Nanomaterials and their Properties
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Lecture - 07
Nanomaterials: Surfaces (Part-I)

Students, welcome to the lecture number 7. Lecture 7 is basically continuation of lectures 5 and 6 as I mentioned in the last class.

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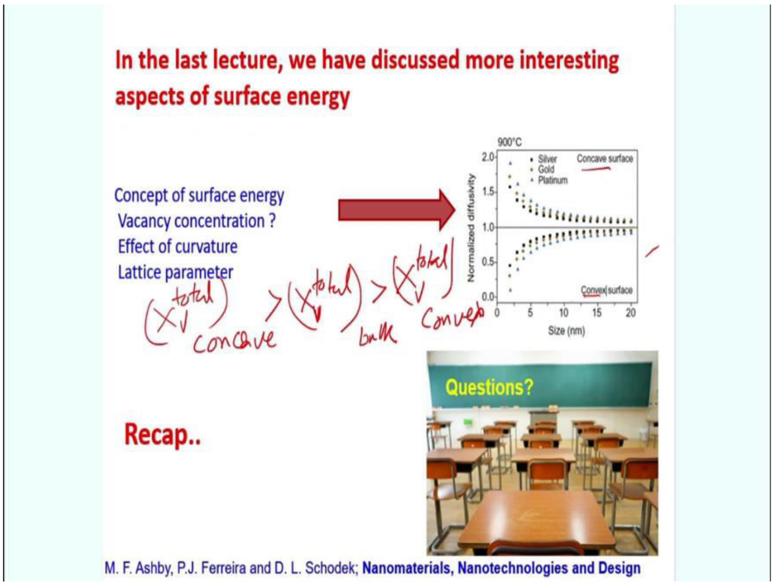

In the last lecture, we have discussed more interesting aspects of surface energy

Concept of surface energy
Vacancy concentration ?
Effect of curvature
Lattice parameter

$(X_V^{total})_{concave} > (X_V^{total})_{bulk} > (X_V^{total})_{Convex}$

Recap..

M. F. Ashby, P.J. Ferreira and D. L. Schodek; **Nanomaterials, Nanotechnologies and Design**

Well, in the last class we have discussed many interesting aspects of surface energy right. We started with concept of surface energy then we went on different aspects of surface energy, most importantly, I discussed about two effects one the effect of curvature. So, curvature will change the basically the aspect of the effect density most importantly the vacancy concentration and as you know vacancy concentration related to the diffusion, right.

So, diffusivities of different metals like silver, gold, platinum all these things I shown you how they are changing depending on the surface, curvature, convex or concave. So, it was shown that the vacancy concentration X_v^{Total} for concave is greater than X_v^{Total} bulk greater than X_v^{Total} convex right, that is because the vacancy concentration is a strongly depend on the local curvature.

Then I talked about something about lattice parameter which I again I will discuss today little bit about to clarify certain aspects and finally, we close the lecture with some examples of sintering of nanoparticles. Please note down your questions which are coming to mind while listening to this lecture and we can discuss these questions when we will meet over some online platform face to face for the class.

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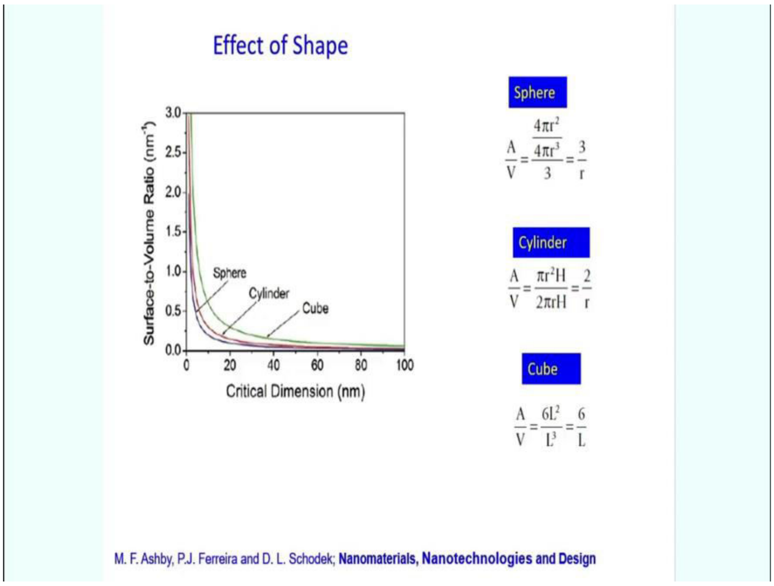

Effect of Shape

Sphere

$$\frac{A}{V} = \frac{4\pi r^2}{\frac{4\pi r^3}{3}} = \frac{3}{r}$$

Cylinder

$$\frac{A}{V} = \frac{\pi r^2 H}{2\pi r H} = \frac{2}{r}$$

Cube

$$\frac{A}{V} = \frac{6L^2}{L^3} = \frac{6}{L}$$

M. F. Ashby, P.J. Ferreira and D. L. Schodek; **Nanomaterials, Nanotechnologies and Design**

Well, few things we like to recap first is the effect of shape. You know nanoparticles have very high surface area to volume ratio, but that is also affected by the shape right. The surface area to volume ratio is affected by the shape of the nanoparticle and we have shown to you that if I change the shape of a nanoparticle from sphere to cylinder to cube, the surface to volume ratio will be changing depending on the critical dimension whether its a radius or length of a cube right. This is something which you have shown you again and again please remember that shape plays a major role in dictating the surface area to volume ratio.

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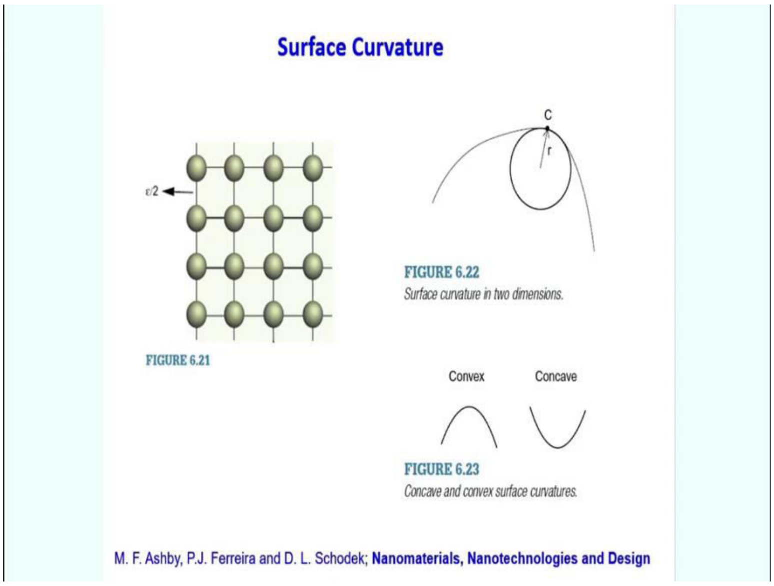

Surface Curvature

FIGURE 6.21

FIGURE 6.22
Surface curvature in two dimensions.

FIGURE 6.23
Concave and convex surface curvatures.

M. F. Ashby, P.J. Ferreira and D. L. Schodek; **Nanomaterials, Nanotechnologies and Design**

Well, surface curvature I have discussed just few minutes back it is an important aspect surface curvature will be changing various things surface energy, vacancy concentration depending on the nature of the local curvature whether its convex or concave this aspect must be taken into consideration.

You know surface will have very peculiar curvature local curvature right it is not like a fixed thing. Sphere means always have a uniform curvature they will have undulations and this undulations are going to be changing the local curvature and that is in turn will change the surface energy that is something we have discussed about it.

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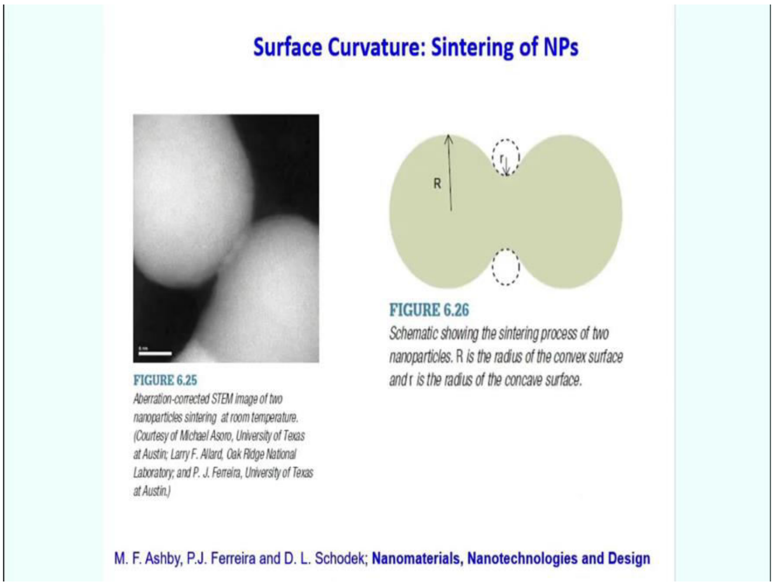

Surface Curvature: Sintering of NPs

FIGURE 6.25
Aberration-corrected STEM image of two nanoparticles sintering at room temperature. (Courtesy of Michael Asoro, University of Texas at Austin; Larry F. Allard, Oak Ridge National Laboratory; and P. J. Ferreira, University of Texas at Austin.)

FIGURE 6.26
Schematic showing the sintering process of two nanoparticles. R is the radius of the convex surface and r is the radius of the concave surface.

M. F. Ashby, P.J. Ferreira and D. L. Schodek; **Nanomaterials, Nanotechnologies and Design**

And this will have a tremendous effect on the sintering of nanoparticles because the vacancy concentration will be changing from the convex to concave curvature regions and that is will affect the motion of atoms or motion of vacancies in turn motion of atoms.

So, that will have a serious effect on the sintering of nanoparticles even at room temperature where diffusivities are normally very low for bulk materials for nanomaterial this will have a serious consequence that is why even if want the ppa nanomaterials storing them is a big question because you cannot avoid these sintering aspects. So, you may start with nanoparticles as synthesized from a particular root, but after a few days you will find that all of them are microcrystalline.

So, all your money and all your time whatever you spend to make these nanoparticles will go into vain will go waste actually, but nobody is going to purchase those things So, how to stabilize them is something which you need to learn and that aspect will be significantly affected by these curvature effects.

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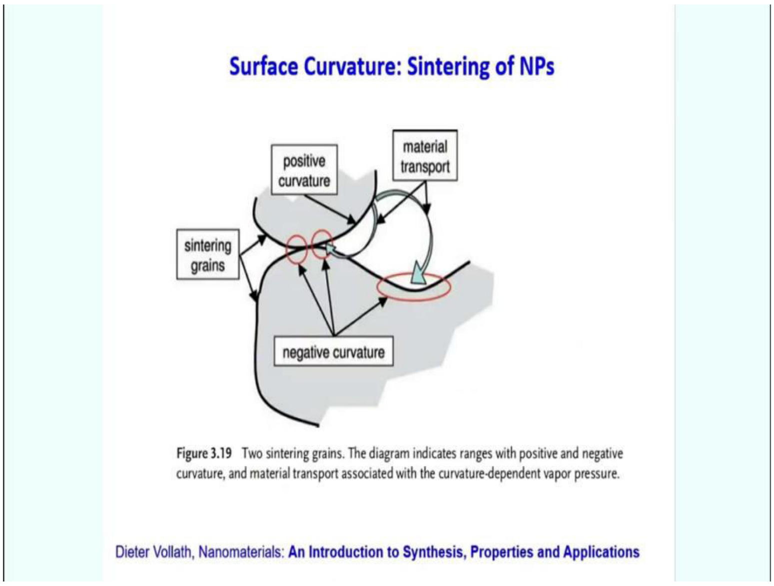

Surface Curvature: Sintering of NPs

Figure 3.19 Two sintering grains. The diagram indicates ranges with positive and negative curvature, and material transport associated with the curvature-dependent vapor pressure.

Dieter Vollath, Nanomaterials: **An Introduction to Synthesis, Properties and Applications**

Well, this is something I discussed again, this slide you see that positive curvature and negative curvature regions and the mass transport happens from the positive curvature to negative curvature regions ok. You know positive and negative curvature define mathematically positive is for convex, negative is for the concave surfaces, right. So, depending on that curvature locally on the surface of these particles mass transport will be determined right and that is something which is going to be in turn affect the sintering of the grains.

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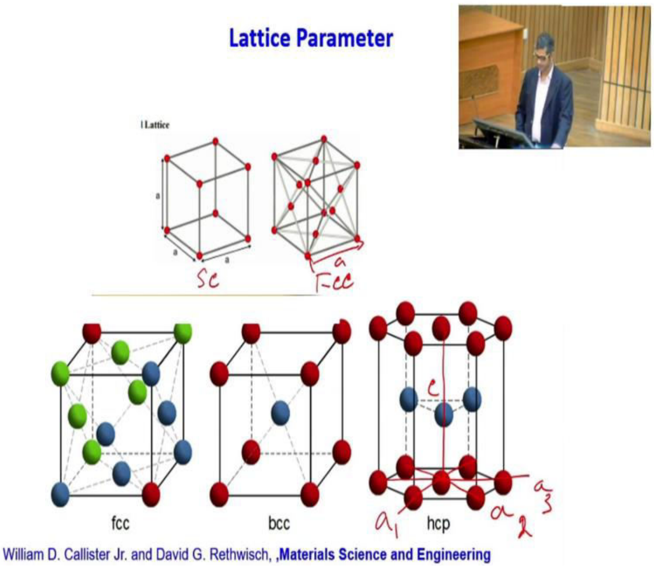

Lattice Parameter

William D. Callister Jr. and David G. Rethwisch, **Materials Science and Engineering**

Well, then I discuss about something of lattice parameters and I will talk about it again here lattice parameter let me just you know open it up, this is something which we have stopped discussing at the end because the time constraint in the last lecture, a lattice parameter is something which is defined by the unit cell right.

This is a simple cubic lattice, lattice parameter is given by: a, this Fc cell lattice parameters given by: a again and again something else for the same thing for fcc and bcc has shown in the color pictures. hcp you have two lines parameters one is c another one is a right a is this dimension right.

So, the 3 a lattice parameter all are same values because this is a regular hexagon say a_1, a_2 another a_1, a_2, a_3 right something like this. So, that means, this lattice parameters are also going to be affected by this surface energy and also the size of the nanoparticles.

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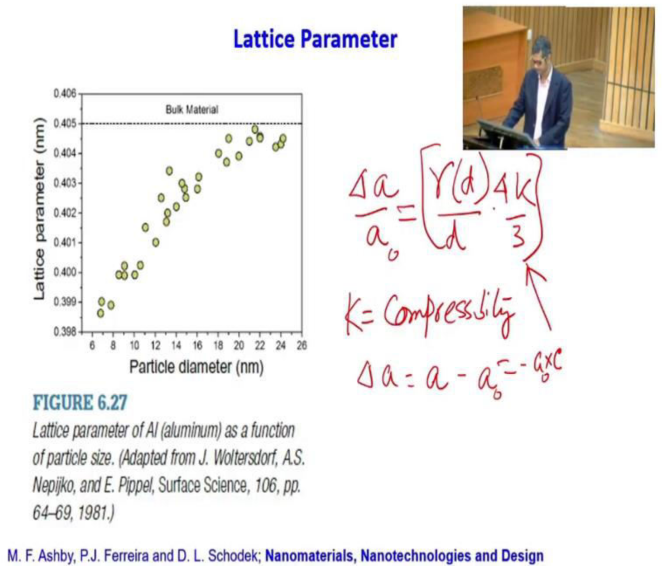

Lattice Parameter

FIGURE 6.27

Lattice parameter of Al (aluminum) as a function of particle size. (Adapted from J. Woltersdorf, A.S. Nepijko, and E. Pippel, Surface Science, 106, pp. 64–69, 1981.)

$$\frac{\Delta a}{a_0} = \left[\frac{\gamma(d)}{d} \cdot \frac{4K}{3}\right]$$

K= Compressibility

$$\Delta a = a - a_0 = -a_0 \times C$$

M. F. Ashby, P.J. Ferreira and D. L. Schodek; **Nanomaterials, Nanotechnologies and Design**

Well, as you have seen the equation which I wrote at the end of this last lecture was something like this. $\frac{\Delta a}{a} = \frac{\gamma(d)\times 4k}{d\times 3}$

Hope you have remembered those aspect, K is the curvature right, K is the bulk not curvature remember kappa is a curvature, K is the compressibility and d is the dimension of the particle maybe it is diameter or its per cube its one of the length of the side, ok it can be any other dimension also possible.

So, as you can see here all the $\frac{\Delta a}{a}$ is inversely proportional to d, but you have to understand γ is also depends on d right. So, it is this aspect of γ which is going to change the magnitude of change of lattice parameter, K will be negative and that is why lattice parameter will be decreasing correct.

Because Δa is $a - a_0$ let us write a_0 this one because there is still lattice parameter at the bulk. So, that is going to be changing. So, therefore, a will be equal to a_0 minus something right some parameter into a_0. So, this factor is going to come into picture, this is going to be $a - a_0 = a_0 c$ which is this am I clear? That is what is the aspect is.

So, because of the γ significantly depending on the gut size of a nanoparticle, your lattice parameter is going to be decreasing otherwise has been observed for different particle diameters for aluminum. As you can see here in this plot taken from this paper by Woltersdorf et al and its very clear compared to the bulk, bulk lattice perimeter aluminum is something like about 4.5 angstrom or 0.45 0.405 nanometers its can go down even 3.99 angstrom. Significantly low at a lattice particle diameter of 7 to 6 nanometers.

That is something which is very significant change is very significant its decreased by 1 nanometer sorry 1 angstrom not 1, 0.1 nanometers and that is means the lattice parameter shrinks a lot when you go down the size and this can be explained using the concept of surface energy please remember these aspects.

This is something which I could not clarify it, but now its clarified ok. Remember please do not get confused that Δa is inverse proportion to d that is what you dictate upon that. So, as d increases this would increase no. Basically γ is also depends on d and γ is basically you know has a significant effect of the decreasing of particles. So, as the particle decreases γ is also going to be changing ok.

So, γ is basically increasing. So, because of these two effects one side is d decreases and then γ increases. So, virtually it will depends on the ratio of γ/d right that is something which will be depending on the absolute values of γ and d at a particular value of d, a particular particle diameter. So, this is something which you need to remember always. So, that is first needs to be calculated using the formula which I have given and then put into this equation and to get the change of delta lattice parameters or Δa.

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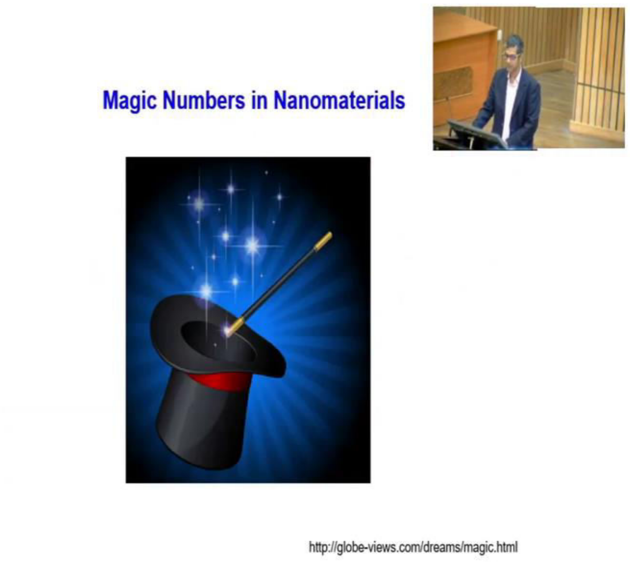

Magic Numbers in Nanomaterials

http://globe-views.com/dreams/magic.html

Well so, that is about the discussions, I spent about 10 minutes to do that. So, let us go to the magic number in nanomaterials. You know magic how can you create magic in science that is something which is very unusual right, but here the nature, Mother Nature has created magic, you can have only few numbers by which you can play with it you do not have a choice of all numbers with you.

So, what are those fortunately important numbers? Ok. Like fortunate guys or girls in the class who get A grades or A plus grades something is important here what are those numbers? But I am first I must explain you what is a magic number how it has developed this is a very not this is easy thing to understand. So, I request you to please concentrate to listen the lecture very well. So, that you understand it well you do not forget it. This is something new completely to you I hope you have never heard of these concepts ever in your curriculum.

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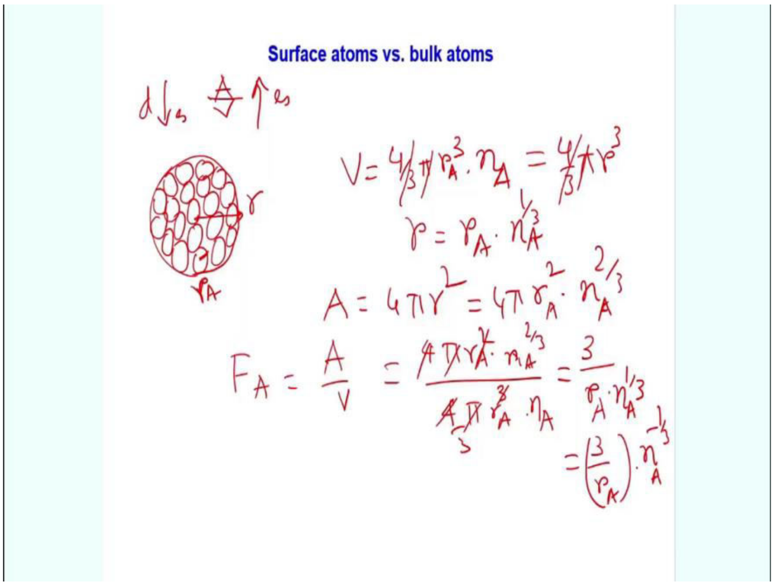

Surface atoms vs. bulk atoms

$d\downarrow,\ \frac{A}{V}\uparrow$

$$V = \frac{4}{3}\pi r_A^3 \cdot n_A = \frac{4}{3}\pi r^3$$

$$r = r_A \cdot n_A^{1/3}$$

$$A = 4\pi r^2 = 4\pi r_A^2 \cdot n_A^{2/3}$$

$$F_A = \frac{A}{V} = \frac{\cancel{4}\cancel{\pi} r_A^{\cancel{2}} \cdot n_A^{2/3}}{\frac{\cancel{4}}{3}\cancel{\pi} r_A^{\cancel{3}} \cdot n_A} = \frac{3}{r_A \cdot n_A^{1/3}} = \left(\frac{3}{r_A}\right) \cdot n_A^{-1/3}$$

Well, first let us talk about surface atom versus bulk atom. What is surface atom by bulk atom? Let us do that. You know we all know as the particle size decreases as the d decreases what happen? Surface area by volume ratio increases right that we know very well.

Therefore, the fraction of surface atoms will also increase as the particle size decreases now can we correlate that as a function of size what is the number of surface atoms versus bulk atoms? Can you do that? Let us do that ok. For that we will consider a very simple step ok it is always better to consider very simple thing and then explain your thought aspects.

So, let us consider a very simple step, what is that? Shape of a sphere ok let us consider that which is a spherical particle it contains many many many atoms and each atom is also like a sphere we are considering them hard sphere and they are sitting like this right. Now, obviously, this is center. So, this is r is the radius of the particle and let us suppose radius of each atom is r_A, A stands for atom right. So, r_A right.

Now, if this sphere has any number of atoms. So, therefore, volume of this sphere will be $\frac{4}{3}\pi r_A^3$ this is the volume of each individual atom. Now I multiplied by n_A, number of atoms units in this sphere. So, that is the total volume, but in doing that we are assuming that there is no space free space in this particle in this sphere all are occupied by this particle that is not true.

So, this is an assumption which you are making. But nonetheless maybe 10 to 20 % or 25 % space will remain vacant thus can be later on counter add it into the calculations. Well for the sake of simplicity we are not doing that right now. We are considering the volume of this unit cell as volume of this sorry volume of the sphere is $\frac{4}{3}\pi r_A^3 \times n_A^3$, where r_A is the size of each radius of each atom n_A is the number of atom in this unit sphere right, correct.

So, this must be equal to $\frac{4}{3}\pi r^3$; obviously, r is the diameter of the sphere. So, volume of the sphere is $\frac{4}{3}\pi r^3$. So, I can cancel 4 by 3rd 4 by 3rd and pi I get what? I get $r = r_A \times n_A^{1/3}$, this is the relationship between the number of atoms and radius of each atom that is easy to calculate for copper you know what the size of copper atoms with a sphere radius right.

So, now correct. So, what is the surface area of these atoms of this sphere basically? So, A is the surface area of the sphere that is nothing, but $4\pi r^2$ sufficient of the sphere. So, that is nothing, but $4\pi r^2 \times n_A^{2/3}$ am I right that is something which is easy to understand.

So, therefore, fraction of our surface atom is A/V. So, that is equal to F_A is this $\frac{4\pi r^2 \times n_A^{\frac{2}{3}}}{\frac{4}{3\pi r_A^3 n_A}}$ that is equal to $\frac{3}{r_A} n_A^{-\frac{1}{3}}$ So, you can see that actually, that is how actually your the fraction of the surface atoms can be obtained. Now, we can actually. So, this calculation is very straightforward for a sphere you will be able to do it for cube or maybe some other geometrics ok. So, what I did is sometime which is confusing to many of you is that, I have put atoms into spherical geometry atoms are also sphere; obviously, they are like a in a hard sphere they touch each other, but they do not deform each other that is the assumption we have made and we also made an assumption that the whole space is jam packed by these atoms, there is no space free space available in this volume right.

So, that means, this with these assumptions I get this is the fraction of surface atoms on the sphere. This I can relate with very easily number of atoms right r_A is anyway specific to a particular particle. So, this copper aluminum or zirconium or something oxygen, but n_A is something which is a variable, n_A will change these F_A significantly and it is $n_A^{-\frac{1}{3}}$.

So, I can write down for a particular species this is a constant term and then its become $n_A^{-\frac{1}{3}}$ ok. So, that is the relationships you get it.

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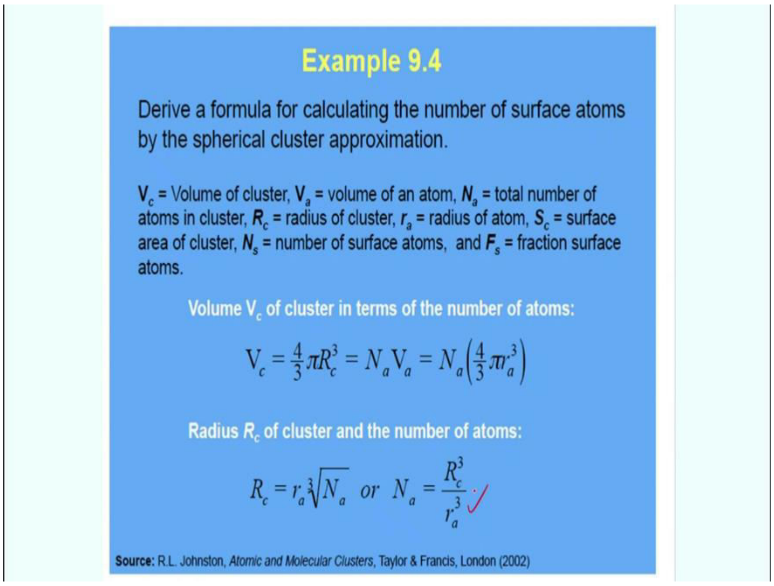

Example 9.4

Derive a formula for calculating the number of surface atoms by the spherical cluster approximation.

V_c = Volume of cluster, V_a = volume of an atom, N_a = total number of atoms in cluster, R_c = radius of cluster, r_a = radius of atom, S_c = surface area of cluster, N_s = number of surface atoms, and F_s = fraction surface atoms.

Volume V_c of cluster in terms of the number of atoms:

$$V_c = \frac{4}{3}\pi R_c^3 = N_a V_a = N_a\left(\frac{4}{3}\pi r_a^3\right)$$

Radius R_c of cluster and the number of atoms:

$$R_c = r_a\sqrt[3]{N_a} \quad or \quad N_a = \frac{R_c^3}{r_a^3} \checkmark$$

Source: R.L. Johnston, *Atomic and Molecular Clusters*, Taylor & Francis, London (2002)

Well, this is something again shown it here very simply the volume of the cluster is $\frac{4}{3}\pi R_c^3$ that is equal to $N_a\frac{4}{3}\pi R_c^3$. So, $R_c = r_a N_a^{1/3}$. So, therefore, $N_a = \frac{R_c^3}{r_a^3}$, you can obtain this way right. This is very simple this is the relationship you know then you can compare N_a and R_c

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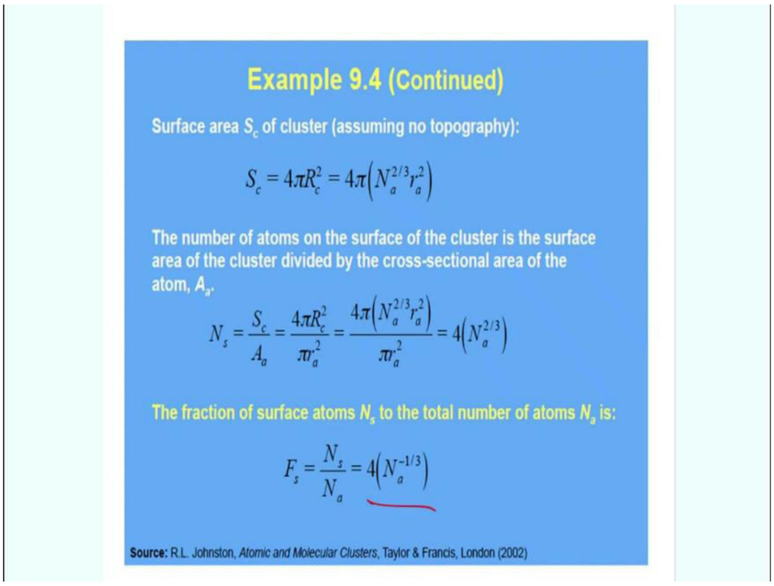

Example 9.4 (Continued)

Surface area S_c of cluster (assuming no topography):

$$S_c = 4\pi R_c^2 = 4\pi\left(N_a^{2/3} r_a^2\right)$$

The number of atoms on the surface of the cluster is the surface area of the cluster divided by the cross-sectional area of the atom, A_a.

$$N_s = \frac{S_c}{A_a} = \frac{4\pi R_c^2}{\pi r_a^2} = \frac{4\pi\left(N_a^{2/3} r_a^2\right)}{\pi r_a^2} = 4\left(N_a^{2/3}\right)$$

The fraction of surface atoms N_s to the total number of atoms N_a is:

$$F_s = \frac{N_s}{N_a} = 4\underline{\left(N_a^{-1/3}\right)}$$

Source: R.L. Johnston, *Atomic and Molecular Clusters*, Taylor & Francis, London (2002)

Now, you can always get a surface area, surface area is given by this $4\pi R_c^2$ we have seen that $4\pi N_a^{2/3} r_a^2$. So, number of atoms in the surface, N_s is basically surface area volume ratio is S_c/A_a ok or they are talking about a right yeah. So, we can do it in this way also that is nothing, but the cluster surface ok S_c is the surface area.

So, that is way you can remove what? We can remove these r_a actually from this. So, that, but finally, it becomes like this a constant term, $4(N_a^{-1/3})$. You can use either way I have kept it open ok this is taken from R. L. Johnston Atomic and Molecular Clusters ok this is also equally good any of these two calculations you can do.

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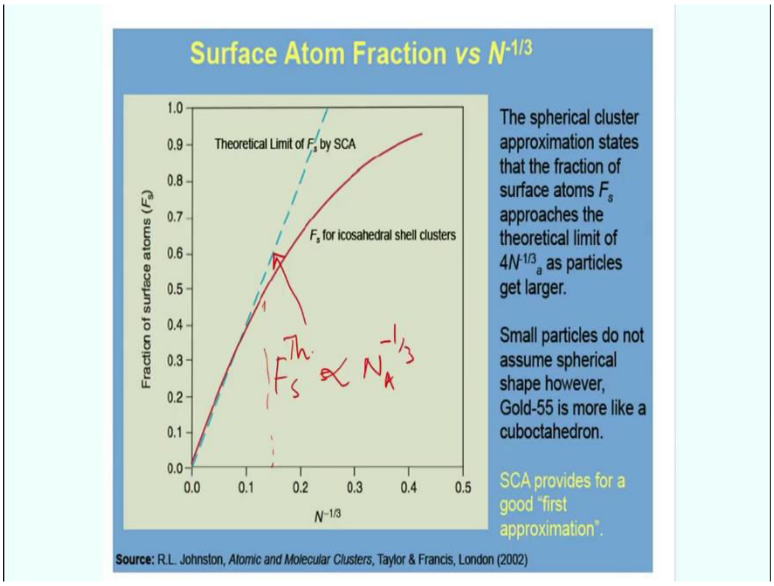

Surface Atom Fraction vs $N^{-1/3}$

The spherical cluster approximation states that the fraction of surface atoms F_s approaches the theoretical limit of $4N_a^{-1/3}$ as particles get larger.

Small particles do not assume spherical shape however, Gold-55 is more like a cuboctahedron.

SCA provides for a good "first approximation".

Source: R.L. Johnston, *Atomic and Molecular Clusters*, Taylor & Francis, London (2002)

So, now we can plot. We can plot this data fraction of surface atoms versus $N_A^{-1/3}$ what do you see? You see this is the theoretical limits this blue dots given by the calculations right that is nothing, but relationship with respect to $N_A^{-1/3}$ that is what it is you can plot it again yourself that is the scaling law. Scaling law says F_s is F_s is basically theoretically I can write down theory theoretically is proportional to $N_A^{-1/3}$ and that relationship is this ok.

Now, we have made many assumptions first of all in the theory earlier many theories may not exactly match with the experimental things. So, you know most easy surface lowest surface energy cluster for the liquids actually for solids yeah do exist, but very rarely is an icosahedral cluster which is nothing, but a 13 atom cluster icosahedron I will show you the picture of that. Icosahedral is the shape which forms this kind of clusters ok.

So, those clusters will not be following these particular relationships and they will deviate it as the N_A goes beyond 0.15 or so, you can see here from there it is deviating significantly. So, larger clusters larger value of N is this deviation is significantly observed for smaller one there is no change between whether you use theoretical limits and the icosahedral clusters ok.

So, this provides a good first approximation for the whole understanding. This is reasonably good right its not deviating as much as we are thought initially, because we are making so, many assumptions in this hard sphere model and the space is fully occupied with atoms those things are actually even if taken a consideration still does not make our calculation way off from the experimental ones ok. So, that is what is something which is very interesting, it does not make the calculation strongly depend on that.

But you know. So, far so, good this is understandable right you can easily do that this maths ok those of you who have knack of mathematics you can easily do these calculations for icosahedral clusters or spherical clusters ok it does not matter, but life does not end there. Most of the nanoparticles that crystalline. Like they could think of gold, aluminum, copper, platinum, silver many many others or you can think of iron, you can think of tungsten.

So, they have definite crystalline structure that crystalline structure will not allow them to go into spherical shape right. Obviously, there is underlying crystalline structure and this crystalline structure determines the surface energy actually. We know that surface energy of these different kinds of the material depends on the shape or the other they dictates the shape ok because it depends on the orientation crystalline orientation.

As a surface energy depends on crystalline orientations their variation will dictate which shape a particular material will take right. Because they are crystalline they are not amorphous if they are amorphous there is no anisotropy of surface energy ok. Surface energy could have been completely isotropic same in all directions, but because they are crystalline and they have definite atomic planes with different densities ok. Surface energy is going to be varying from one plane to other planes.

And you know surfaces the materials are very clever very intelligent, they will always try to create a surface which is the least surface energy. Then it spends less energy right we also like that given a choice you will not listen to my lecture you will like to go and back to your room sleep or something do something else, but definitely not listening to this kind of these lectures who will take understand that. So, that is what it is that is materials also like this ok.

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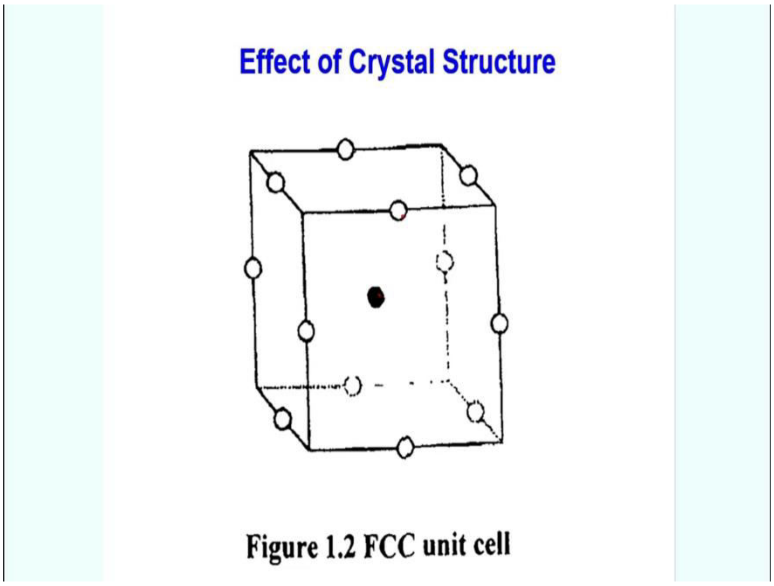

Effect of Crystal Structure

Figure 1.2 FCC unit cell

So, what is the effect of these you know what do you say this crystalline structure? Well, because underlying crystalline structures are built in now we discussed something about that and as I said ok. And as you know 70 percent of these periodic tables are basically metals am I clear there are metals and many of these surface centered cubic structures and what about in phase center cubic structure?

This is the phase centered cubic lattice ok as you can clearly see is it or not. Well, is it is not right it is this FCC unit cell, but shown in a different way right these are your phase center atoms ok corner atoms are displaced ok. So, now as you clearly see if I put an atom inside this unit cell there are 12 neighbors right how do you know?

4 plus 4 plus 4 right and FCC and hcp unit cells we know the coordination number is 12, there are 12 atoms this is way of representations to show in a different way so, that you can understand there are 12 realities atom otherwise you have to calculate it you have to

go and find it but you know that there are 12 nice tables right. So, now, this shows the whole perspective view.

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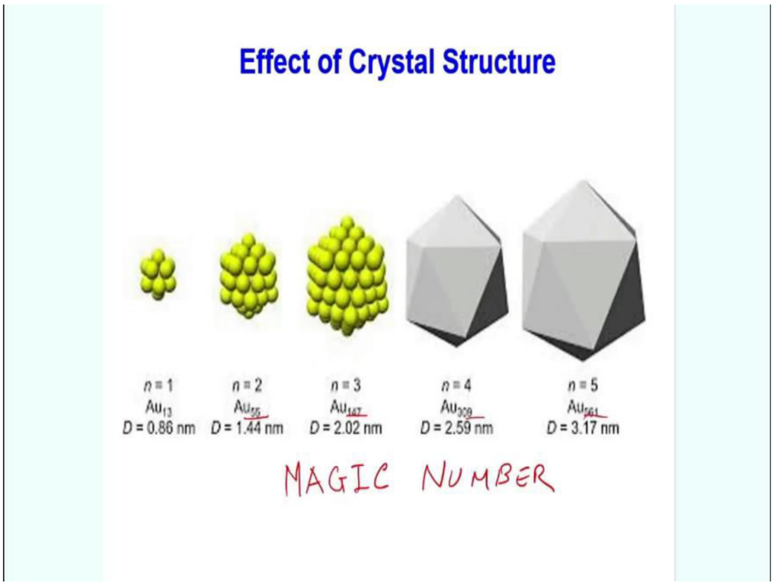

Effect of Crystal Structure

$n = 1$
Au_{13}
$D = 0.86$ nm

$n = 2$
$Au_{\underline{55}}$
$D = 1.44$ nm

$n = 3$
$Au_{\underline{147}}$
$D = 2.02$ nm

$n = 4$
$Au_{\underline{309}}$
$D = 2.59$ nm

$n = 5$
$Au_{\underline{561}}$
$D = 3.17$ nm

MAGIC NUMBER

So, now the single layer ok. So, we will go back yeah. So, this is along with this the 13 atoms in its right and that retains the fcc symmetry right 12 coordination number and fcc symmetries. Symmetry is basically dependent on the crystalline underlying crystalline structure ok and cube most important is your direction is three-fold directions ok f 3 m bar f m 3 bar m right and the 2 mirror planes.

So, now question is this, if this is a coordination and by which you want to form a nanoparticle 13 atom cluster basically ok then it has there is a single layer right and these all these atoms are sitting on the surface am I clear? Except the central atom. Central atom is within the bulk and all the atoms are sitting on the surface correct.

So, these aspects must be built in we are only thinking of spherical icosahedral clusters that is not be true always. So, what is important is to consider the underlying shape of the crystalline structure of these material to generate these shapes. So, now let us do that. Now suppose therefore, in single layer of the surface atoms 12 surface atoms am I clear?

And so, that is called single layer n equal to 1 that is my gold 13 atom cluster right you can understand that and it is a diameter of 0.86 nanometers you can do that by knowing simply diameter of gold atom you can calculate that, that is not difficult because you know the fcc structure.

So, now if I want to retain this symmetry of fcc structure, if I want to do that I put another layer right. So, if I put another layer you might be thinking 13 into 13 will be 26 no. If you really want to retain the symmetry what you need to do is to create a cuboctahedron symmetry which will come to little later ok correct.

So, as you see this is that cuboctahedron symmetry ok of this is what is the cuboctahedron symmetry shown on the right side it will have about 13 atoms again, but this is a 14 sided solid unlike cube 6 sided solids or 14 sided solids ok and because of the 14-sided solids with the 6 square faces and 8 equilateral triangles ok. I do not know whether I will show you that ok where is that.

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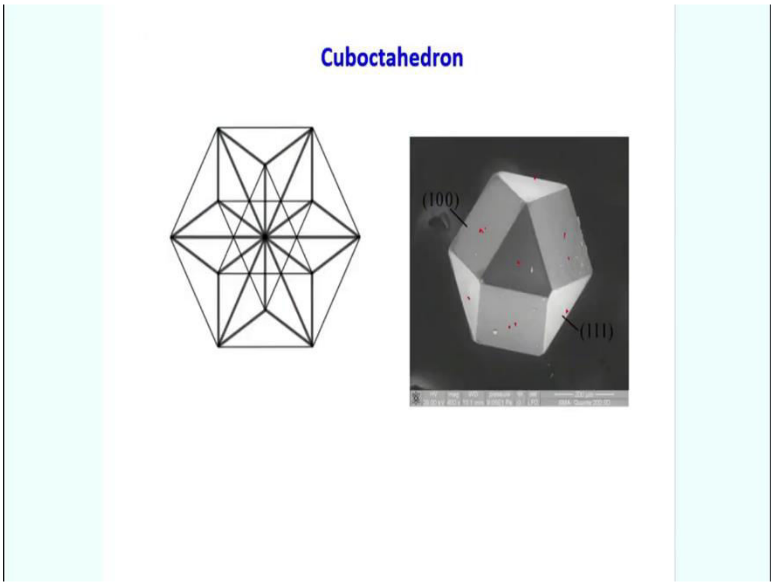

Cuboctahedron

This is what it is this is a cuboctahedron ok you can see that actually. There are 6 square faces these are the square faces and this is another one, 1 2 3 you can clearly see and 8 equilateral triangles 1, 2, 3, 4 you can clearly see that. So, 8 on the other side. So, 6 and 8. So, there are 14 solid sides ok do not worry I will explain in detail terms.

So, what will happen then? So, these 13 atom nanoparticles, which you created with one layer the moment you want to put a 2 layer shape will be cube octahedron the one I showed you with the 14 face side solids. If you want to retain the symmetry if you do not know the retain symmetry then forget about it can take any shape, but most of the fcc crystals they like to form a cuboctahedral shape, but that is the lowest energy shape ok.

Well in the next lecture I will discuss about it why this kind of shapes forms because that is very important for you to understand, but for the sake of generality please accept my viewpoints that the shape will be cuboctahedral why it will cuboctahedral come back to (Refer Time: 30:42)?

Now these 14 faces solids will be having 55 atoms ok because atoms can see in the corners as well as the center of these faces also that is what and then these things goes on that is what see then you have 3 layer, 4 layer. So, that is why 2 layer will have 55 atoms together and 3 layer will have 147 atoms, 4 layers will have 309 atoms, 5 layer of 365 65 1 atoms these numbers are called magic numbers ok they are called magic numbers here they are coming from magic correct.

Now, you understand why they are called magic number. This number you see that is what 13 is always a good number right, but we always think 13 is a bad number 13 55 147 309 and 561 and so, what goes on these numbers are there. So, now let me explain in a detailed manner to you ok.

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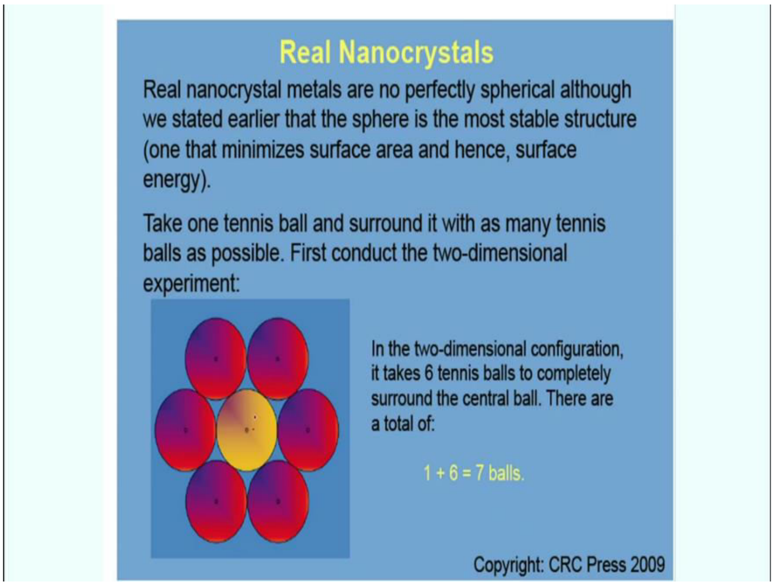

Real Nanocrystals

Real nanocrystal metals are no perfectly spherical although we stated earlier that the sphere is the most stable structure (one that minimizes surface area and hence, surface energy).

Take one tennis ball and surround it with as many tennis balls as possible. First conduct the two-dimensional experiment:

In the two-dimensional configuration, it takes 6 tennis balls to completely surround the central ball. There are a total of:

1 + 6 = 7 balls.

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Real nanomaterials nanocrystals are metal with no perfectly spherical although symmetry. Although we stated earlier the sphere is the most stable structure take 1 tennis ball simply tennis ball and you can surround it with as many as tennis balls. So, first you construct the two-dimensional experiments what is that? In a two-dimensional experiments this one you have done in your crystallographic courses right. You have a single tennis ball I can only surround same size tennis balls of 6 so; that means, there are total of 1 plus 6, 7 atoms right this is the 2D close packing.

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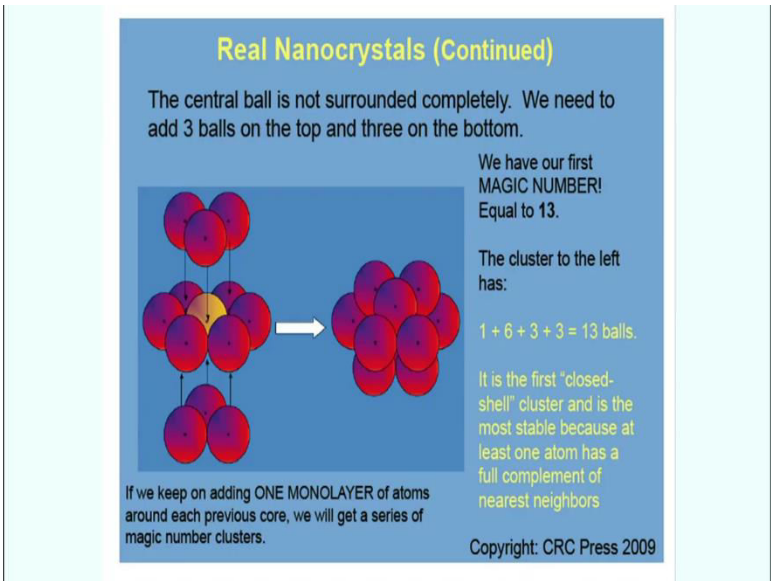

Real Nanocrystals (Continued)

The central ball is not surrounded completely. We need to add 3 balls on the top and three on the bottom.

We have our first MAGIC NUMBER! Equal to **13**.

The cluster to the left has:

1 + 6 + 3 + 3 = 13 balls.

It is the first "closed-shell" cluster and is the most stable because at least one atom has a full complement of nearest neighbors

If we keep on adding ONE MONOLAYER of atoms around each previous core, we will get a series of magic number clusters.

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Now, if you want to do a 3 D closed packing central ball is surrounded completely we need add 3 balls on the top of each central ball is surrounded completely we need to add 3 balls on the top and 3 balls at the bottom to cope to satisfy the boards of these 6 atoms surrounding the central ball right. So, the magic number is 13 you see that 6 plus 6 plus 1. So, if I consider this central ball is completely satisfied with bonds that becomes a bulk atom.

On the other hand, these red color atoms are surface atoms that is becomes my first shell right. So, 1 then 6 and then 3 plus 3 that is the fcc structure right a b c, a is the central layer, b is the second layer, c is the third layer that is the fcc structure you know that you have a forgotten right. So, in the first closed pack cells cluster this is the 13 atom clusters is the most stable because at least one atom has a full complement of nearest neighbors what is that?

The central atom center tennis ball, right. So, now if we keep on adding one monolayer atom around each previous core, we will get a series of magic numbers what is that means? So, now, you can create another layer and so obviously, when you create another layer each of these atoms red color atoms will also be surrounded by other surface atoms right that is satisfaction you have to do.

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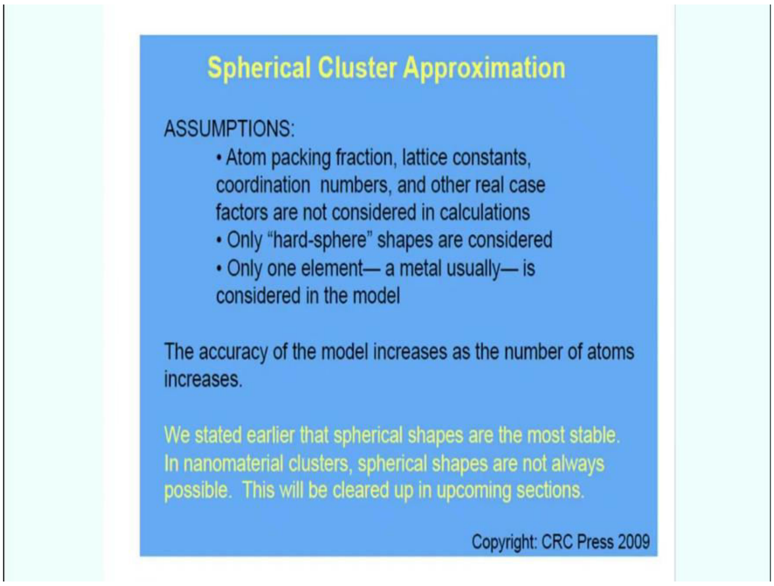

Spherical Cluster Approximation

ASSUMPTIONS:

- Atom packing fraction, lattice constants, coordination numbers, and other real case factors are not considered in calculations
- Only "hard-sphere" shapes are considered
- Only one element— a metal usually— is considered in the model

The accuracy of the model increases as the number of atoms increases.

We stated earlier that spherical shapes are the most stable. In nanomaterial clusters, spherical shapes are not always possible. This will be cleared up in upcoming sections.

So, in order to do that you need to add more and more atoms.

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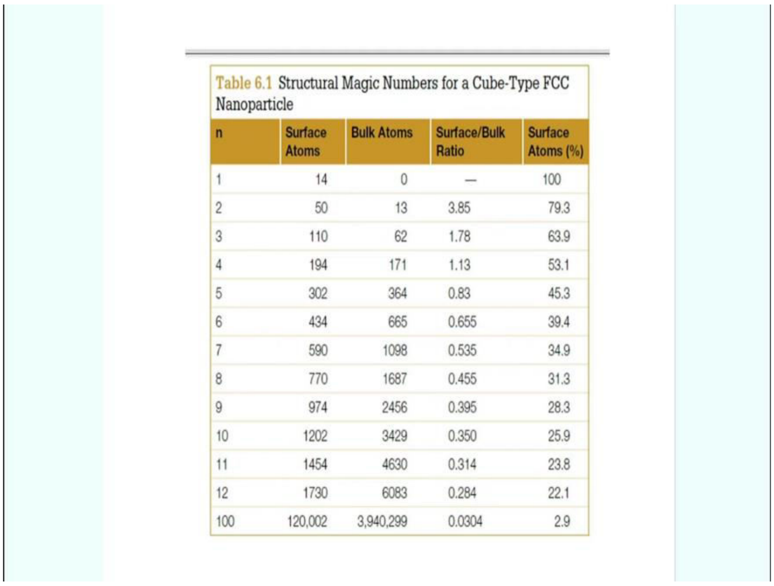

Table 6.1 Structural Magic Numbers for a Cube-Type FCC Nanoparticle

n	Surface Atoms	Bulk Atoms	Surface/Bulk Ratio	Surface Atoms (%)
1	14	0	—	100
2	50	13	3.85	79.3
3	110	62	1.78	63.9
4	194	171	1.13	53.1
5	302	364	0.83	45.3
6	434	665	0.655	39.4
7	590	1098	0.535	34.9
8	770	1687	0.455	31.3
9	974	2456	0.395	28.3
10	1202	3429	0.350	25.9
11	1454	4630	0.314	23.8
12	1730	6083	0.284	22.1
100	120,002	3,940,299	0.0304	2.9

That is what it is. So, now, if you do for a simple sphere this is cube only cube structure.

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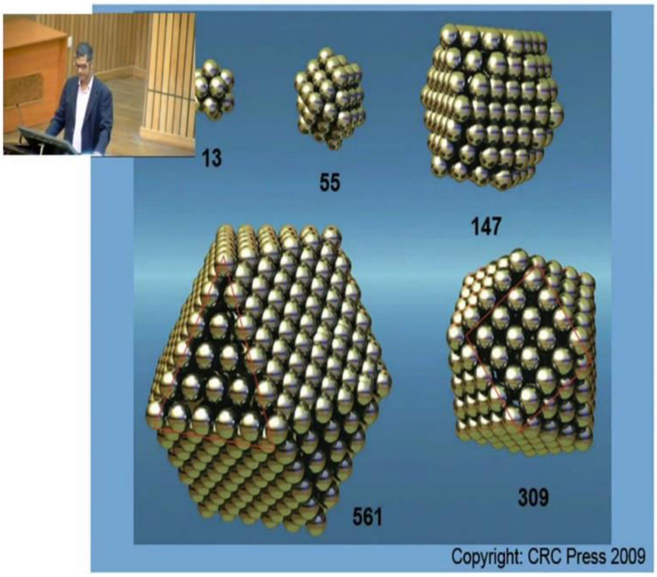

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So, that is the 13, 55, 147, 369 and 561 are the magic numbers right.

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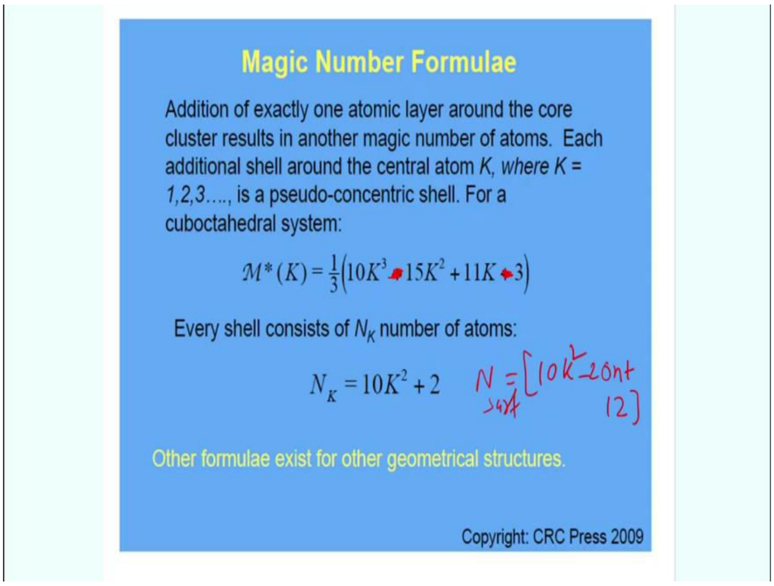

Magic Number Formulae

Addition of exactly one atomic layer around the core cluster results in another magic number of atoms. Each additional shell around the central atom *K, where K = 1,2,3….,* is a pseudo-concentric shell. For a cuboctahedral system:

$$\mathcal{M}^*(K)=\frac{1}{3}\left(10K^3 - 15K^2+11K - 3\right)$$

Every shell consists of N_K number of atoms:

$$N_K = 10K^2+2$$

$N_{>4Y4} = [10K^2 - 20n + 12]$

Other formulae exist for other geometrical structures.

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So, you can do a little bit maths also and the math says ok like this magic number formula ok addition to addition of exactly one atomic layer around the core cluster results in another magic number of atoms ok that is. So, this is something which you know for the cuboctahedral symmetry this M^* is the number of atoms of in this fcc nanoparticles given by ok its $\frac{1}{3}(10K^3 - 15K^2 + 11K - 3)$ yes.

So, now and the number of surface atoms surface atoms are less. So, I can write down surface atom is $N_{surf} = (10K^2 - 20n + 12)$. You must be wondering where from this formula are coming well this formula are coming by the geometrical constructions you can do that yourself. I am not doing it because that will take a lot of time, but these are available literature and please do this ok for your understanding.

So, that is something which you need to know very well and ok I am not doing it again and again for you because you also need to do some homework right there will be no mid-sem exam looks like not sem exam online lecture. So, your home assignments will be this and there you will not get very easily from different internet sources you have to really think and do it.

So, you got it. So, there are other formulae exists for other geometrical structures this is for cubic crystals with cuboctahedral structures right. This is very important for you to understand. So, what do you understand? So, far whatever you discussed first thing you understand.

So, let me go back I will come back again our magic numbers first you understand that we can calculate for a specific number of atoms in a cluster ok surface fraction of surface atom and it is very easy to do it for spherical ok spherical shape actually. So, you can do that and this becomes $n^{-\frac{1}{3}}$ the fraction of surface atoms.

And you can see that that is a theoretical limit $n^{-\frac{1}{3}}$, but real crystals will have shapes because of these crystalline shapes, it will have a definite number of atoms which will be stabilizing the structures and that is what is the magic numbers ok.

We started with fcc unit cell then slowly we built up the structural layer by layer and showed you how this magic numbers are coming correct. Please remember this which I have just shown you this is your for your understanding how you can create a 13th clusters atom.

And, then you can do the second layer how the 55 cluster atom will be created I also discussed this cuboctahedral shape of 14 side is 14 face solids. And, then number of atoms sitting as that. So, 42 is the number of atoms in there in that cuboctahedral shapes right; obviously, 13 is here, 42 is there then you become 55. So, now let us show this table I think I have somewhere there.

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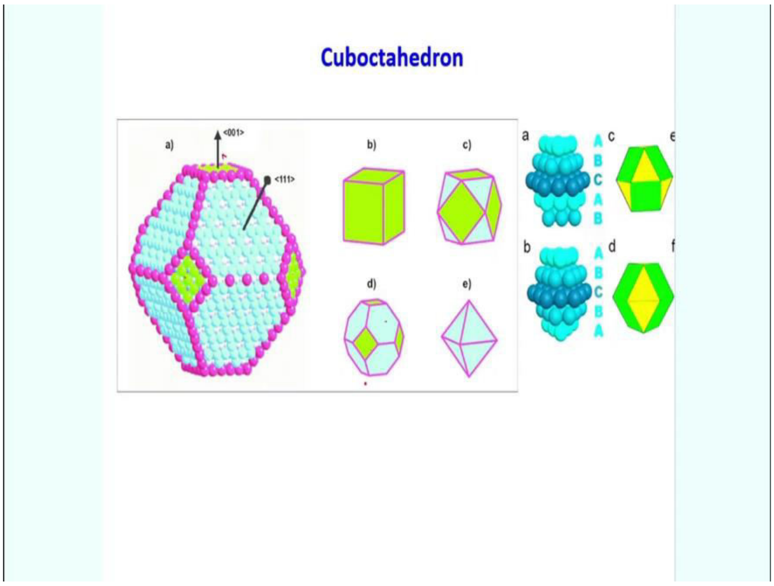

Cuboctahedron

So, this is the cuboctahedron structure and this is better to here ok. So, what do you see here? In a cuboctahedron you have this square face ok there are 6 square faces and then you have triangular faces ok. So, that is you see here correct and you can create a structure by this way by adding atoms very easy to do that this is something which is there in the books.

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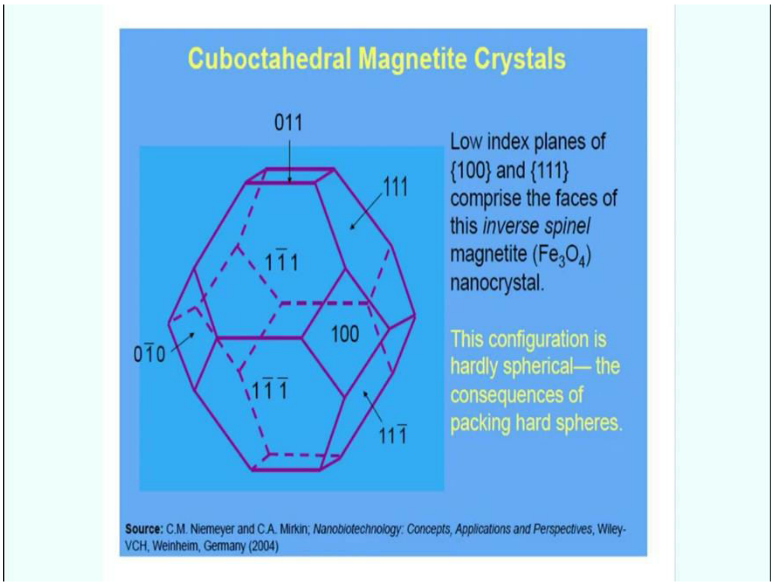

Cuboctahedral Magnetite Crystals

Low index planes of {100} and {111} comprise the faces of this *inverse spinel* magnetite (Fe_3O_4) nanocrystal.

This configuration is hardly spherical— the consequences of packing hard spheres.

Source: C.M. Niemeyer and C.A. Mirkin; *Nanobiotechnology: Concepts, Applications and Perspectives*, Wiley-VCH, Weinheim, Germany (2004)

And, this is on the magnetite crystal, these are the different planes of the atoms. Configuration is hardly spherical-the consequence of packing hard sphere ok low index explains {100} {111} comprise the faces of inverse spinal magnetite nano crystals ok this is what is observed in cubic structures, this kind of shapes are stabilized.

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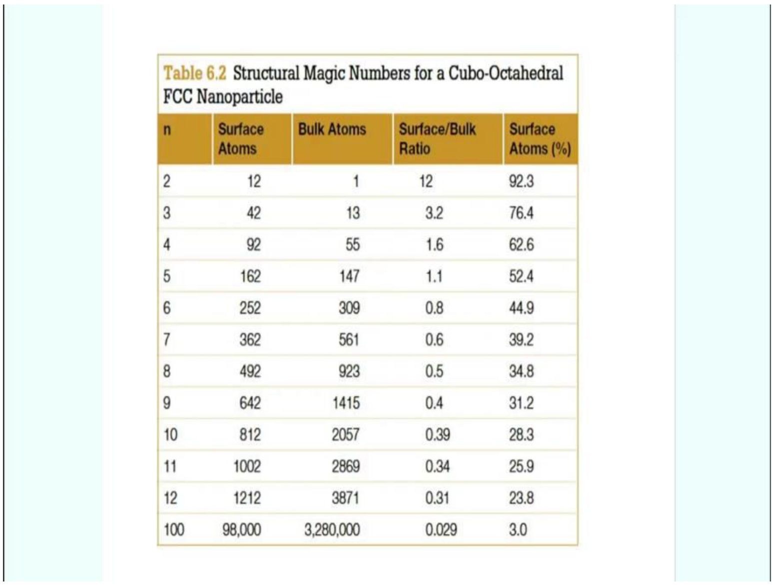

Table 6.2 Structural Magic Numbers for a Cubo-Octahedral FCC Nanoparticle

n	Surface Atoms	Bulk Atoms	Surface/Bulk Ratio	Surface Atoms (%)
2	12	1	12	92.3
3	42	13	3.2	76.4
4	92	55	1.6	62.6
5	162	147	1.1	52.4
6	252	309	0.8	44.9
7	362	561	0.6	39.2
8	492	923	0.5	34.8
9	642	1415	0.4	31.2
10	812	2057	0.39	28.3
11	1002	2869	0.34	25.9
12	1212	3871	0.31	23.8
100	98,000	3,280,000	0.029	3.0

Well, so, therefore, this is the magic numbers of that. So, the if of n is equal to 1 ok remember that this is not 2 ok basically why it is calling 2? There is a central atom and then you are putting around that there are 12 atoms then become 13 atom clusters, the central atom become 1 and the surface atom become 12 that gives you surface to bulk ratio 12, the fraction of surface atom is 92 percentage.

If you create another layer, your surface atom become 42 because all these cubo octahedral atoms goes to surface atoms bulk atoms become 13, so the ratios get changed. So, you can keep on doing that ok and these numbers are called the magic numbers right 13 55 147 309 561 923 1415 and so on. So, you can create bigger and bigger bigger bigger clusters right. So, that is something which you should remember.

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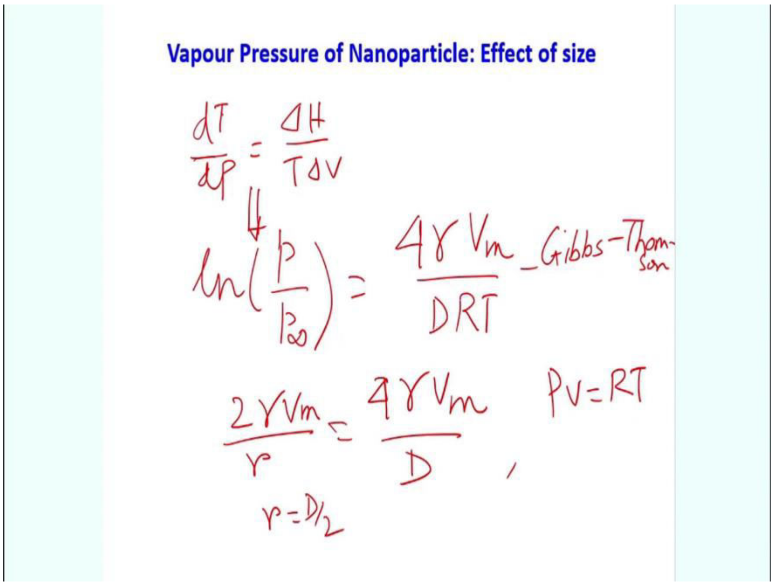

Vapour Pressure of Nanoparticle: Effect of size

$$\frac{dT}{dP} = \frac{\Delta H}{T\Delta V}$$

$$\Downarrow$$

$$\ln\left(\frac{P}{P_\infty}\right) = \frac{4\gamma V_m}{DRT}$$ _Gibbs-Thomson

$$\frac{2\gamma V_m}{r} = \frac{4\gamma V_m}{D}$$ $PV = RT$

$r = D/2$

Now, in the last part of my lecture which I am going to do is, to show you something new something new means something which you have not read about it. You know vapor pressure of nanocrystalline material also depends on the size and the surface energy right.

Those of you who are well conversed with Clausius and Clapeyron equation, that tells you the dT/dP and that is equal to what temperature time by temperature pressure equal to what? Is that it says yes this is $\frac{dT}{dP} = \Delta H/T\Delta V$.

This is the Clausius Clapeyron equation if you pressure on the ice it melts to water because ice has more volume than water that is comes from these ok. Now, we can modify this equations taking into consideration the size of nanoparticles ok and this is can be easily done by using concept of free energy which I am not doing that. So, therefore, if you do it properly, the equation I am writing here I am not discussing much of detail then it will be massive.

So, lnP/P_∞ is basically solid to vapor pressure solid to vapor or liquid to vapor here we are talking about solid to vapor liquid have no shape right solid only. So, this will be equal to $4\gamma V_m/DRT$. So, let me just tell you why it is coming you know that $\frac{2\gamma V_m}{r}$ that you know or you do not know you must be knowing it this is what it is?

This is this pressure created because of the soap bubble right you know that and this is nothing, but $\frac{4\gamma V_m}{D}$ because r $=D/2$, γ is the surface and the V_m is the molar volume this is something which you know.

And because we know that the vapor can be treated as a gas. So, therefore, $Pv = RT$for one mole and that is why the RT term comes in the picture right this is understandable? So, I can always write down from this equation only this comes this is not very different from that and this is known as a Gibbs Thomson equation, correct

So, as you can clearly see the vapor pressure p, p is infinity for the bulk and p is for the nano particle of size diameter d right that is significantly scales with gamma and d ok that gamma is also depending on the surface diameter of the particle, but d is also depending on the diameter of the particle d is. So, that I can write down this whole equation gamma is also function of d right.

So, this is something which will be changing the behavior of the nanoparticles, when they are in contact with their vapor right. So, all of them nanoparticles will not be prone to vaporizations, but some of them, for them the vapor pressure will decrease substantially as the size decreases. So, stability of them will be depending on the size that is something which is to know.

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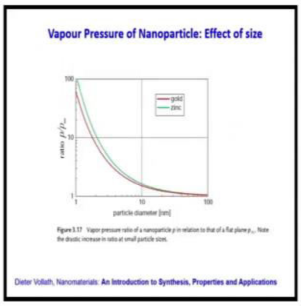

Vapour Pressure of Nanoparticle: Effect of size

Figure 3.17 Vapor pressure ratio of a nanoparticle p in relation to that of a flat plane p_∞. Note the drastic increase in ratio at small particle sizes.

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So, now I am plotting here with P/P_∞ for gold and zinc as a function of particle diameter. So, what do you see as the particle diameter decreases this P/P_∞ is increasing in very high value right and this is one atmospheric pressure 10 and 100. So, therefore, ok P_∞ is basically bulk that is a flat surface. So, the drastic increase in the ratio a small particle size huge increase not drastic, it will be huge increase of ratios for the particles.

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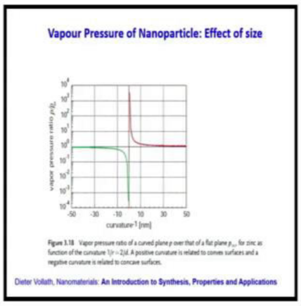

Vapour Pressure of Nanoparticle: Effect of size

Figure 3.18 Vapor pressure ratio of a curved plane p over that of a flat plane p_∞, for zinc as function of the curvature $1/r = 2/d$. A positive curvature is related to convex surfaces and a negative curvature is related to concave surfaces.

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Now, next plot which is the last plot for this class is if vapor pressure ratio of a curve plane p over a flat plane p for zinc ok and this is $\frac{1}{r}$ what do you see here? There are two sets of curves ok why? Because one is for convex other one is for concave. So, therefore, not only size, but also the curvature will also dictate the vapor pressure why? Because $\frac{1}{d}$ is basically curvature right we have seen that $\frac{1}{r}$ can be related to $\frac{1}{d}$ basically curvature.

So, therefore, both the sides as well as the curvature will dictate the vapor pressure ratio and that is something which is important to consider. So, as you prepare nanoparticles, they will have different sizes different curvature locally and that will affect this ok. So, let me stop here. So, we have discussed lot of things very important, but difficult aspects which you need to ask to understand.

First one is the magic number concept which is not easy to conceive nicely to get it please listen to the lecture properly and read books and also the effect of size and the local curvature on the vapor pressure these are two things we discuss. In the next lecture we will discuss about the equilibrium shapes of the nano crystalline materials ok. I will bring about new concepts for that.