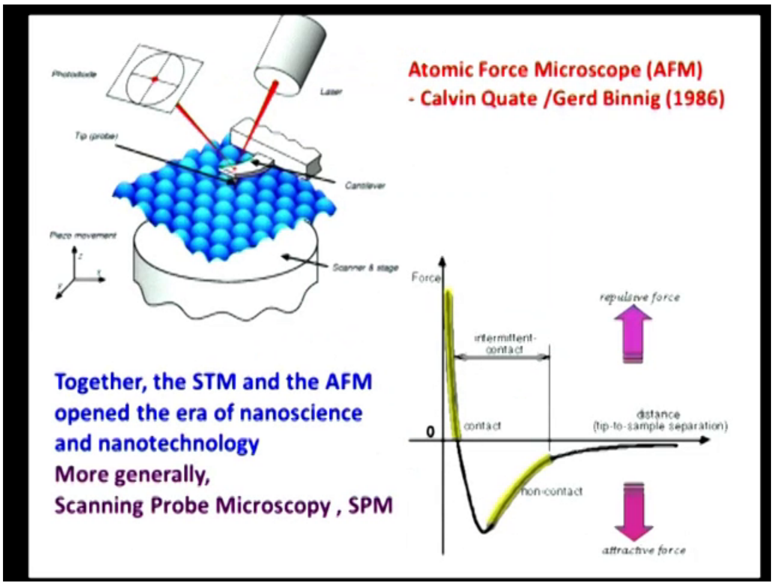

Soon after followed the atomic force microscope in 1986 while the limitation of this scanning tunneling microscope was that it could only look at electrically conducting or metallic objects the atomic force microscope is different in the sense that it really measured the force between an atom on a sample and a tip on the at atom at the tip of your probe so, that it did not depend on the electrical conduction that would we required in an STM.

This force actually exist between any 2 atoms and therefore, it makes no distinction between a conducting surface and a non conducting surface, as a result of it was possible to probe the surfaces of any kind of a material whether conducting or non conducting and in fact, the Atomic Force Microscope has really become the principle on which a more general technology known as scanning probe microscopy through which one can measure electrostatic forces, magnetic forces and so, force spheres of forces.

In all these technologies that are based on this AFM it has been become possible to look at objects on a very fine scale, equally importantly the atomic force microscope and the scanning tunneling microscope of today can look at objects in the ambient while objects had been looked at in electron microscopes those generally require a vacuum and a pretty elaborate systems. The atomic force microscope really enabled the birth of nanotechnology of today because it is possible through an AFM or a similar device to look at objects in the ambient on a table top so to speak, you could say that the current era of nanoscience and technology began with the Atomic Force Microscope.

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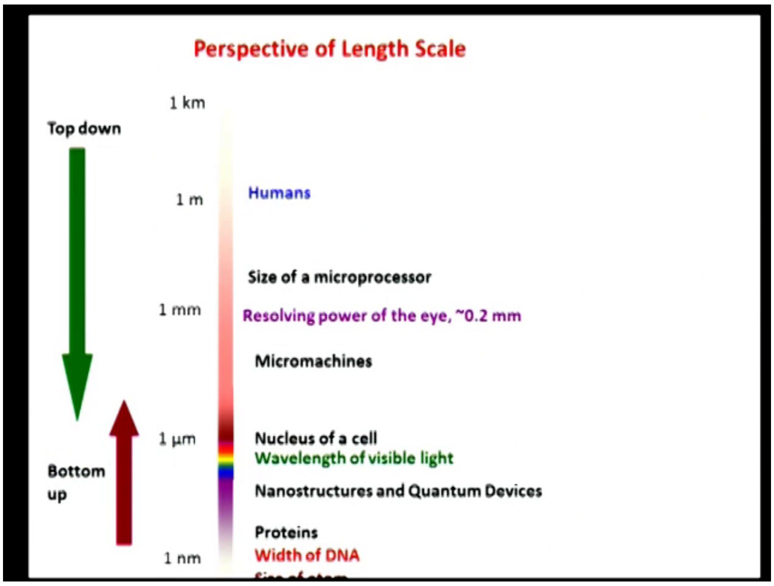

Now, some idea of the lens scales involved, what I have shown here is the scale of things human scale show as opposed to the microscopic scale, we are interested at the bottom of the scale on the view graph where we are talking about somewhere between 1 and 100 nanometres where different kinds of nano structures and quantum devices and of course, natural objects like proteins and DNA and so on belong.

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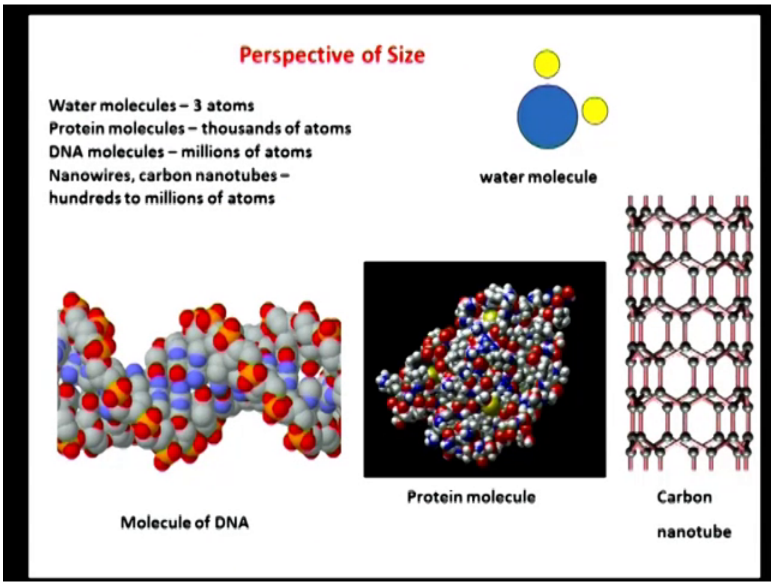

These are examples where we have a molecule of a DNA which can contain millions of atoms nanowires and carbon nano tubes which can contain hundreds to millions of atoms depending on the length and so, forth, these are all objects of interest in the current nanoscience nanotechnology a context.

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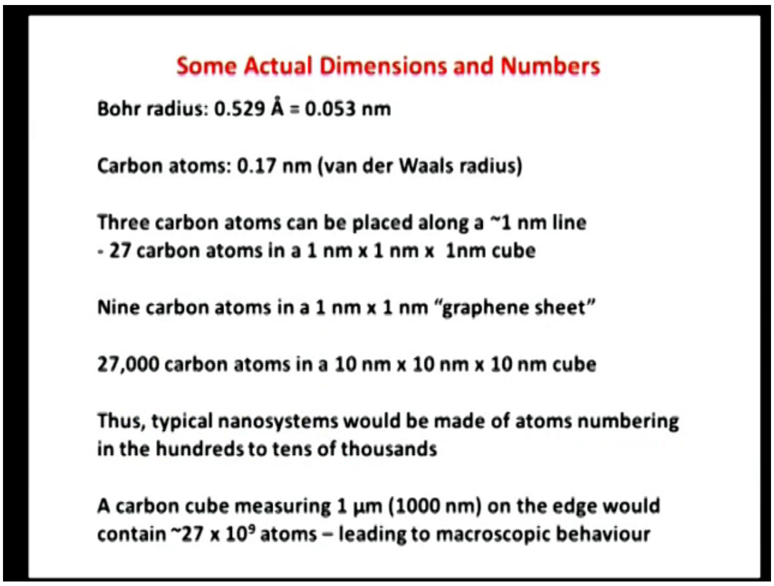

It is always useful to have an idea of actual dimensions and numbers the Bohr radius which is the radius of the first orbit in the hydrogen atom measures 0.053 nanometers or half an angstrom. The van der Waals radius of a carbon atom is about 0.17 nanometre, 1.7 angstroms and it is possible to line up 3 carbon atoms along a 1 nanometre line. If you had a cube measuring 1 nanometre by 1 nanometre by 1 nanometre of carbon atoms it will contain 27 carbon atoms or in the current graphene sheet which is a 2 dimensional object measuring 1 nanometer and 1nanometre then you would have 9 carbon atoms and in a cube of 10 nanometers on the edge there would be 27,000 carbon atoms.

Now you could say that a typical nanosystem would be made of 100 to 10s of 1000s of atoms, by comparison if you had a carbon cube measuring 1 micrometer on the edge or 1000 nanometers on the edge it would contain something like 27 billion carbon atoms that is already a large collection it is no longer in the nano region and the behaviour of a such a an object or a particle would be the same as the behaviour of a microscopic object, it is no longer in the nano region.

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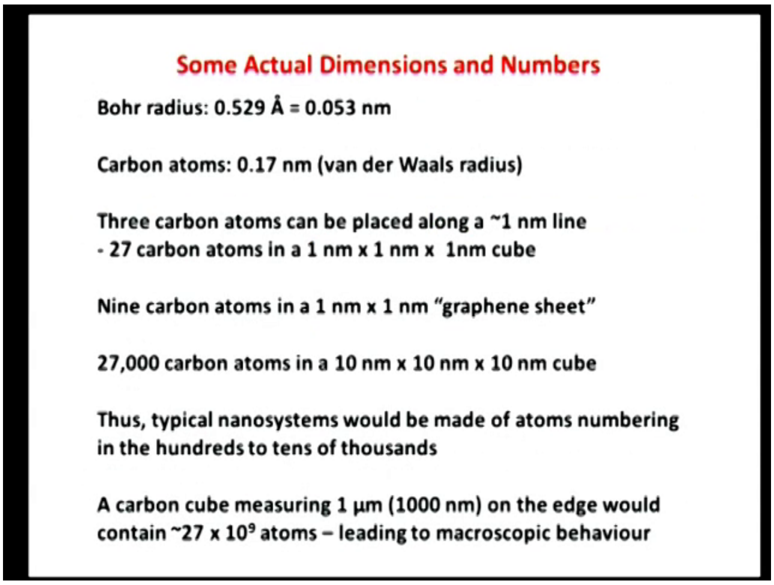

Now, atoms we all know for example, the Bohr radius the treatment of the atom and the hydrogen atom and so, on requires a proper understanding of the behaviour atoms requires quantum mechanics, it is necessary to apply quantum mechanics understand the behavior of atoms.

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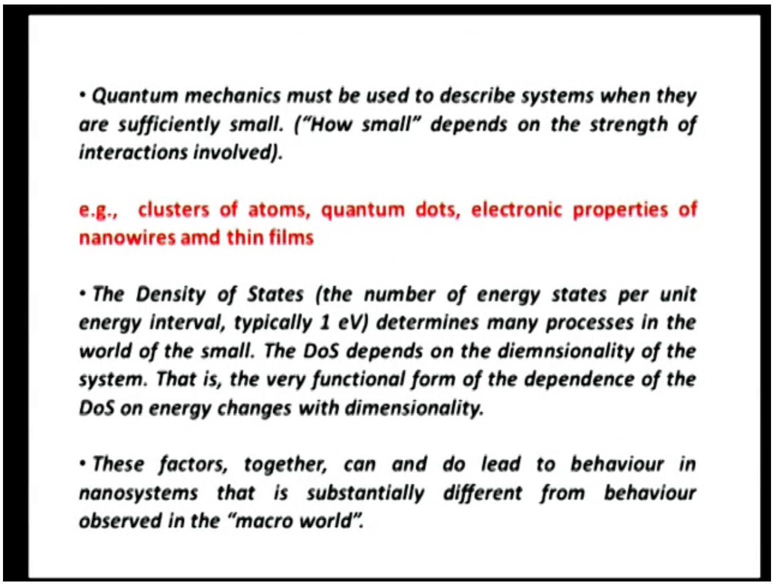

When does the in other words quantum mechanics is required when systems are sufficiently small, how small that is depends on the strength of in interactions involved will come back to that, for example, clusters of atoms, quantum dots, electronic properties of nanowires and thin films and so, forth would require quantum mechanical description to be able to understand the behaviour fully. In essential aspect of s such an approach is the concept of the density of states that is the number of energy states per unit energy interval, typically 1 electron volt. This density state determines many of the processes in the world of this small it depends on the, it is important to know that the density of states depends on the dimensionality of the system.

That is whether it is a one dimensional 2 dimensional 3 dimensional system or even 0 dimensional therefore, the very functional form of the dependence of the density status on energy depends on the dimensionality. These factors that you require quantum mechanics to describe nano systems and important sense of the density of states together can and lead can and do lead to the behaviour in nano systems that is substantially different from the behaviour observed in the macro world.

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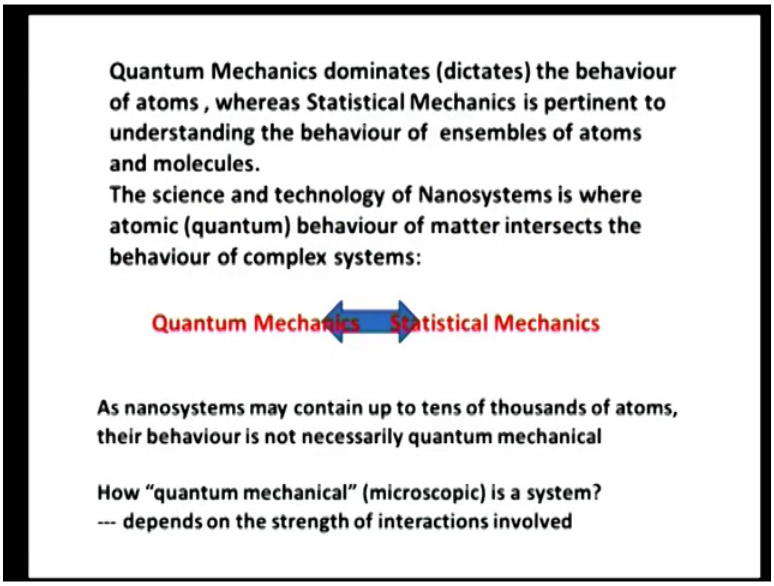

As I just said quantum mechanics dominates or even dictates the behaviour of atoms where as a different discipline statistical mechanics is actually pertinent to the understanding of the behaviour of ensembles of atoms that is large collections, microscopic collections of atoms and molecules are described with the help of statistical mechanics because it is not possible to follow the motion of individual atoms in a large collection.

Therefore they can such a large collection can be described by statistics now on the one hand you have nano systems where your are atomic systems where you require quantum mechanics, on the other hand you have nano systems where you have 100s or 1000s of atoms that are involved. So, actually the science and technology of nano systems where is where the quantum behaviour the atomic behaviour of matter intersects with the behaviour of complex systems which requires statistical mechanics. So, you have an intersection now of quantum mechanics and statistical mechanics that is up appropriate to understand nano systems as I said nano systems may consist of 10s or 1000s of atoms and the their behaviour is necessarily quantum mechanical and as I said how quantum mechanical how microscopic depends on the strength of interactions of a particular system will talk to that later.

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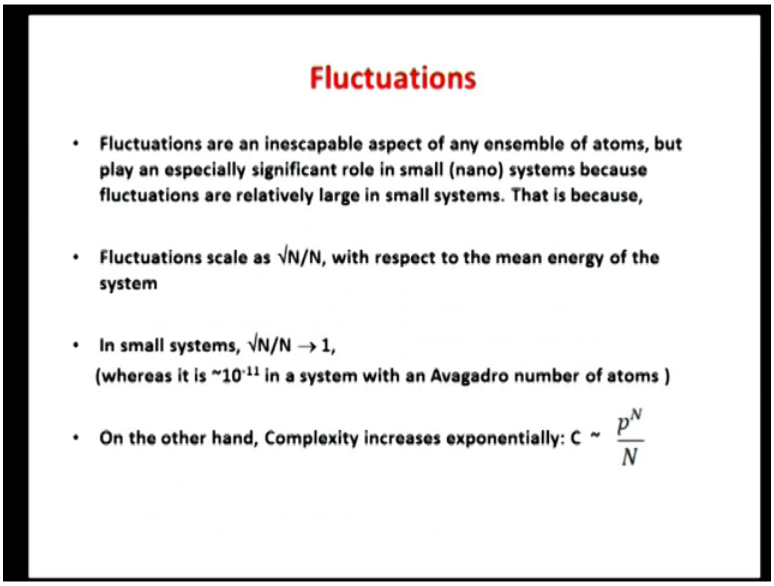

One of the necessary aspects of statistical mechanics is that fluctuations are important when you have large ensembles as I said you cannot describe every particle in an ensemble.

So, while you can describe an average there can also be fluctuations therefore, fluctuations are an inescapable aspect of any ensemble atoms and these fluctuations play an especially significant role in small or nanosystems because fluctuations are relatively large in small systems. That is because fluctuations scale as square root of N by N or one over square root of N with respect to the mean energy of the system.

This comes out to statistics or statistical mechanics in small systems this square root of N by N approaches unity although of course, it is less than unity is of the order of unity, where is this ratio is much smaller of the order of 10 to the power minus 11 in a microscopic ensemble of let us say an Avogadro number of atoms. Therefore, fluctuations are hardly important in microscopic systems where as they become very important in microscopic systems or nano systems. On the other hand complexity of this system that is the complexity of the behaviour of these systems is an exponential function you can say it varies as P to the N divided by N.

Therefore on the one hand you have a set of fluctuations that are important in nanosystems on the other hand you have complexity that increases with N, one may to look at these things is to recognize for example.

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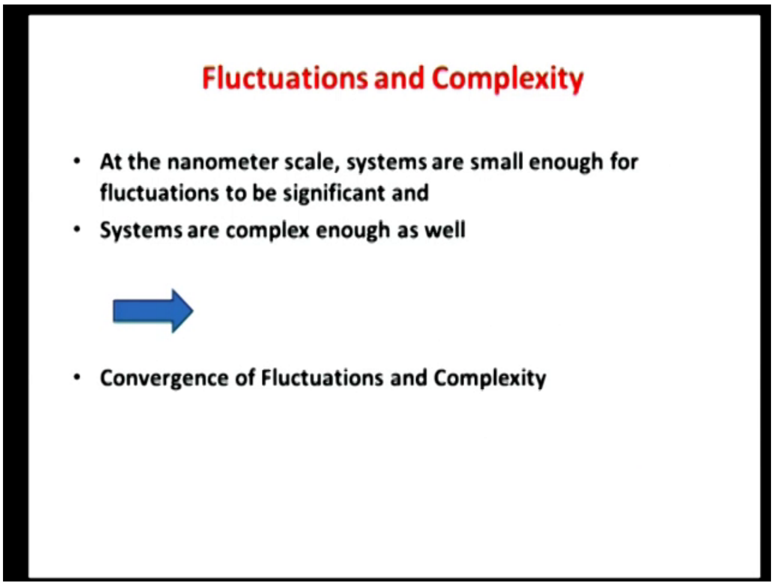

That at the nanometre scale, systems are small enough for to fluctuations to be significant where as the systems are also complex enough therefore, at the nanoscale you have a convergence of fluctuations and complexity now this can be looked at in the following fashion.

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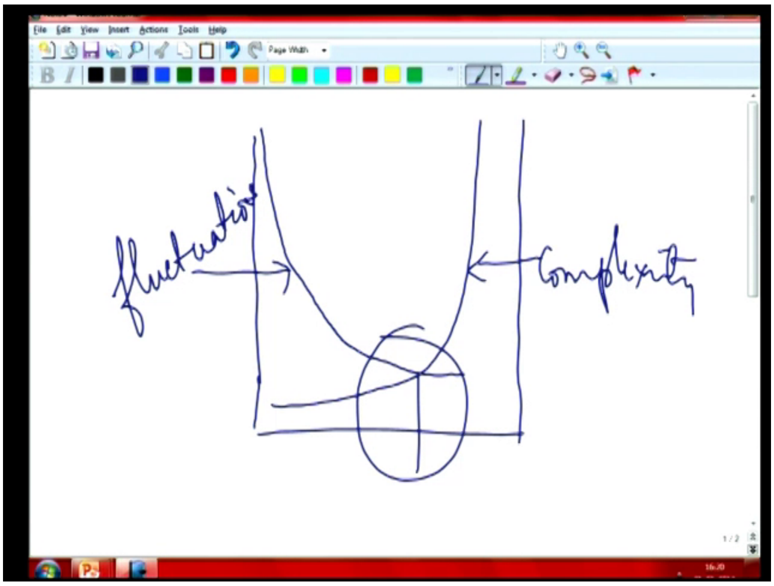

One can draw a graph that describes on the one hand fluctuations come down as a size increases where as complexity goes up as size increases, on the, this is complexity and this is fluctuation. So, you really have a region here where in the nanosystems you have the simultaneous importance of fluctuations and complexity. That is what actually signifies nano systems and as I said we will come to this a bit later and try to elaborate on these things.

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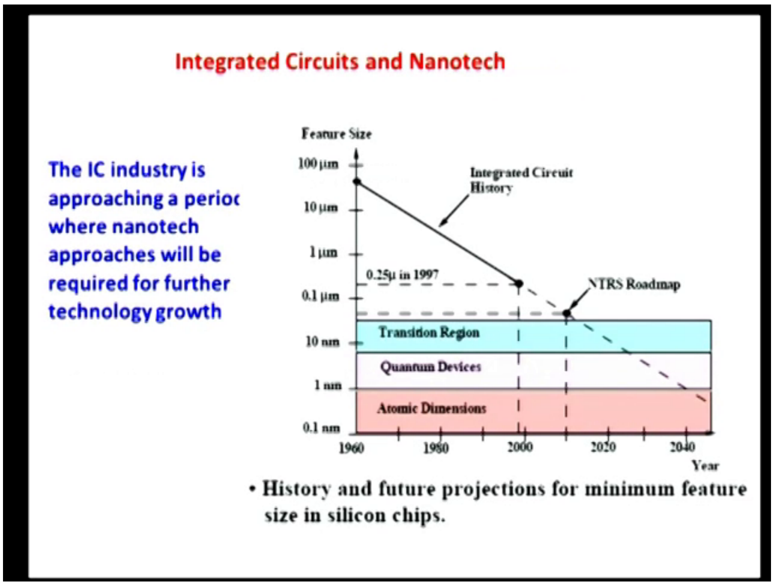

Now, fluctuations have become important in a way that is understandable from the context of VLSI integration I am not really going to talk about the scaling and so, on, but what is happening now is that because of the extremely small dimensions the feature sizes in today's integrated circuits in production. There is actually a factor that comes into play that is due to fluctuation that is you have millions and millions you know even billions of circuits in a single wafer and you are subjecting them to various kinds of processes and these processes have to take place on a very verifying scale nanometre scale on a wafer for example.

Therefore, there can be variations from let us say spot to spot, to speak in on the wafer and therefore, there can be a an influence of these fluctuations that can affect the yield of a semiconductor manufacturing process, this is not really to do with nanomaterials as such,, but I wanted to point out how fluctuations can come into play in the actual fabrication or devices as the dimensions really come down to very small sizes.

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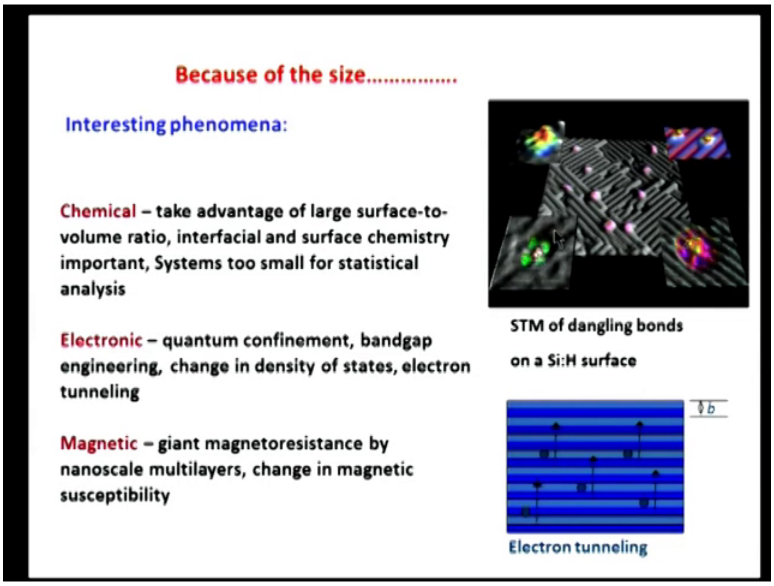

Now, why do we want to study nanomaterials and nanostructures there are very interesting phenomenon that arise which is actually the subject of this course, there are chemical aspects taking advantage for example, of the large surface to volume ratio interfacial surface chemistry become very important and these can be exploited to advantage there are very significant electronic and optical effects due to a something known as quantum confinement will come to change the density of states electron tunneling and.

So, force some of these things are already evident in today's circuits because after all when the gate oxide thickness comes down very much than tunneling which is quantum mechanical effect is already beginning to be important in VLSI circuits and then there is this, called giant magneto resistance effects which evident from nano scaled multilayered thin film structures. Which was actually invented around the same time as a atomic force microscope and today already it is part of the magnetic storage devices, in other words it is nano technology actually implemented in practice that is a part of the nano effects in magnetism.

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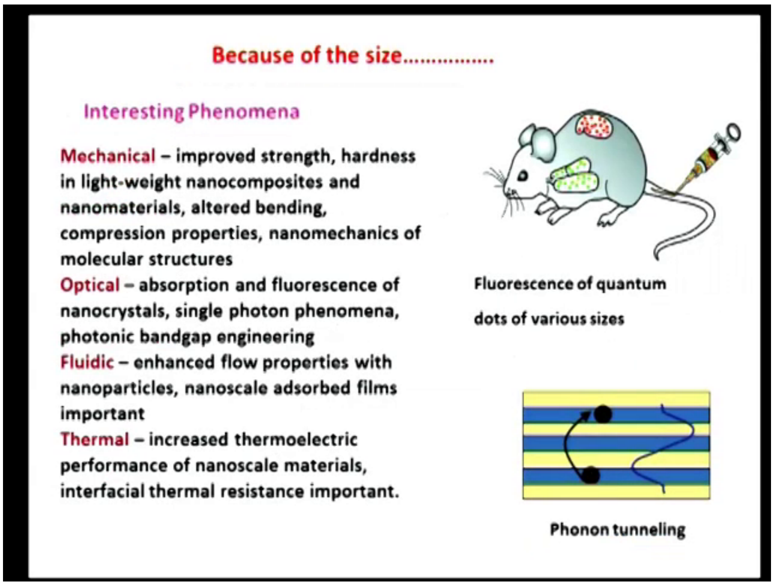

There also interest in mechanical effects for example, improved strength of materials, optical effects which is really the other side of the electronic effects single photon phenomena and so, forth and photonic band gap engineering which is, already a well developed technology nanofluidics and thermal effects such as increased the thermoelectric performance in nanoscale materials and so on. These are all examples of the motivation for studying nano materials for the expansion of nanoscience and the development of nanotechnology.

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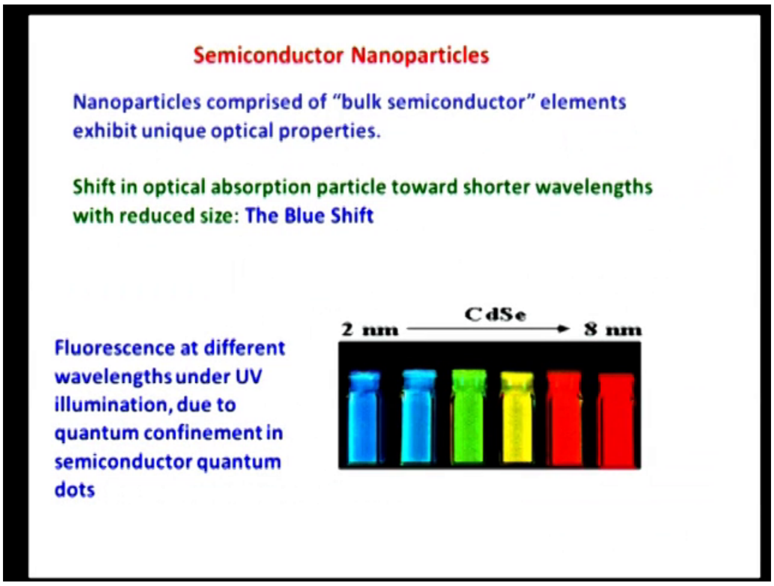

A couple of vivid examples on this what is shown here is the progressive change in the appearance of nanoparticles of cadmium selenide which is a direct band gap semiconductor as the size of the particles is increased from 2 nanometers to 8 nanometers or reduced from 8 nanometers to 2 nanometers. What you see here is the same material under fluorescence on the fluorescence on the same material under UV illumination you can see that. In fact, because of the change in the size of the particles progressively from 8 nanometers to 2 nanometers you have a complete change in the appearance from read all the way to blue as the size reduced and this. In fact, is a quantum mechanical effect something known as the blue shift which arises from quantum confinement that we will refer to as we go along that we learn about soon, this is semiconductors.

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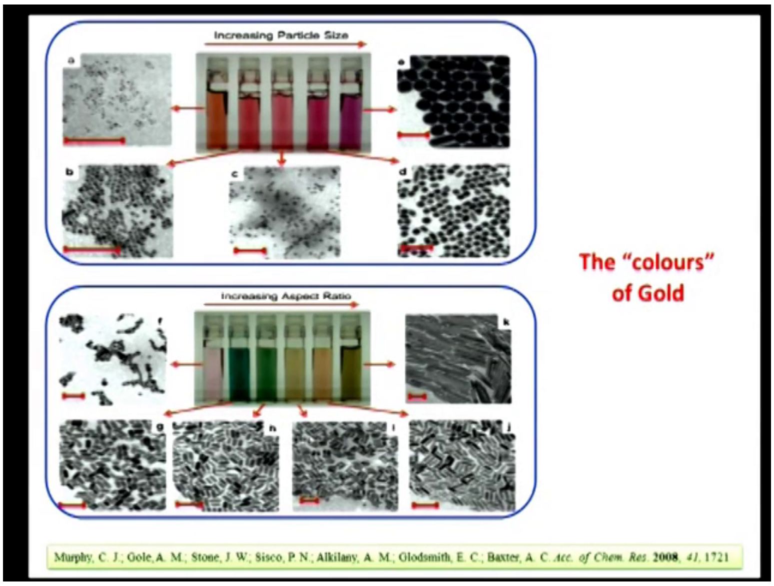

Now, gold I mentioned nanoparticles of gold actually Michael Faraday made them 150 years ago now we all think of gold as having well gold an appearance yellowish appearance, but when you size it down as you can see here in this view graph when you bring down the size of gold in nanoparticles or in nanorods then the colour of gold changes it can even be green as suppose to being yellow. So, that depends on the size of the nano particles in the top view graph are in this on the aspect ratio of nanorods in the bottom one where the aspect ratio changes changing the colour of gold as we see it. These are vivid examples of how the properties of materials can be altered by controlled nano structuring of materials.

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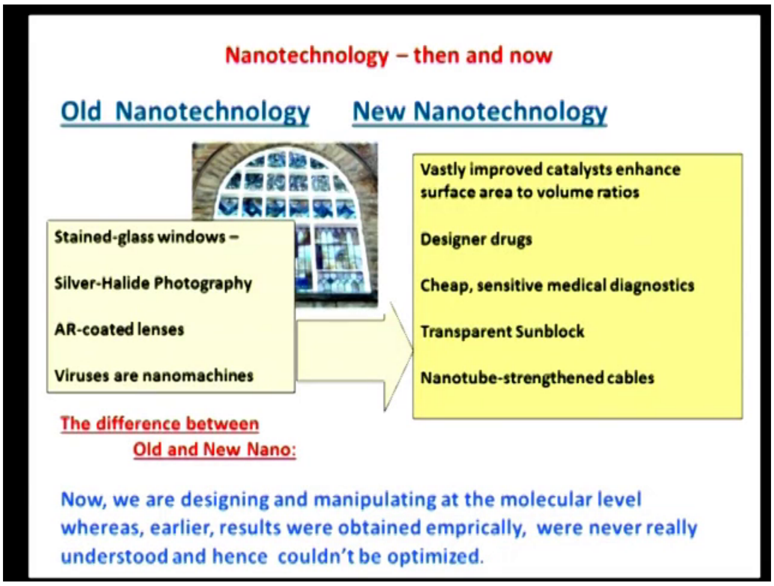

Already said that nanotechnology is not knew we had the industrial catalyst and the stain glass windows one thing I forgot about is the silver highlight photograph, photography the divide photography which is of course, more or less which is vanished now, but all these are examples of what may be called old technology.

The new technology is a list that I have shown here which is just partial list designer drugs and so forth, the difference between the old technology and the new technology is that many times because of the lack of ability to explore and understand the behaviour of particles on a very fine scale. There was no clear understanding of the principles of work working off for example, let us say the stain glass windows it was a sort of a black magic as to why spectacular colours were achieved in those context where as we now are now in a position to be able to understand these things in a systematic fashion and therefore, develop them in a systematic fashion.

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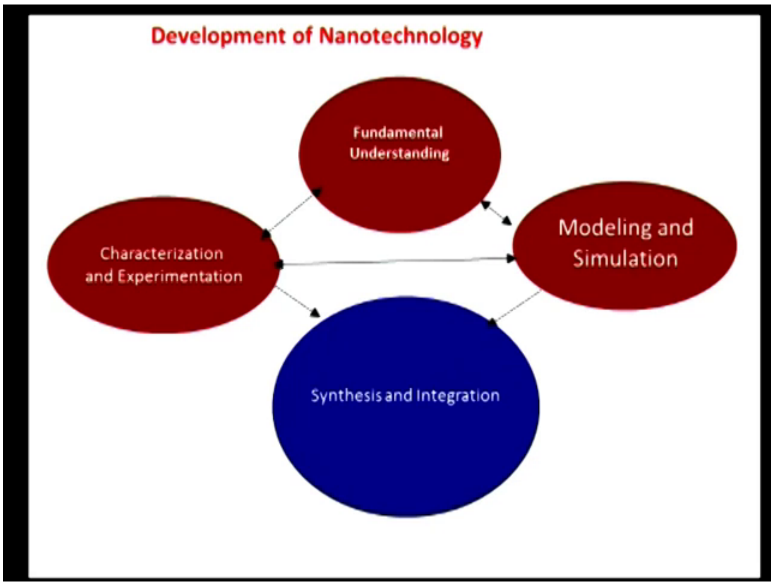

So, a matrix of sorts can be defined where you obtain fundamental understanding that comes through characterization and experimentation we know the laws of physics that apply and therefore, modeling and simulation are possible and therefore, it is possible to integrate this knowledge into useful devices and actually employee them, this is the development of nanotechnology of the current day.

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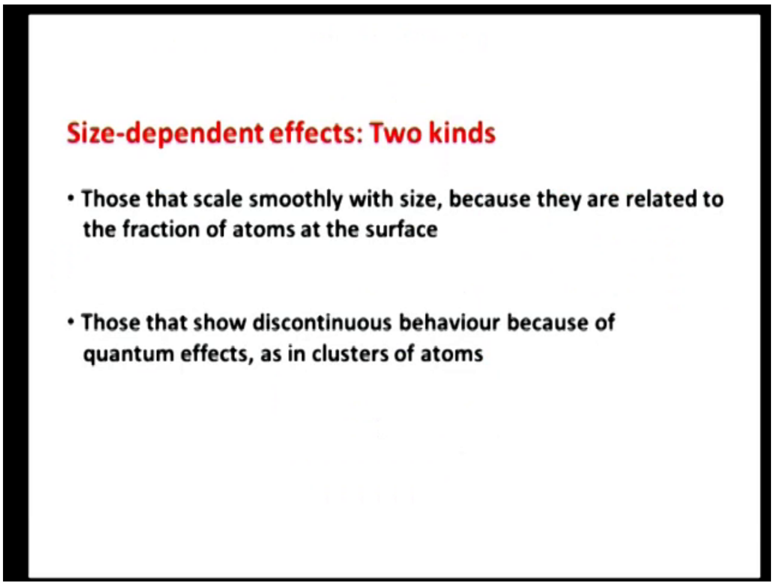

Have you given this somewhat lengthy introduction we are probably in a position to proceed further what we need to understand more formally is that there are size dependent effects in materials, that is as uses size it down from microscopic scale to nanometric scale of the way of the kind that we defined, there are 2 different kinds of size dif dependent effects that one can observe. The first kind is those that scale smoothly with size and these are related to the fraction of atoms at the surface of a particle or surface of a nano system. The other kind is those kinds of effects which show discontinuous behaviour because of quantum effects and one example is in the cluster of atoms which we will describe as you go along.

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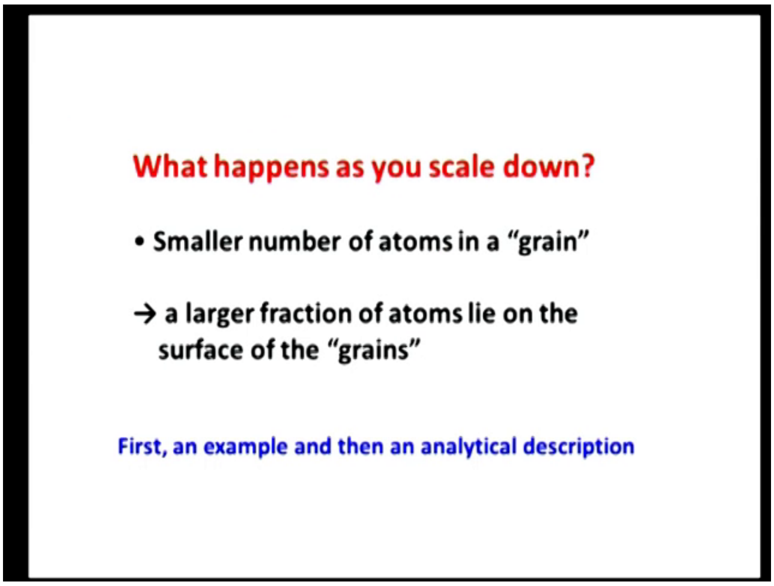

First we come to the kind that very smoothly with size and we ask what happens when you scale down the obvious thing that happens when you scale down is there is a smaller number of atoms in a grain of material in a particle of material, automatically it also means that therefore, a larger refraction of the atoms within that grain are at the surface they lie on the surface of the grain.

Let us look at a simple example and then go to an analytical description of what is meant by this.

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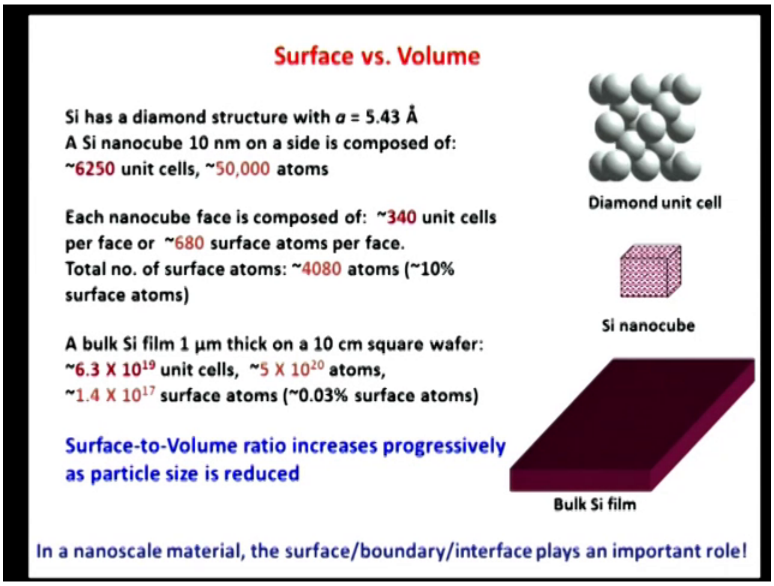

Let us take silicon, the prototypical semiconductor we are all familiar with silicon has the diamond structure with a lattice constant of 5.43 angstroms and with the knowledge of these dimensions it is possible to you simple arithmetic to show that a silicon nanocube 10 nanometers on the edge is made of about 6,250 unit cells or about 50,000 silicon atoms.

Now each of these nanocubes measuring 10 nanometers on the edge is composed of mean it has 6 faces of course, and each of these faces is made of 340 unit cells per face or 680 surface atoms per face there are 6 faces, therefore there are about 4,000 atoms of silicon on the surface of this 10 nanometer cube, which has a total of about 50,000 atoms therefore, something like 10 percent of the atoms in this nanocube lie on it is surface. Whereas if you go to a bulk silicon film which measures about one micrometer thick I already said that a micrometer is already a very large dimension in this world because it comprises millions of atoms or billions of atoms therefore, we are in the microscopic world when you come to a micrometer thickness (Refer Time: 30:47) to nanometers.

If you had a silicon film one micrometer thick on a 10 centimeter square wafer it is easy to show that there are about 5 into 10 to the power of 20 atoms in this one and also to show that about 1.4 into 10 to the 17 of these are on the surface. That is only about 0.03 percent as supposed to 10 percent in the earlier case are on the surface. Therefore, the surface to volume ratio increases progressively as you reduce the particle size, this is just a numerical example and this indicates in a rather vivid fashion that nanoscale materials the surface of the boundary of the interface is very important.

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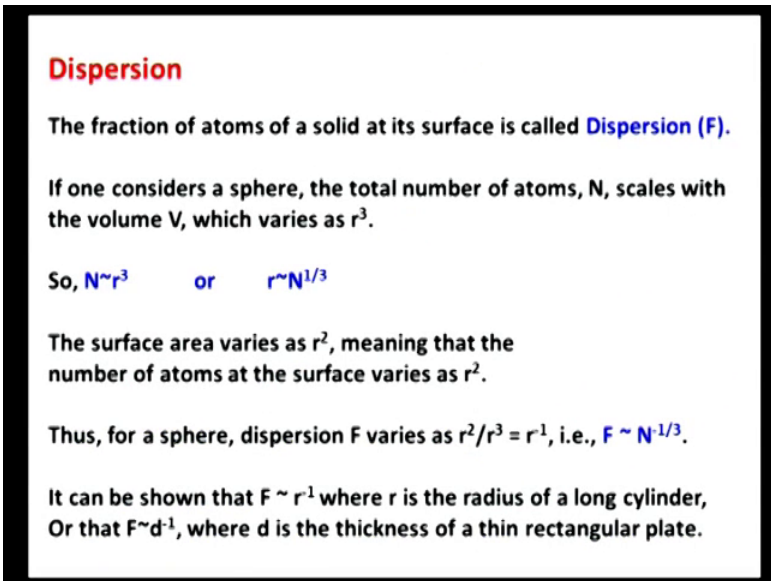

Now, there is a analytical way to describe this progression under quantities called dispersion, dispersion is the fraction of atoms of a solid at it is surface, dispersion is denoted by F and it is a fraction of atoms of a solid at it is surface. If you consider a sphere the total number of atoms N, scales with the volume which varies as r cubed 4 by 3 pi r cubed as you know, therefore, N goes us r cubed or r goes as N to the power of 1 third. The surface area varies as r squared meaning that the number of atoms at the surface varies as r squared, thus for a sphere dispersion F varies as r squared by r cubed or dispersion F goes as r to the power minus 1, which means that dispersion F goes as N to the power of minus one-third.

That is scaling law for a spherical object, but one can show readily that this relationship this functional relationship is valid for a long cylinder or for a thick film or a rectangular plate. So, this is a general result that the dispersion goes as n to the power of minus one third, this is Scaling law.

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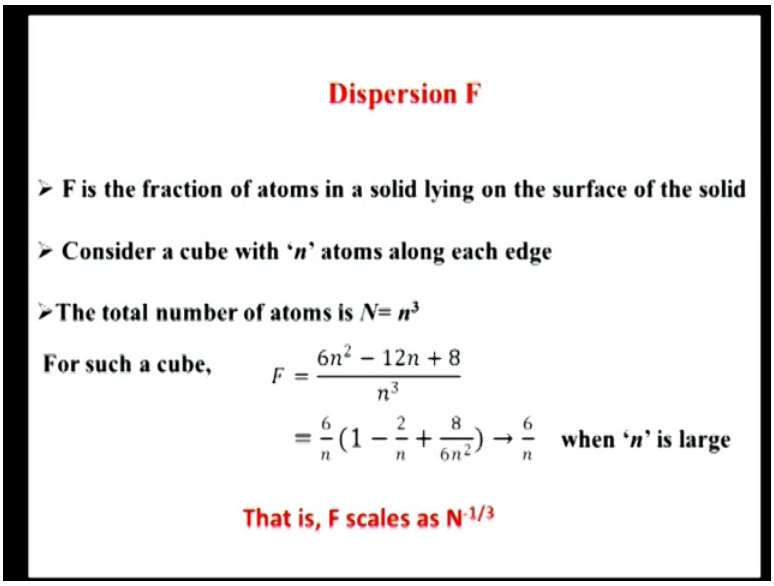

One can actually consider a different kind of a geometric shape to look at dispersion and that is a cube, now consider a cube with n atoms along the each edge let us try to draw this.

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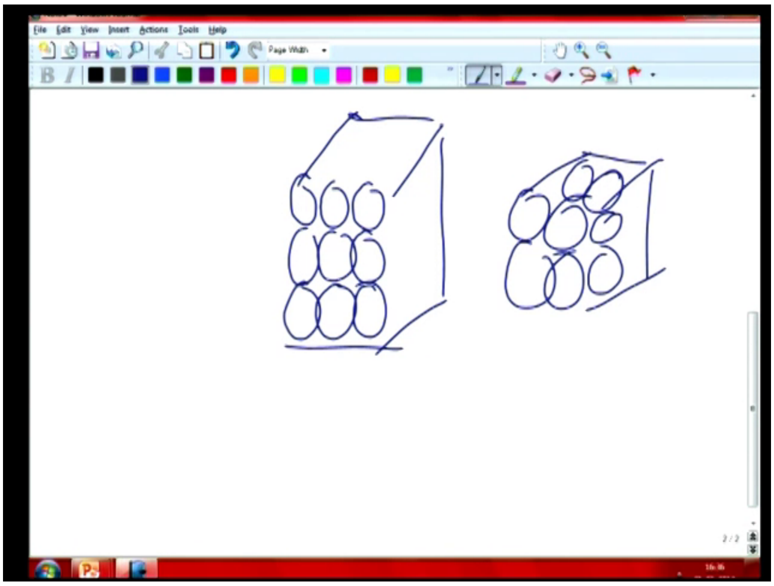

We have a cube let us say a cube with 3 atoms on the edge, you can imagine that this course is face as a cube; such a cube would have as you know 27 atoms. Now what we will do is to consider the number of atoms in such a cube on lying on the surface, if you had only a cube with 2 atoms on the edge, then every one of them all the 8 atoms would lie at the surface, where as if you had a cube with 3 atoms on the edge with the total of 27 you can readily satisfy yourself that 26 of these atoms in a cube in this cube would like at the surface.

Therefore, the dispersion here is 26 divided by 27 those lying at the surface is 26 and those lying in the interior is only one and therefore, the dispersion is 26 by 27. If you actually go through this exercise and do this for cubes with different number of atoms n on the edge then you can see that it is possible to come up with this general formula F is equal to 6 n square minus 12 n plus 8 divide divided by n cubed.

Now the reason for this form 6 n square it defines the number of atoms on all the 6 faces together with the 6 faces of the cube, it is 6 n square because a cube has 6 n 6 faces, but when you consider this 6 faces what happens is that you have to subtract your double counted the edges they have 12 edges double counted them therefore, you have to subtract 12 n, but then when you subtract this atoms on the edge to avoid double counting you will have removed all the 8 corner atoms and therefore you have to add 8 therefore, 6 n square minus 12 n plus 8 is the total number of atoms of on the surface of a cube with n atoms on the edge.

Therefore, the dispersion is 6 n square minus 12 n plus 8 divided by n cubed this can be simplified as you can see and for large n you can readily see that this F would go as 6 divided by n. Now n this small n is equal to n cube rather the capital N is equal to n cubed the total number of atoms is equal to n cubed and therefore, you can see from this simple example that F scales as n to the power of minus one third which is really what we had earlier also therefore, the scaling law for the dispersion is n to the power minus one third.

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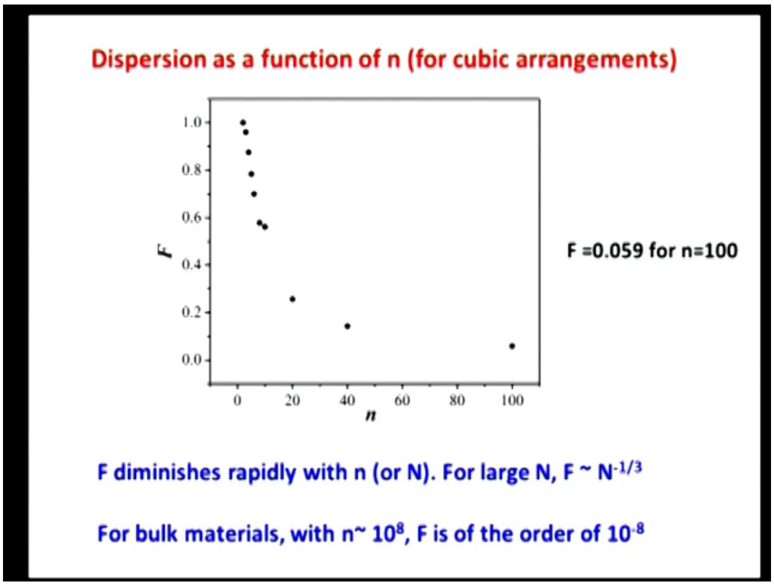

Now, one can actually plot this dispersion function for this cubic arrangement that I just mentioned as a function of N the number of atoms on the edge of this cube. So, you have the case where F is equal to 1 for n is equal to 2 that is capital, small n is equal to 2 F is equal to 1 and so forth and it declines rapidly.

When you have a cube with 100 atoms on the edge then F in that case is 0.059 in other words 5.9 percent of the atoms in a cube of 100 atoms on the edge would lie at the surface is still a pretty large number, but for bulk materials where you really have Avogadro number of atoms of the order of 10 to the 24, let us say then n this small n the number of atoms on the edge of a cube would be about 10 to the 8 and therefore, F the dispersion is 10 to the power of minus 8 therefore, you can see how much of a difference it makes when you go from the macroscopic world to the microscopic world namely that the dispersion increases greatly when you size it down.

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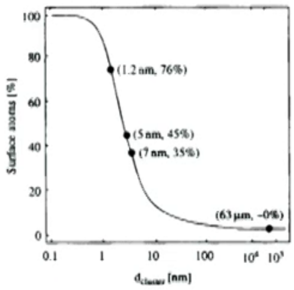
Palladium Clusters



The percentage of surface atoms changes with the palladium cluster diameter.

[C. Niitzenadel, A. Ziittel, D. Chartouni, G. Schmid, and L. Schlapbach, Eur. Phys. J. DS, 245 (2000).]

Here is an example of the case of Palladium, Clusters of palladium made of different sizes varying from 63 micrometers all the way down to 1.2 nanometers and in the clusters of palladium measuring 1.2 nanometer you can see that 76 percent of the atoms are at the surface of these clusters, this is a practical illustration of what happens when particles are sized down.

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An elementary way to look at scaling

Consider a cube of edge a. Its surface area is $6a^2$.

If the cube is divided into smaller cubes of edge (a/n),
The total number of cubes would be n^3, each with a surface area of $6(a/n)^2$.

The total surface area of the n^3 cubes is $n^3 \times 6(a/n)^2 = 6na^2$.

Thus, by dividing the cube by a factor of n, the total surface area has been enhanced by a factor of n.

This accounts for the effectiveness of "finely divided" metal particles as catalysts.

One can look in a very elemental way at these scaling what happens consider a cube of edge a, it is surface area is 6 a square, if the cube is divided into smaller cubes of edge a divided by n then the total number of cubes would be n cubed each with a surface area of 6 into a by n whole square.

The total surface area of n, n cubed cubes is there for equal to 6 n a squared, that is we have gone simply by dividing our large cubes in large cubes into a large number of small cubes we have gone from a total surface area of 6 a squared all the way to 6 n a squared where n is the factor of division therefore, this can show us readily that by sizing it down the total surface area of an object can be greatly increased and coming back to our finally, divided material what it shows is that such finely divided material would have a large surface area which people understood a long time ago was very important for catalytic action, it accounts for the effectiveness of catalytic action of finely divided metal particles.

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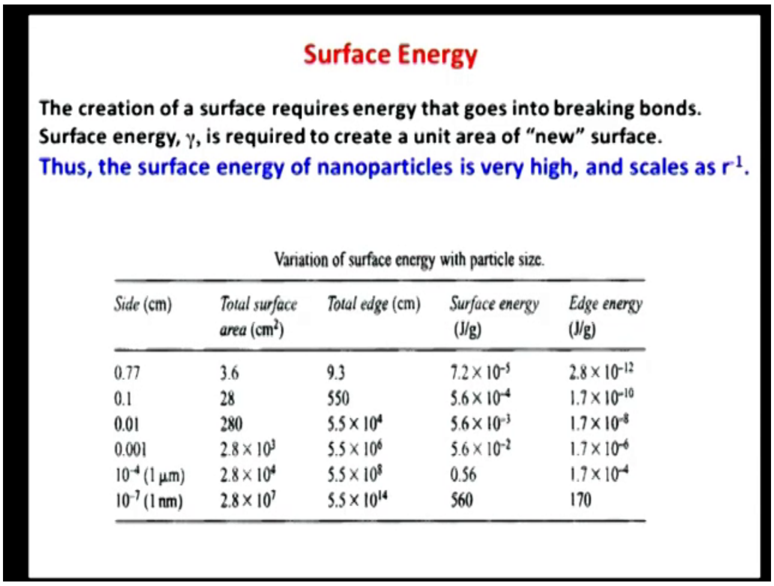

Variation of surface energy with particle size.

Side (cm)	*Total surface area* (cm^2)	*Total edge* (cm)	*Surface energy* (J/g)	*Edge energy* (J/g)
0.77	3.6	9.3	7.2×10^{-5}	2.8×10^{-12}
0.1	28	550	5.6×10^{-4}	1.7×10^{-10}
0.01	280	5.5×10^{4}	5.6×10^{-3}	1.7×10^{-8}
0.001	2.8×10^{3}	5.5×10^{6}	5.6×10^{-2}	1.7×10^{-6}
10^{-4} (1 μm)	2.8×10^{4}	5.5×10^{8}	0.56	1.7×10^{-4}
10^{-7} (1 nm)	2.8×10^{7}	5.5×10^{14}	560	170

Surface energy, another important aspect of scaling, now when particles are divided I have been as we just did for a cube it is important to recognize that energy is necessary to create a new surface because you have to break bonds. This energy that is required to create a new surface is called surface energy and you measure it in, many joules per unit area. Now as you can see because of the very large surface area that becomes possible when objects are scaled down the surface energy of nanoparticles is very high and it goes inversely as are the radius of the particle and what I have here is a table that shows how the surface energy of a particle varies when the size reduced from macroscopic sizes that is centimeter level sizes all the way down to nanometers. It since it goes inversely as a dimension you can see if the surface energy varies from 10 to the power of minus 5 joules per gram in the case of macroscopic objects all the way down to all the way up to 570 joules per gram when the size is reduced to one nanometer.

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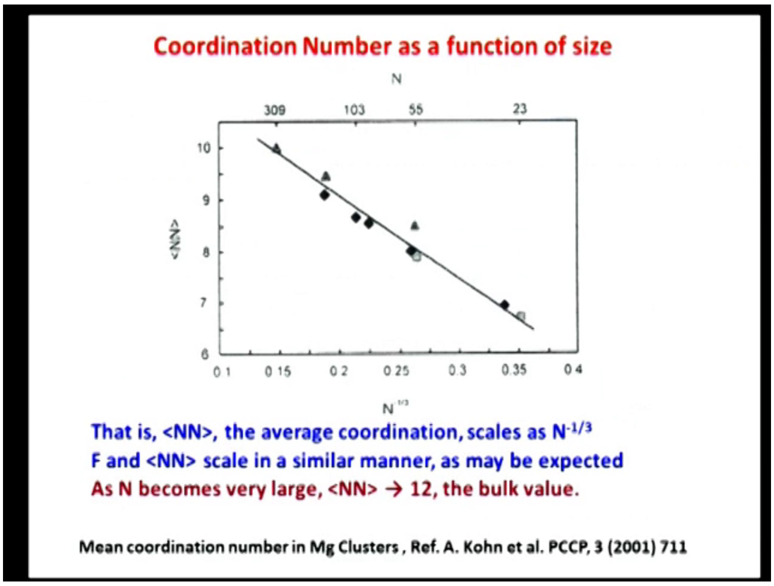

Coordination number, what is coordination number, coordination number is the number of atoms, number of nearest neighbours that an atom is bonded to. So, it is the number of bonds it has got and that is a coordination number, now atoms at the surface are in a way partially (Refer Time:43:46) because they do not have atoms to bond to above the surface therefore, as you can see that the bonding of a an atom at the surface of an object is weaker in other words it is coordination number is smaller one refers to therefore, the average coordination number of a material because a surface atoms have a lower coordination than those in the interior of a solid.

What is shown here is the mean coordination number of magnesium clusters that is calculated as a function of the cluster size. So, the mean coordination number is on the y axis and the number of atoms in the cluster is on the x axis and the linear scaling here shows that the coordination number goes as N to the power of minus one third that it is it scales the same way as the dispersion function.

Now this can be expected because as this scale of this as the size of the object is scaled down then the surface area increases and therefore, the number of surface atoms increases, therefore the average coordination is diminished. In the limit of bulk objects then you can see that the coordination approaches the value of 12 which is what it is for a close pet magnesium crystal.

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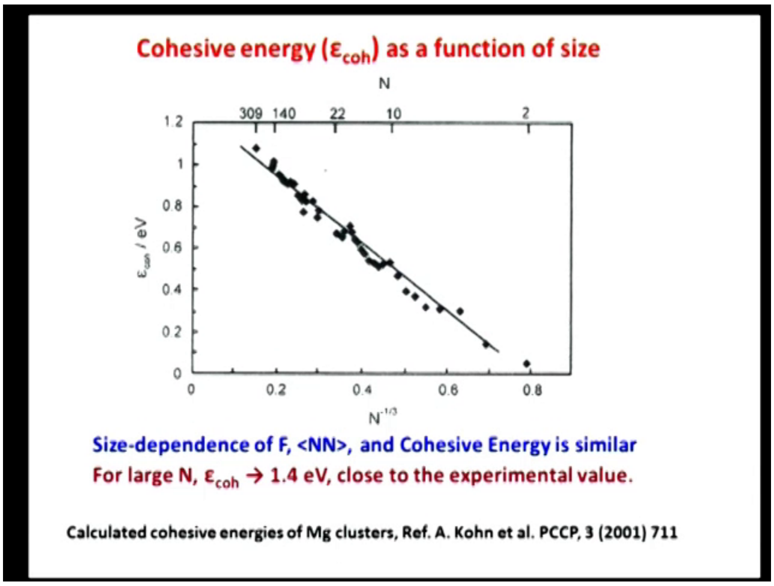

Cohesive energy this another one that scales the way that the dispersion does, cohesive energy is the energy that holds solid together we could say that it represents is strength of bonding in a solid, what is shown here is the graph of a average cohesive energy of magnesium clusters as a function of the size of the cluster, what is shown here is a linear part again that is this scaling is now the same as the scaling for the dispersion and for the average coordination number therefore, all the quantities dispersion average coordination number on cohesive energy they all have the same scaling law they go as n to the power of minus one third. In this graph you can see if you extrapolate for large values of N which represents which is on the left hand side of the x axis for large values of N this cohesive energy approaches the value 1.4 electron volts which is close to the experimental value for magnesium crystals.

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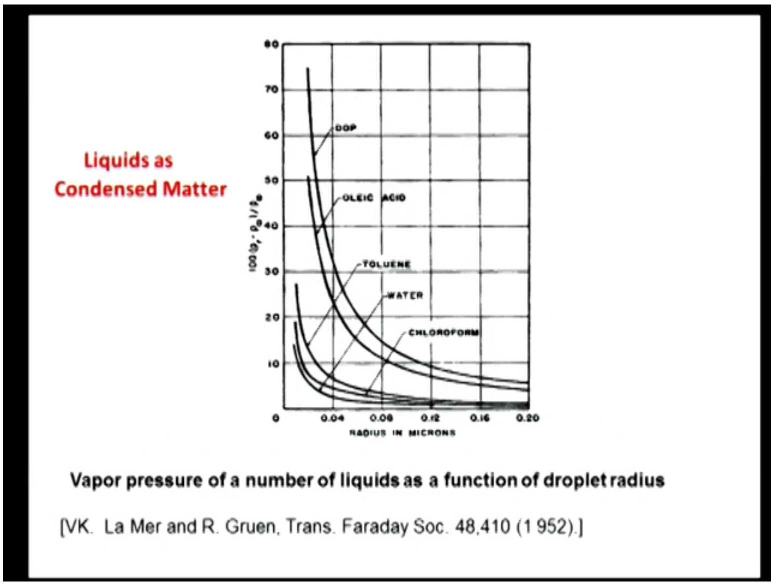

Now, for just a moment let us look at liquids as condensed matter.

What is shown here is the vapor pressure of different liquids as a function of the radius of drops of these liquids different liquids like chloroform, toluene, water are shown here, what you can see is that as the radius of the drops or droplet us of these different liquids comes down to very small values the vapor pressure increases exponentially what is vapor pressure how is this generated it comes out of the boiling of atoms at the surface into the vapor phase that is from liquid to the vapor phase.

Now as you size it down as you size that liquid drop down what is happening is that a large fraction of the atoms of the droplet are you at the surface and these are less well bound then the atoms in the interior and therefore, they can escape or they can boil off which is really what vapor pressure is due to. So, this illustrates again that in the condensed liquid phase as well the effect of the coordination being low at the surface leading to higher vapor pressures.

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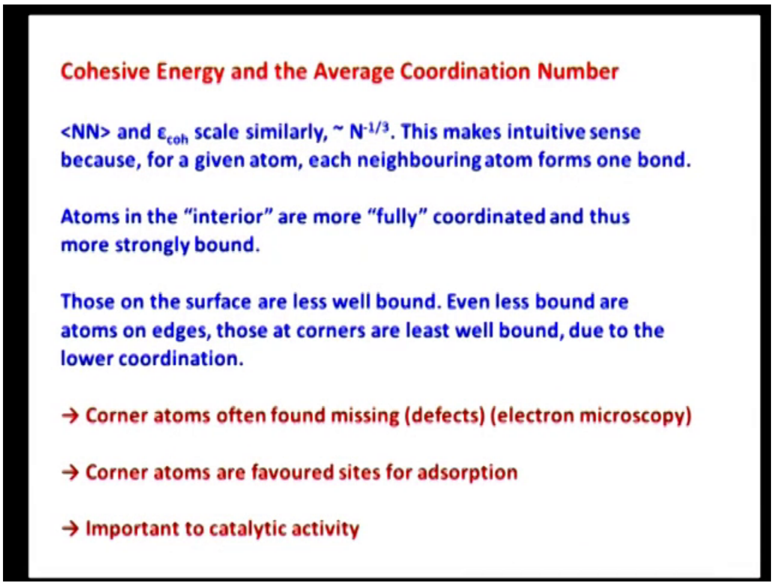

Now, to repeat the average coordination numbers as well as the cohesive energy scale similarly go as N to the power minus one third this makes you intuitive sense because, for a given atom, each neighbour forms one bond. So, it has if it has fewer neighbors than it has fewer bonds and therefore, a lower cohesive energy. Atoms in the interior are more fully coordinated and they are most strongly bound. Those on the surface are less bound, even less well bound are atoms on the edges of a cube for example, that we just went through and those in the corners are least well bound because they have the fewers coordination.

All of this is actually illustrated by experimental evidence for example, if one examines in an electron microscope, microscopic samples of let us say metals one finds often that the atoms at the corner are missing even under thermodynamic equilibrium conditions these are defects and these are arise because of the low coordination at the corners for same reason corner atoms are favored sides for absorption that is if you want to develop a catalyst than one of the things that is important is that you really make sure that you have particles that have a lot of corners in them because these corner atoms are hungry for absorption which is what is required for better catalytic actions.

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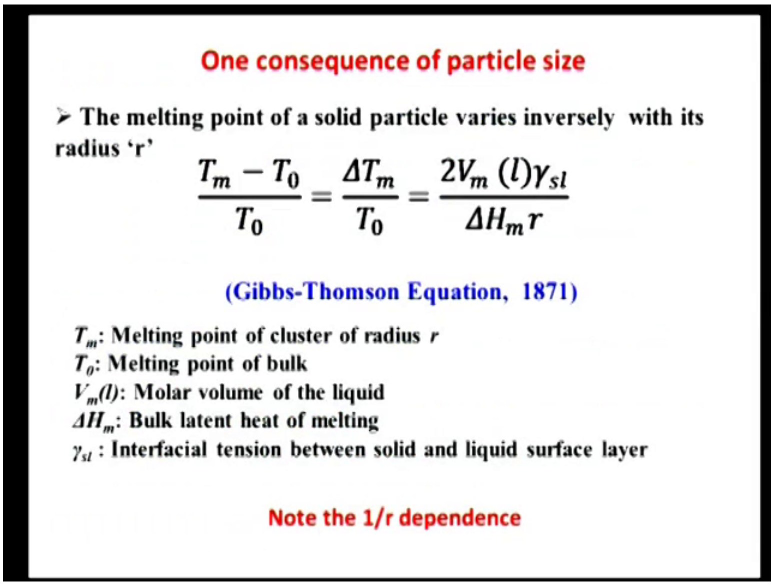

One of the consequences of particle size is related to the cohesive energy you have already mentioned, but at different physical properties affected by that actually this is a well known experimental result as well as a theoretical result dating back to 1871 the Gibbs Thomson relationship where the variation of melting point of a solid is related to the particle size, it is well known even such a long time ago that the melting point would be lower if the particle size is smaller, I wanted to note the one over all dependents which is similar to the dependents of these other quantities that we have just discussed.

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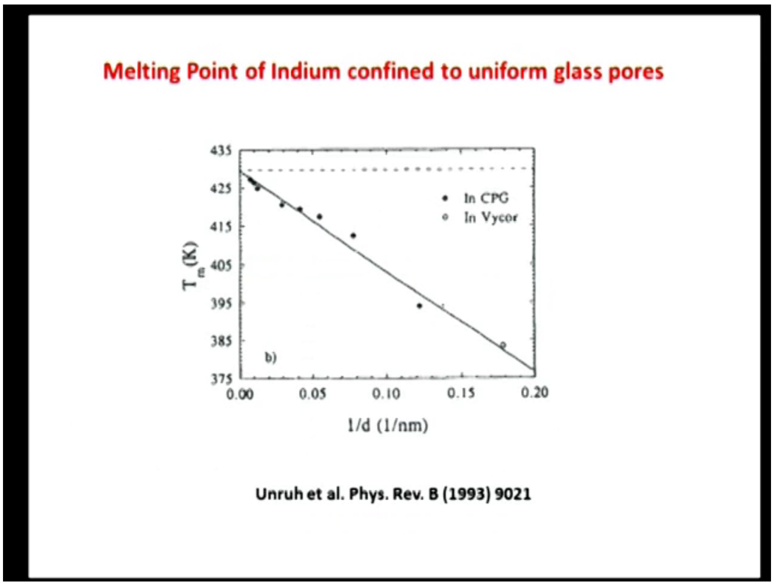

The melting point of a solid as I said the days when the size of the solid is reduced size of the particle is reduced one particular experimental manifestation of this or experimental verification of this is the measurement of the melting point of indium in glass pores of well defined size.

So, what is plotted here is the melting point on the y axis as the function of the inverse diameter of glass pores of different sizes and what I wanted to see is the linear relationship that is exactly the same that is the functional relationship is that exactly the same as the scaling of the dispersion of the cohesive energy and now the melting point.

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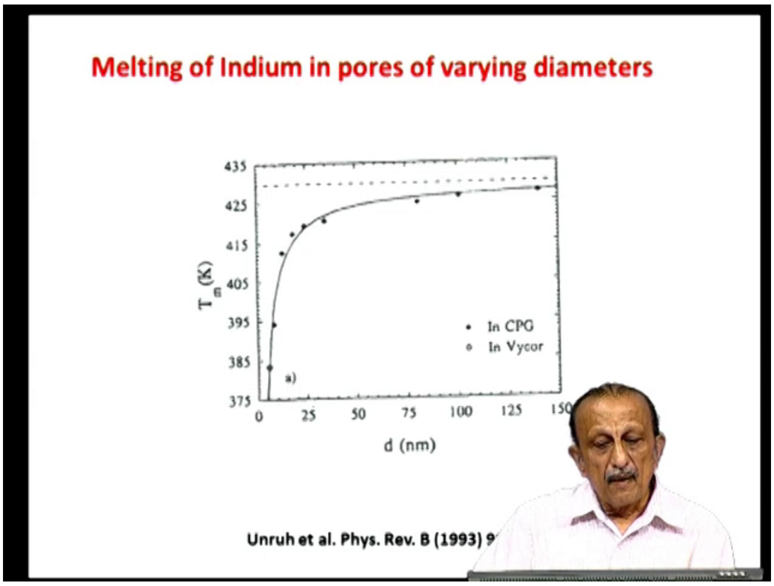

All of this scale smoothly with the size of the particles and this is really the same result where the melting point is shown as a function of the diameter earlier it was the inverse diameter, now it is the diameter and what you see here is the approach of the melting point to the bulk value as the pore size of the glass pores in which indium is confined.

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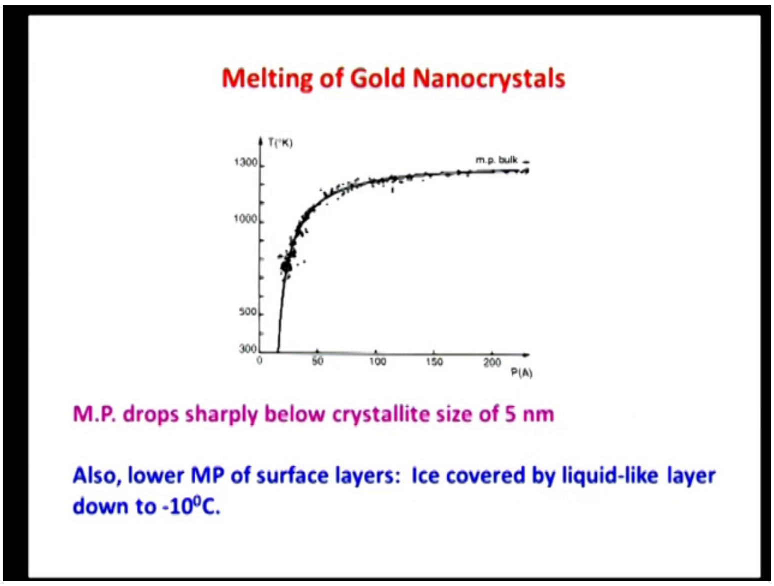

That pore size increases and then the melting point indium approach is the bulk melting point of 430 Kelvin's. Now gold just as a rather well known example gold melts at about 1336 in the bulk thirty 6 Kelvin's in the bulk what is shown here is experimental results of the melting point as a function of gold particle size it turns out that it is possible to make gold particles of extremely well defined sizes, called mono disperse gold particles where an entire sample has a very narrow size distribution for example, you can make gold nano particles measuring 5 nanometers almost exactly and so forth.

The melting point of gold of these different measurements has been experimentally determined and the melting point of gold false dramatically when it is size down of about 5 nanometers or below. It is also a context in which we can recall that there is a different experience that we all probably we are familiar with that is the lower melting point of surface layers of objects or materials that we are familiar with for example, Ice is covered by a liquid like layer even down to minus 10 degree celsius where as it is supposed to solidify at 0 degree celsius under atmospheric pressure, this is because of the relatively poor bonding at the surface which makes it possible for a liquid like layer to be seen on eyes all the way down to minus 10 degree celsius.

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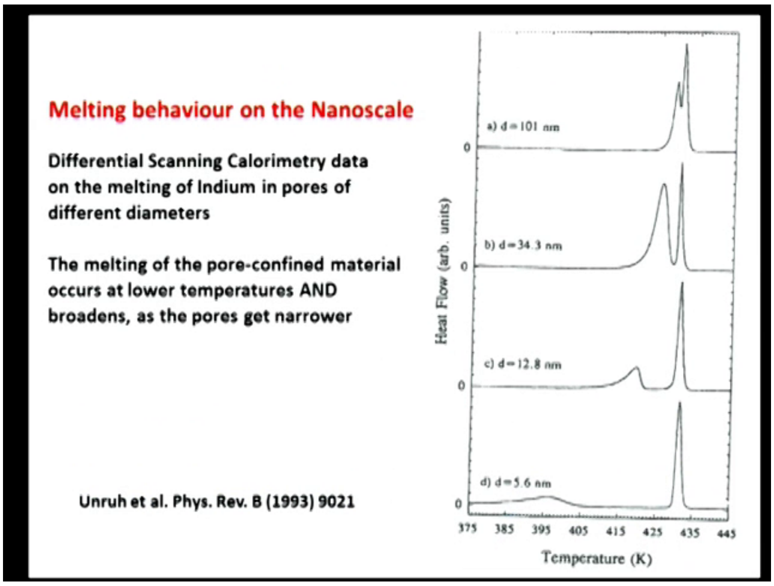

Another aspect of another demonstration I should say of the melting behavior on the nano scale is this set of data that shows the melting of indium in pores of very well defined diameters I mentioned this to you earlier what is shown here is calorie metric data, on the y axis is the amount of heat that is absorbed for the melting process to takes place on the x axis is the temperature and what I wanted to see is that as the pore diameter is reduced from 100 nanometers all the way in to 5.6 nanometers the endotherm that belongs to the bulk indium melting which is at 435 gradually moves to lower temperature.

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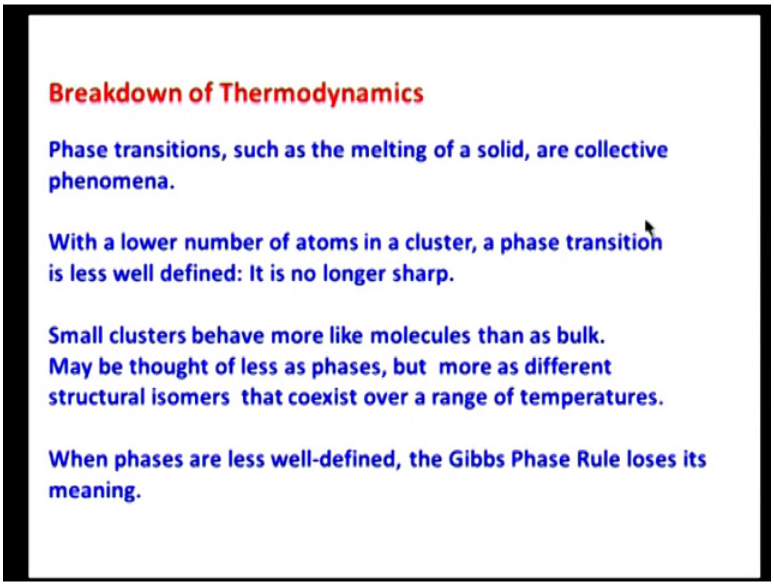

That is when the pore size is 101 nanometers the melting point is below 430 degree celsius and then as the pore size is reduced this temperature or melting of indium within these nano pores becomes lower and lower. As well as these peaks are no longer sharp what this is showing is that because of the low coordination that is available to indium atoms with in this confined pores smaller number of atoms to born to therefore, the melting point of gold of indium diminishes regularly as you size down the pores and also it is no longer as short.

Now this can be understood in the following way the melting of a solid is a phase transition is of first order phase transition and these phase transitions are collective phenomena that is it occurs through the participation of millions of atoms together. When this collection is smaller when there is a lower number of atoms in a cluster for example, a phase transition now is well defined is not well defined is no longer shown. Small clusters behave more like molecules than as bulk material one may think of them less as phases than as different structural isomers that coexist over a range of temperatures, when these phases are less well defined as in this case as in small clusters the Gibbs phase rule loses it is meaning.

So, you could think of nanomaterials as a point where thermodynamics that we normally know can break down and of course that the reason for that is you no longer have a large collection of atoms and in effect thermodynamics deals with bulk material. So, what we have done in this session so, far is to have a introduction to nanomaterials in a rather general way, but later on to go through this scaling that applies to certain properties of materials when you bring them to nanoscale, that is, called smooth scaling in the coming classes we will deal with the effects of quantum phenomena where there is abrupt scaling as supposed to smooth scaling and in the coming classes because it is necessary to understand the basis of the basics of quantum mechanics we will go through the elements of quantum mechanics in order to be able to understand nanomaterials.