Nanomaterials and their Properties
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Lecture - 12
Surfaces and Interfaces-II (Contd.)

We are going to start the lecture number 12 and as you know the first few lectures on thermodynamics we have already spent quite a bit of time like lecture number 9, 10 and 11, but we are going to continue some more important aspects because that is very vital for the discussions on properties of nonmaterial's later part.

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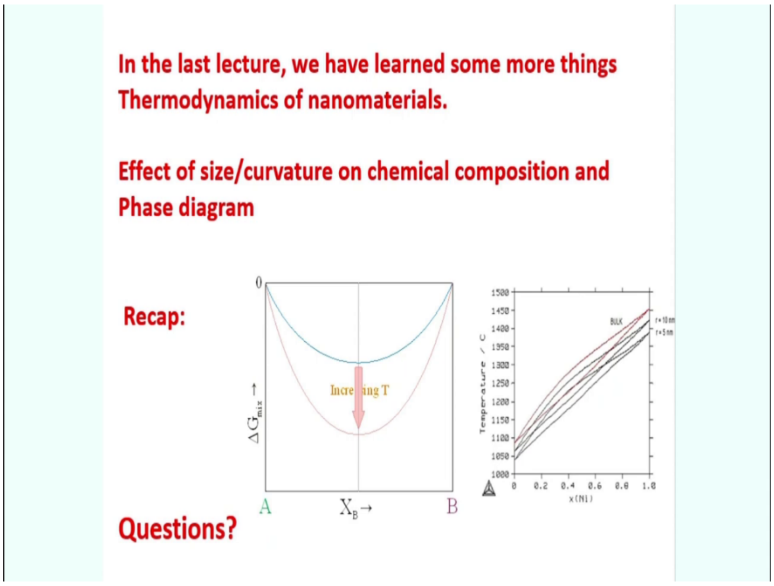

In the last lecture, we have learned some more things
Thermodynamics of nanomaterials.

Effect of size/curvature on chemical composition and
Phase diagram

Recap:

Questions?

And,well in the last lecture what you have learned?You learned various aspects of thermodynamics of nanomaterial, right?Most importantly because a nano is areduced scale system like size of the particles are normally less than 100nanometers or so.

So, we have to always talk about effect of size.This will come repeatedly to you and you should not bother too much because that is what is the thing which makesnano materials more important, but as you know as you decrease the size you have a effect of curvature, andthe curvature affects many things.Curvature affects melting temperature, curvature affects vacancy concentration, we have seen curvature also affects the chemical compositions.

If you have a alloy if an if you have an alloy or a mixture of two elements or more than twoelements the distribution of the elements in the nanomaterial is severely affected by the curvature local curvature.And, depending on the convex or concave curvature this can even have serious consequences.

Well, then in the end of the lecture I discussed something about the phase diagrams – how does the phase diagrams are also affected by the size.Phase diagrams are very classic things in material science right because they depicts the relationship between temperature and the composition about the presence of different phases or phase mixtures at equilibrium.

And, that is why actually we need to know about thermodynamics more.You knowwe started discussing about the entropy of mixing enthalpy of mixing and free energy of mixing in the last lecture and then I talked about little bit about the quasi-chemical theory which is a very popular one that is widely used in the literature.

And, then I derived various expressions to show you how it is important to know these expressions again and again because thermodynamicsis very vital for any kind of phenomena, any kind of phenomenon or whatever you see in the context of material science that is very vital.And, that is what you need to know about it and that is what we will do is a little bit of recap of that.

Then, we will go into the detailed discussion of the phase diagrams, the effect of size on the phase diagrams, how it can be brought about using different thermodynamic analysis.But, I would like to tell you very important thing here, most of these analyses are mathematical.Obviously, they are more of mathematics and physics together, but mostly mathematical.

So, therefore, you need to practice it.This derivations, mathematical analogies and the kind of boundary conditions, constraints and most importantly the aspects of the thermodynamical concepts of free energy, chemical potential you need to refresh and you need to know about it.

Obviously, I cannot do justice to those kind of aspects in this course because this course is not meant for purely on thermodynamics and I do believe most of you have had opportunities in the past to learn about thermodynamics,metallurgical thermodynamics especially or maybe thermodynamics from chemical point of view like chemical engineering or chemistry point of view and you can refresh up little bit those aspects.

And, in the course of these lectures I will talk about a little bit and I will also put various repositories in the course websitelater on sothat you can understand them very well, but what I mean to say is that you need to spend some time on these derivations.

And, if you face any problems on these aspects please do raise questions and thesequestions will be answered when you talk face to face over in online platforms or to discuss about some of these things again.

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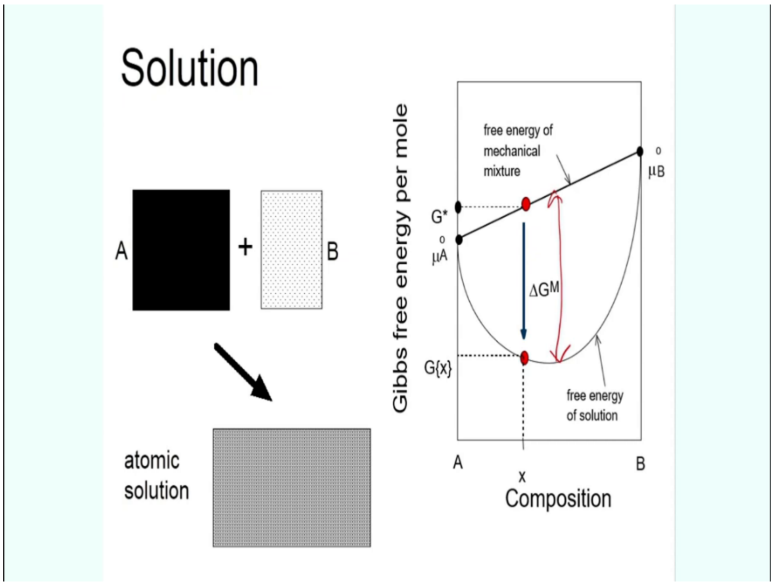

Solution

Well,so, as you know we have started with solute solutions, ok.Solute solutions are actually like a liquid solution in solid state and they are atomistically mixed; that means, they are mixed with the level of atoms.They are not like a physical mixture like a sand and salt, and anyway you whenever you do this kind of atomistic solute solutions.

Atomistics you have to say atomic actually,not atomistic,sorry.Atomic solute solutions what will happen the free energy will be severely affected by the entropy of mixing and free energy you will undergo a drastic jump you can see here drastic jump.That is happens because of the entropy of mixing increasing because of due to the mixture happening at the atomic level and this we have discussed a lot in our previous few lectures.

This is very basicallythe basis for formation of solute solutions.Why?Solute solutions are more stable than the physical mixtures that is the thing which is basically something to do with entropy of mixing.Configurational entropy of mixing is drastically increased because of these configurations entropy normal compression is possible during this formation of solute solutions.

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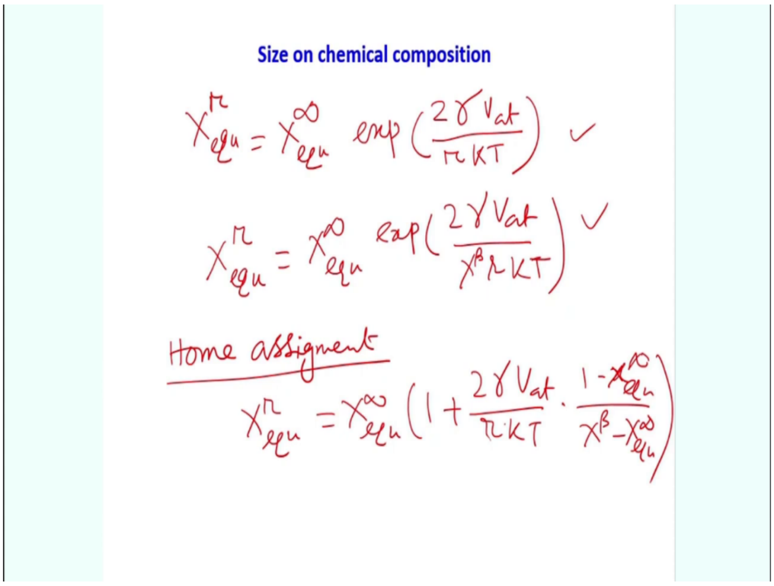

Size on chemical composition

$$X^{r}_{equ} = X^{\infty}_{equ} \exp\left(\frac{2\gamma V_{at}}{rKT}\right) \checkmark$$

$$X^{r}_{equ} = X^{\infty}_{equ} \exp\left(\frac{2\gamma V_{at}}{X^{\beta} rKT}\right) \checkmark$$

Home assignment

$$X^{r}_{equ} = X^{\infty}_{equ}\left(1 + \frac{2\gamma V_{at}}{rKT} \cdot \frac{1-X^{\infty}_{equ}}{X^{\beta}-X^{\infty}_{equ}}\right)$$

$$X^{r}_{equ} = X^{\infty}_{equ} exp\left(\frac{2\gamma V_{at}}{rkT}\right)$$

$$X^{r}_{equ} = X^{\infty}_{equ} exp\left(\frac{2\gamma V_{at}}{X^{\beta} rkT}\right)$$

Home assignment

$$X^{r}_{equ} = X^{\infty}_{equ} exp\left(1 + \frac{2\gamma V_{at}}{rkT} . \frac{1-X^{\infty}_{equ}}{X^{\beta}-X^{\infty}_{equ}}\right)$$

And, then we talked about the effect of size in compositions. Effect of size it come it comes actually in terms of curvature actually. So, we have derived various expressions; as you know, the first one is that we have derived is this is $X_{\text{equilibrium}}$ composition for the particle size of r can be given is equal to $X_{\text{equilibrium}}$ composition.

Remember, we are writing equilibrium because we are talking about phase diagram things we are talking about thermodynamical equilibrium, that is equal to $X_{\text{equilibrium}}$ of infinite size particles; that means, a flat surface basically without any curvature in front side is just like a bulk material also you can think about it. But, in infinite means, it is definitely very large as compared to the nanoparticles; r denotes the radius of the spherical particle,

And, that is we have seen is that is equal to exponential, then there is a factor which comes into few the gamma is the interfacial energy free atomic volume ok V_m, ok. I think that is for the any phase we are talking about it alpha, beta, whatever divided by divided by r multiplied by KT ok that is the first approximations when you do.

Now, basically it is really true for very very dilute solutions, ok and then I also ask you to you know this basically comes from an equations asymptotic solutions of a equations, ok, different conditions you apply on the equations that is the equation you derived.And, you can also have another kind of solution exist where sorry, it should be X, not kappa $X_{\text{equilibrium}}$ particle is r is equal to what?This is what we have seen in the last lecture. I think you can actually see it that is equal $X^{r}_{equ} = X^{\infty}_{equ} exp(\frac{2\gamma V_{at}}{rkT})$

This X is basically coming from one of the compositions of one of the phases like let us suppose this X is the composition of beta phase if any alpha beta mixture is present, then

$$X^{r}_{equ} = X^{\infty}_{equ} exp(\frac{2\gamma V_{at}}{X^{\beta} rkT})$$

And, there is another one which is also available, and that is you are going to derive, ok. It was part of your home assignment.

$$X^{r}_{equ} = X^{\infty}_{equ} exp(1 + \frac{2\gamma V_{at}}{rkT} . \frac{1-X^{\infty}_{equ}}{X^{\beta}-X^{\infty}_{equ}})$$

If you do the maths properly, what you will see? You will see that is the most complex one.

So, these two are good for dilute solutions. So, on the both sense of the phase diagram very easily applied.Third one is basically for the concentrations which is much higher than the dilute, ok. So, by the way by using thermodynamic analysis you can derive all these expressions very easily.That is what you should focus, you should know.This will be used for different kinds of assignment problems which I am going to solve later on, ok. That is something I discussed.

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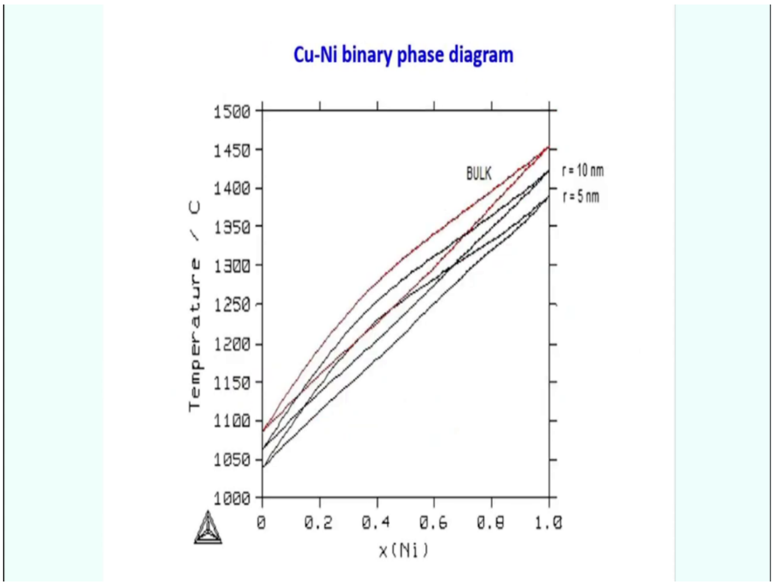

Cu-Ni binary phase diagram

Then I would go in discussing about the binary phase diagrams how they are affected by size and that is what we are going to do that.This is for copper – nickel which is isomorphous system; that means, it is basically a single phase forming from the liquidkind of systems in which there is no other than no other reaction other than liquid going to the solute solution phase, ok.

This is severely affected by the size you could see bulk to the phase diagrams which are corresponding to the radius of 5 nanometerand 10 nanometer is different in on the size.This can be derived using computer conclusions which you can do it actually.It is not difficult to get it.

We also do it as a part of our research activities, but this can be done.This is not a at all a complex composite calculations nowadays.These are routinelydone on computers that you should be able to do it.

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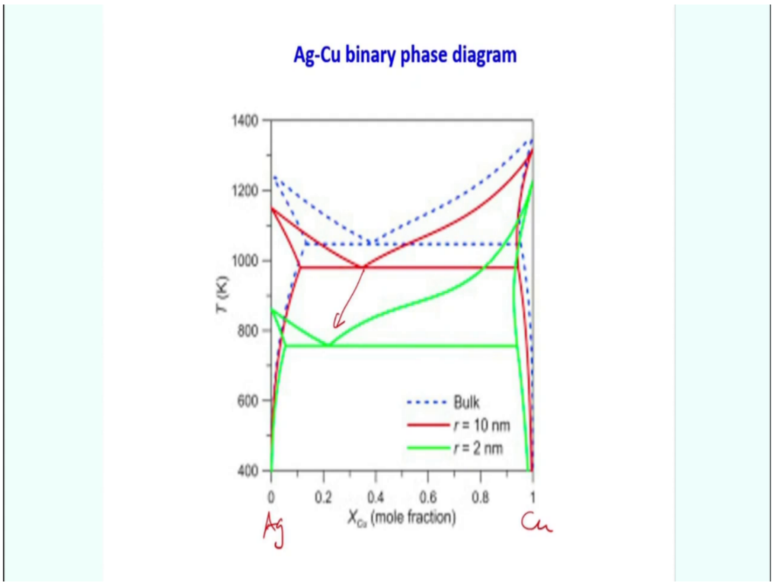

Ag-Cu binary phase diagram

This is a little bit complex.It is on a silver – copper eutectic systems here you see the eutectic temperature has gone down as a temperature as well as composition wise also the left side.That means eutectic composition has become rich in big A rich in silver this is silver end and this is copper end rich in A, that is very nice.That is mainly because of this composition changes can be explained using those equations which are just now shown in the last couple of slides ago, ok.

So,so that means, what?The temperature goes down composition changes.This isthis effects can be also explained using those equations.But, when you have a large pool of compositions you can not do this.You have to use the computational tools to do that.

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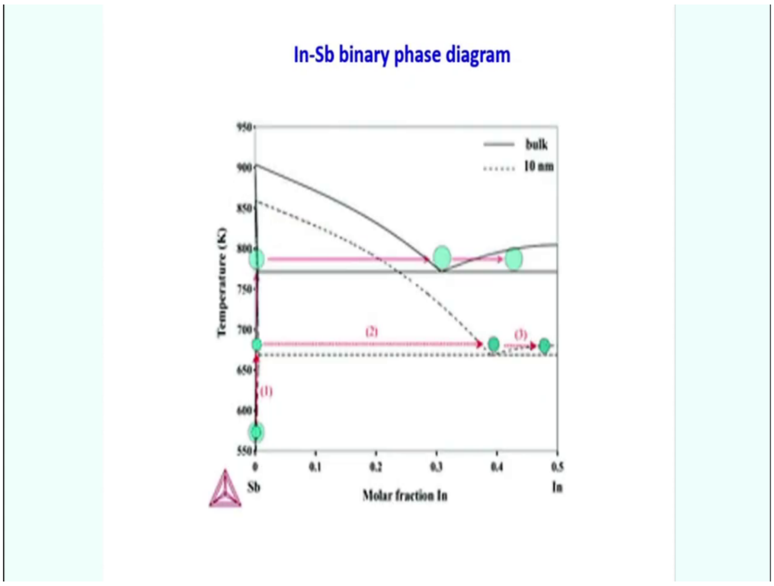
In-Sb binary phase diagram

Well, this is on indium – antimony phase diagram where also there is eutectic and eutectic temperature goes not only down.Compositions of you rright side it become indium rich.This, these are the things you should look at it how this aspects are can be easily theoretically explained. You do not need to do any experiments to determine these phase diagrams anymore.You can do this using computational tools very easily.

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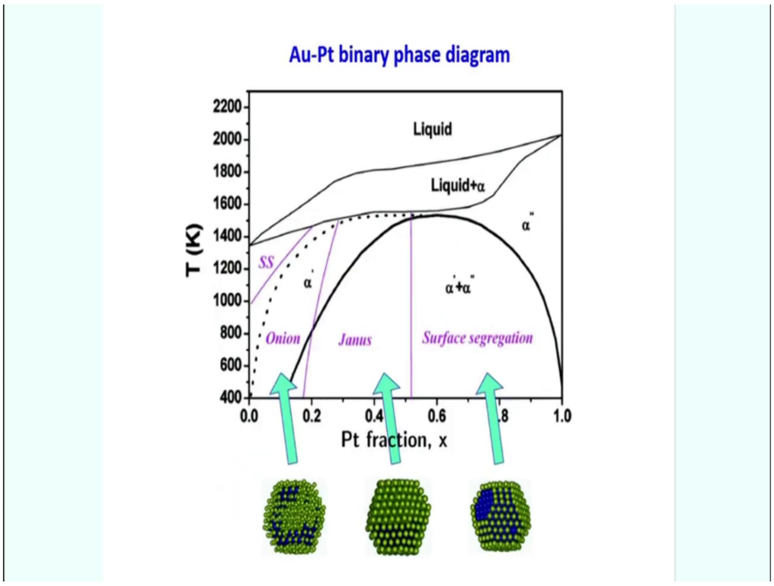
Au-Pt binary phase diagram

Well, this isa gold – platinum phase diagram which is more complex there is a phase separation. So, those of you who do not know about phase separationsforget about it.Do noteven bother about it. I just put it to show you that this is this kind of phase diagrams also do exist.

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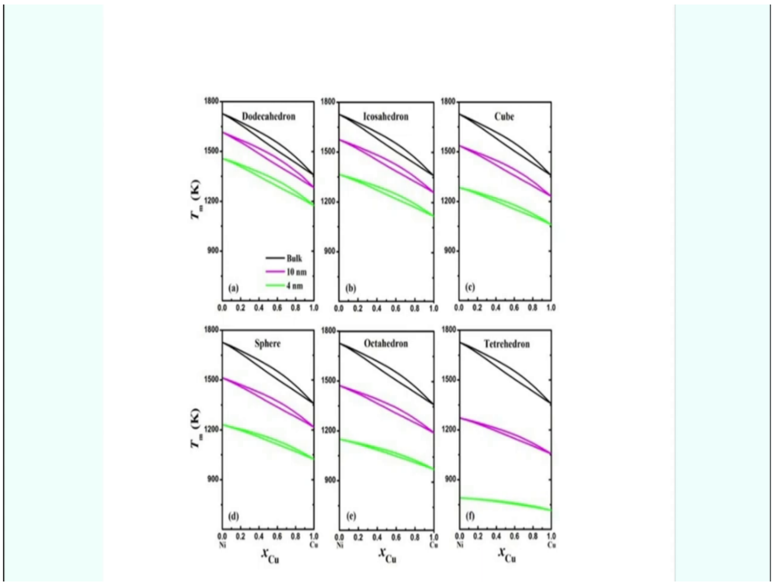

Well,so,and you knowthese are all very important aspects of this is also the phase diagrams is also they are already depending on shape whether you are using dodecahedron, cube, sphere,octahedron, tetrahedron size particles they are severely affected by this vector shape at allshape by this shape ok.

And,the and you can see the dispositions of the curves for copper nickel phase diagram actually here again isstrongly dependent on the shape and that is understandable.The shape factor comes in the fundamental equations which you will discuss now.

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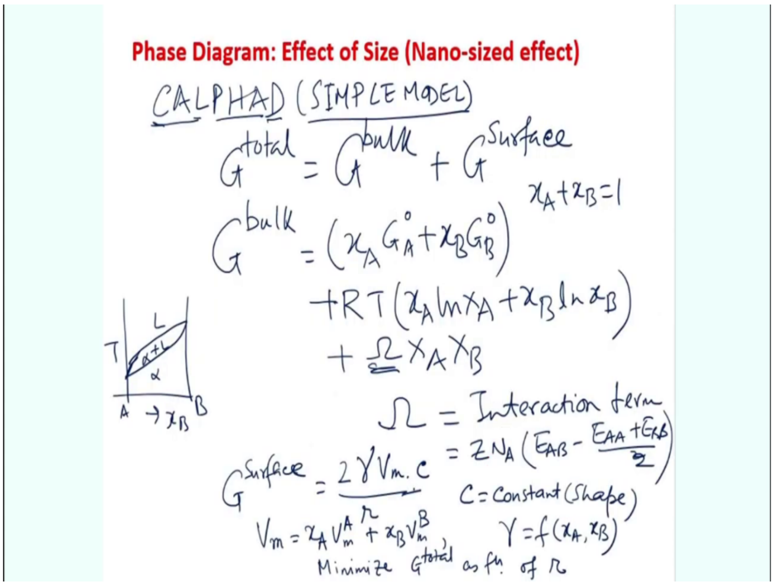

Phase Diagram: Effect of Size (Nano-sized effect)

CALPHAD (SIMPLE MODEL)

$G^{total} = G^{bulk} + G^{surface}$

$x_A + x_B = 1$

$G^{bulk} = (x_A G_A^0 + x_B G_B^0) + RT(x_A \ln x_A + x_B \ln x_B) + \Omega x_A x_B$

Ω = Interaction term $= ZN_A\left(E_{AB} - \frac{E_{AA}+E_{AB}}{2}\right)$

$G^{surface} = \frac{2\gamma V_m . C}{r}$

C = Constant (Shape)

$V_m = x_A V_m^A + x_B V_m^B$, $\gamma = f(x_A, x_B)$

Minimize G^{total} as fn. of r

$$G^{total} = G^{bulk} + G^{surface}$$

$$G^{bulk} = x_A G_A^0 + x_B G_B^0 + \mathrm{RT}(x_A \ln x_A + x_B \ln x_B) + \Omega x_A x_B)$$

$$x_A + x_B = 1$$

Ω (intraction parameter)= $ZN_A(E_{AB} - \frac{E_{AA}+E_{BB}}{2})$

$$G^{surface} = \frac{2\gamma V_m c}{r}$$

C=constant

$$V_m = x_A V_m^A + x_B V_m^B \gamma = f(x_A, x_B)$$

Minimizes G^{total} as function of r.

Ok now, so, what we are going to do? We are going to talk about it interms of thermodynamical mathematical formalisms, let us do that. So, that you understand it very well, ok.As you know the most important approach which is used to calculate phase diagram is known as a CALPHAD,ok.

And, this CALPHAD is very popular because it allows you to do very calculations easily.CALPHAD terms of ok calculation of phase diagram. So, calculation C or CAL is of C ok calculations, PHA is phase and D is the diagram. So, these threewords together is put a CALPHAD ok and that is the simplest model of CALPHAD tells that basically it depends on the free energy.

So, as you know total free energy of the system can be written simply for two aspects – one is bulk, other one is the surface.When you talk about a free particle this is surface when you talk about a structure like a tung crystalline material like copper, silver, gold or even alloys of copper – silver or copper – nickel this $G_{surface}$ become $G_{interface}$.That is actually similar, but not same, ok.We will talk about it little later.

And, you know so that means, G_{total} is the total Gibbs free energy the system now consisting of two parts – one is the bulk, other is the surface $G^{total} = G^{bulk} + G^{surface}$

For big material big cell materials this $G_{surface}$ goes to 0; you do not need to bother about it; only for the nano size materials $G_{surface}$ is substantially large, and this must be considered in the calculations, ok.This is something which is important ok.

Now, G_{bulk} is very easy to write this consisting of a binary system consisting of A and B like two metals this will be $x_A G_A^0$ that is the part of this free energy pure A G_A^0 superscript 0 means pure A; when you have pure A, that is the free energy. Now, if you multiply the X_A the mole fraction of A in the material then this become the contribution for the pure A; that is basically I have talked about here this is nothing, but physical mixture free energy.

And, then $x_B G_B^0$ corresponds to the again for the pure B and because it is B is present about X_B moles fractions. So, we have adding multiplying with X_B. The G_A^0 is for mole fraction of A, the X_A is equal to 1, but in alloy you have a X_A moles fraction of a X_B mole fraction of B; X_B and X_A is equal to 1 ok in a alloy you know $x_A + x_B = 1$

always because this is a mole fraction and that concept you already been talked about it ok. So, this is the physical mixture.

Now, when you have an atomically mixed solute solution, you also have an entropic effect, right. So, the entropic effect comes in terms of $RT(x_A \ln x_A + x_B ln x_B) + \Omega x_A x_B)$. So, ln term is basically log term, right. Now, with this, we have to this is basically physical mixture the top two terms the first two terms on the right side and then you have entropic because of configuration entropy of mixing because of mixing your change in the configuration entropy you have the second term.

And, then, but you know then obviously, when you mix two materials together always mixing will lead to change of volume, change of bond energies. So, you need to add that effect ok. This does not consider that this only considered the physical mixture plus the entropy change. It does not consider you know bond characteristic change volume change because of the addition of two elements the solute solution does not consider; you can see that.

So, this aspect is always added in terms of interaction parameter gamma, ok. Interaction parameter multiplied by X_A into X_B this we have seen actually in the last lecture how this can be derived and this gamm at his term the what is called this one is interaction term this term is written like Ω (interaction parameter)= $ZN_A(E_{AB} - \frac{E_{AA}+E_{BB}}{2})$ ZN_A, N_A corresponding to Avogadro number Z corresponding to the coordination number like FCC it is 12, BCC is 8 simple cubic, it is 8 ok. So, that is the coordination number N is the Avogadro number because that is per mole basis.

And, then you have seen this term $(E_{AB} - \frac{E_{AA}+E_{BB}}{2})$ that is the bond energy term, correct? In addition, we also need to know. So, that is, you know G_{bulk}, right. So, what about $G_{surface}$? $G_{surface}$ we have seen very easily it can be written $G^{surface} = \frac{2\gamma V_m c}{r}$, ok.

Here γ is the surface energy, Vm is the molar volume, r is the size of spherical particle is in terms of the radius of the spherical particle, and the C is basically a constant and it depends on size; sorry, it depends on the shape. I am sorry it is not size depends on the shape size is already considered. So, that means, the constant which is basically related to shape. Just now we show some phase diagram based on the shapes, right. So, this is the aspect must be built in.

So, therefore, you have you know G_{bulk} you know the $G_{surface}$, very easily, right.There is no nothing you need to do.For a binary system AB this parameter is known.What is that parameter? This parameter is known because you know the bond energy differences, right.You know the atthe coordination number, you know the crystal structure and the coordination number and you also know the Avogadro number.

So, you know the this parameter very easily G_{A0} is known this is for the pure A and G_{B0} is also known; gamma is something which may not be known, but you can calculate theoretically or you can actually measure experimentally. Molar volume easily if you know the density you know the molar mass like this molar mass divided by density is a molar volume,C is a constant which will depend on the shape that can be tabulated.

So, now you can actually use these equations and find the total G as a function of r as a function of size, right. Well, you also need few more things. You also need this one the molar volume of the alloy when you are mixing two elements together; this will also depend on V_m $=x_A V_m^A + x_B V_m^B \gamma = f(x_A, x_B)$,where V_m^A is the molar volume of pure A V_m^B is molar volume of pure B and X_A and X_B are the mole fractions, right.

Well, and sometimes people do consider, but that is we are going to deal it much later, not now, ok.You know the gamma, the surface energy is also dependent on X_A and X_B. So, you can consider, but for the simple things which is which you were talking about is a simple model, right.The CALPHAD is a simple model and the simple model does not need complex things; this is the complex thing actually ok, fine.

So, therefore, this whole thing I can then minimize G^{total}. So, the finally, what is done you have to minimize G^{total} as function of r. So, once you get it then you get the phase diagram the minimization. It gives you at a particular temperature values of X_A and X_B.

That is what a phase diagram needs phase diagram is basically nothing, but the binary isomorphous phase diagram is a temperature versus composition, right.You know the copper–nickel phase diagram, right.It looks like this liquid alpha for a liquid alpha, right.

So, that is what you need then you can calculate this phase diagram very easily, well.This is the simplest possiblemodel we can one can discuss. So, I spent about 15 minutes, so, you must be bored.So, before we go into the complexities involved we will go into the complexity involves,I would like to tell you few important things, ok.See this mathematical derivations are very simple.

They are not complex derivations andwhat you need is basically a little bit of practice and going back to your basics of thermodynamics and that is something which normally people forget that is I have seen semester to semester students do forget on different things.They do not remember, it is as if their memory is just like a hard drive, you format it.It gets over ok.So, something happens to you.

So, therefore, if you do like this you need to go back and understand it nicely ok againand that is something good it will help you to make yourself ready for various kinds of interviews which you will be going on to get jobs or something or maybe some things, ok.

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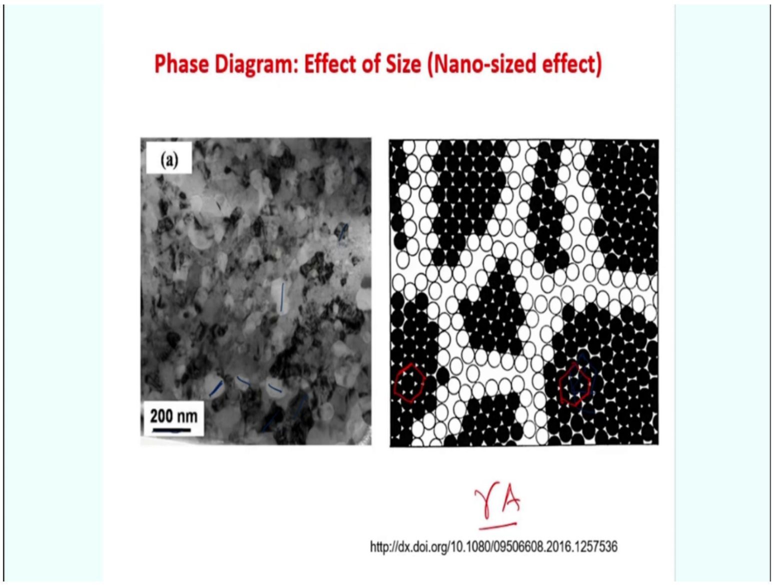

Phase Diagram: Effect of Size (Nano-sized effect)

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Well, before we go into the complex things, let me just tell you something very interesting, ok. You know nanomaterials can may be what is called the stand-alone like spherical particle sand is sitting on the surface, right. You can also have nanomaterials which are basically bulk-like tung of copper. You take a copper, deform it heavily, you can get nanocrystalline copper.

So, you have small grains of copper; you can see here many many grains of copper ok and this is 200 nanometer bar that they will be all less than 100nanometer, ok. You can see the small grains of copper everywhere, the black, white ok. So, atomistically what we can we think about it.

Atomisticallyyou can think about it the grains are separated by boundaries between them. That is why you see separate grains, and all of you have seen microstructure or optical microscopes. You have seen the grains and grain boundaries, right.

So, between two grains there is a boundary. So, what is the structure of the materials at the boundaries? Ok, what do you think of structural materials at the boundaries? Well, people have, you know, thought about it many, many times and people scientists have come across that you know grain boundary is basically consisting of atomic configuration which is haphazard which are not periodic which are random basically.

Obviously, it cannot be purely random the way you think about it. Still, there is randomness that exist in the grain boundaries, ok and you know you can see that there is a complete disorder arrangement of the atoms at the boundaries, which are shown by the kind of spheres which are unfilled.

And, in the grains, the filled squares are shown and the black or filled square you can see these squares actually nicely arranged in the grains. You can see in this grain they are arranged very periodically ok.

You can also see that they are arranged you know very nicely within this, ok. So, if this very easily can be shown by drawing a hexagon which is regular ok or everywhere you can see that actually in all the grains actually see I can draw that.

So, that indicates the atoms are arranged in a very periodically nice ordered manner, but on the grain boundaries between the two grains there are boundaries; you can see that these are shown by the unfilled circles, and these are actually not arranged like that.

You cannot draw such kind of nice hexagons by using the atoms (Refer Time: 28:04)you cannot. So, that means, what? Going to this disorder atomic arrangements grain boundary exist in a relatively high energetic state. That is what it is because they are not yet sitting at the minimum energy positions; they are at a high energy position.

So, therefore, energetically they are at a high energetically states, and these add up to the total energy. Obviously, right if they are random, they are not at the ground state then there is add up to the energy state; think about yourself.

If you are running and then all of a sudden you stop your run at the ground, what happens? You are not at the lowest energy level. So, it takes time for you to get cool down, temperature grows, you sweat hard, you may need some fan to cool it down and finally, then use energy states energy goes down.

So, grain boundaries are like that. They are like a running at the high-speed atoms are not the time to find out good neighbors, good friends around it so that they can relax; they can feel relaxed. So, the atoms are actually completely unrelaxed; that is why they have high energetic states ok. So, therefore, nanomaterials nanocrystalline grains materials actually have a relatively strong tendency to reduce the like total grain boundary areas because that is what is the energy is coming from consuming that.

So, in order to do that, so, they will always try to increase the grain size. So, once that the they increase the grain size, they will not remain in the nanocrystalline region. So, that is why it is very difficult to stabilize the grain size of various metals like copper, nickel; nickel is very even more serious. Nickel grains can go at room temperature.

Although melting temperature nickel is 1400 plus 1453 degree Celsius, but nickel another this nickel if you keep it room temperature the grains will grow, right. The reason is this.The grain boundaries have high energy that propels this process of growing of the grains and by that they can reduce the grain boundary areas and by using the grain boundaries, the total energy of the grain boundaries can be reduced, ok.

So, this is something which is very common and so, therefore, here there is no surface of grains, but there are interfaces of grains in between the two grains, there is say grain boundary which is nothing, but an interface. So, we need to consider if you want to model such a kind of things which is readily available and which are actually really the systems which are normally we deal with in real applications, we need to talk about thermodynamic stability of this kind of things.

Now, how do you do that?Ok so, that is something which you will discuss. So, you understand, right? You understand the atomic structures of grains and the grain boundaries, ok.This is a model which is proposed by professor Gleiterfrom Germany long back, and it is accepted model that, and you can see the grain boundary area is quite large even in this 2-dimensional picture also, right.

So, therefore, total energy is basically gamma multiplied by A,right surface energy or interfacial energy.So, A is also increasing, then this total energy is also increasing. So, hence the as the grain boundaryarea is more total energy of the material is also high, well. So, therefore, we need to tilt the problem little bit differently, but we will do it. So, I will go back.So, here we talked we did not talk about everything like that, we talked about very simple thing.The standard particle of this energy, that is all.

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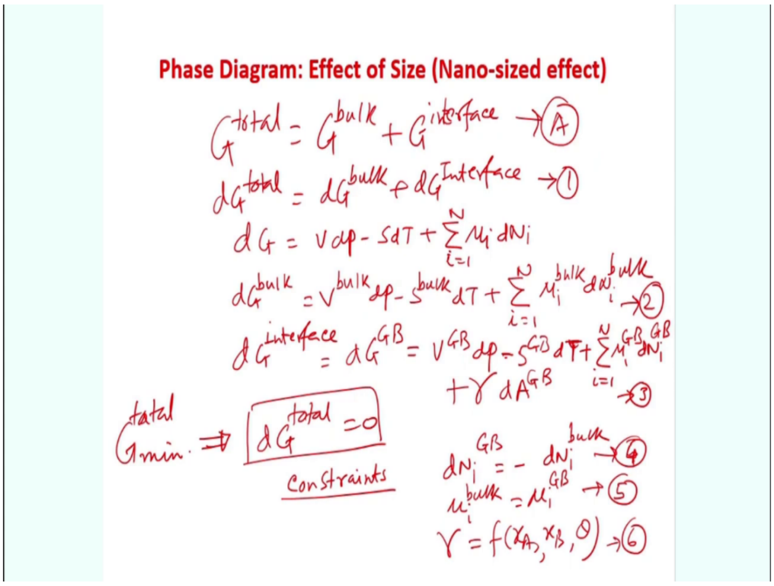

Phase Diagram: Effect of Size (Nano-sized effect)

$$G^{total} = G^{bulk} + G^{interface} \rightarrow (A)$$

$$dG^{total} = dG^{bulk} + dG^{Interface} \rightarrow (1)$$

$$dG = Vdp - SdT + \sum_{i=1}^{N} \mu_i dN_i$$

$$dG^{bulk} = V^{bulk}dp - S^{bulk}dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} \rightarrow (2)$$

$$dG^{interface} = dG^{GB} = V^{GB}dp - S^{GB}dT + \sum_{i=1}^{N} \mu_i^{GB} dN_i^{GB} + \gamma dA^{GB} \rightarrow (3)$$

$$G^{total}_{min.} \Rightarrow \boxed{dG^{total} = 0}$$

Constraints

$$dN_i^{GB} = - dN_i^{bulk} \rightarrow (4)$$

$$\mu_i^{bulk} = \mu_i^{GB} \rightarrow (5)$$

$$\gamma = f(x_A, x_B, \theta) \rightarrow (6)$$

$$G^{total} = G^{bulk} + G^{surface} \ldots\ldots\ldots\ldots\ldots\ldots(A)$$

$$dG^{total} = dG^{bulk} + dG^{interface} \ldots\ldots\ldots..(1)$$

$$dG = VdP - SdT + \sum_{i=1}^{N} \mu_i dN_i$$

$$dG^{bulk} = V^{bulk}dP - S^{bulk}dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} \ldots\ldots..(2)$$

$$dG^{interface} = dG^{GB} = V^{GB}dP - S^{GB}dT + \sum_{i=1}^{N} \mu_i^{GB} dN_i^{GB} + \gamma dA^{GB} \ldots\ldots(3)$$

$$G^{total} = dG^{total} = 0$$

Constraints

$$dN_i^{GB} = - dN_i^{bulk} \ldots\ldots\ldots\ldots.(4)$$

$$\mu_i^{bulk} = \mu_i^{GB} \ldots\ldots\ldots\ldots\ldots.(5)$$

$$\gamma = f(x_A, x_B, \theta)\text{…….(6)}$$

In this case we are going to little bit change our way of derivations but, we will start with the same thing. Again $G^{total} = G^{bulk} + G^{surface}$. It is no longer surface because we are talking about grain boundaries, boundaries between the grains this is an interface between the two grains. So, then obviously, if you take total derivative $dG^{total} = dG^{bulk} + dG^{interface}$ right that is easily can be done.

And, you know that in dG for an alloy is you have done that actually $dG = VdP - SdT + \sum_{i=1}^{N} \mu_i dN_i$ or i can be any number ok 1,2, 3 we normally deal with two-component systems. So, i will be 2 A and B, ok. So, i can go from 1 to N, right.This is something we have seen.

We have derived for pure materials this $\mu_i dN_i$ goes to 0 because dN_i is 0 pure water there is no dN_i because this is N_i is equal to 1. So, dN_i is 0. So, that case is basically VdP- SdT. Please go back to my earlier lectures; we have discussed this about a lot.

Now,I can write down **then** dG^{bulk} ok what you can write down dG^{bulk} very easily. How can you do that? ok that is $dG^{bulk} = V^{bulk}dP - S^{bulk}dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk}$, right. We have only done that in the last or maybe last to the last lecture, correct. So, this is something which you understand this is for the bulk, right. So, what about the interface? Here interface is grain boundary. So, $dG^{interface}$, $dG^{interface} = dG^{GB} = V^{GB}dP - S^{GB}dT + \sum_{i=1}^{N} \mu_i^{GB} dN_i^{GB} + \gamma dA^{GB}$

That is my equation number 3, right. Well, that is not the correct equation, right.

Why? Because you need to add the grain boundaries energy. So, that is means you have to write gamma into dA^{GB}; gamma is the grain boundary energy. So, otherwise, bulk and interface will have almost similar values, although it will not be similar because the $\mu_i^{GB} dN_i^{GB}$

and μ are are their μ will be definitely different V or dS entropy or volume may not be so much difference it will be different.

But, that is ok. Let us forget about it if it is different or not, entropy will be different because there is more randomness in the grain boundaries.The volume will go different because they occupy much different volumes than the grain interiors right, but γdA^{GB} are definitely going to be there in the grain boundaries; it will not be there in case of bulk, right. So, you understand that.

So, once you do such a kind of calculations, your additional constraint put in, ok, what are the additional constraint you put it in? So, you know that to minimize this free energy, if you want to minimize the top equation, ok, this I write down if you want to minimize that what you need to do? Minimization required G^{total} to be equal to 0, correct, that is the minimization of if you want to minimize that is the mathematical formulism which is always used for minimization, fine.

So, what are the constraint here like or the condition, but we if these are not condition actually these are more like constraints,ok. I should be very careful about the spelling. Students are now they may be very good, or some of you may be good in English. So, the first condition is that obviously, the first one is what is easy to write dN_i^{GB} ok, yes. So, I forgot to write. The mass change must be the same. So, this is complete closed system of grains and grain boundaries.

So, there is a mass transfer from grain boundary to grain,the mass going from grain boundary to grain it is equal to minus of mass coming from the grain to grain boundaries.There is the total mass to be constant; that means, dN_i^{GB} plus dN_i^{bulk} equal should be 0 or $dN_i^{GB} = -\ dN_i^{bulk}$. If you add some mass from grain boundary to the grain, it is nothing, but loss from grain boundary by grain to the grains, ok grain to the grain, ok that is the one thing.

Second important, so, that is my point number 4, which is the constant number 1 ok constant 1. Second constant is the chemical potential. So, the chemical potential at the boundary between the grain and the grain boundary should be the same that is the Gibbs law of any componentwhether it is AB does not matter the chemical potential must be the same across the boundary,($\mu_i^{bulk} = \mu_i^{GB}$), otherwise, the grains and grain boundaries will be not at equilibrium that is the equilibrium conditions.

But you know the these are the two constant which to be used to solve this equation G^{total} to be equal to 0. But, we have to understand one thing here that the gamma here can never be considered to be constant ok which you have done γdA^{GB} right that is the term we have added for the grain boundaries, but that is gamma will not be constant at all because gamma will depend on not only composition segregation but also orientation.

Remember that we have already discussed the gamma it depends on orientation cos theta plus sin mod theta; remember that equation ok go back. So, this is my equation number 6. So, whenever you put this aspect into gamma, this equations will become non-linear.

It will be not easy to solve analytically; you have to go back to computational tools to solve this equations. Well, that is something which is not at all easy in while doing the calculations ok. So, how does the gamma will depend on the orientation of things $\gamma = f(x_A, x_B, \theta)$ let us see that. I think I have some pictures for you ok.

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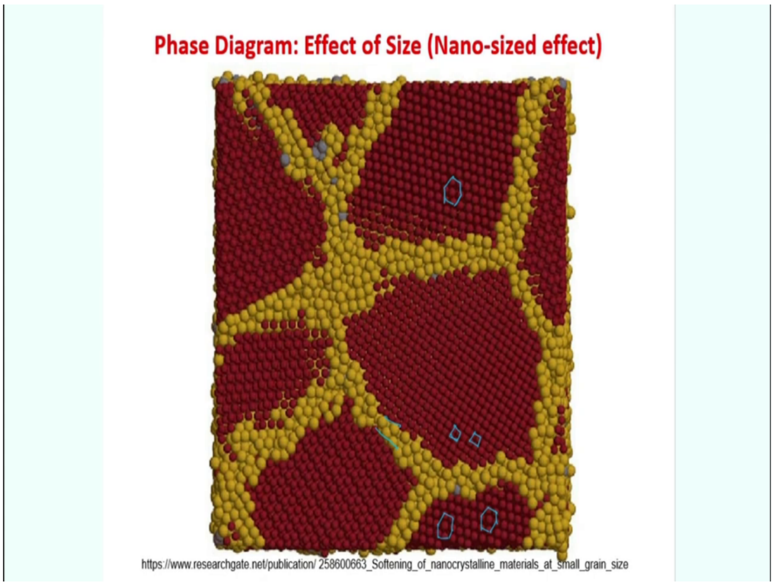

Phase Diagram: Effect of Size (Nano-sized effect)

https://www.researchgate.net/publication/ 258600663_Softening_of_nanocrystalline_materials_at_small_grain_size

Yes, wait for that let me just tell you some nice pictures; these are all taken from different journals. So, this is a structure of grain centred boundaries and a 3,correct.You can see that grains are nicely arranged a crystal lattice ok, atoms are arrangedin nice manner, ok.You can see here there is a cube, there is a square you can draw, there is a hexagon you can draw, this is a good picture actually, ok.

I can draw a better hexagon here 12 3,12 3, right, and you can draw a nicely square here. You can you can do this hexagon there also here. But, on the grain boundaries, atoms are haphazard; this is a 3D picture, actually. How does it look like? They can form a very interesting paper which is given here. So, this is structure. So, that means, this interface has a lot of energy, ok, and equilibrium depends on the chemical potential equality of any component, correct.

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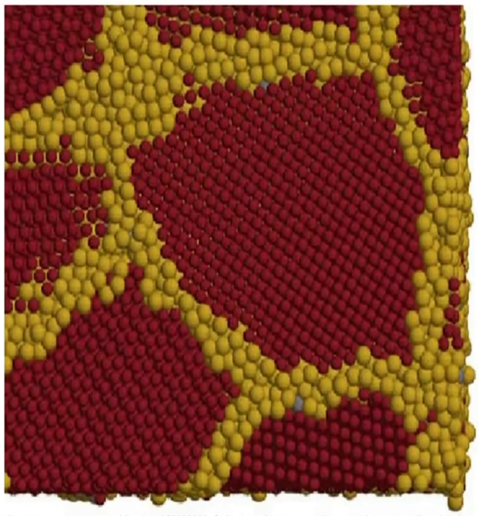

https://www.researchgate.net/publication/ 258600663_Softening_of_nanocrystalline_materials_at_small_grain_size

And, it is shown in a much nicer view here.You can see very clearly how the grain and grain boundary structures looks like. A nano crystalline material, this structure is very important. This structure is having a large surface area large grain boundary area. So, that is how this energy is pretty high.

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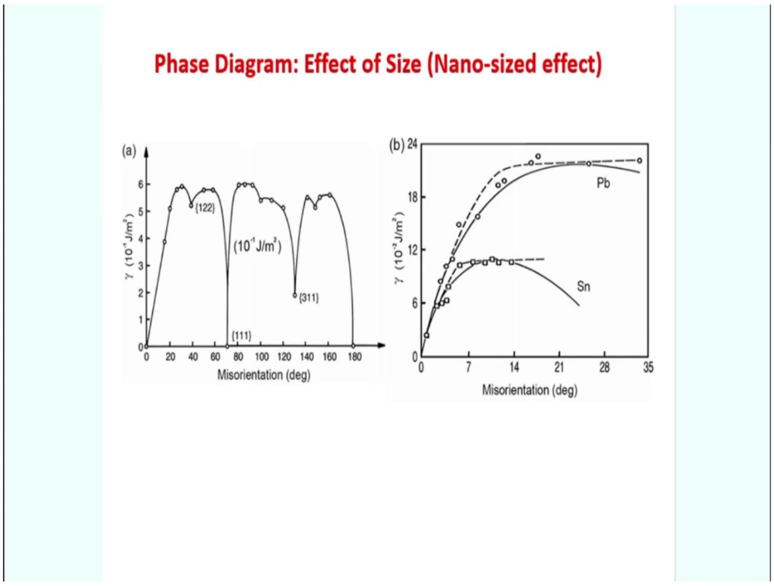

Phase Diagram: Effect of Size (Nano-sized effect)

Well, so,how does this grain boundaries and the grain energy will depend on orientations that is what is this is see gamma as a function of misorientation angle andon the left side and you can see that there are dips ok like the orientation of {112}, {122} and {311}have dips; most important dip is at {111} that we have discussed.{111} is the closest factor line in an FCC structure that is why this comes at 64 points some angles some degrees 58 or something angle.

So, the 60.58 angle theta, ok misorientation, and this is the lowest energy. Everything else has different energy. So, therefore, depending on this crystallographic orientation, that is what I showed you in this picture ok, depending on the crystallographic orientation of the grains, this grain boundary energy will change, right.

Once you have seen you have seen here somewhere your square and hexagon. So, that orientations are different and the boundary if the things will be different from both side. So, this will change the energetics of the system, right.

So, similarly, you can also have chemistry (Refer Time: 43:18) like a lead and tin gamma will also depend on how in lead and tin alloy how lead and tin have present in the material amount. Suppose, in grain, if you have a lead and tin concentration something like whatsay50

– 50, you will have one kind of gamma value; then you have a 60:40 or 70:30, ok that is something that will change the gamma quite drastically.

So, in a nutshell what is important here? Now, you go back my derivation here. So, I can no longer ignore gamma as a function of X_A, X_B and theta.This is not possible anymore. You mustyou know you must not forget that gamma is a very serious function of these and that dependence is so much that you can no longer ignore that correct, well that is something which you have probably understood.

But, how to deal with it? How you can deal such a kind of aspects. So, in the next couple of or next 4 – 5 minutes, I am going to tell you the scheme of dealing with it, but little discussion I will do in the next lecture that is the lecture number 13 ok, well. So, how it is done? First let us talk about you know let us first considered G_{bulk}, ok.

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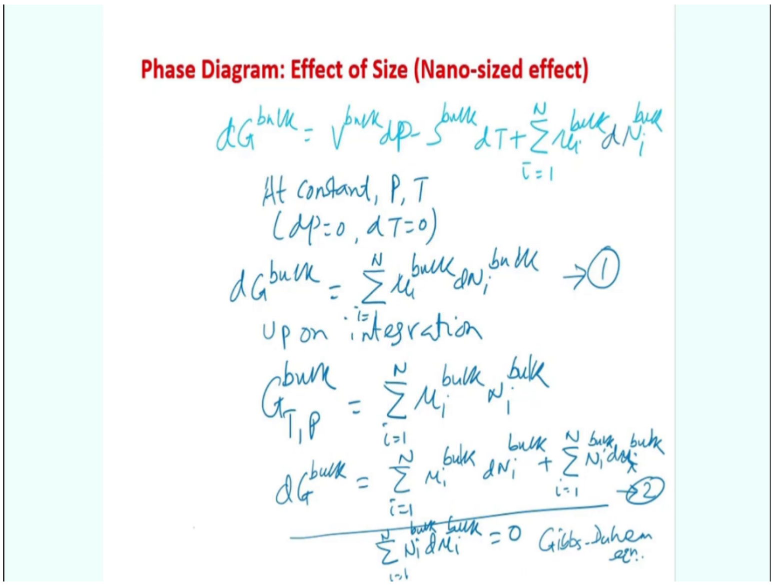

Phase Diagram: Effect of Size (Nano-sized effect)

$$dG^{bulk} = V^{bulk}dP - S^{bulk}dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk}$$

At constant, P, T

$(dP = 0, dT = 0)$

$$dG^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} \rightarrow ①$$

Up on integration

$$G_{T,P}^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} N_i^{bulk}$$

$$dG^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} + \sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk} \rightarrow ②$$

$$\sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk} = 0$$ Gibbs-Duhem eqn.

$$dG^{bulk} = V^{bulk}dP - S^{bulk}dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk}$$

At constant P and T

$$dP = 0,\ dT = 0$$

$$dG^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Doing intrigation

$$G^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} N_i^{bulk}$$

Upon differentiation

$$dG^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} + \sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk} \ldots\ldots..(2)$$

$$\sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk} = 0 \text{ Gibbs – Duhem equation}$$

This equation remember that $dG^{bulk} = V^{bulk} dP - S^{bulk} dT + \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk}$ Wherein going to 1 to N, correct. So, come on different so many availability of colors, this correct still this color is different ok,anyway it does not matter. So, that is ok. So, at At constant P and T, $dP = 0,\ dT = 0$, and $dG^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk}$, right. Now, if you do integration, this is total differential; if I do an integration, what you will get? $G^{bulk} = \sum_{i=1}^{N} \mu_i^{bulk} N_i^{bulk}$ right, that is correct? That is understandable or not? That is easy to understandable, ok.Very easy to understandable that is not at all difficult thing to do. So, this is what we gotat constant temperature pressure. Now, we can differentiate it, right easily.You can get a differentiation of that. So, if you do that dG$_{bulk}$ become total differential $\sum_{i=1}^{N} \mu_i^{bulk} dN_i^{bulk} + \sum_{i=1}^{N} N_i^{bulk} d\mu_i^{bulk}$, right. I just taken differentiation μ constant n change n constant μ change this is $d\mu i$, correct.

So, you see this equation let us stamp this equation at two, and this equation is 1, compare them. So, what do you understand? Very clearly, you understand that summation $N_i^{bulk} d\mu_i^{bulk}$ =0, this term must go to 0, then only these two can be equal. So, this is known as Gibbs – Duheme equation in the literature for nanocrystalline materials.Obviously, this will or rather boundaries, actually. You have to see we have to have some other terms also there.

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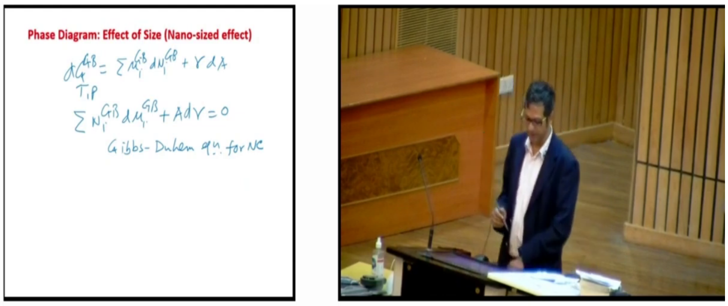

Phase Diagram: Effect of Size (Nano-sized effect)

$$dG^{GB}_{T,P} = \sum \mu_i^{GB} dN_i^{GB} + \gamma dA$$

$$\sum N_i^{GB} d\mu_i^{GB} + A d\gamma = 0$$

Gibbs- Duhem eqn. for NC

So, we have seen dG^{Gb} at constant temperature pressure ok that is the condition you always use right because when you are doing experiment, you are doing at 1atmosphere atmospheric pressure and constant temperature. So, you can always assume this. This is the correct assumption. So, that becomes $\sum_{i=1}^{N} \mu_i^{GB} dN_i^{GB} + \gamma dA$, correct.

So, if you do this maths again integration and all these kinds of things, whatever we did in the last slide, correct, so, what you will get the same Gibbs –Duhemse euation will become that will modify. So, therefore, I write down I can write down $N_i^{GB} d\mu_i^{GB} + \ Ad\gamma$ to be 0 that is the Gibbs – Duheme euation for nanocrystalline material correct, well.

So, I am just giving you starting the whole thing, how we can deal with the gammas orientation dependence and all these grain boundaries how we can do things theoretically more sound. So, this is something which you will discuss further because this requires more discussions. Well, by the way, before I end the lecture, you know, you must be thinking why the professor is doing so much of mathematical derivations.

Well, I am not doing much mathematical derivation; let me tell you, these are very standard derivations. This directly comes from the textbook, and the only thing I am applying is the concept of grain boundaries concept of surface gamma dA term gamma into a term all this aspect adding into it.

We are not adding much to these whole things, correct, but then next lecture, we will be adding quite a lot of new concepts, ok, how it is this kind of this concept this gamma as a function of theta and X_A X_B can be plugged into it in the model.But, you know the important aspect is you need to do these derivations on your own. Do not just watch the lectures on your mobile phone or on your laptop.

Please do this using a piece of paper as I am doing it. You may find some mistakes of mine also. If you, please do point it out, but most importantly you will be able to practice this so well so that you do not forget it, but most of you just learn to, and that is why you will not be able to do it properly when it comes to exam or interviews or something.

So, better actually practice this so that you have a lot of you know thoughts process clear into it, otherwise you can do mistakes here and there, and the whole thing will be completely faulty, ok.With that is I should stop it here; we will come back to the next class on these aspects again.

Thank you.