Nanomaterials and their Properties
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Lecture – 05
Nanomaterials: Surfaces and Interfaces – I

So, welcome students, today we are going to start the lecture on surface energy; this is lecture 5 and this is this section of the lectures from lecture 5 to 6, 7 , 8 will be on surface energy related things and you need to understand this particular aspect very well.

Because as you know nanomaterials have very high surface area to volume ratio; this is an important characteristic of nanomaterials, which provides them important mechanical, physical, electrical, electronics, chemical, magnetic and all kinds of structural and functional properties. So, it is important to know, I am using important word again and again, important to know these aspects very well.

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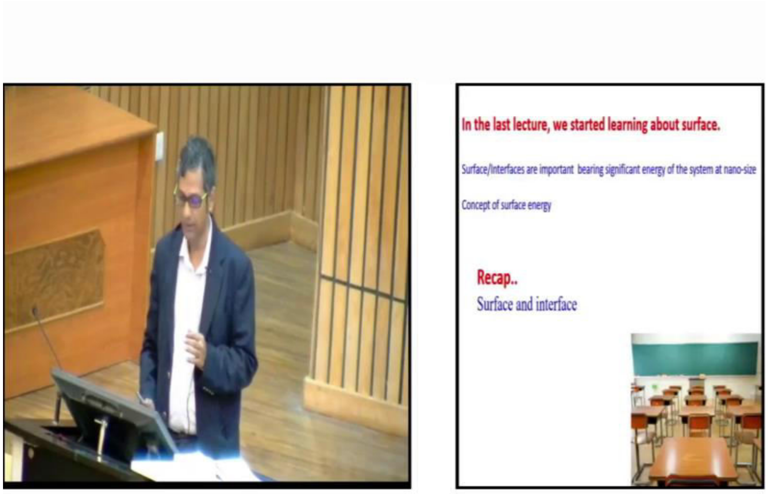

In the last lecture, we started learning about surface.

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

Concept of surface energy

Recap..

Surface and interface

Well, in the last lecture, we started learning about the surface, right. So, surface are important, interfaces are important; because they bear significant energy of the system at the nanoscale and that is why I started the concept of surface energy. So, now, I am going to make some recap of that surfaces interfaces, how do they you know play role, how to characterize them, how to make understanding of the whole thing, ok.

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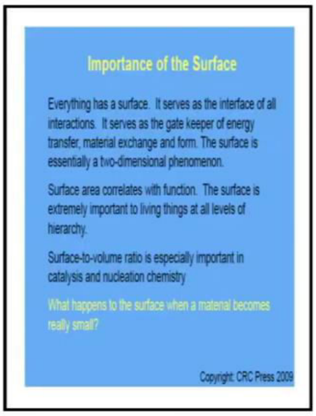

Importance of the Surface

Everything has a surface. It serves as the interface of all interactions. It serves as the gate keeper of energy transfer, material exchange and form. The surface is essentially a two-dimensional phenomenon.

Surface area correlates with function. The surface is extremely important to living things at all levels of hierarchy.

Surface-to-volume ratio is especially important in catalysis and nucleation chemistry

What happens to the surface when a material becomes really small?

So, as you know surface is everything has a surface, your body has a surface like a scheme, ok. It serves as the interface of all kinds of interactions; because that is to this agent only, the surface only everything happens. It serves rather as a gatekeeper of energy transfer, material exchange and even change of forms of steps. Surface essentially a 2-dimensional phenomenon, ok.

Now, surface area is what characterize the surface and also the relative surface energy, that is the surface energy per unit area. So, these are the two important aspects we will focus on; one is the surface energy per unit area, other this surface areas itself. Surface is extremely important for inanimate object or living objects, an important aspect is the surface to volume ratio, correct.

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Nanocrystalline Objects and Surfaces

So, now, you know why they are important? Let us look at only these aspects, these pictures are taken from various sources. As you know this is grapheme, this is several layers of grapheme, the single wall nanotube and this is a multiwall nanotube right; this is Single Wall Nano Tube, SWNT and this is multiwall nanotube, right.

So, now if you look at carefully, once you open up, whether it is a single layer of carbon or several layers of carbon or it is basically a nanotube single or multiple layers; once you open it up, what is happens is forms a surface. And, if you look at carefully this picture the bottom ok, let us consider atom inside; forget about red and white and blue, first concentrate that each wall is an atom, focus on that, do not forget about everything else. So, if I comes in the atom like this here ok, this one you see let me put a different color, so that you can see nicely. So, I am putting a green color, I am talking about this atom, ok.

So, this atom is bonded nicely with this white atom, this white atom, this red atom, this white atom, this red atom, this white atom, this red atom, nicely bonded; that means all it is bonds are nicely satisfied. It does not have any hunger to get attached to some other thing else some other molecules or something else right, because it is bonds are saturated.

Now, if you look at atoms sitting on the surface, let us consider a different color, ok. I will consider red; because that is a very bright color, right. If you consider this atom right, you see that this is the one I am marking away the atom.

So, now this atom you could clearly see, it is bond from the top is not satisfied; because there is no atom existing on the surface top of the such thing ok, only down the plane is bonds are satisfied. Unlike this atom, which is sitting inside the bulk of the material, the atom sitting on the top of this plane is unsaturated right; it has dangling bonds, it has bonds which are not satisfied.

Now, what will happen to these bonds? Because they are not satisfied, the extra electron present on the outer shell of this atom which are not bonded with anything. So, therefore, it has hunger to get bonded to something and this hunger leads to what is known as attachment of molecule onto it, it is reactivity many other things.

Now, in a bulk material, like if you consider this cell phone; this is a big material right, this is a very big cell phone. In a bulk material, surface area is very small compared to the the atom in the surface is very small compared to the bulk, compared to the atom in the bulk right, that means number of atoms on the surface like this is very very minimal as compared to the number of atom like this.

And these aspects gives you very important thing, what is that? Because of that the properties of the material is determined by the atoms in the bulk, they are not determined by the atoms on the surface; because the volume percentage of the atoms in the surface for a bulk material like a book ok, like you know water bottle or like a you know cell phone or like a duster, like even this pen, that is almost like 2 to 5% of the total number of atoms and we ignore their effects.

But, in nanomaterials, where the surface area is pretty large; that means number of atoms on the surface area is very large, you can no longer ignore that. And, this is quantity scales with the surface area, scales with the size of a nanomaterial; as the size goes down, this quantity increases. So, this is a very simple analogy which you need to understand, now, ok.

Now, how do you do that, ok? So, as you understand, surface is nothing, but surface is related to energy that you understood right; because surface has this kind of atoms, whose has dangling bonds, whose bonds are not satisfied, right. Now, let us suppose surface energy per particle, ok.

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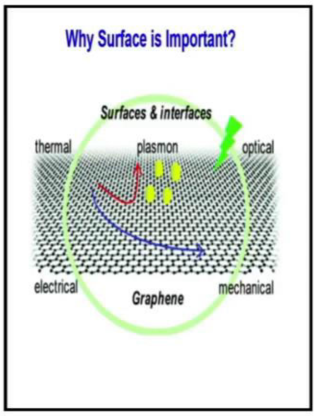

Why Surface is Important?

So, before you do that, again it becomes a single atom, all these properties thermal, electrical and plasma resonance, optical, mechanical everything is related to surfaces; because there is it all the atoms in a grapheme, singular graphene is a surface atom, there is no bulk here, every atom is sitting on the surface. So, therefore, they have 100 percent atom sitting on the surface for a graphene.

Have you ever thought of it? Never right, because a single layer of carbon, then nothing below, nothing above. So, only thing which is important for such a kind of aspect is the surface energy and surface energy of this aspect, because surface area is infinite is very as large as the material. So, surface energy what is known as a gamma per unit area is that is what is important for such a kind of material.

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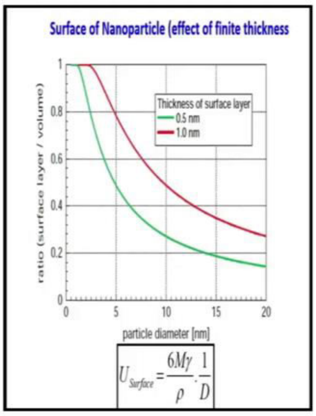

Surface of Nanoparticle (effect of finite thickness

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

Well this is something we discussed about it. But on a any other nanomaterial, surface is not a mathematical entity ok, it has a finite thickness, right. So, finite thickness means, it is a thickness consisting of several layer of atoms correct; this is an exercise I have done in the last lecture, you can go and follow that. And so, if I consider the thickness of the layer from 0.5 to about 1.5 nanometers, that is standard normally what people have observed it by doing different experimentations.

And if you look at ratio of surface area to volume as a function of particle diameter ok; here a spherical nanoparticle is considered, that is why particle diameter has come into picture. And if you look at carefully below 5 nanometers, the percentage atoms on the surface per 1 nanometer thickness of the surface is about 80 % and for about 0.5 nanometer thickness, surface let us about 50 %, it is a huge difference.

So, therefore, depending on the surface thickness, this value that is the ratio of surface area to volume will be drastically changing. And, that is exactly happens in normal nanomaterials, unlike grapheme; if you consider single wall, multi wall nanotubes or basically single wall nanotube exactly same as a grapheme, if you consider multilayer nanotubes, surface layer and the inside layer has bonding characteristics of the carbon atoms are different, same thing is valid for any other shapes. So, therefore, these concepts do actually apply.

Now, as we consider this case, we will first get an estimate of surface energy as a function of a diameter of a nanoparticle, let us do that, ok.

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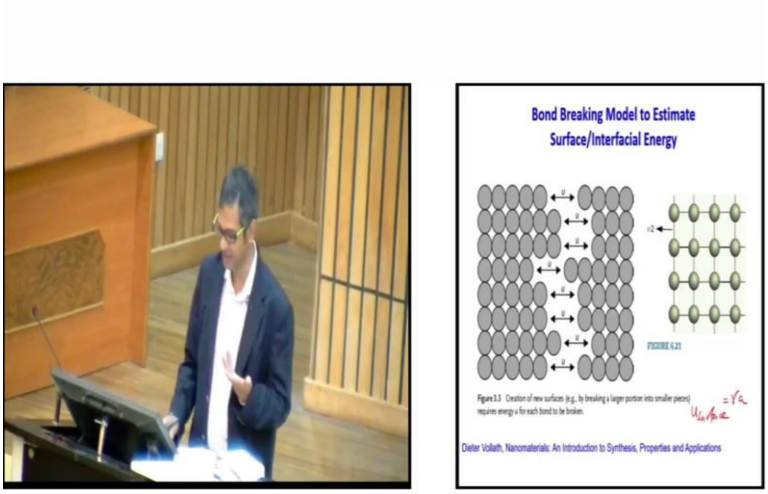

Bond Breaking Model to Estimate Surface/Interfacial Energy

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.

$U_{surface} = \gamma a$

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So, before I do that, again I am sorry, you know what is the reason for surface energy; that I have already discussed with you just now, let me rewrite ok, surface energy is because of the bond which are broken.

So, now if I consider that, if I consider the bond energy between atom is u, small u actually and you know or you know this is taken from Vollath; that is why they have used u, this is taken for mass b, we have taken epsilon ok as the bond energy.

So, bond is between 2 atoms right, this is very clear. Now, with the surface energy per particle is $U_{surface}$, let us write it $U_{surface}$, surface energy per particle, ok. And thus, obviously will be equal to γa. What is γ? γ is a surface energy per unit area and a is the total area of the surface right, that is clear, right.

Now, as you know, as we told you that the origin of surface energy is the number of bonds broken, right.

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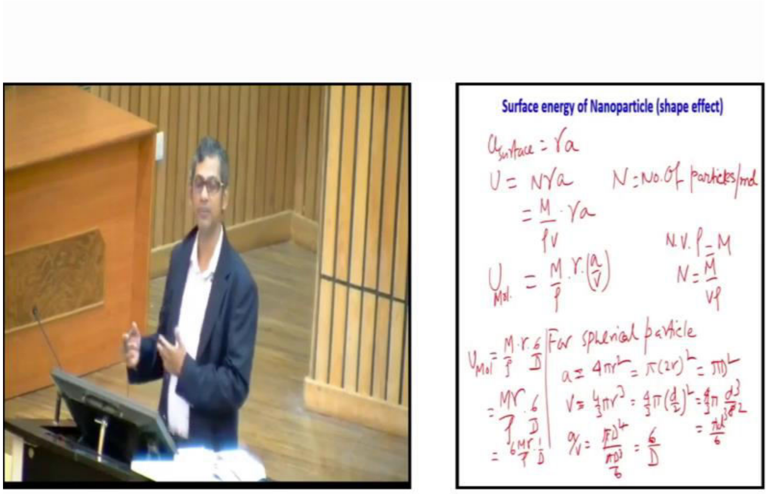

Surface energy of Nanoparticle (shape effect)

$U_{surface} = \gamma a$

$U = N\gamma a$ $\quad N$ = No. of particles/mol

$= \frac{M}{\rho V} \cdot \gamma a$

$N.V.\rho = M$

$N = \frac{M}{V\rho}$

$U_{Mol.} = \frac{M}{\rho} \cdot \gamma \cdot \left(\frac{a}{V}\right)$

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

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

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

For spherical particle

$a = 4\pi r^2 = \pi(2r)^2 = \pi D^2$

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

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

So, suppose there are N number of atoms in a 1 mole of material, N is the number of atoms in 1 mole of materials, let me do that. So, $U_{surface} = \gamma a$; gamma is the surface energy per unit area, a is the total area. So, suppose one particles of area a and surface energy per unit area is gamma, the total surface energy of the particle is Ua.

Now, in a one mole of material, you have N number of particles; then total surface energy we can write down is what $U = N\gamma a$, where N is the number of particle per mole, right. So, I can write down this thing very easily, that is equal to M by this. What is this quantity? M is the molecular mass or molecular weight right, ρ is the density and V is the molar volume right, that is what it should be. So, that is multiplied by γa, it can be written like this, ok.

So, we can modify this. So, now, question is this, I can write down very simply M by gamma. So, you understand how this has come, N is the number of particle, right. So, now, if you consider each particle has a volume of V right, each particle has a volume of V, correct.

If each particle has a volume of V, ok, each particle has a volume V; N particle has a volume of NV. Now, if you multiply this one with density, that is become mass. So, $M = NV\rho$, because we are considering one mole of material, am I clear.

So, therefore, I can write down $N = \frac{M}{V\rho}$, where this V is the volume of each particle, ρ is the density of each particle and M is the molecular weight. So, I can write down this expression like this, am I clear. So, that is become $\frac{M}{V\rho}\gamma a$. a is what? a is the surface energy sorry surface area of the particle, right.

So, now for spherical. So, this is what U is the total energy for surface energy for one mole, very simple calculation you can do that. So, this is per mole actually ok, let us write down that. Now, for a spherical particle what will happen? For spherical you can do yourself that one for other steps, I will doing for spherical ok, spherical particle, let us erase it up. So, spherical particle what is area, tell me the area? Area, a = $4\pi r^2$, right.

We can write down that as a $a = \pi(2r)^2$, So, it will become $\pi(D)^2$. What is the volume? Volume is four third ok, do not ask me that you do not know what the volume of a sphere is, that is well known; $V = \frac{4}{3}\pi r^3$ right, as $r = \frac{D}{2}$, I can write down $V = \frac{4}{3}\pi(\frac{D}{2})^3$. So, that will becomes; $V = \frac{\pi}{6}D^3$.

So, what is $\frac{a}{V}$ ratio then? $\frac{a}{V} = \frac{6}{D}$. So, this become $\frac{M\gamma 6}{\rho D}$ or this is the $\frac{6M\gamma}{\rho}(\frac{1}{D})$

So, what do you understand? You understand that, surface energy is not only depends on the size; but it scales with the size, for a spherical particle it scales $\frac{1}{D}$. So, that means if I plot U_{mole}, U surface energies per mole as a function of D for a spherical nanoparticle, it will be a $\frac{1}{D}$ kind of curve right, parabolic curve you will understand that, right.

So, if I plot that, let me erase it some part, this part ok, hope you understood it; I am using this as my board ok, you have to understand that, this is the problem.

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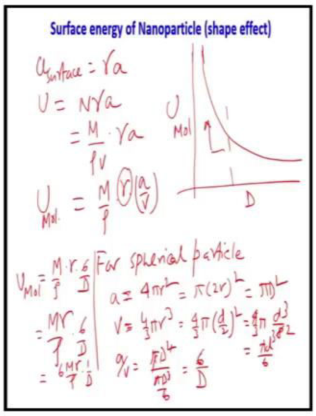

Surface energy of Nanoparticle (shape effect)

$U_{surface} = \gamma a$

$U = N\gamma a$

$= \frac{M}{\rho V}\cdot\gamma a$

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

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

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

We are normally comfortable with board. So, this is U_{mole}, this is D; how it will look like? It is $\frac{1}{D}$ right, this will be like this. So, for very small size particles, surface energy is very very high right; that is basically coming from the area concept, remember we have not made anything about gamma, you want to understand that.

We simply made a calculation based on surface area to volume ratio, that is so simple calculation; you do yourself, you will understand; that tells you the spherical particle, this is what is going to be the thing happening, right. So, I am drawing again, because that drawing was not good. So, you do it properly.

So, you can clearly see, after a certain size, surface energy increases rapidly as a function of particle diameter. So, if you deduce the particle diameter, surface energy will exponentially sorry, now sufficiently will rapidly rise; do not say exponentially, that is not a correct language, rapidly will rise, ok. So, that is for the basic concepts of surface energy from the perspectives of surface area.

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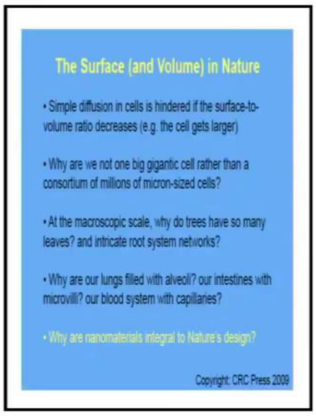

The Surface (and Volume) in Nature

- Simple diffusion in cells is hindered if the surface-to-volume ratio decreases (e.g. the cell gets larger)
- Why are we not one big gigantic cell rather than a consortium of millions of micron-sized cells?
- At the macroscopic scale, why do trees have so many leaves? and intricate root system networks?
- Why are our lungs filled with alveoli? our intestines with microvilli? our blood system with capillaries?
- Why are nanomaterials integral to Nature's design?

Now, you know as I said, it depends on the surface to volume ratio right and there are hundreds of example nature, where this thing actually happened. Simple diffusion in cells is hindered by if the surface to volume ratio decreases, right. This is what happens in your Aquaguard or in the case of your what is that called RO give us some osmosis process; you need a large surface area for the for the diffusion osmosis to happen.

Why not we, why not have one, why do not I have a one gigantic cell rather than a consortium multiple millions of micron sized cells, right? That is because surface area of this intercellular bond boundary increases, that is what happens in a material like; you want to be nano size material, then again size raise increases.

At the macroscopic cells, why do you 2 have, so trees have so many leaves, ok? Have you ever thought about it? No, think about it. Or why do they have intricate rooting system? Why are the lungs filled with alveoli? This is what I told you right, our intestines has microvilli, our blood systems of capillaries.

So, nature makes the design of the things based on nanoscale material, this is what, just now I discussed and that is mathematical analysis has a simple corollary in nature, you understand that.

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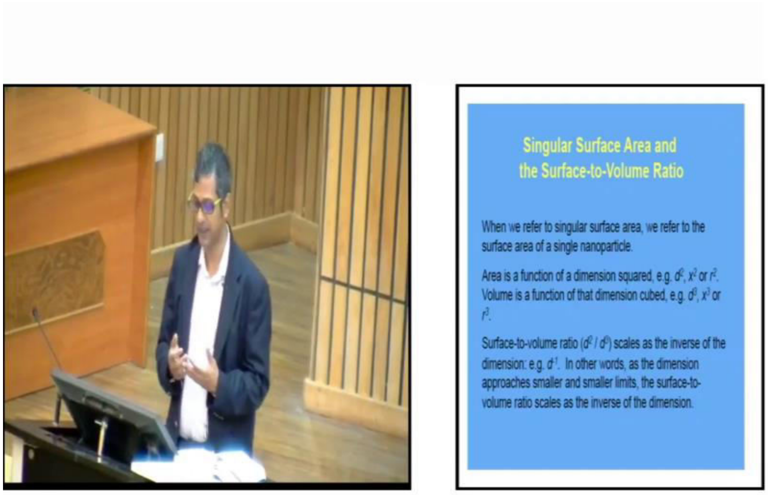

Singular Surface Area and the Surface-to-Volume Ratio

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.

Well, so you have seen that, that $\frac{1}{D}$ rule is valid for spherical nano particles, this can developed by many other things.

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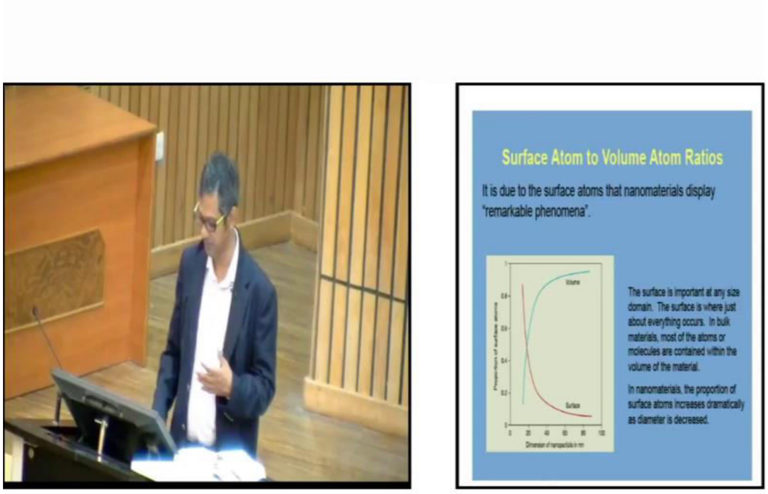

Surface Atom to Volume Atom Ratios

It is due to the surface atoms that nanomaterials display "remarkable phenomena".

The surface is important at any size domain. The surface is where just about everything occurs. In bulk materials, most of the atoms or molecules are contained within the volume of the material.

In nanomaterials, the proportion of surface atoms increases dramatically as diameter is decreased.

But before you go into it, let us discuss first what is the surface energy per se, ok.

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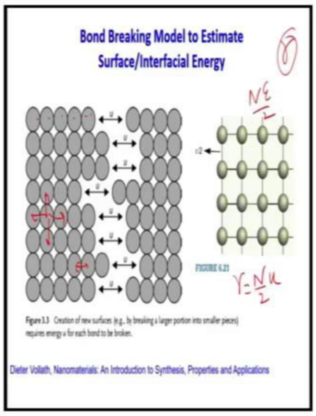

Bond Breaking Model to Estimate Surface/Interfacial Energy

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.

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I will not, I will come back, I will go back to their side again. So, this picture is splashed you know, we only talked about how the surface related volume ratio can change the surface energy; we did not talked about γ, right. γ is a specific surface energy; how does it control, how does it control the surface energy of the systems, let us look at that aspect also, that is very important, ok.

So, before I do that, you know this concept is well known in material science and surface energy is one of the areas or one of the gray areas, which has not been understood properly, but still, we have some fundamental concepts. So, fundamentally surface energy is basically because of dangling bonds or the unsatisfied bonds.

So, any surface energies can be explained by simply considering a model, in which the particles are produced by breaking a large solid into small pieces. In order to achieve this, it is necessary to cut the bonds between the neighboring atoms; that is very important, you have to cut the bonds, because you are breaking a big particle into smaller one, like taking a big chalk, breaking it down to small pieces. So, you are breaking bonds, that is obvious, right.

In simplified explanation ok between 2 atoms in the largest energy of bonding; there are atom 2 atoms are bonded right, that is what is shown here, these 2 atoms are bonded, these 2 atoms are bonded ok, shown by arrows right and you want to separate one bond energy.

You want to separate one bond; you have to spend energy, u; because that is the bond energy between 2 atoms. But the moment you separate, or you break a bond, you separate 2 atoms; so that means by spending energy, u, you are breaking 2 atoms. So, that means per atom energy is $\frac{u}{2}$, that is why written here $\frac{\epsilon}{2}$ ok, as we have done rightly.

So, therefore, if I have one mole, the surface energy is simply $\frac{N}{2u}$ or in as which terms is $\frac{N\epsilon}{2}$, that is what is epsilon energy in a very simplistic form. So, within the entry of the particles, within the entry of particle suppose this one ok, this one is bonded nicely, bonded nicely, bonded nicely, bonded nicely, correct.

But what about surface atoms? Are they bonded nicely or not, right? That is very important thing to understand. Well, we are going to a very important concept. So, maybe we can take about half a minute of you know break, so that you can come back.

So, you understand surface energy is the critical. So, think about you know surface energy for your body, right. So, if you have less number of fingers, you have less surface energy right; you have more number of fingers, you have more surface energy. Think of the people you have 6 fingers; one finger has lot of extra surface energy right, surface area. Well, let us come back fine, that is a joke, ok.

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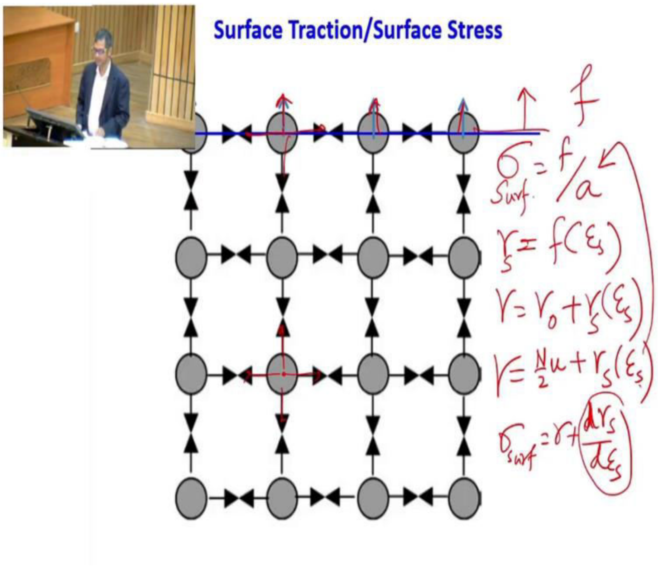

Surface Traction/Surface Stress

$\sigma_{surf.} = f/a$

$\gamma_s = f(\varepsilon_s)$

$\gamma = \gamma_0 + \gamma_s(\varepsilon_s)$

$\gamma = \frac{N}{2}u + \gamma_s(\varepsilon_s)$

$\sigma_{surf} = \gamma + \boxed{\frac{d\gamma_s}{d\varepsilon_s}}$

So, now what will happen to the atom sitting on the surface? Let us look at it that carefully. So, I told you this atom sitting inside the crystal, this atom is bonded nicely, bonded nicely, bonded nicely, bonded nicely, correct. But what about this atom? This is bonded nicely, bonded nicely, bonded nicely; no bond on this side right, same thing is valid for this, valid for this. So, at a plane surface correct, this aspect that reduced number of bonds correct, creates a force acting on the atom perpendicular to surface. So, this is the surface.

So, because of these dangling bonds or unsatisfied bonds, a force, f, act thing on this or basically a force, f, acts on these atoms perpendicular to the surface. Why it is perpendicular surface? This is the surface, this is the perpendicularity right; oops I should be able to draw it properly now, I am doing all kinds of mistake. So, right this is the direction of the force is acting and force is acting on each of these atoms and this force is f, am I clear?

Now, at a plane surface, this does not cause any hydrostatic pressure, you know hydrostatic pressure right; you think about the cycle tire, it is inflating. So, any element inside the type of surface the tire is basically you know hydrostatic pressure, that is why you are putting an air; you can otherwise you can have a solid tire, but this will not have basically work. So, you need a hydrostatic pressure inside that.

So, the because of this force, this force will not get any hydrostatic pressure on the material; but this will lead to stays on the surface. You will be thinking about why is this? Very simple, because this force is acting perpendicular to this plane surface; so this will lead to stretching of the atoms, a stretching means a force.

So, now this force is known, the stress, $\sigma = \frac{f}{a}$; of each atom, a is the area of the each atom and f is the force ok, σ is again not done properly. So, σ is the stress and this stress is known as the surface stress. So, we can write down surface, this is the stress acting on each of this atom and this is known as the surface stress, this is something new, correct.

Now, this surface stress will depend among the amount of stretching, amount of stretching will depend on the force. If you have only single bond dangling for each atom, the force is one kind; but you have a 2 or 3 bonds dangling, force will be more. So, more the force is, more will be the stretching; as the more is the stretching, more is the stress, force more means more is the stress. So, you understand that this surface stress depends on the stretching.

Now, this surface stress has been modeled and remember this one will affect the surface energy; you must be thinking why, because you are generating extra stress in the material, you are generating extra stress on the surface of the material. So, that will be affecting energy of the system, is it not; because that is an extra energy you're paying or extra energy you are creating because of the surface dangling bonds. So, that has to be paid up.

So, now obviously, the surface free energy or gamma will be depending on this amount of stretching, amount of stretching is ϵ_s How much this bond will get stretch, because of this force, f acting on them, that will be deciding this surface energy also, much like a stretching upper our screen. So, as you know, gamma can be now written as $\gamma = \gamma_0 + \gamma_s(\epsilon_s)$, which will depend on ϵ_s, right. You got it, that is very clear. And this $\gamma_0 = \frac{Nu}{2}$ and this is $\gamma = \frac{Nu}{2} + \gamma_s(\epsilon_s)$; So, now I know these aspects and I know this ϵ_s, ϵ_s is related to the surface stress, right. So, γ_s depends on ϵ_s, $\epsilon_s$depends on the surface stress sigma. So, I can do a simple maths, which I am not doing that, I am leaving it to you. So, I can write down $\sigma_{surf} = \gamma + \frac{d\gamma_s}{d\epsilon_s}$; do you understand that, this will directly come from that, ok.

Well, it assumes that the γ, σ_{surf} and ϵ_s they are directly related; they have they are not complex related, they will have you know linear or kind of relationship, that is understandable. In the elastic stretching regime, you can always apply Young's law, right. So, you can do that, ok.

Now, for a liquid, this term for a liquid, this term goes to zero, correct. For a liquid, the stretching of atom or stretching of the surface flame will not lead to change of surface energy or basically not lead to any create of any surface stress rather, correct. For a solid it will, and this will depend some amount of force or amount of stretching. So, more the stretching, more is the surface stress and more will be surface energy for solid.

So, this part is never dealt when you talk about the effect of surface area on the total energy surface energy system right, this was ignored. So, you understand that surface energy is first and foremost important thing is in a nanomaterial, solid nanomaterial; surface energy is critically going to depending on this surface stress, ok.

So, that means surface energy has two components; one is the bond breaking, that is given by $\frac{Nu}{2}$ in a per mole, other one is your because of stretching, correct. It is very difficult to estimate this; there is no experimental procedure in the world available today, which can allow to estimate this γ_s.

So, what you can do? Well, you can actually calculate γ_s, if you can know the total gamma and if you the number of bonds broken. But in most of the cases is very difficult to know how many number of bonds are broken, bond energy you can be known for a material.

Let us talk about graphene actually, you can easily get these things; you know graphene sheets are basically not a flat, they have lot of undulations and this undulation is basically because of stretching, ok. There are many reasons for boundary region surface stress, right. So, that is leads to change in the surface energy of your system. Well, that is one part of it. So, you understand right, I hope. So, I am not talking much about it, I hope so you understand it, ok.

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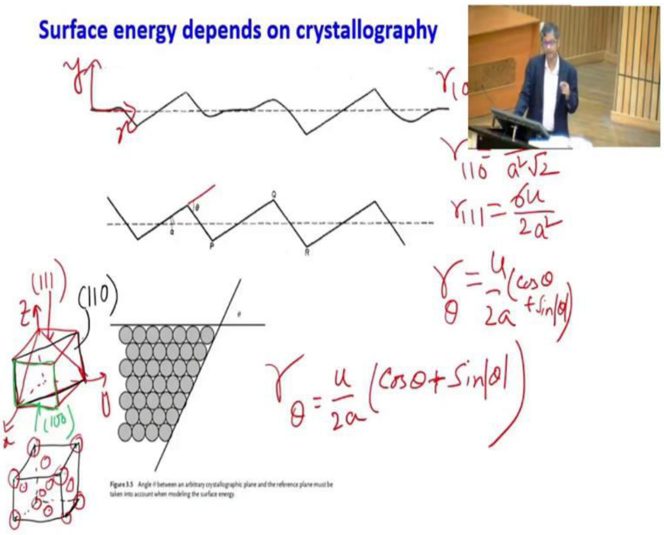

Surface energy depends on crystallography

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

$$\gamma_{110} = \frac{}{a^2\sqrt{2}}$$

$$\gamma_{111} = \frac{6u}{2a^2}$$

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

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

Next couple of slides what I am going to do is this; the surface energy also depends on the gamma basically, also depends on orientation. How? Yes, that is very important, how do you know that. Well, think of a cubic crystal ok; I will draw it here, because I need to use this part. So, I draw a cube fcc crystal ok; I will draw 2 fcc crystal, one with atom and one without atom, this is with atom, without atom, right.

So, let us mark 3 important planes (1 1 1) and ok different color. This one is what? This one is (1 1 0) right, let me write down and this one is red one is (1 1 1). How do you know that? This is x, this is y, this is z; you do it yourself, along x 1, along y 1, along z infinity. So, that is a (1 1 0) along x 1, along z 1, along y 1, (1 1 1). And what about this plane, ok? Let us use a green thing right, this is what, (1 0 0), that is a plane which is cutting x axis 1 parallel to y and parallel to z. So, these are the 3 prominent planes in a fcc crystal.

So, now I drop the atoms, ok. So, let us use a black color to draw the unit cell, I am sorry; because it is the end of the slide, still it is ok understandable. Now, I put the atoms, corner atoms; you can do yourself right, corner atoms are very easy. Then you have all light corner atoms, then face center atom; top surface, bottom surface, side surface, side surface, side surface, side surface.

Now, you tell me, if the origin of γ is a bond broken; now if I consider first, one is your surface, that is this one the green, ok. How many bonds are broken? So, you can count 1, 2, 3, 4, and 5; 5 atoms are sitting on the surface, correct. So, bonds of those 5 atoms are broken and subtly surface series a^2, correct. So, γ is basically total number of bonds broken. So, for each atom you know if you know how many bonds are broken; then you can calculate easily, let does not do that, ok. And if you know the bond energy among them and divide by the surface area, that is a square.

So, what about (1 1 0) plane, how many atoms are there? You can see 1, 2, 3; 1, 2, 3, 6 number of atoms are different also. This is the plane which is surface plane, then 6 atoms will be sitting on the surface right and their bonds will be not satisfied. So, if you for the sake of simplicity if we assume 6 bonds are not satisfied, $6u$ multiplied by what area; area is different here, $a^2\sqrt{2}$. So, $a^2\sqrt{2}$, right.

So, that is thing. So, I can write down $\gamma_{110} = 6u\sqrt{2}$, right. γ_{110} will write here, $\gamma_{100} = 5ua^2$. What about γ_{111}? Well, that is very easy on the (1 1 1) plane, 1 atom, 2 atom, 3 atom, 4, 5, 6, 7; 6 again 6 right, 6u. And what is the area? $2a^2$.

So, you tell me, are they all same? Obviously not, correct; they are all not same. So, that means this gamma in fcc crystal depends on the orientation. What is the surface, that will repeat dictate the gamma? So, as you understand in a real crystal, the surface will be like this zigzag, correct. And you can actually calculate the orientation by angle theta. So, if you use a laboratory frame of reference x and y ok; this is y, this is x, 2-dimensional plane, you can calculate the angle theta or alpha, correct.

So, then you can measure, you can know how the surface energy is depending on the angle angular related ok, orientation dependent, right. That is you can do it, because this is for a single crystal, one unit cell; but material will never be one unit cell, it will be a large unit cells whatever the dimension.

So, there depending on the surface it will be depending on the how these planes are oriented with respect to your frame of reference. So, if your frame of reference is like that, I have drawn it x and y and then you put this crystal on this on that plane of references, the angle, the each surface will make with respect to that is what is the that is what is the orientation.

So, and now it has been calculated. If you consider say such a kind of constructions, this is taken for Dieter Vollath again; if you take input as I can construction, $\gamma_{\theta} = \frac{u}{2a}(cos\theta + \sin|\theta|)$.

So, θ may be; because in case of sin, minus plus makes different, that is the $\sin|\theta|$. So, let me write it down again very big way. So, that $u_{\theta}$is $\gamma_{\theta} = \frac{u}{2a}(cos\theta + \sin|\theta|)$, not u_{θ}; again I am making some mistake, $\cos\theta + \sin\theta$, this is another relationship in a 2 D.

So, that means if you know bonds energy, if you know the distance a, a is basically diameter of the your atom and if you know the angle theta, each plane one plane is making with a laboratory frame of reference and your frame of reference, then you can calculate this. So, first thing is that, I told you gamma depends on the surface stress, remember that a surface traction; then I told you gamma also depends on orientation of the each plane.

So, you understand that, we started with; let us not complicate things, because this will confuse you. We started with gamma into area and first we made a relationship between how the size will change the surface energy. And I told you for spherical size, it is basically $\frac{6M\gamma}{\rho}(\frac{1}{D})$, it will vary depending on the cubic particle, you know you have particle shape like a cylinder or something, that you can do yourself, we will come back to it maybe today or in the next lecture.

Then I we talked about how the specific surface energy gamma will behave, you understand that. So, gamma in a solid depends on the surface stress right; you see this, the surface traction. And I told you how it is going to be happen. And, third thing, we discussed today is surface energy also depends on crystallographic orientation, right.

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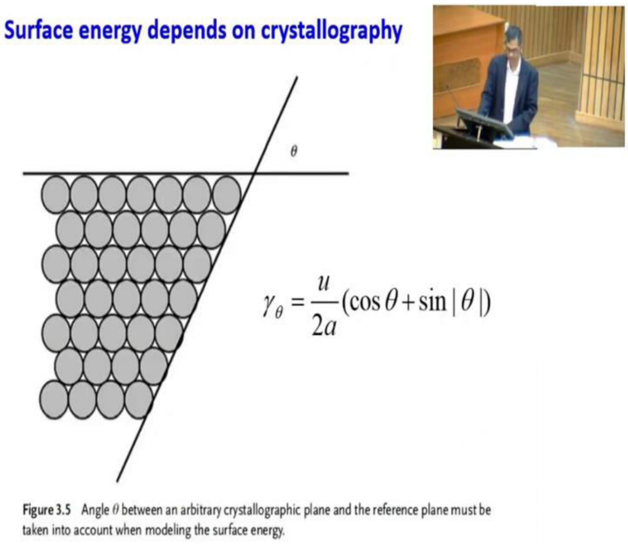

Surface energy depends on crystallography

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

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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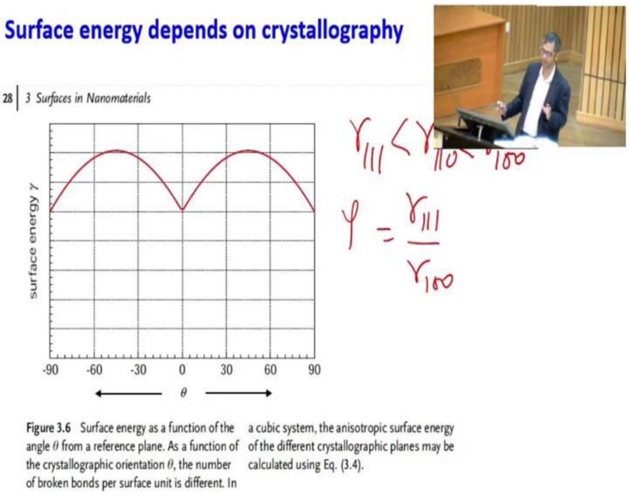

Surface energy depends on crystallography

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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).

$\gamma_{111} < \gamma_{110} < \gamma_{100}$

$\varphi = \frac{\gamma_{111}}{\gamma_{100}}$

So, next 5 minutes or so yeah, this is what it is shown this equation nicely, taken from Dieter Vollath's book is there. Now, if you plot surface energy function of theta from any reference plane, ok. So, as you see, the crystallographic orientation function theta, number of broken bonds per unit surface is different, ok.

So, in a cubic system anisotropic surface energy of different crystallographic planes may be calculated by this. So, now, we can always define, as you can clearly see surface energy of (1 1 1) plane is lower than surface energy of (1 1 0) plane is lower than surface energy of (1 0 0) plane.

So, you can define as cubic parameter, which is known as ok; we should not use epsilon, let us do some other things, because you will confuse otherwise. So, let us use this parameter. So, this is actually known as like this, but this will be all in less than one, this is called anisotropic parameter.

So, that means surface energy is not isotropic in all crystallographic directions; it is anisotropic and it depends on the crystallographic direction, that is what it tells you. And how strong is anisotropy is dictated by the ratio, $\frac{\gamma_{111}}{\gamma_{100}}$

So, now one can a cubic anisotropic of cubic crystalline, one can tetragonal symmetry tetragonal crystals, one can have orthorhombic hexagonal, different kinds of crystalline, different kind of anisotropic parameters. And, that is how we can actually get generalized expressions of γ, which we will may discuss sometime later, not now, ok.

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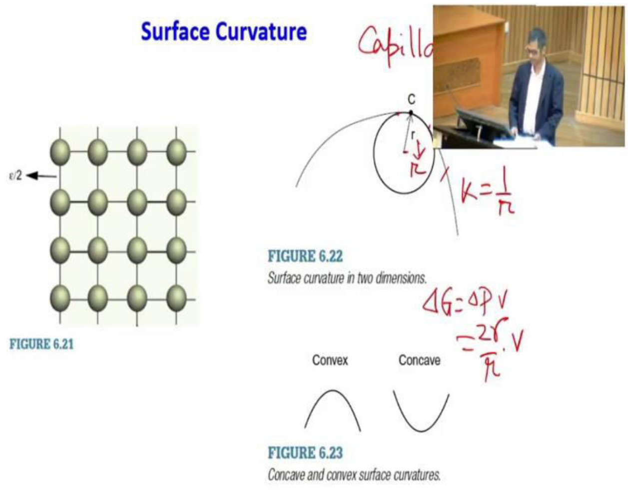

Surface Curvature

Capilla

FIGURE 6.21

FIGURE 6.22
Surface curvature in two dimensions.

$K=\frac{1}{r}$

$\Delta G=\Delta P V$
$=\frac{2\gamma}{r} \cdot V$

FIGURE 6.23
Concave and convex surface curvatures.

The last thing which I like to talk about it, surface energy also depends on curvature and I leave it to their. How it is? Well, that is very simple here, we do not need to talk about much right; how it will depends on surface curvature you know that right, all solid materials have finite sizes, they are not infinite. So, because of that, you know it has some local curvature right, you know that right; it is not, I do not tell you this.

So, it important aspect to the geometry of this surface. So, specifically geometrical surface will be the curvature of the surface, am I clear? And, that is actually effects in normally knows a capillary effect. You must be wondering, why this is known as a capillary effect?

Because all the experiments to study the curvature or effect of curvature was done on capillaries or glass tubes basically, that is why it is known as the capillary effect very interesting. In olden days people used to use glass tubes and to look at a pole liquid and see how the curvature changes, that is how the capillary term came.

So, we are talking about 2 dimensional curves. And in this figure, you see I have shown you a curve like this and now then I have drawn a circle with radius r touching the curve at point c. So, that means we can define the curvature by a term known as radius of curvature ok, $\kappa = \frac{1}{r}$, this is r. So, $\frac{1}{r}$ is what is known as a radius of curvature; it is not gamma, it is κ. So, p will be I think it will better I write properly ok, that is γ and r will be confusing, right correct. So, this is also so, this is known as a curvature, correct.

So, as you see this curvature will change depending on the location of the curve, this is at point c. So, if you move power from point c, if you go to here or there or here; it is changing, this is not same. And for to determine that you get everywhere, you have to do a circle touching that point on the curve and then only you will know what is the curvature. Well, that is very important, am I right.

So, as you know curvature can be 2 types, convex and concave, by nomenclature; this is not my nomenclatures, this is a standard nomenclature, for the convex surface radius of curvature is positive. So, it is not yes, radius of curvature; for the concave, it is negative. So, magnitude of that is depending on the type of curvature, convex or concave.

So, now you know the, all of you know soap bubble experiments right; you have done in your plus 2 or maybe later on. If you want to calculate, what is the pressure inside of bubble; you can do that, that depends on $\frac{2\gamma}{r}$, right. So, if I have to calculate free energy in this because of this curvature, this is it will be pressure change into volume; pressure change means, pressure inside the curved surface and outside this.

That is what is happening soap bubble; you have done the experiment $p_2 - p_1 = \frac{2\gamma}{r}$ and this is your again r, I should write like that, confusing otherwise for many of you, that is it. This is what you should know, $\Delta G = \Delta pV = \frac{2\gamma}{r}V$

So, you understand because of curvature, now for the convex and concave curvature, this ΔG will vary; because for a convex it is positive $\frac{1}{r}$, for concave is negative $\frac{1}{r}$, this estimate of the ramification on the nanomaterials.

So, I am going to stop here and I will come back in the next lecture, on this aspect only. Till then have a nice time.