Nanomaterials and their Properties

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Lecture – 06
Nanomaterials: Surfaces and Interfaces-I (contd…)

Hello students, hope you are enjoying the lectures. We are going to move into lecture number 6, but before I start that, let me just tell you that you can always have questions regarding every topic I am teaching and post it to me by email. Anyway, we are going to create a website also which will be interactive so that you can understand how to use the interactive media.

Nonetheless, let us start our lecture.

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In the last lecture, we have been learning about surface.
We shall continue on it.

Surface/Interfaces are important bearing significant energy of the system at nano-size

Concept of surface energy
How surface area affects surface energy?

Recap..
Surface energy

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

Well, as you know in the last lecture that is lecture number 5, we have been learning about surfaces. We started lecture number 4, deliberated on lecture number 5 and in this lecture we are going to continue on it.

As you know surface and interfaces are very important for nanomaterials, because surfaces or interfaces bear a significant part of energy of the system when the size is at the nanoscale. I discuss something about concept of surface energy, the bond making model and then, I discuss something about how surfaces, surface area affects the energy of the system right, and finally I talked about something about surface energy.

So, in this lecture, we are going to talk about more, about the effect of the surface energy. By the way, you have any questions? You can always write it down and post it to me. So, what do you have learned; that every nanometer material have surfaces and surface area is pretty large, a surface rate of volume ratio is pretty large so, the effect of surfaces cannot be ignored.

Why it is, how it is manifested or how it is done? If you consider the surface atoms sitting here ok; let us put a kind of a pen or something like that and using a color. So, if you look at any atom here, there are sufficient number of dangling bonds on this atom and these dangling bonds are unsatisfied. And, because of this aspect, because of unsatisfied bonds, these atoms are going to have more energy, ok. And when you have large number of such atom sitting on the surfaces, then this energy is going to be significantly high, correct.

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Nanocrystalline Objects and Surfaces

So, let us, you know this is very important for several important several materials not only the carbon based one, but I like to show you this one because you know we know that carbon can form a single layer graphene, ok where every atom of carbon is a surface atom right, it is, it does not have any connection with underlying material or on the top side right; it is a single layer. So, there are lot of unsaturated bonds present on this surface of the graphene and these unsaturated bonds carry lot of energy.

As you know carbon atoms on the in the plane, they are connected with bond right each carbon atoms, but an outside the plane, there should be two bonds, these bonds are missing. Because these bonds are missing so therefore, there are unsaturated electrons present associated to each carbon atom and they are adding up the energy your system. So, if you roll it up, you form a single wall nanotube, carbon nanotube; again, the surfaces remains same instead of becoming a flat one, it become a curved surface or if you put several of these roll layers, you can make a multi-wall nanotubes, then you can have actually some of the bonds of the carbon atom on the top surface are satisfied.

Well, this is something which is very important for every nanomaterial in this world, ok what are is a carbon or some other species does not matter, it is a aspect which is very common.

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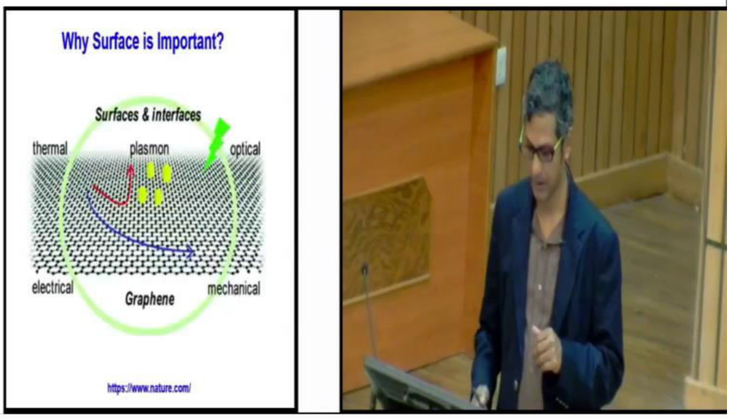
Why Surface is Important?

https://www.nature.com/

Graphene is more predominant because many of these properties are basically because of these dangling bonds, like surface plasmons, thermal, optical, electrical or mechanical properties of graphene you understand. The graphene is much more stronger than a graphite, this graphite has Van der Waal bonds between the layers which are easy to break. But the graphene there is no Van der Waal bonding, it is basically a covalent bonded carbon layer, So, that is why elastic modulus of graphene is in the tera-pascal design not in mega Pascal or the giga Pascal, this is the reason is this. So, there are many many such properties which we will discuss in many of some of the lectures later on are because of these surface energy of grapheme.

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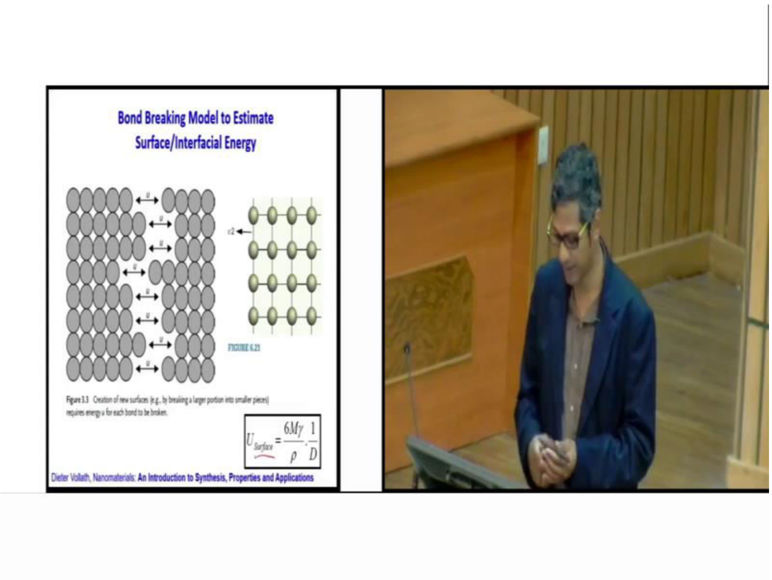

Bond Breaking Model to Estimate Surface/Interfacial Energy

Figure 3.3 Creation of new surfaces (e.g., by breaking a larger portion into smaller pieces) requires energy u for each bond to be broken.

$$U_{Surface}=\frac{6M\gamma}{\rho}\cdot\frac{1}{D}$$

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

Now, I also discussed about the origin of surface energy. Origin of surface energy is because of the breaking a bonds right. So, every atom is connected to the other atom by a some bond, we have already told about talked about it about carbon. And so, if I break a bond and if the bond energy between the two atoms are U, then basically per atom you are breaking you are spending energy of $\frac{U}{2}$ or $\frac{\epsilon}{2}$, correct.

So, this bonds which are broken to create a surface or this bonds which are dangling actually in case of surface already created are responsible for surface energy right, ok; it can happen by interfacial also interfacial energy also. So, we have done some mathematical analysis using spherical particle and we have shown that the surface energy depends on inverse of the size. It also depends on density, depends on the total sub energy, depends on the molecular mass, but most importantly scale to the size that is the critical aspect ok.

So, as you decrease the size, $U_{surface}$ increases; you see $U_{surface}$ will increases decrease size exceedingly at a very high rate ok. So, that is something which is also an important aspect, not only size degree reduction leads to increase of surface energy but it scales with the size. So, therefore, we need to understand how does a scale with different kinds of shapes is this only true for spherical one, but what will happen if you have a cuboid or you have a cone or you have a cylinder that is something which we will discuss today.

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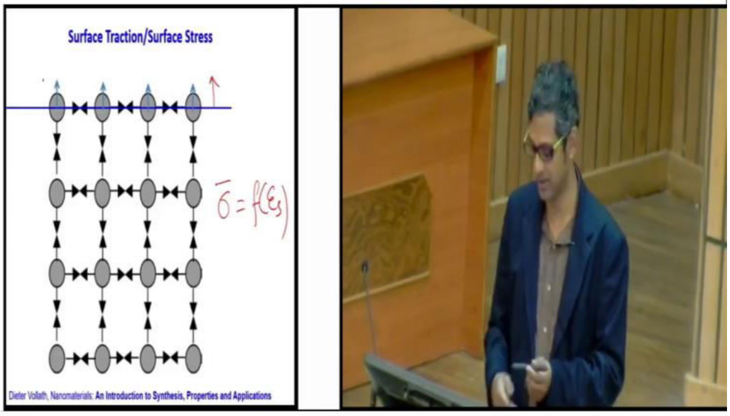

Surface Traction/Surface Stress

$\bar{\sigma} = f(\varepsilon_s)$

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Well, not only that, you know if you have a surface, atom sitting in the surface on a solid ok these atoms are filling some kind of extra force, because of the dangling bond. And, this extra force is acting perpendicular to this surface and this leads to what is known as traction force or in a larger scale surface stress. And surface stress basically will depend upon the stretching ok, how much these bonds are stretch is obviously, because there is no bond on this side, the surface atoms will be stretch just like a rubber or a skin of a rubber right exactly, it will be stretched.

If you pull a rubber band, you are stretching the rubber band so, atoms sitting on the surface are also getting stretched, exactly same thing happens here. The moment you create a surface on nanomaterial or any material actually whether for the sake of understanding, this surface atoms are filling a force, acting perpendicular to the surface and this will lead to stretching of the surface atoms and this stretching is manifested in terms of surface stress; the surface stress will be a function of stretching, amount of stretching, right.

Then, we have shown how to deal with it in the last lecture, I am not going back into that.

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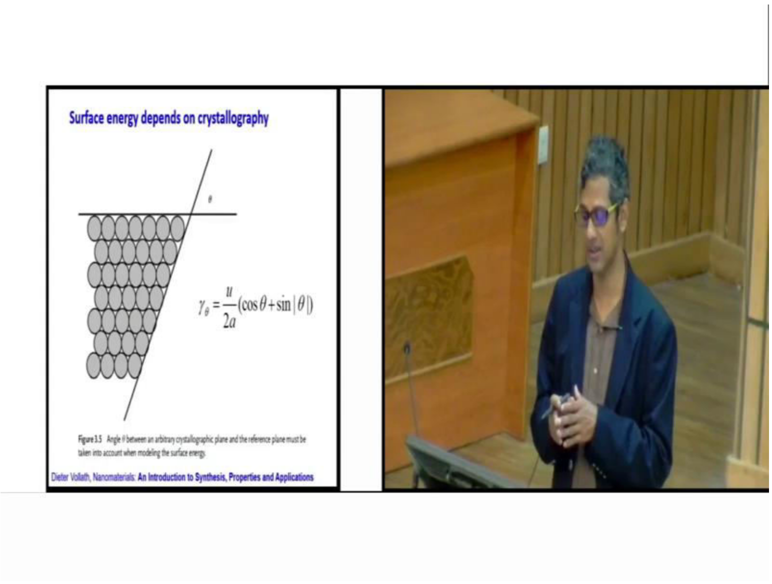

Surface energy depends on crystallography

$$\gamma_\theta = \frac{u}{2a}(\cos\theta + \sin|\theta|)$$

Figure 3.5 Angle θ between an arbitrary crystallographic plane and the reference plane must be taken into account when modeling the surface energy.

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Surface energy also depends on the orientation of the plane. I have discussed this using a cubic FCC structure and this is the formula which is used to calculate how surface energy will change as a function of orientation of the plane ok in a 2D, correct. I think it is for you two-dimensional situation is enough, you do not need to go into two-dimensional, 3D it will have more complications ok. But if you are interested, you can look into these textbooks which I given their 3D things are also discussed.

Well, by the way, so these are the aspects you should know.

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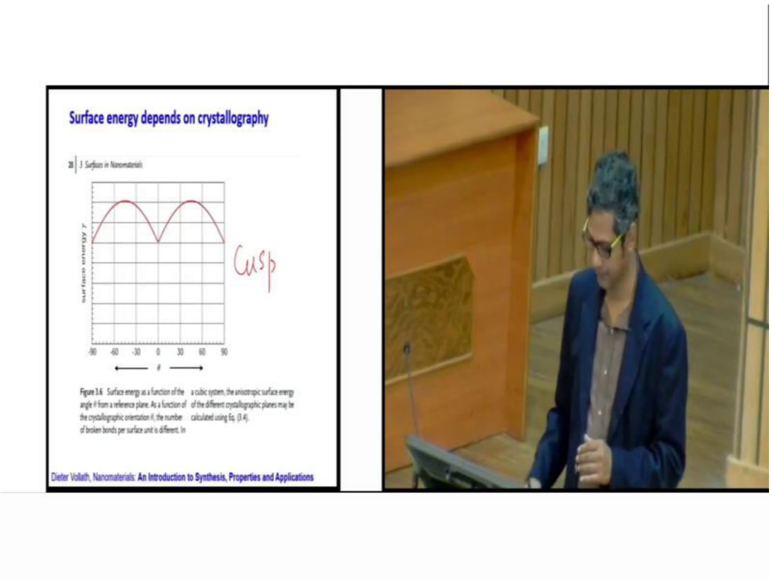

Surface energy depends on crystallography

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Figure 3.6 Surface energy as a function of the angle θ from a reference plane. As a function of the crystallographic orientation θ, the number of broken bonds per surface unit is different. In a cubic system, the anisotropic surface energy of the different crystallographic planes may be calculated using Eq. (3.4).

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Now, as if you can see that in this diagram which is taken from Vollath's book of Nanomaterials, it is shown how surface energy is going to change as a function of theta positive and negative side, ok. Obviously, sin it will not better matter because sin is basically sin mod theta, but cos it is going to be changing as a function of theta. Now, this is its creates two cusp ok, you can see that. And these cusps are actually our origin of the variation of the substances function of orientations.

So, there are maximum, minimum value of the surface energy because of orientation change, ok. You can find out if your laboratory frame or reference is 0^0, then at a different angle 30, 60, -90 or +90, how surface energy is going to be varying with respect to this angle.

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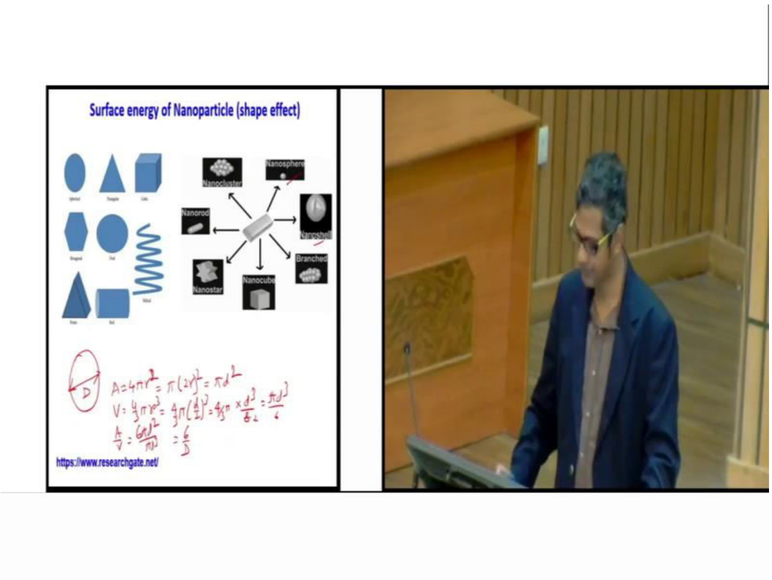
Surface energy of Nanoparticle (shape effect)

$A = 4\pi r^2 = \pi(2r)^2 = \pi d^2$

$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{4}{3}\pi \times \frac{d^3}{8} = \frac{\pi d^3}{6}$

$\frac{A}{V} = \frac{6\pi d^2}{\pi d^3} = \frac{6}{D}$

https://www.researchgate.net/

Well, now let us discuss of today's lecture. Surface energy also will depends upon shape, I already discussed about it ok for the spherical shapes right as you can really understand; why it will depend on shape is very easy to understand, ok.

So, if I have a sphere and this is the diameter of the sphere ok, so as you understand the you know spherical particle surface area is $4\pi r^2$ right is it not and that is equal to pi into ok; let us erase it up $\pi(2r)^2$ that is equal to πd^2, this we have done. And volume is $\frac{4}{3}\pi r^3$; $\frac{4}{3}\pi r^3$ I should be very careful because this pen always goes that means, it is about $\frac{4}{3}\pi\left(\frac{d}{2}\right)^3$. So, $\frac{4}{3}\pi\frac{d^3}{8}$. So, this is equal to $\frac{\pi d^3}{6}$. So, Area to volume ratio; $\frac{A}{V} = \frac{6}{D}$

So, you just say, A by V is $\frac{6}{D}$. Suppose as you also scale as a function of $\frac{1}{D}$ ok, 6 can be done as a constant factor ok. So, this is true for if you have a spherical shape to triangular shape, cubic, hexagonal or prismatic or even rod like a cylinder or even a helical, correct. So, by the way, you can create these steps from a single entity by different treatments, you can create nanospheres, you can create nano shell, you can create cube, 7-stars, nanorods, nanoclusters or even branch structures, right.

So, all the geometrical things which you have learned in your plus 2 and even subsequent studies to calculate area to area and volume will come into picture and we will have one lecture for these two how to calculate these aspects, when we will discuss more about it ok; that is in online lecture which I will discuss more on that aspects.

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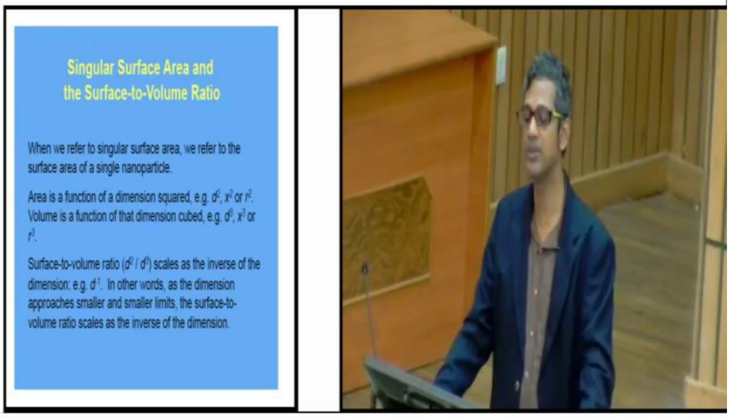

Singular Surface Area and the Surface-to-Volume Ratio

When we refer to singular surface area, we refer to the surface area of a single nanoparticle.

Area is a function of a dimension squared, e.g. d^2, x^2 or r^2. Volume is a function of that dimension cubed, e.g. d^3, x^3 or r^3.

Surface-to-volume ratio (d^2 / d^3) scales as the inverse of the dimension: e.g. d^{-1}. In other words, as the dimension approaches smaller and smaller limits, the surface-to-volume ratio scales as the inverse of the dimension.

So, let us see how it is going to be changing ok, I will not do all of them. So, when you refer to a you know singular surface area, we refer the effect is particle area of a single particle right. Area is a function of square of the dimensions all of you know that ok, it is it says unit of meter square or centimeter square so, inch square. So, it will have a dimensions of; any dimension whether length or is a side of a you know cube or diameter square right, volume will have a have a always a function of cube.

So, surface to volume ratio will be $\frac{1}{d}$ it is expected, but the constant terms will change. So, dimension as the dimension approaches or these particles become smaller and smaller surface to volume ratio will be much higher.

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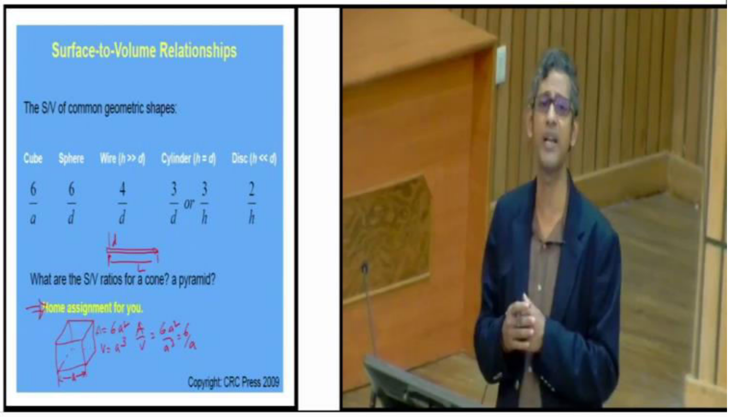

Surface-to-Volume Relationships

The S/V of common geometric shapes:

Cube	Sphere	Wire ($h >> d$)	Cylinder ($h = d$)	Disc ($h << d$)
$\frac{6}{a}$	$\frac{6}{d}$	$\frac{4}{d}$	$\frac{3}{d}$ or $\frac{3}{h}$	$\frac{2}{h}$

What are the S/V ratios for a cone? a pyramid?

Home assignment for you.

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

$V = a^3$

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So, now you can clearly see I have already done for spheres is $\frac{6}{d}$, right. What about cube? You can do yourself that is very easy, if you cannot do, I can do this for you that is something which is easy to understand. So, I have done it probably or let me do it again there is nothing wrong.

So, if you know that cube has 6 surfaces and cube has each of these sides as a length of a. So, surface area is $6a^2$. Why a square; a into a right, this is the surface area of total surface area of the cube ok. Now, what is the volume? Is obviously a^3 that I need did not discuss even. So, what is the area of a volume ratio? It is $\frac{6a^2}{a^3}$ that is everybody can do $\frac{6}{a}$ a, right.

So, now, we can you know get it for where is like this, where is the diameter d, a length L so, you can do that right or a cylinder ok or it a disc or you can do it for cone or pyramid ok. So, this is this is something which I think you should do, it is a home assignment for you that is what I mentioned, right. If you, do it for a wire, cylinder, disc, pyramid, cone all kinds of shapes. Do not worry, if you are not will do, I will do it for you, but you must try, you should try how to do it, this is very easy.

See idea is for you to do is that to understand how the surface to volume ratio is going to be critical for nanomaterials, if you create different shapes. So, you it gives you size is one aspect, size of nanomaterial is one aspect right that is what we have been talking about it size, size, size, size, size. But shape, which we have not discuss is very critical that is why different shapes has different kinds of manifestos in terms of properties.

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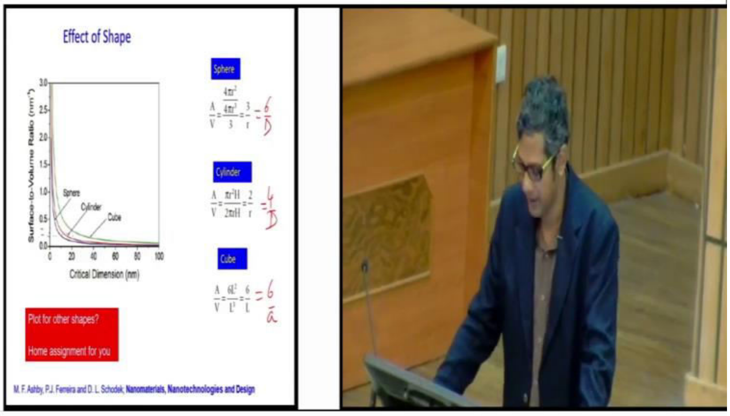

Effect of Shape

Sphere

$$\frac{A}{V}=\frac{4\pi r^2}{\frac{4\pi r^3}{3}}=\frac{3}{r}=\frac{6}{D}$$

Cylinder

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

Cube

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

Plot for other shapes?

Home assignment for you

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

Well, if you can clearly see if I plot surface area to volume ratio in nanometer inverse as a function of critical diameter or critical dimensions in nanometers for three shapes sphere, cylinder and cube, let us see how it happens. For a sphere I have already done is $\frac{3}{r}$ or $\frac{6}{d}$, right. For a cylinder is very easy, again it is done here $\frac{\pi r^2 L}{2\pi r L}$ and is becomes $\frac{r}{2}$. For a cube, $\frac{6}{L}$ or $\frac{6}{a}$; $\frac{6}{a}$ actually we have done that is ok, L is the length suppose of the things ok, it does not matter you can write down $\frac{6}{a}$ also am I clear.

So, this is equal to $\frac{4}{d}$ this should be $\frac{4}{D}$ not small d capital D, it is always like that right; $\frac{6}{D}$, $\frac{4}{D}$ and $\frac{6}{a}$. So, as you can clearly see the change at which it changes physically sphere and the cylinders, they are well, all of their behavior is similar, but only difference is that the way they are changing ok.

So, as you clearly see the for the critical dimension of less than 10 nanometers so, that 20 nanometers, there is its effect is very significant for all the shapes. But when it become very small of the order of 2 nanometers to 3 nanometers, all of them will be having similar effects not much difference, ok. All the ratio will be almost between 2.5 to 3, but between 0.2 to 2.5 that is why the most of a things happen; this is 0.2 actually so, you can see this something about 15 nanometers show the effects are very very very rapid. So, that is why it is very small scale, the shape will dictate how the surface energy is going to be changing, this is something we should which you should always remember ok, you should not forget that ok.

So, now, I would like you to also plot, make the similar plots for other shapes like cone or maybe pyramid or disc, you can do it right, this is an also home assignment for you. Just try, you can use computer to plot ok, you do not need to plot yourself, but just see how these plots will behave as a function of different shapes. If you can do it all the different geometries in one plot and send me, it will be great, I will be appreciating your efforts for that, ok.

So, that is something which is very important.

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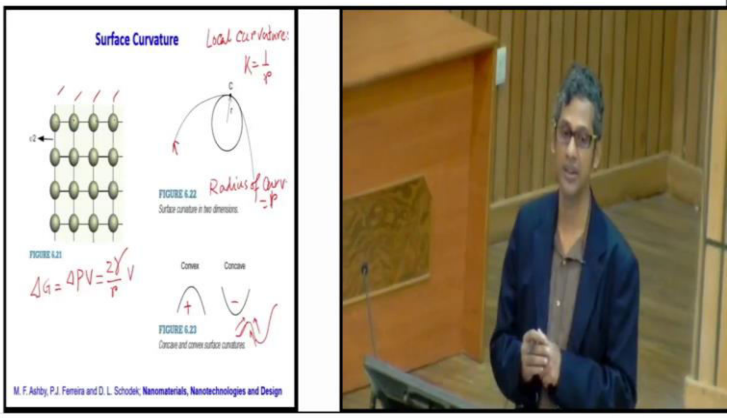

Surface Curvature

FIGURE 6.21

FIGURE 6.22
Surface curvature in two dimensions.

FIGURE 6.23
Concave and convex surface curvatures.

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Now, I am going to come to another important aspects ok. So, we have spent about 20 minutes so. As you know all of you know about curvatures right, because you have been studying about curvatures from your plus 2 or even 11th standard right or 10th standard correct. Curvature is has a very important effect because most of the geometries we see are curved, they are not flat ok; like you can say sphere, you consider a cylinder, you consider the pyramid, you consider a cone, they are all curved, they are not flat. So, therefore, curvature is inbuilt in these shapes and you should understand; what is the effect of surface curvature on the surface energy. This is something which we will discuss in a detailed manner.

Now, let me just tell you that as you know surface energy is basically dictated by the bonds which are broken or dangling bonds; like the ones which are sitting here you can see, these atoms have dangling bonds like this. So, therefore, they are having excess energy. So, here I need to compute this excess energy, we will see how to be done.

So, first let us talk about how surface curvatures are defined. You know the surface curvature is defined by this way. Suppose this is a curve ok, you can see outside one, this one I am talking about it correct. I want to know the curvature at point C on this curve. So, what I do? I draw a circle which will be touching the point C. As you see if I draw an circle; if I draw a circle, the radius of the circle will be r right.

So, therefore, local curvature at point C or radius of curvature is basically; radius of curvature is basically given by $\kappa = \frac{1}{r}$ right, correct. So therefore, this is what is very significant right radius of curvature radius of; sorry I think this is the local curvature, radius of curvature is local curvature, ok. So, radius of curvature is what? Radius of curvature is r ok, this is the local curvature. This is the problem with this pen difficult to write, in a blackboard you can easily write it up and so; and radius of curvature is r right, let me write down, correct.

So, as you know there are two types of curvature, convex and concave. Traditionally or mathematically, we considered this k to be positive for concave; convex ok, this is positive and for concave, it is negative. This is what is traditionally accepted because this this has to be differentiated, concaves versus convex must be differentiated. So, differentiate we consider convex one as a positive curvature, concave one is a negative curvature, am I right. So, that is what is we always that is how we can differentiate. Now, remember these aspects.

So, now question is as we have begun our discussion what is the effect of the surface curvature on the surface energy as in fact, how it is going to play a role? Well, change in surface energy as you should know change in surface curvature will lead to change in free energy, and this is written like this ok. This is very easy is equal to change in pressure multiplied by volume; what is the meaning of that? Let us consider this one is basically a bubble. Now, ΔP is nothing but pressure difference from inside and outside that is $P_2 - P_1$. If P_2 is the pressure inside, P_1. is outside, then ΔP is $P_2 - P_1$ and V is the volume right that is understandable.

So, this can be written as like this 2γ, this is γ, this is not r; now I have to change the symbol of rγ by ΔPV right. This derivation of; $\Delta P = \frac{2\gamma}{r}$ is you have done in your plus 2 standard even ok. If still not able to understand, I we can do it in when we discuss about this lecture. But for the sake of time constant, let us consider this is the delta P.

So, you know as you know ΔG is inversely proportional to r. So, as the psi decreases, r decreases, ΔG increases even if γ is not changing much γ will also depend on many aspects, but assume γ is not changing on those aspects. So, ΔG is a strong function of r, and inversely proportional to r, right.

So, inside you know; so, now, this inside pressure P will also depends on the kind of curvatures whether convex or concave. In case of convex, it will be positive, in case of convex, it will be negative that we have already discussed right. So, ΔG, sign of delta G will be changing depending on the type of surface. In one case, it will increase the energy of system otherwise it decreases energy of system right; that is clear. And, this is coming from mathematical treatment of convex and concave curvatures, we have to differentiate between them, right.

So, therefore, these negative and positive signs are placed to that they are not same. You can always also have a curve like this right, you can see this is convex, this is concave. So, how this will affect ΔG you can understand. So, this part of the curve convex one has a positive ΔG, this part of the curve will have a negative ΔG. So, this will lead to even mass transport, energy transport, all kinds of things.

So now, we are going to discuss a very specific thing the effect of this ΔG on equilibrium vacancy concentrations in nanomaterials, because of this curvature ok. I am going to derive it ok. So therefore, please listen to me and also, try to follow my step.

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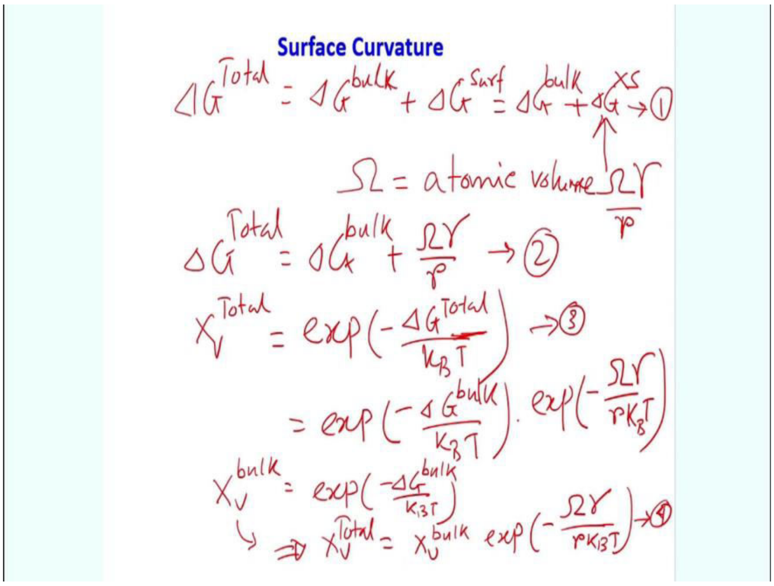

Surface Curvature

$$\Delta G^{Total} = \Delta G^{bulk} + \Delta G^{Surf} = \Delta G^{bulk} + \Delta G^{XS} \rightarrow ①$$

$$\Omega = \text{atomic volume} \quad \frac{\Omega \gamma}{r}$$

$$\Delta G^{Total} = \Delta G^{bulk} + \frac{\Omega \gamma}{r} \rightarrow ②$$

$$X_V^{Total} = \exp\left(-\frac{\Delta G^{Total}}{K_B T}\right) \rightarrow ③$$

$$= \exp\left(-\frac{\Delta G^{bulk}}{K_B T}\right) . \exp\left(-\frac{\Omega \gamma}{r K_B T}\right)$$

$$X_V^{bulk} = \exp\left(\frac{-\Delta G^{bulk}}{K_B T}\right)$$

$$\Rightarrow X_V^{Total} = X_V^{bulk} \exp\left(-\frac{\Omega \gamma}{r K_B T}\right) \rightarrow ④$$

So, total energy, total free energy of any system suppose you consider of any system, we will have two parts right, $\Delta G^{Total} = \Delta G^{bulk} + \Delta G^{XS}$, bulk and surface correct. Many people write this ΔG^{XS} as $\frac{\Omega \gamma}{r}$. And this one, this extra term is basically because of curvature effect. So, that we can write down $\frac{\Omega \gamma}{r}$; this one is known as atomic volume, volume of one atom, correct. So, I can write down $\Delta G^{Total} = \Delta G^{bulk} + \frac{\Omega \gamma}{r}$; right. So, this is our equation 1, this is our equation 2, am I right?

So, how many of you know how the vacancy concentration depends on ΔG, you should know that ok, it is given in literature. So, you know the volume fraction of vacancy, which is nothing but X_v^{Total}, X is always is used as a fraction right, ok. This is not volume pressure, this is basically like a solid concentration we define mole fraction. This is equal to $\exp\left(-\frac{\Delta G^{bulk}}{K_B T}\right)$. Now, I like to discuss about this aspect.

Why we use $K_B T$? When ΔG^{Total} is in energy is given in ev electron volt, you can use Boltzmann constant, it is given in joules, you can use R, R is the gas constant, right. So, both of these are correct. So, that is my equation number 3. So, I can expand this $\exp\left(-\frac{\Delta G^{bulk}}{K_B T}\right) \times \exp\left(-\frac{\Omega \gamma}{r K_B T}\right)$ that is what it is, correct.

Now, as you know I can always write down X_v^{Bulk}, the concentration of vacancy in the bulk as $\exp\left(-\frac{\Delta G^{bulk}}{K_BT}\right)$. So, this gives me, this one will give me finally, X_v^{Total} is equal to $X_v^{Bulk}\exp\left(-\frac{\Omega\gamma}{rK_BT}\right)$ that is equation 4. So, that means the X_v^{Total} is dependent X_v^{Bulk} and the exponential term, $\exp\left(-\frac{\Omega\gamma}{rK_BT}\right)$.

So now, let us go to the next page.

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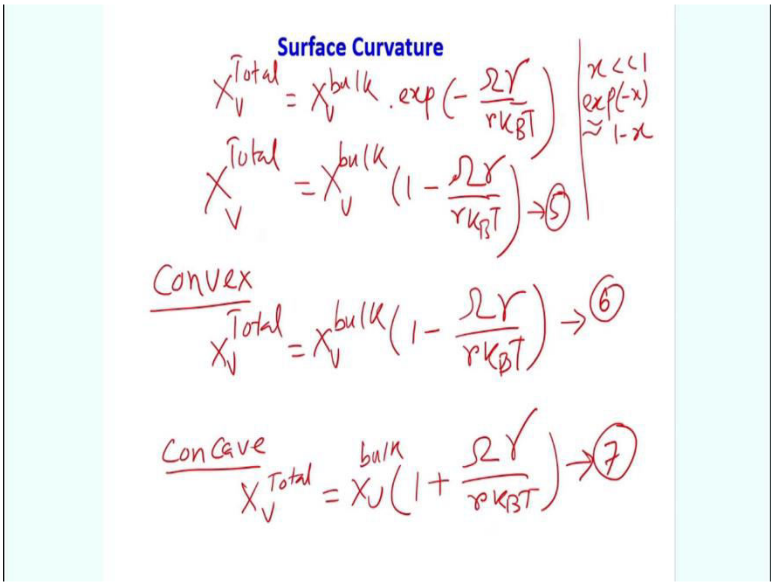

Surface Curvature

$X_v^{Total} = X_v^{bulk}.\exp\left(-\frac{\Omega\gamma}{rK_BT}\right)$

$x << 1$
$\exp(-x) \simeq 1-x$

$X_v^{Total} = X_v^{bulk}\left(1-\frac{\Omega\gamma}{rK_BT}\right) \to ⑤$

Convex

$X_v^{Total} = X_v^{bulk}\left(1-\frac{\Omega\gamma}{rK_BT}\right) \to ⑥$

Concave

$X_v^{Total} = X_v^{bulk}\left(1+\frac{\Omega\gamma}{rK_BT}\right) \to ⑦$

We will again write the same equation you may forget; so $X_v^{Total}= X_v^{Bulk}\exp\left(-\frac{\Omega\gamma}{rK_BT}\right)$. So, when you know when exponential minus ok let us do this maths on the right side is x is very small ok. Then as you understand r is small, K_B is small, but T is large so, this γ is also very small, atomic volume, this sorry the sigma, correct. We can write down $\exp(-x) = 1 - x$, you know exponential can be expanded 1 minus x plus x square by factorial 2 minus x square factorial 3, I am just stopping at x because if x is very small other terms will be very small ok. So, I can write down this $X_v^{Total}= X_v^{Bulk}(1 - \frac{\Omega\gamma}{rK_BT}), ok.$

Now, let us bring in the concave and concave surface effects. So, for the convex and for the concave. For the convex, this will be $X_v^{Total}= X_v^{Bulk}(1 - \frac{\Omega\gamma}{rK_BT})$, because r is positive; 1 by r is positive, this will remain same, $\Omega\gamma$ and rK_BT. For the concave, $X_v^{Total}=$

$X_v^{Bulk}\left(1+\frac{\Omega\gamma}{rK_BT}\right)$; look at what will happen? This will be positive because r is negative so, it will be a positive. So, we can write down this is the equation 5, this is equation 6, this is equation 7.

So, for concave and convex, the huge difference. One case you are adding up this term, other case you was subtracting this term right. So therefore, one case, the vacancy concentration will increase much more than what is the bulk vacancy, other case it will decrease substantially, right.

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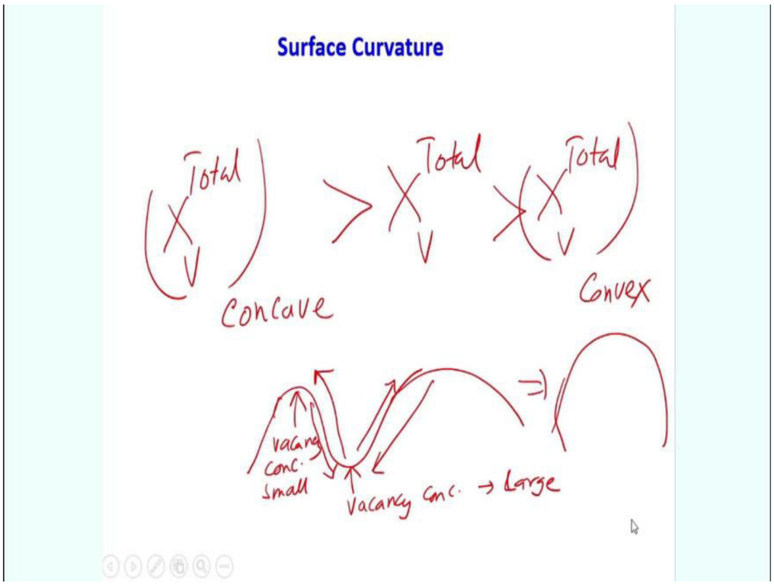

Surface Curvature

So, what you can write down from this? We can write down from this very simple thing that (X_v^{Total}) for concave must be greater than X_v^{Total} ok when there is a flat surface or whatever it is ok flat surface, convex. This is very interesting, right.

If you have a surface like this so, vacancy concentration will be large here, vacancy large. Here, vacancy concentration small. So, vacancies will move from here to there right, and the vacancy is moving here to there, mass will move from here to there thus obvious right, that is what something we should always remember that is obvious correct. So, this is going to happen.

So, if you have a surface like this which is most likely the case is convex, concave convex again, vacancies move, mass will move. So, if the mass is moving from higher to lower region so, finally, whole thing will this thing will become like this, they will join together. Well, you are not able to understand it more, let me give you some example to make it clear.

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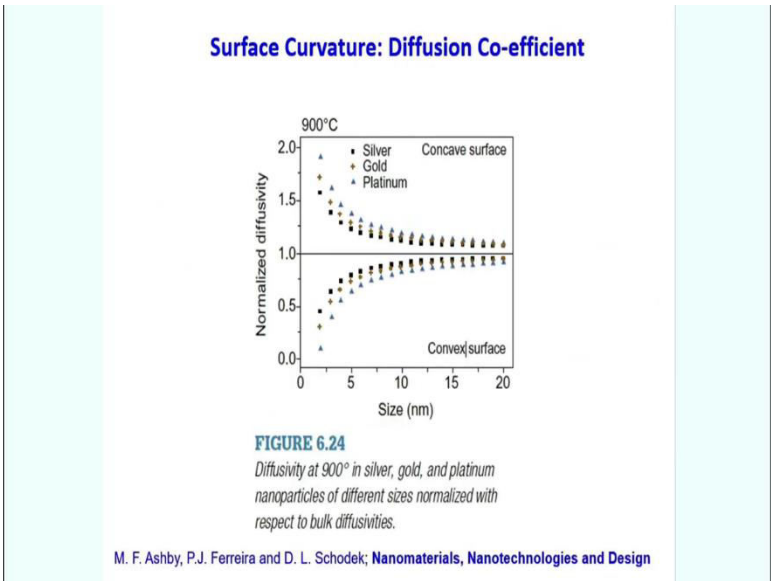

Surface Curvature: Diffusion Co-efficient

FIGURE 6.24
Diffusivity at 900° in silver, gold, and platinum nanoparticles of different sizes normalized with respect to bulk diffusivities.

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Before that so, that means, the diffusivity is diffusion is related to vacancies, right. So, diffusivity is we just talked about it will depend on the size; so this is convex, this is concave. So, as you see for the concave, vacancy concentrations will be more, diffusivity will be high right, that is what it saws, and this depends on size. About beyond about 10 nanometers so, effect is not so significant, but below that effect is very significant.

On the convex side, it is going down ok, it is going down to very small values diffusivity. This is normalized, means normal respect to the flat surface that is what is normalized ok. A flat surface has one diffusivity that diffusivity is used to normalize diffusivity with concave surface and diffusivity with convex surface. And this is diffusivity a 900 in silver, gold, platinum, nanoparticles, a different size normalized with respect to bulk diffusivities that is why I told you bulk ok. I am sorry I did I told you so, flat, no it is a bulk. Bulk means there is surface effects are not there, it is a big size piece of gold, silver, platinum.

So, you can clearly see how the precipitation 900 is going to change.

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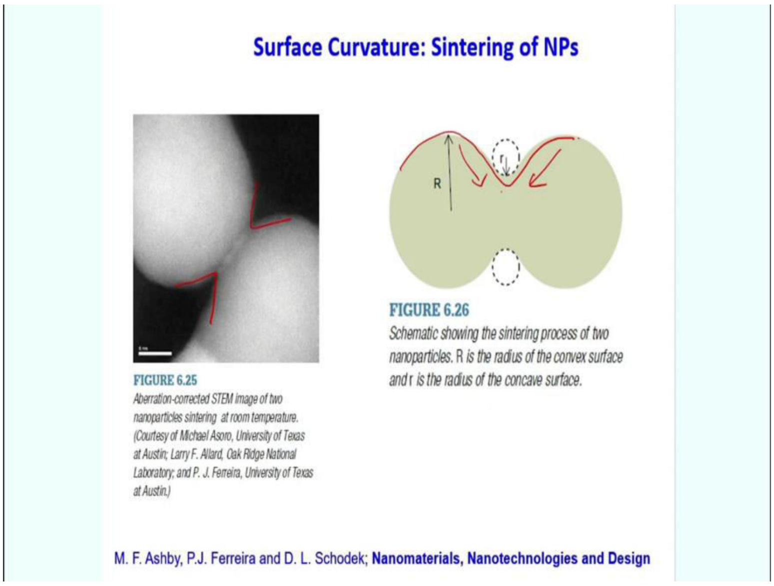

Surface Curvature: Sintering of NPs

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.

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What are the effect of that? This is a significant effect on the sintering of nanoparticles that is why if you prepare nanoparticles, even room temperature they will sinter. Let us look at it. See this, I told you this is a curvature just now I told convex, concave, convex. So, because of vacancy differentiation between this point and this point, the convex and the convex, the vacancies will move; there is a concentration difference that will lead to migration vacancies and the opposite direction mass will move, right.

So, as the mass moves, this particle will join one by the other so more and more mass will move from this top region to the bottom or to this part and this will lead to increase its particle size. That is what happened on something sinter, you can see that ok. This exactly same geometry is happening there also at the atomic scale.

So, I hope this part is clear.

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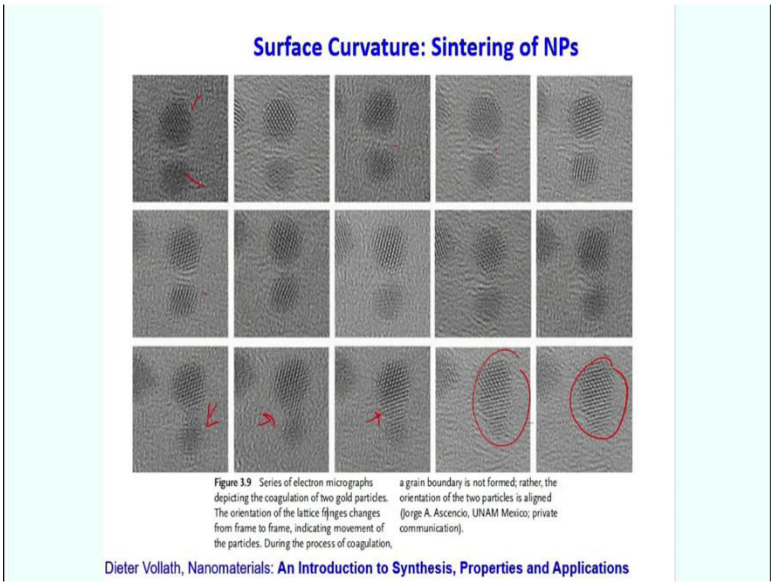

Surface Curvature: Sintering of NPs

Figure 3.9 Series of electron micrographs depicting the coagulation of two gold particles. The orientation of the lattice fringes changes from frame to frame, indicating movement of the particles. During the process of coagulation, a grain boundary is not formed; rather, the orientation of the two particles is aligned (Jorge A. Ascencio, UNAM Mexico; private communication).

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Now, some people have done experiment, this is taken from little Dieter Vollath, an experiment of sintering of two gold nanoparticles. Here, you can see one nanoparticle here, one nanoparticle there. And then, then coming close, coming close, coming close, coming close and they are joining here and slowly, slowly, slowly and I think in they are joining here, here also they are joining, joining and then finally becomes single particle, single particle.

This happens at room temperature, you do not need to do it at high temperature that is the important aspect that is mainly because of the surface curvature. So, as is become a curved particle, surface curvatures are going to be changing. So, you understand how important it is the curvature and most of the geometries we see having curved surfaces and that will have different curvatures. This is something which you need to read and understand from the books also.

I hope I made it clear, how it is important by mathematical derivations which I did here ok. So, these derivations are basically from thermodynamics we are using.

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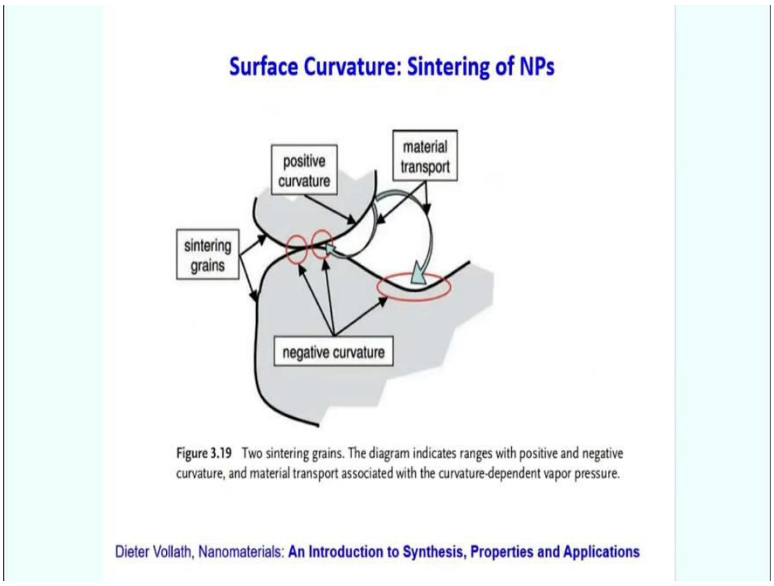
Surface Curvature: Sintering of NPs

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.

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Well, this is again shown in a detail manner here, this is taken for Dieter Vollath. You can see the negative curvatures right; negative curvature means concave and convex are lead to positive curvature. So, mass will transport, you see here material transports will happen from negative curvature to positive curvature and these two guys will join together. This is something which is easy to understand.

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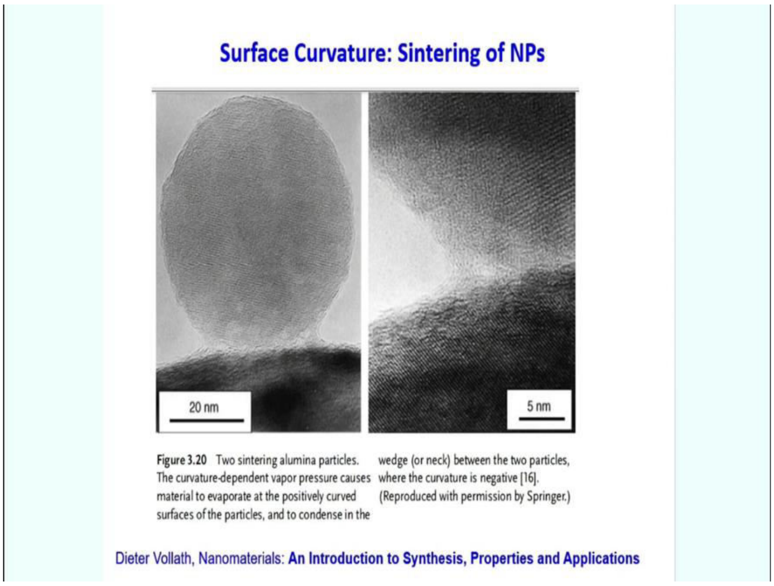
Surface Curvature: Sintering of NPs

Figure 3.20 Two sintering alumina particles. The curvature-dependent vapor pressure causes material to evaporate at the positively curved surfaces of the particles, and to condense in the wedge (or neck) between the two particles, where the curvature is negative [16]. (Reproduced with permission by Springer.)

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This picture is very very favorite picture of mine. You see this is alumina particles, two aluminum particles ok. Here when curvature will change the vapor pressure ok which I do not know, I may discuss next class, I will still I am thinking about it this is not part of a syllabus but still it is easy to understand. Curvature can change even by Clausius-Clapeyron equation will bring about it, curvature can change even the your vapor pressure. And this will lead to change of mass transport, something will evaporate from the convex region to the concave region and join and neck will increase.

This is also possible.

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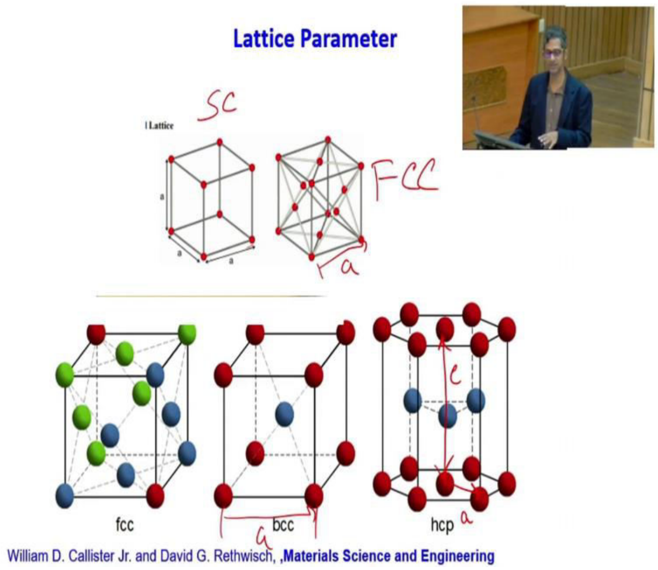

Lattice Parameter

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Well, the last thing in today lecture we are going to discuss in 5-7 minutes is how the lattice parameter is going to be changing right; that is something which you need to do. So, as you know lattice parameters if you do not know, let may just discuss about it. You know the unit cells ok, in a cubic crystal structure there is simple cubic is a simple cubic lattice, this is body centered cubic lattice, this is body centered cubic lattice and you have also hexagonal crystal structures. These are mostly observed that is what I have shown.

So, in a simple cubic structure, lattice parameter is given by a, FCC also this is the lattice parameter ok, bcc also this is the lattice parameter, hcp you have two lattice parameters, one is the c, other one is a correct, but this is how the lattice parameter is defined. Now, because of the size lattice parameter can also get changed, how ok?

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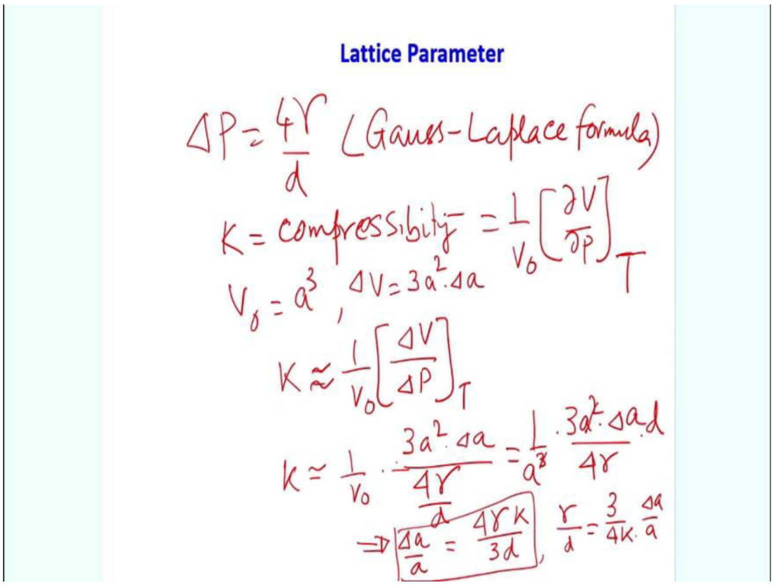

Lattice Parameter

$\Delta P = \frac{4\gamma}{d}$ (Gauss-Laplace formula)

$K = \text{compressibility} = \frac{1}{V_0}\left[\frac{\partial V}{\partial P}\right]_T$

$V_0 = a^3$, $\Delta V = 3a^2 . \Delta a$

$K \approx \frac{1}{V_0}\left[\frac{\Delta V}{\Delta P}\right]_T$

$K \simeq \frac{1}{V_0} . \frac{3a^2 . \Delta a}{\frac{4\gamma}{d}} = \frac{1}{a^3} . \frac{3a^2 . \Delta a d}{4\gamma}$

$\Rightarrow \boxed{\frac{\Delta a}{a} = \frac{4\gamma K}{3d}}$, $\frac{\gamma}{d} = \frac{3}{4K} . \frac{\Delta a}{a}$

Let us do simple mathematical calculation. Well, all of you should know that Gauss and Laplace, you know they gave a formula about the pressure difference of a soap bubble ok. And this is something which many of you read about it, just now I did it is $\Delta P = \frac{2\gamma}{r}$ so, that is become $\frac{4\gamma}{d}$ and this is basically many people call, this is basically Gibb Thomson effect; Gauss-Laplace, right. So, P is; ΔP is the pressure difference between interior of a liquid droplet and outside. Exactly, same thing happened in solid soap bubbles.

Now, we can always define another important parameter called K, K is known as compressibility. What is it? Well, compressibility is what? Compressibility means if I have a gas, 1 liter of gas and if I apply pressure, how come how much compression I can do? This can happen for solid also, but it will be difficult to understand, it can happen liquid also correct, but gas can compress easily, more you can compress, liquid can be compress little less, solid can be compress in much less. So, that means, compressibility is a parameter which is very unique, this is used and this is defined like this visualizes initial volume and this is done as constant temperature as well, $\frac{\Delta V}{\Delta P}$.

So, now, let us consider a simple cube ok, which has a volume of a^3 right. So, therefore, I can write down ok let me just not do it here, we will do this one. So now, I can write down K so, $K = \frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T$.Well, ∂V is infinitesimal change, ∂P is infinitesimal change, they are no longer differentials, but the infinitesimal changes, correct. So, that is what I write almost equivalent, K is almost equivalent.

So, now, I know V ok, $V_0 = a^3$, $\Delta V = 3a^2\Delta a$, you should write Δa mathematically, you should be right very clear. So, and you know ΔP. So, now let us put together; $K = \frac{\frac{1}{V_0}3a^2/\Delta a}{\Delta P}$ and what is ΔP? $\frac{4\gamma}{d}$ where d is the diameter, like γ is the surface energy. So, now, I can even put value of V_0 right. So, that is equal to a^3 and d go above, correct.

So, I will simply simplify which you can do let us do that. So, this a^3, a^2 get cancelled correct. So, let $\frac{\Delta a}{a}$; this becomes $\frac{4\gamma K}{3d}$, alright. That is what it is, or you can write down this way also $\frac{\gamma}{d}$ is $\frac{3\Delta a}{4Ka}$. So, this is your lattice parameter change, correct.

So, that means, if γ is finite, K is finite so, lattice parameter change will depends upon $\frac{1}{d}$, 4 and 3 are constant, γ is also can be considered constant and compressibility is obviously, constant for a particular material, a is lattice parameter the bulk so, for the lattice parameter change it is $\frac{1}{d}$. So, you can clearly see as the particle size decreases, lattice parameter will also change.

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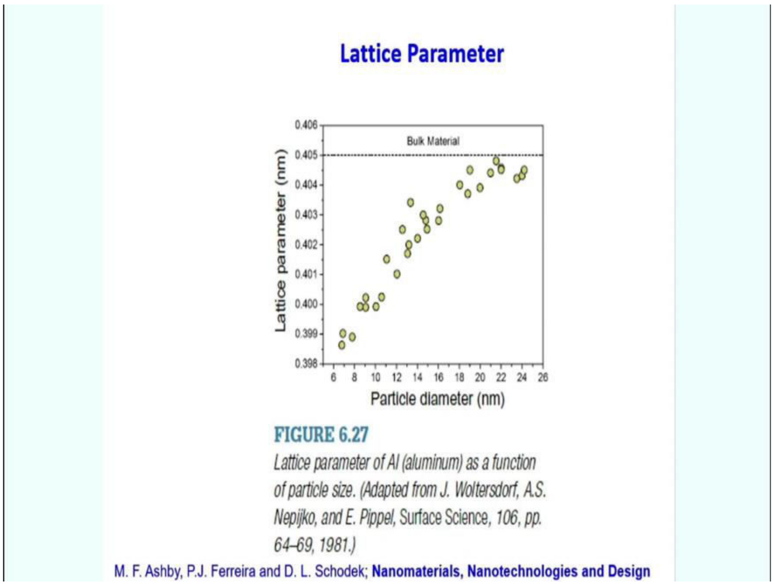

Lattice Parameter

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.)

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And it is been observed that as the particle size decreases, lattice parameter decreases, you compare the bulk. And this can be explained using this formula I have given it ok, that will depends obviously, on $\frac{\Delta a}{a}$ value because as you see $\frac{\Delta a}{a}$, this is depends on the value of compressibility γ, they are very small scale and 1/d ratio, ok. If compressibility is negative, Δa will be negative. If compressibility is positive, Δa will be positive. For most of the solids that is what is happening. This is for aluminum as a function of particle size.

So, what do you understand from this lecture today? First, we discussed about effect of shape on the surface energy, how it is going to be changed and depending on different shapes, you have different kinds of formulae. Then, we discussed about the curvature. Depending on curvatures, surface energy is going to be changed and that will lead to change the vacancy concentration. And, this in turn will affect the diffusivity and diffusivity will then affect the sintering of nanoparticles. And, this is so strong, the effect is so strong even at room temperature nanoparticle can sinter like gold, platinum, silver have been bound to be sintering. And then finally, I discussed about lattice parameter effect or the effect of size in the lattice parameter.

We will continue discussing on this in the next lecture, ok.

Thank you.