**Nanomaterials and their Properties**
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Lecture – 14
Effect of Size on Phase Diagrams

Today is going to be the last lecture on Thermodynamics of Nanomaterials. You must be feeling little bored, so many lectures on thermodynamics and surface energy. Well, we have not done with surface energy yet sometime again, we will come back to surface energy aspects, but as far as thermodynamics is concerned, we are going to wind up today and then start a new thing or new aspects of the course.

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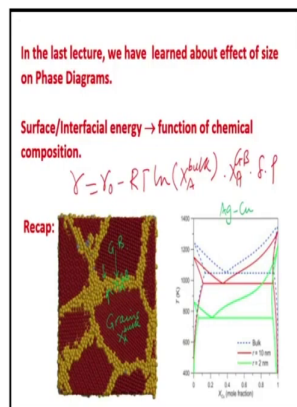
First of all in the last lecture we learned I hope quite a bit about effect of size on the phase diagrams, right and you know phase diagrams depicts information about various phase formations and the as a function of temperature and composition. So, it is important to know how these phase fields are affected by the size of the nanomaterial or the curvature of the nanomaterial.

And, in the end, I did show you that the simple model can be use to calculate phase diagrams. However, the simple model does not consider the surface energy as a function of

composition. We always use surface energy as you know isotropic. We do not consider that this is a function of composition at all.

Nonetheless, one can do actually, calculate the surface energy as a function of composition, and plug into the model and calculate. So, finally, we derive an equation which is like this; $\gamma = \gamma_0 - RT\ln(X_A^{bulk})\delta\rho X_A^{GB}$ right. We have explained everything.

So, what it does it do? It does connects the bulk composition and the grain boundary compositions with a surface energy. That is what is need to be known, because in bulk nanomaterials you have both grains and the grain boundaries, right. You have grains as well as grain boundaries both are there you can see clearly these are the grain and this is the grain boundary.

So, you we need to know the composition of X_A in the grain that is call X_A bulk. Obviously, atoms inside the grain is like in bulk, because it is bonds satisfied in all the directions. So, therefore, one can consider the composition inside the grain as X_A bulk, but at the composition in the grain boundary is X_A grain boundary. We have discussed why this composition has to be different in the grain boundary and the grains, right let us not go back to it.

So, then once we have information's about this gamma as a function of composition we can put it the model, simplistic model we discussed, we are not going to go back again because of time constraints and many other issues and one can do this. A delta is the thickness of the grain boundary and rho is the density of the grain boundary. That is a difficult term to calculate.

Well, that can be calculated by knowing the grain boundary structure whether it is a high angle low angle grain boundaries, let us not go about all these details you can assume some numbers and do this calculations, but delta is the thickness which can be measure experimentally by looking at the microstructure using transmission electron microscopes, it is possible to do that.

And, the right side I am showing you phase diagram between silver and copper and with the effect of size, right; effect of size means, for the spherical particle radius of 10 nanometres

and 2 nanometres is shown and there is a drastic change in the melting temperature, eutectic temperature as well as the composition you can see that.

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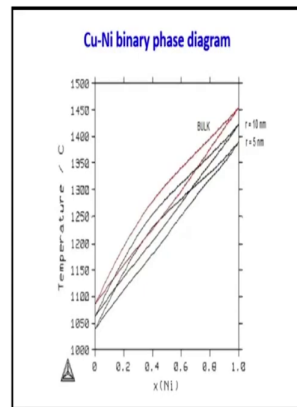
Well, and this is the few copper nickel binary phase diagram I am showing you repeatedly because this is the simplest possible phase diagram in the in the metallic system available. That is why this is this aspect of effect of size can be easily understood by looking at this simple phase diagram very easily, ok. So, ok let us not go back.

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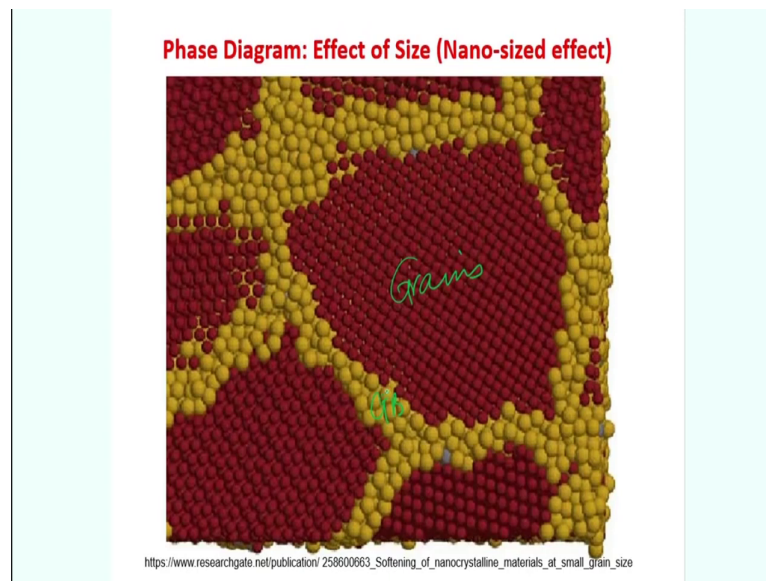
So, that means, what? This whole discussion was built on grain and grain boundary structure and the composition difference of grain and grain boundary, right. And, we assume that grain boundary has different composition the grain that is basically observed in fact, even in many of the nanomaterials by doing experimentation people have seen it. This mainly because of the grain boundary acts as a much different identity than the grains; grains has atoms nicely ordered and their bonds are satisfied in all the directions.

In the grain boundaries atoms are haphazard, quite a bit of randomness is there in an atomic arrangements as well as the atom mixing actually has lot of freedom to move from one place to another. So, that is why grain boundary structure is different from the grains and grain boundary can accommodate solute segregation. Segregation of the solute like in an alloy of A and B, B is a solute. So, solute can easily go and segregate the grain boundaries and change the characters to grain boundary.

And, that can lead to lot of different kinds of things in the grain boundaries, grain boundaries can corrode easily. Nano-crystalline materials have low corrosion resistance because they have large grain boundary areas. The grain boundaries will be having more solutes. So, they will corrode easily when it comes in contact with a acidic or a basic solution or even in water, ok.

So, therefore, this model which I have discussed can be extended by considering the whole thing grains and grain boundary together this whole thing grains and the grain boundary and GB together as one system, and then we can develop a single thermodynamical parameter and that thermodynamical parameter can then be minimized to obtain that.

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How do you do that and that is why actually a scientist called Weissmuller provided what he did. It is very simple equation he provide you know. , G_{nano}^{total} for the nanosystem, $G_{nano}^{total}=$

$(x_A G_A^0 x_B G_B^0)+RT[\{x_A^{bulk}\ln(x_A^{bulk})+ x_b^{bulk}\ln(x_b^{bulk})\}+ x_A^{GB}\ln(x_A^{GB})+ x_b^{GB}\ln(x_b^{GB})]+ x_A^{bulk}[H_{mix}^{bulk}+$

$H_{mix}^{GB}]+\gamma A^{GB}$ ok. It is obviously, the physical mixture, all right and then your entropic term is going to come into picture. We have seen in an Euler's case. An entropic term will have two parts one because of grains, other one is because of grain boundaries. This is something unique, right.

You are treating same material grain, as one entity grain boundary as one other entity and this is ok. This is ok why because in the grain atomic structure is different from the grain boundaries. So, one can look at entropic effect in the grain and the grain boundaries distinctly different way. So, how do you do it? Ok. So, for the grains we can write down $RT\{x_A^{bulk}\ln($

$x_A^{bulk})+ x_b^{bulk}\ln(x_b^{bulk})\}$, ok and then for the grain boundaries $RT\{x_A^{GB}\ln(x_A^{GB})+ x_b^{GB}\ln(x_b^{GB})\}$. So,

you have physical mixture and the entropic term. You must be wondering why a physical mixture is not changing ok physical mixture is basically is not at all considering the effect of atomic mixing, ok. So, therefore, there is no change of that part because of the grain, grain boundary treating as two different entries entities, right.

But, then you know we need to also consider excess right excess free energy and excess free energy can be treated like this, that is also has to be at be treated like that $x_A^{bulk}[H_{mix}^{bulk}+H_{mix}^{GB}]$, right and one can do this in the sense that we can treat grains and grain boundaries two distinct entities of the material.

And, in nanomaterial in addition to this we have to add the surface energy term, right that is γ A^{GB}. So, you must be seeing oops, such a big equation, but equation is very simple. We started with simple equation and then added keep on added terms. So, now, if I want to calculate only for the grains, you can remove the grain boundary terms and get it. If I want to calculate for the grain boundary, you can use that, right the you can ignore the grain terms.

And, totality the system will allow you to calculate the free energy together. Now, we can easily do this we can assume a spherical particle ok a spherical basically grain if you assume a spherical grain ok of diameter D so then what will happen then you can clearly see $A^{GB}=\frac{6}{D}$ V. Well, you must be thinking how do $\frac{A}{V}=\frac{4\pi r^2}{\frac{4}{3}\pi r^3}=\frac{3}{r}=\frac{6}{D}$ I get it very simple, right.
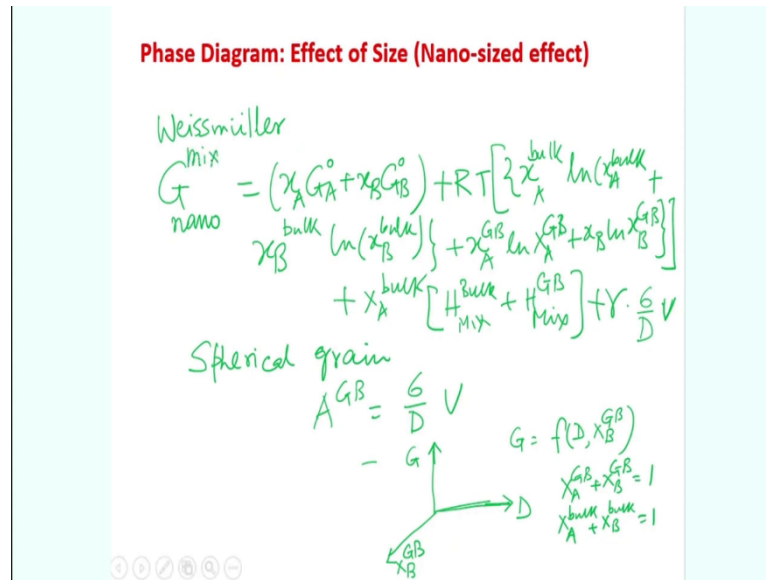
Volume of grain can be calculated easily right, even from the microstructure you can calculate correct that is not difficult to do. So, now we can see that whole G can be plotted as a function of two things: as a function of D which is the size of the grain or diameter of the grain right and also as a function of the composition of the grain boundaries. Well, you know that is what something, which I need to discuss.

If I take an alloy let, we take an alloy of composition with some 20 percent of B; that mean, it contains 80 percent of A. Now, in the grains it will have the same composition, it will not vary too much ok. Why? Because the structure of the grain in such that it will try to accommodate atoms in the same ratio of 80:20 80 A 20 B, but because grain boundary structure is different; grain boundary can have segregation of solutes.

So, therefore, grain boundaries will behave differently and therefore, grain boundary composition will not be same as the composition of the alloy. This is true for ceramic system; this is true for polymeric system also. You can have two polymer metal mixing and producing nano all mixed polymer, there also same thing can happen. If you have a grain and grain boundaries is still in polymer this will happen; obviously, I want because there is no concept of grain boundaries so, why to worry about it, ok.

So, that is why this whole G is basically G has three important basically two important variables not three. So, if I have G ok one is function of D, other one is a function of X_B grain boundaries, correct. So, this is a 3D plot correct. So, $G=f(D, x_B^{GB})$ It is must be thinking why only x_B^{GB}, why not x_A?

Well, $x_A^{GB} + x_B^{GB}=1$. Similarly, x_A^{Bulk} and x_B^{Bulk} bulk if you add together that is $x_A^{Bulk} + x_B^{Bulk}=1$. So, therefore, this is a single variable right, one you know other one is easily calculated. So, that means, I can actually use this expression of Weissmuller and plot G as a function of D and x_B^{GB} that is possible solute, where B is a solute actually, ok.

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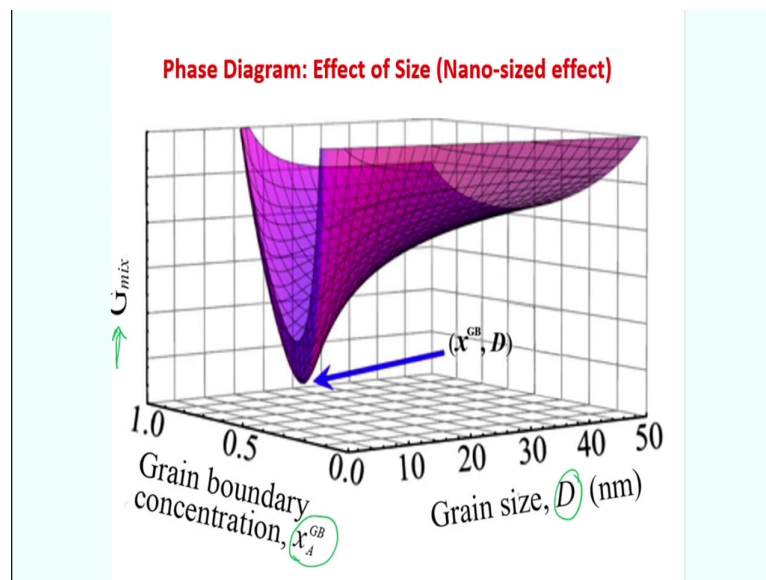
And, that is exactly was done I will come back to it exactly was done by the Weisemuller and you can see here this is G^{mix}, ok. By the way, I should write this is G^{mix} it is not G^{total}, otherwise you will get confused this is G^{total} only, but you are writing in terms of mix, right.

Phase Diagram: Effect of Size (Nano-sized effect)

In terms of mix, you are writing it up. So, $G = f(D, x_B^{GB})$ does not matter I told you just now, because both are actually having related to each other and so, this is what is plotted as a function of x_B^{GB} and as a function of grain diameter (D).

So, what you do? You see a 3-dimensional plot and 3D plot has a minimum or minimum basically minimum ok and that minimum is what you should get, because of thermodynamic reasons because of stability that is the energetically minimum position and that is correspond to certain value of grain boundary concentration of the element ok x_B^{GB} and also diameter (D).

So, you can see that we can actually have this functionalism or this functionality of G^{mix} and get the complete picture in the nano scale by doing such a kind of thermodynamic analysis, ok. So, that is my first part of my things. That is where the most of thermodynamical discussion ends.
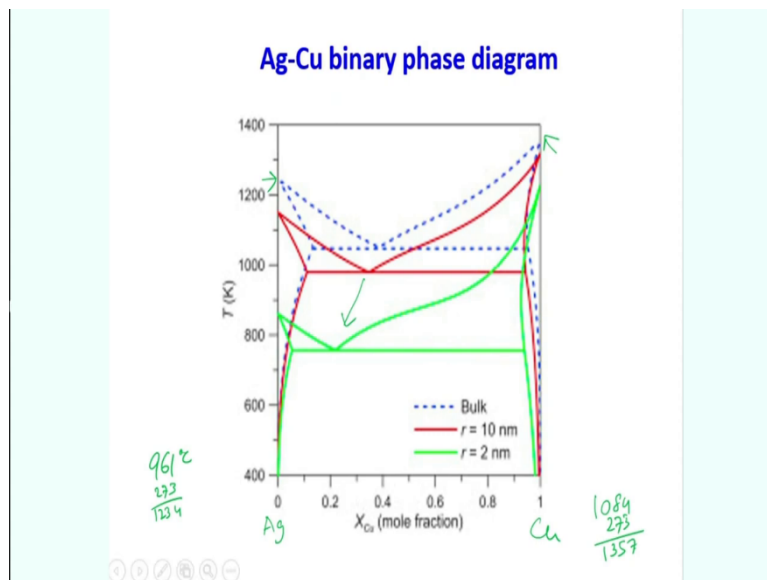
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Phase Transformation temperature of nanomaterials: effect of size

At $T = T_{tran}$ $G_{old} = G_{new}$ $(G_{liquid} = G_{solid})$

But, we are going to also look at something which is unique, ok. What is the unique aspects, correct? at $T=T_{trans}$ $G_{Old}=G_{new}$

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Ag-Cu binary phase diagram

Well, you know as you have seen in this diagram you see the melting temperature of pure silver and pure copper has gone down the dotted line is bulk this is the melting temperature of pure copper. That is about 1084 degree Celsius. So, 1084 plus 273 that is 1357 degree

Celsius, ok. So, similarly silver has a melting temperature of 961 degree Celsius if you add 273 this becomes 1234, right. That is what you see here, correct?

These melting temperatures have gone down although they are pure ends, but these melting temperatures have gone down actually. You can see that this melting temperature has gone down; eutectic temperature also has gone down. So, can I you know do a simple thermodynamical model to understand how you to calculate that and for spherical particle? You will see a very simple analogy you can get.

Well, so, when you are talking about phase transformations you know at the phase transformation temperature.

So, at suppose T is T transformation $T=T_{trans}$ $G_{Old}=G_{new}$ G=H-TS Why? Because, the free energy is must be equal at the transformation temperature.

Below the transformation temperature, that solid will have higher lower free energy than the liquid and above the transformation; temperature liquid will have higher free energy than the solid. This is true for any transformation if you are talking about the ceramic phase transformation also where you have suppose you know in case of cubic zirconia and tetragonal zirconia the same thing will be valid, ok. Free energy of cubic and tetragonal zirconia must be same at the transformation temperature.

Well, now by knowing that what I can write down? I can write down this G ok let us remove this aspect this will otherwise you know make more complication later on.

So, let me write. Why do I write T_{rans}?

$$H_{Old} - T_{trans}S_{old} = H_{new} - T_{trans}S_{new} + (_{new}A_{new} - _{old}A_{old})$$

Because this is the change because of transformation change of enthalpy because of transformation change of entropy because transformation change of free energy because of transformations, ok.

$$\Delta G_{trans} = G_{new} - G_{Old}$$

$$\Delta H_{trans} = H_{new} - H_{old}$$

$$\Delta s_{trans} = S_{new} - S_{old}$$

So, this is for the normal bulk systems. The moment you have surface energy, then you have to add these two terms, $(_{new}A_{new} - _{old}A_{old})$, $_{new}$, A_{new}, $_{old}$, A_{old} terms are surface energy and surface area for the new and old, right. You know even in nanocrystalline system also you can have transformations from one nanocrystalline cube zirconia to nanocrystalline tetragonal zirconia, nanocrystalline copper to nanocrystalline sorry nanocrystalline FCC, a titanium to nanocystalline HCP titanium – so, these transformation are possible, then also you

have surface energy and the surface area will change. So, we must consider these aspects in the nanoscale.

So, this will be plus then gamma new A^{new} minus gamma old A^{old} ok, fine. So, this is something which one can derive very easily from the normal thermodynamics by adding these terms of gamma and A, right, this is for the nano terms, alright. So, now, consider spherical part.

So, spherical particle why do we assume? Because that makes our life easy. You can do is for cubic also cuboid or other things also. So, for spherical particle you know area can be related to volume you know that $A = \frac{6}{D}V$ and then volume can be related to mass divide by density or not mass molecular weight by density so right that is condoned. So, you can clearly see that is $V = \frac{6}{D}\frac{M}{\rho}$.

So, this easily one can do. Now, but you know when you transform a phase from one to other you do not change the mass, right. You may change density that may lead to change in volume or you may change surface area, but mass is not going to be change because you know and you remember the you know very basic thing the mass cannot be lost mass cannot be gained, ok.

Well, we are not talking about Einstein to means of that where mass and energy can be, but we are talking about the normal thermodynamics ok where mass cannot be altered. So, if that is what is case I can write down mass M is spherical particle ok

$$M = \frac{4}{3}\pi r_{old}^{3}\rho_{old} = \frac{4}{3}\pi r_{new}^{3}\rho_{new}$$

So, what is the thing now? $\frac{r_{old}}{r_{new}} = (\frac{\rho_{new}}{\rho_{old}})^{\frac{1}{3}}$ $\longrightarrow$ $\frac{D_{new}}{D_{old}} = (\frac{\rho_{new}}{\rho_{old}})^{\frac{1}{3}}$

D new by D old; D is the diameter, r is the radius, right of this spherical particle.So, what are the two important relationship we got? Those are the two things we will remember right, ok and rest of the thing we will we forget.

So, we have seen that A can be related to this, right. We have also seen that the diameters of the particles can be related to density old and new phase. This is something you have learned how to do it, right. This is one.

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Then I can erase out this one also. I may use this space for my new calculation, right. So, it is understood, right, so far whatever we have done? Ok. So, then what we can do? So, we can come take this equation. You can take this equation and do further calculation. You can see that you know area and the diameter they are related, correct. You can see area is related by D and D is related to density. So, if you do the maths properly, $\Delta G_{trans}=\Delta H_{trans}$ - $T_{trans}\Delta s_{trans}$ +

$(_{new}\frac{6M}{\rho_{new}D_{new}})$ -$(_{old}\frac{6M}{\rho_{old}D_{old}})=0$ at the transformation temperature because $\Delta G_{trans} =$

$G_{new} - G_{Old}=0$ correct. $A = \frac{6}{D}V=\frac{6}{D}\frac{M}{\rho}$

So, one can actually modify this expression further.

$$M=\frac{4}{3}\pi r^3_{old}\rho_{old}=\frac{4}{3}\pi r^3_{new}\rho_{new}$$

$$\frac{r_{old}}{r_{new}} = (\frac{\rho_{new}}{\rho_{old}})^{\frac{1}{3}} \longrightarrow \frac{D_{new}}{D_{old}} =(\frac{\rho_{new}}{\rho_{old}})^{\frac{1}{3}}$$ correct. So, now, I erase the ups.

So, that you can understand easily I erase the up side upper side of the slide. You can also

taken down everything. So, no problem as far as erasing is concerned one can actually note down or if one can look at the video again and again.

So, then I can write down well, I can write down.

$$\Delta G_{trans} = \Delta H_{trans} - T_{trans}\Delta s_{trans} + (_{new}\frac{6M}{\rho_{new}D_{new}}) - (_{old}\frac{6M}{\rho_{old}D_{old}}) = 0$$

$$\Delta G_{trans} = \Delta H_{trans} - T_{trans}\Delta s_{trans} + (_{new}\frac{6M}{\rho_{new}D_{new}}) - (_{old}\frac{6M}{\rho_{new}}(\frac{\rho_{new}}{\rho_{old}})^{\frac{1}{3}}) = 0$$

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So, then I can also write down well, I can write down

$T_{trans} = \frac{\Delta H_{trans}}{\Delta S_{trans}} - \frac{6M}{\rho_{new}D_{new}\Delta S_{trans}}[1 - \frac{old}{new}(\frac{\rho_{new}}{\rho_{old}})^{\frac{2}{3}}]$, correct that is what you can get very easily by doing this mathematical jugglery terms, it will obviously right, otherwise this equation will not get. So, now, one can always think about this ratio as a bulk temperature you know you how to get it very simple $\frac{\Delta H_{trans}}{\Delta S_{trans}}$, ok. You do not know? All of you should know this.

$\Delta H = \Delta S T_{bulk}$ because $\Delta G = 0$. So, you can always get that. So, this is the bulk. So, that is why you can get. You do not understand we can discuss further, ok. This minus this minus, what?

$$\frac{\Delta H_{trans}}{\Delta S_{trans}} - \frac{6M_{new}}{\rho_{new}D_{new}\Delta S_{trans}}\left[1 - \frac{old}{new}\left(\frac{\rho_{new}}{\rho_{old}}\right)^{\frac{2}{3}}\right]$$. So, that is what you get. Now, I erase this part further and you can complete the mathematical relationship easily, so that you can understand and get that those temperatures by simply applying this relationship, which we are going to derive by this thermodynamical derivation, fine.

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So, then I can write down

$$T_{trans} = \frac{\Delta H_{trans}}{\Delta S_{trans}} - \frac{6M_{new}}{\rho_{new}D_{new}\Delta S_{trans}}\left[1 - \frac{old}{new}\left(\frac{\rho_{new}}{\rho_{old}}\right)^{\frac{2}{3}}\right]$$

$$T_{trans} = T_{bulk} - \frac{6M_{new}}{\rho_{new}D_{new}\Delta S_{trans}}\left[1 - \frac{old}{new}\left(\frac{\rho_{new}}{\rho_{old}}\right)^{\frac{2}{3}}\right]$$

$$\Delta T_{trans} = T_{bulk} - T_{trans}$$

$$\Delta T_{trans} = \frac{6M_{new}}{\rho_{new}D_{new}\Delta S_{trans}}(1-\beta) \quad \text{where} \quad \beta = \frac{old}{new}\left(\frac{\rho_{new}}{\rho_{old}}\right)^{\frac{2}{3}}$$

If $\beta \cong 0$

$$\Delta T_{trans} = \frac{6M_{new}}{\rho_{new} D_{new} \Delta S_{trans}}$$

$$\Delta T_{trans} \, \alpha \, \frac{1}{D}$$

So, this tells you that the change of melting temperature the change of mean transformation temperature is basically change one by D correct that is what you get that is very easy to understand and this law is applied, but to do the calculation you should know molecular weight, you should know gamma new phase, rho density of new phase and also delta S that is the entropy change.

Entropy change can be easily calculated if you know the heat change in the transformation like in the case of melting you require to know only the enthalpy of melting that is the latent heat; in case of cubic to tetragonal transformation you need to know what is the transformation heat of transformation. That is what is very important. So, simply by doing this mathematical formalism one can actually do the whole analysis. You can see thermodynamics is so powerful it gives you all the fundamental relationships, which you have derived so far, ok.

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Figure 7.6 Reduction of melting temperature of aluminum as a function of particle size. Note that the surface term causes a significant reduction in the melting temperature.

Dieter Vollath, Nanomaterials: An Introduction to Synthesis, Properties and Applications
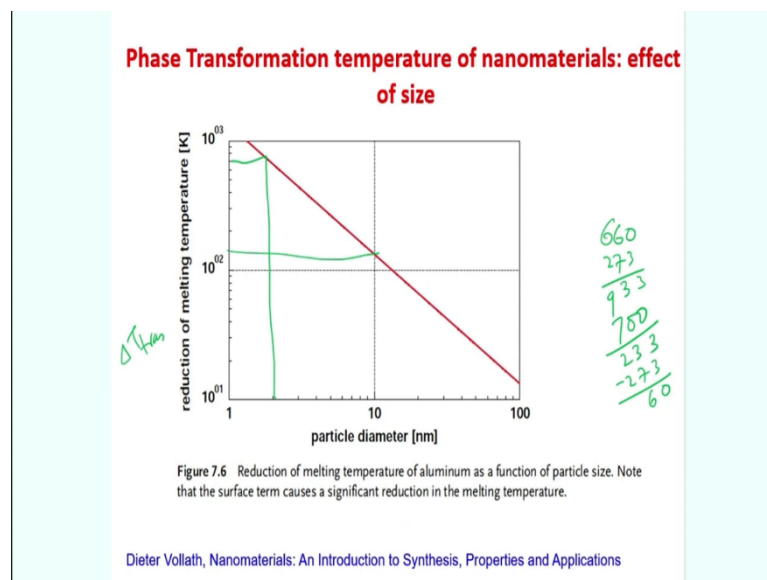
So, this is the same thing taken from Dieter Vollath's book, reducing reduction of melting temperature again delta T as a function of particle diameter for aluminium, ok and you can

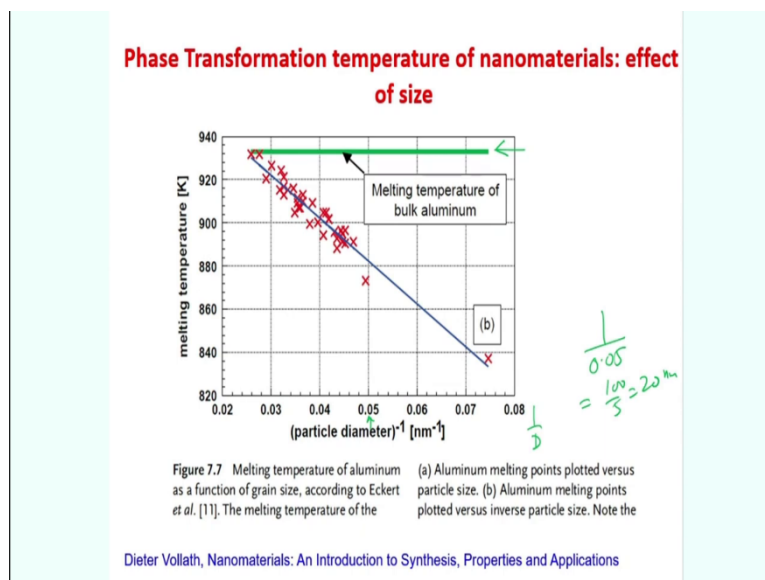clearly see that temperature is going down from 10 to the power 3 to 10 actually as you basically, change in temperature is pretty large as you go down to 1 nanometer, it is substantially large.

It is something on sometime it is people do not even believe such a kind of change can happen for nanoparticles; it is a massive change, ok. This is basically ratio oh sorry, reduction delta S delta T trans this is basically delta T trans that is massive. So, for about say then this is about couple of 100s, correct. 10 nanometres and if you go to 2 nanometres it is become very large close to even 800 nm that is unbelievable in low for aluminium, ok.

That means, aluminium as a melting temperature 660 degree Celsius if you have a add 273 660 plus 273 is 939. So, you subtract this 1700 so how much you get. 1433 and then you divide minus 273 is becomes what? It becomes around minus 60 degrees. This is impossible actually such a kind of thing cannot happen, but you cannot produce 2 nanometer aluminium particle it will not be stable it will be fully oxide. It is so reactive with this to the atmosphere.

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Figure 7.7 Melting temperature of aluminum as a function of grain size, according to Eckert et al. [11]. The melting temperature of the

(a) Aluminum melting points plotted versus particle size. (b) Aluminum melting points plotted versus inverse particle size. Note the

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

Well, same thing has been shown here to be done. Here it is plotted as a function of 1 by D ratio, correct. So, higher the ratio smaller is the particle diameter, right. Lower the ratio larger is the particle diameter you can see if it is 0.05 by 1, it becomes what hundred by 5 is 20

nanometer. So, 20 nanometer is the smallest one you know somebody has got some smaller than that also, correct.

20 nanometer is 0.2 correspond to 0.5 and then you go up to about hundred nanometers and this is the bulk multi temperature 930 how much 933 degree Celsius temperature is what is the bulk melting temperature of aluminium. So, you can clearly see even the experimental data points follow the theoretical curve. So, that means, the whatever thermodynamic analysis we have been doing it, it is true actually. It is not wrong it follows the experimental data, which has been for you know plotted in this case. So, these are all available in Dieter Vollath's book.

So, I will say you know upload some of these portions for your benefit, but please do the calculations or the derivations yourself do not forget to do that because derivations are very important to know the theory and then you want to apply for various problem solving this is what you need to know, ok.

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Now, so far whatever time I have about 10 to 15 minutes maybe 10 minutes time we are going to switch over and talk something new. Something new means something new because we are going to start the description of. So, we have discussed about what? Hierarchical things of nanomaterials, availability in nature, then we talked about surface energy, then we

talked about thermodynamics right that is that is total something about 14 lectures has been spent.

Now, we are going to talk about properties and at the end we are going to talk about characterization of these nanomaterials, right. So, before we talk about properties you must know how nanometals are synthesized. Well, that is itself a big subject, ok. Obviously, I cannot talk so much, but I will be able to give you perspectives to that so that you can understand you know synthesis of nanomaterial is a big subject and in the book of Michael Ashby and others lot of things have been written here, ok.

So, you can produce 1-D, 0-D and 2-D nanomaterials by different techniques like discrete nano objects can be produced or you can produce you know surface nano features or you can produce bulk ok by different routes. So, for discrete nanoparticle you can use inert gas condensations, colloid methods or even you can do you know templating you can even use electro deposition PVD, CVD self assembly, ok.

For surface nanostructures, you can do CVD, PVD, lithographic techniques or you can do electro depositions or CVD and PVD. For the bulk you need to use different kind of techniques like equiangular extrusion, milling cryogenic, room temperature or even you take a particle powder particle consolidator sinter to get a nanostructure material bulk. You can always incorporate nanotubes and rods in the polymeric or the metallic matrices; you can also do rotating starter PVD or CVD cyclic electrodeposition so that you can have a bulk thicker material possible, right.

So, these are all you know where different routes are done. Now, we are going to discuss some of these routes there are even many many routes which are not been discussing.

Synthesis of Nanomaterials
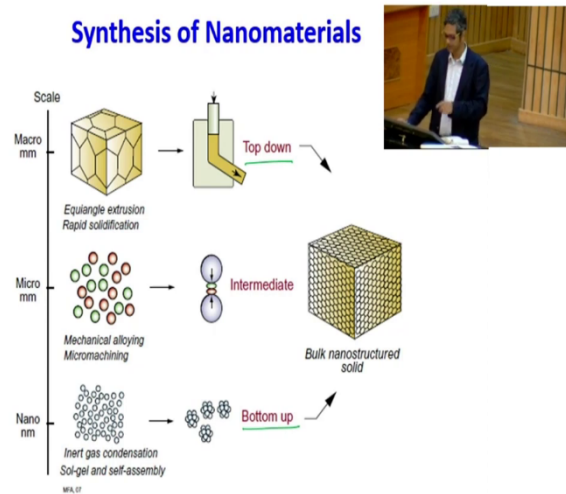
M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

But, you know in a nutshell if you want to produce synthesis nano synthesize nano materials, there are two processes which are used – one is top down, other one is a bottom up ok. Very funny names you can see bottom up, top down, top down bottom up, right.

So, in a top down approach you can start in a micro on millimeter size grain structure; millimeter size – big grains, you can see by your naked eyes and then you can break it down into small, small, smaller pieces just like you take a chalk ok piece of chalk and then you use big chalk and then you one by one break and break particle dust from dust you can make through nanocrystalline particles, right.

Or you can do you know you can start with atoms ok like you can take evaporation of any metallic things it will produce vapour; vapour is nothing but atoms. So, those atoms then can actually condense and produce small you know nanocrystalline materials. This is known as a bottom up approach. You start from atoms then get down to nanomaterials that is why it is called bottom up.

You can also be intermediate things like mechanical alloying or micro machining; mechanical alloying you can start with bigger size particles, break it down to intermediate one produce nanomaterials or you can actually form an alloy to form a nano from a pure materials even from a alloy also. Machining also same thing you can do a machining operation on the

surface and deform the surface to heavily and form nanostructure materialism, it was just called intermediate things.

But, mostly you have two types of things one is top down one is bottom up.

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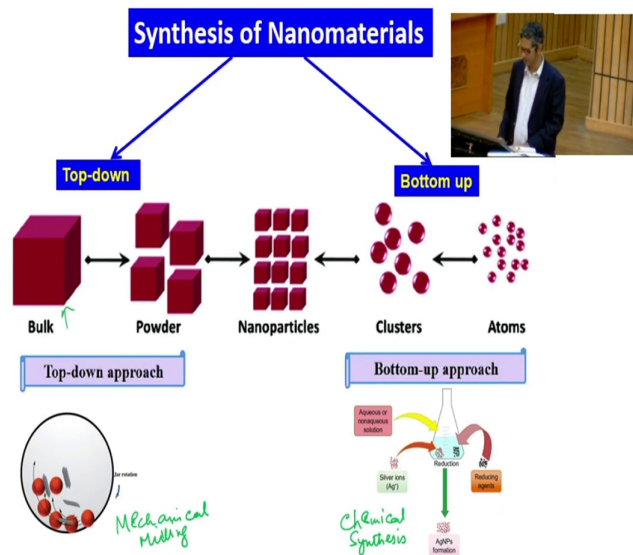
Next slide we will also explain in details manner. In a top down approach you can start with the bulk as I said; bulk means it is about this pen, it is a big thing, xyz all the things grain structure everything is big millimeter or micron ok, grains are very big. Then you can make a powder, break it down, break it down, break it down, break it down and get nanoparticles, right.

So, this is basically a destructive process you break things down. You completely break then you still get a nanoparticles or with the bottom up you start with atoms like a vapour, metallic vapour, their atoms loosely bonded, then they come condensed from clusters and then clusters grow they form nano particles, right.

So, the top down approach makes example is your ball milling or mechanical milling, right. Bottom up approach – chemical synthesis, all the chemical synthesis groups comes under that. You can have you know salts like have people here using silver salts and then silver salts

as silver ion, reduce it and you can get silver nano particles by doing something right that we will discuss later on how you can be done.

So, you understood right these are the two classic techniques by which you can produce nanomaterials, there is no other technique available in this world. All the techniques which you are you will be studying or knowing they will fall under these two. There are some intermediate techniques of micromachining or something I discussed.

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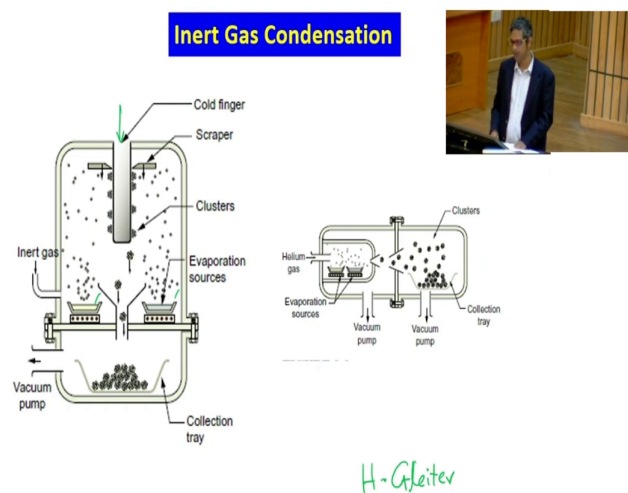
M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

Well, first one we will discuss few of them today's lecture. First one is known as inert gas condensation. This was basically you know this basically adopted by Herbert Gleiter. H. Gleiter in his classic work in 1960s and even 70s 19 late 1960s and 70s, ok.

So, in the time of nano starting off, what is done in this case? Well, let me first tell you this is a vacuum system, ok whole thing is evacuated whole thing whole chamber. And, in this evacuated chamber you have source like this. This is one, this is another one; basically source means nothing, but metal or maybe whatever you want to do you produce nanoparticles and then you heat them up.

You know, any metal if you heat up it will evaporate, correct? Only thing it is required sometime high temperature like tungsten or things, but normal materials under vacuum it will evaporate and produce vapour, correct. And, then you can actually allow inert gas like argon

and helium; helium is better than argon, but argon can also be used. You can let this inert gas go inside, right.

Inert gas molecules, then will make this vapour to move forward because there will be kind of collusion of atoms of inert gas molecules and these evaporated things. So, once they are actually moved away from the source because of evaporation, then if you put a cold finger, what is the cold finger? Nothing, but a rod which is cold because of flow of liquid nitrogen.

So, you can actually have flow of liquid nitrogen inside this rod a liquid nitrogen is very low melting temperature like minus 196 degree Celsius or 77 Kelvin, right. So, if you flow that, the whole rod surface will be very cold. That is why it is called a cold finger, correct. So, what will happen because this vapours have all moved up due to inert gas movement inert gas flow, they will all condense on this cold finger very easy because this will this will act as a sink, ok.

And, all the vapours because their vapour will reduce the energy by forming clusters on the surface of this cold finger and then you can take a take this cold finger down, ok or basically you do not need to put it down you can have a scraper mechanical scrapper which will scratch the surface of this cold finger, then you can get nanoparticles in a collection tray how simple is the technique, right.

It is simple, but the moment you want to devise such a kind of a chamber with all these things, it takes lot a lot of planning and understanding and they also effort to do that, correct. So, that is something which is widely used very widely used, ok. So, this is known as inert condensation which has been proposed by Herbert Gleiter in Germany long back.

You can also have inert gas expansion, what is that? Well, that is something which is very very interesting, ok. This is even much better because here what happened because you have condensation of these clusters on the surface of this cold finger, some of these the clusters will be agglomerated; that means, one cluster will fall on each other and this will lead to agglomeration of nanoparticles and agglomeration means size cannot be controlled, ok.

So, an agglomeration will be more and more if the condenser is basically vaporization rate, evaporation rate is very high that agglomeration will be more. So, that is something which is

difficult to control actually. Although, you can change with check the temperature control the flow up inert gas, but still those are not enough to have you know such a kind of things.

So, what you can do in instead is have a you know two chambered system. One chamber in which you have evaporation sources both are evacuated, ok. You can see the vacuum pumps and then these molecules are inside this small chamber, then you can allow you know inert gas flow into this like helium gas flow into this chamber and then once it flows it comes out, it expands you can have a volume expansion.

So, because of volume expansion what will happen? There will be adiabatic cooling you understand that you are not using any cold finger here, but you are making this gas to be cooled adiabatically because of expansion. If you if you immediately expand a gas volume there will be temperature drop because of adiabatic cooling. This volume is expanding, system is working against it, so, temperature will decrease.

So, as the temperature will decrease, in this gas these clusters will inform as nanoparticles, they will condense and form nanoparticles. So, there will be no kind of agglomerations will be much lower here and this is later on develop method maybe 10 to 15 years after Gleiter Herbert Gleiter developed it and this is a good one in which you can get good quality of nanoparticles easily.

So, this is the first technique which is widely used by the initial days of nanomaterial processing and you can make these and then you can get powder actually, then you can sink to this powder to get bulk.

Inert Gas Condensation
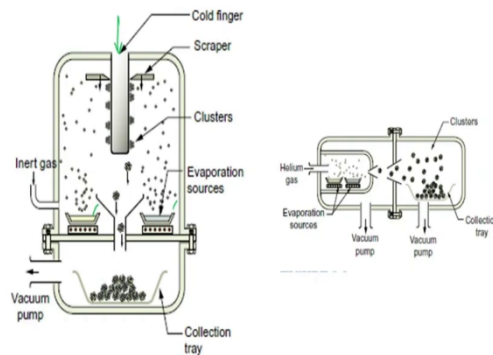
M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009, Chap 8

One can use many other things like sonochemical or sol gel synthesis, ok. So, I will not discuss those things today, but in the next couple of lectures we will discuss about all this processing roots in detail manner. This is available in the chapter you know chapter 8 chapter 8 of this book. You can read it thoroughly, it is available very nicely.

Thank you.