**Phase Transformation in Materials**
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Lecture - 17
Interfacial free energy, Solid/Vapor Interfaces

So, students today we will start a new chapter that is on interfaces. Basically crystal interfaces and microstructures. That is correspond to the chapter 3 of the book which are prescribed you. In fact, what I am going to deliver lecture today is directly taken from the book of proton is telling. So, if you want you can directly refer to the book for details. Interfaces are very important for phase transformations, because phase transformation means formation of a new phase many cases.

Therefore, it involves nucleation and growth and whenever you have a new phase forming in a old or parent phase there is interface. But only discussing about those kinds of heterogeneous interfaces is not going to give you the whole perspective that is why you start with the very basic concepts and slowly, now introduced the new or concepts.

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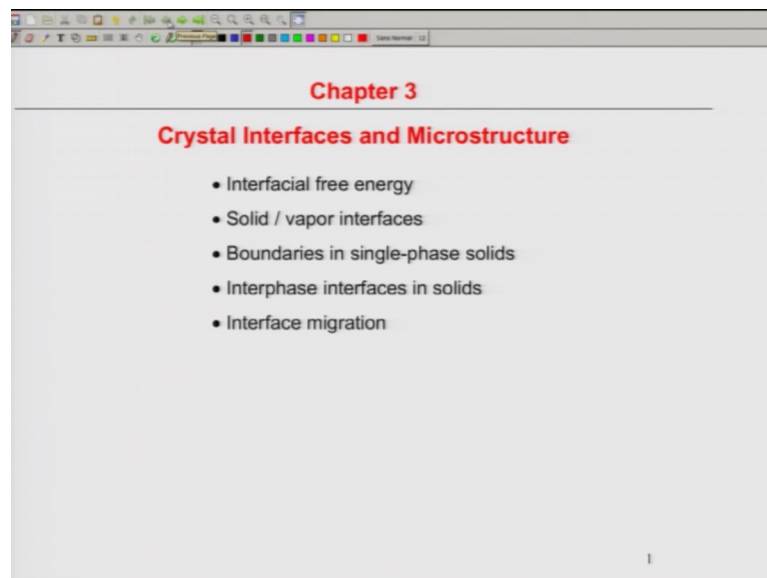
Things which will be discussed is basically what is the meaning of metal basic free, energy then I will talk about different interfaces. First one which is the most simplest one is the solid and vapor interface then grain boundaries that is the boundaries in a single

phase material, and which are one which I talk to the beginning that is the interface interfaces in the solids.

Finally, will briefly talks upon how are the meaning of the interfaces in those migration, but that is the whole thing maybe it will be cover in next 2 3 lectures. So, let us first look into what is the meaning of interfacial free energy. By the way before I move there are 3 types of interfaces which are important.

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One as I told you the free interfaces that is the vapor. And other 2 actually either interface between the same grains same phase of the same grains or in interface between the 2 other 2 phases whatever the situation you got to deal with interfacial energy.

So, whether it say solid way of my interface or alpha interface or is alpha beta interface, we are going to deal with boundaries and boundaries full up energy. And this energy is always defined as a interfacial free energy. This is a part of free energy which I have discussed, but different type of free energy. What is that in the free energy system is basically you will always consider thermodynamics as a bulk thermodynamics, you never consider in thermodynamics the interfaces.

So therefore, free energy always given as say G of the bulk, that is where there is many value effect of the interfaces. But the moment you have an interface where is a surface or interface we are going to have a extra energy. The extra energy basically coming from

the surface area, or interfacial area multiplied by the energy of the unit area. So, that is basically nothing but surface area and the free energy of gamma, which is defined as a per unit area. So therefore, total and the system will be equal to G 0 plus A gamma to G 0 is the energy of the bulk, where there is no interface.

Now, movement you have bringing into interface you had you are going to add up A into gamma term, and A is this total area where the system and gamma is the surface energy of unit area. Now so that means, gamma is what this excess free energy, this is nothing but excess free energy which is coming because of the material lying at the close to the surface of interfaces, ok.

So, please make it clear that this is a kind of a free energy, but this is excess free energy, something which is adding external system. That is the main difference between free energy and the surface free energy. It will be there in a b system where there is a interface or surface, you cannot actually complete ignore it. Only when we have a very large grain or very large suppose you know material the surface area is very small compared to the volume of the material, then you can ignore it. Otherwise you cannot ignore this kind of things.

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So, how do we are actually calculate? You know there is a means conceptual between surface tension and surface energy.

Let us we clear about the beginning, surface tension is what? Now this is a basically valid for the liquids. Now if I simply consider a frame that is like these on the right side shown; this is a frame you can see here. And in between the frame there is a thin film. Now you know the one of the bar of the frame is movable, other 3 bars actually are immovable. So, simply we are moving this right side bar by a force F I can increase the length of the surface area of the flame, because we are changing the dimensions. So, let us suppose if I apply force F per unit length parallel to this surface. So, what will happen at the force? We will write a small that thin film is small distance, because of that surface we will increase by small amount is called dA that is why it I defined.

So, because of this force the work done is what? Work done is nothing but force multiplied by the how much is the surface area increased that is F into dA. So, we know that d G is basically d G 0 plus A gamma that I have shown. So, d G is nothing but dA gamma dA plus a d gamma right that is obvious. Because G 0 is constant, it does not depends on anything. It is basically bulk energy, at a constant temperature pressure this is no change. So therefore, only change will happen on the A gamma. And if I total difference will A gamma is gamma dA plus dA d gamma. So, that is the change of the total free energy. That must be equal to the force multiplied by the area change that is the work done. So, that is why if I equate that is F becomes gamma you can clearly, see this is a simple equation nuts with nuts a very difficult want to understand F is nothing but A gamma plus a multiplied by d gamma by d n right.

Now, for liquids surface energies always independent of the area that I will explain why; that is why for liquid all I assume dA d gamma by dA to be 0. And that is why F becomes completely equal to gamma, why does it so? Because liquid is you know liquid is not we will not be able to support any shear stress. If I apply shear stress liquid will liquid items will basically rearrange themselves. And that means, this stretching of this flame by a place on the force a F is nothing equivalent to like a place on shear force on a liquid.

Even if you stress it the atoms on the bar raise of the liquid will rearrange themselves because that is a huge mobility. And because of that a constant surface structure can be maintained. There will be no difference between the structure of a liquid in the in the thin flames in the center and other boundary, because the rearrangements is very easy to possible. Because of that the gamma will be independent of any change of surface area. Gamma will not change because the atomic structure is remaining almost similar all

throughout the thin flames, and that is why in liquids the surface energy and the surface tensions are equal, but on the other hand solids in fact with the similar stuff.
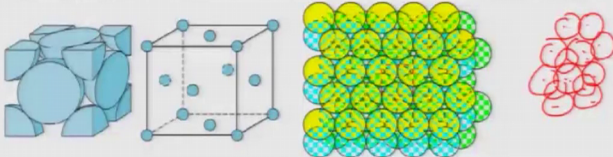
So, solid suppose solid thin film no atoms movements are very slow so the free arrangement is not possible. And therefore, we cannot assume in a solid this d gamma by dA term to be going to 0. That (Refer Time: 07:57) in fact, but most for solids it is not equal to 0. And that is why I am solid surface energy and surface tensions are different, and they are differed by this term a d gamma by d m, that is image a different in the solid and liquid. So, that is very, very you know that is why I am solid surface energy surface free energy and surface tensions are not identical. We had to know; what is the dependence of gamma on surface area, or stretching up that and that is why the In fact, that is what will be major discussion for the next few slides which will see.

Now, question is this to understand that let us first assume you know solid because liquid surface tensions are represent the similar there is no point in discussing what the liquids much. So, let us consider first solid may be interface. Because solid liquid solid interfaces are little more complex, first we will consist solid vapor interface. Remember any solid say equilibrium with this vapor always; so surface energy let us suppose if I consider FCC crystal, let us very easy to understand.

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And this is what is see a FCC crystal here, atoms are sitting at these phase centre positions right. And you know let us also suppose that surface is bounded by 1 1 1 plane

of the physical to structure. Because 1 1 1 plane is the dense pack structure, dense pack plane So therefore, let us suppose that. And we know that 1 1 1 plane; obviously, in FCC structure is a 12 coordinated atoms all atoms are 12 coordinated.

So, it is you know it if you consider surface of that if I draw it is done here. If I draw a simple one layer simply it is A 1 atom is surrounded by 6 atoms, correct? We can do that similarly I can do the same thing here this atom is surrounded by 1 2 3 4 5, 1 2 3 4 5 6 6 atoms right. So, all this atoms will be surrounded by that. Now if you look at carefully 3 dimensional space, this is if suppose this is what is the plane of the surface which is shown here by these yellow marked the yellow colored moles. You know there actually 3 neighbors outer 12 piece absent on the top, there is understandables if I consider that there are 6 neighbors on the early is plane and there has to be 12. So therefore, the bottom there will be another 3 and the top there will be another 3. Because this is suppose in FCC physical structure is a b C stacking right.

So, this is A and the b layer will be somewhat like this one atom there this was vacant another atom there is vacant another atom right. So, (Refer Time: 10:50) bottom also there will be another layer below that. So, if this 3 bonds are at the surface; that means, 3 of the 12 bonds will be broken. That is very clear. Now if the bond we will sense is suppose let us assume this is say pure metal. So there of a bond sense of every bond is similar that is equal to given by epsilon. So, each point can be considered as lowering in the internal energy, by gamma epsilon by 2; obviously, because each point is form by 2 atoms.

So therefore, I have to considered that the lowering of the interfacial energy by epsilon by 2, because there are 2 atoms involved. So, per the atom it is epsilon by 2. Therefore, every surface atom will with 3 broken bonds will have an excess energy of 3 gamma by 3 epsilon by 2, because there are 3 bonds broken. So, 3 into epsilon by 2 is what is the what is these excess interfacial energy, that is what is the surface of the bulk of atom with the bulk.

Now, how do I estimate epsilon simple way of estimate epsilon is related this 2 heat of sublimation. Because is a solid vapor heat of sublimation means what? Solid is became a vapor phase. So that means, the all the bonds in the in the solid state I have broken, and they are becoming vapor. That is why vapor there is no bond, I mean in the atoms there is

bond, but bulk bonds are there. But basically bond characteristics changing from solid to vapor, when is something becomes something sublimants. So, (Refer Time: 12:24) latent heat sublimantation must be equal to the sum of the latent heat, or the equal to the some latent heat of the fusion and the latent heat of vaporization, that we no basically. First something has to melt then in (Refer Time: 12:35) can vaporize.

Now let us suppose forget about the all the stuff let us suppose there are one mole of solid that is vaporized. So that means what? Total 12 into N a number of bonds are broken, N a is the Avogadro's number. So therefore, I can write down latent heat of this sublimation must be equal to total number of bond multiplied with it bond energies thus epsilon by 2. That you can see is basically that gives you epsilon is nothing but L s by 6 N a, that is simple or other (Refer Time: 13:03) calculation will give you this is L s by 6 N a, that is L s if I know latent heat of vaporization I know. And if I one mole I have one mole pieces.

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So, then I can simply calculate the bond energies is equal to L s by 6 N a.

So now if I have that idea what I can do. So, assume that is this surface energy is basically because of this 1 1 1 surfaces. So therefore, that must be equal to 3 epsilon by 2 I have already considered. And epsilon is what L s by 6 N a. So, that is gives me surface energy s equal to 0.25 into L s by N a right if I simply do the calculations basically you can see this is 12 this is 3. Therefore, 1 by 4 and 1 by 4 become 0.25 and this is L s by N

a, that means, different crystal will have different values of surface energies, solid vapor surface energies because Taylor different values of L s. Or rather this simple model allows you to calculate solid vapor interface energies simply by knowing the heat of sublimation.

That is; what is the important information you can take from these simple derivation that, if I know basically the latent heat of sublimation I can calculate; what is the solid liquid vapor interfacial energy. That is why in the literature you will see initially from 1870's to about 1940's then I extent the research work done on solid vapor interfacial energies, because this is very easy to conceive and understand. There is nothing no difficulty at all. But things will change slowly.

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Now, how does is scale with the real experiments? That is what we will always like to know. You know real surface energies actually atoms we always considering the whole derivation the atom access as a jisur fear. And they are not able to move, this things are not actually correct. But there is another thing which we have not considered here. Surface atom surface to will have more freedoms. Why because they are sitting the surface therefore, there bonds are broken they can move more than the bulk.

Secondly there is a higher thermal entropy this is the surface atoms, why? Because this you know extra configuration, because atoms actually at some atoms are there no bonds. So, they can configure it more way then a bulk. Atom in a bulk atom cannot sit

configuration of the atoms are more than more fixed you cannot change is surface it can changed. So, because of this configuration variations of the surface atoms, I can see to with a if I am surface atom I can see it near a vacancy or near some other atoms, I can move also little bit because of thermal energies.

So, because of that this excess entropy of computational entropy will lead to change in the model. That is model did in consider that. So, surface energy crystal will be there associated with the excess entropy done that excess entropy of not considered in our model. We simply ignore that. And because of that because of you have a lot of freedom more freedom surface more freedom. So, that is why the configuration can be easily changed, that is why the values of gamma what are the calculated will be less than what we have the model. And people have seen the value actually is point one 5 multiplied by L s by m A is not 0.25. 0.25 is little above estimation compare to what is the what are the assumption which you have meant.

So, if you clearly see that is already given this value this is again taken from the literature for the thin aluminium silver gold, copper delta iron platinum and tungsten. So, we have basically FCCN and BCCN. So, tin as bct and depending on the melting temperature the values of gamma solid vapor interface will be change, thin has the lowest melting temperature here 232 kel degree Celsius. It has about 680 mille joule per meter square is surface energy solid vapor surface energy.

On the tungsten has the highest mille temperature about 3400 degree Celsius, it has the highest value. 2650 is solid the equation interfacial energy mille joule per meter square for the tungsten. So therefore, is obvious more. Higher the milligram to higher the bond energies the higher the bond energy is has the value of it is sold vapor interfacial energy. So, it is very easy to actually deal with solid vapor. Interfaces very easy you can actually clearly see that simply by considering a bond broken bond model like this way, we can get into the values; obviously, model what estimates little bit, but that is can be even consider you know in the real world correct.

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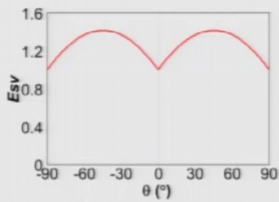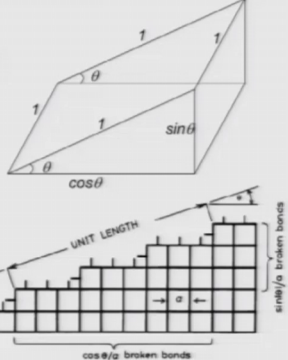
But you know reality is little bit about different, we are assumed what we have assumed only 1 1 1 plane, which is still low index plane which is the bounding surface. Or you can assume it actually 1 1 1 0 planes. But if suppose all the surfaces will not be bounded by 1 1 1 plane, there will be reconstruct surface also. Let us suppose surface is bounded by a odd plane or a irrational plane. How do you deal with it? In only such a case the broken bond model will still be applied, but we have to considered different wave we have to considered the interface like this which is shown here which makes an angle cos theta here. And so, what whether let us consider the bottom picture broken bond model.

What you see here? It is a it is basically step surface is no longer here flat surface. So, if you have a step surface, because you have different kind of you know planes actually sitting on the surface somewhere it is 1 1 1 plane somewhere it is 1 1 0 plane. Somewhere it is different 1 1 is a plane, because different planes are sitting on the surface. So therefore, the bonds number of bonds broken are also different they are not same because the atom sitting on the top surface of 1 1 1 plane is different from the number atoms sitting on the top surface of a 1 0 0 plane or may be some other plane. So, that is why we need to consider such a generalized situation in which this broken bond broken bonds can be have different types on this surface ok.

Now, if I assume that there are 2 things we have to assume which is it is not a no longer 2 dimensional surface A 3 dimensional surface. So there are bonds which are broken

which are parallel to the surface perpendicular to the surface. That is this is the surface suppose which is somewhere one my scheme of the projector, and also there is a surface perpendicular to that. Obviously, it is done into the plane of the of the board or the plane of the projector. So, because of that we need to consider, bonds broken parallel to the surface and terminal surface. There are 2 type of bonds are there easy to understand in any solid surface I do not know whether I can show it you there is a duster. Any solid surface if I considered like this if this is my surface. This is the parallel to the surface this is the perpendicular to the surface.

So, you can also have a bond broken on the surface, and bonds with the extended. This is surface is like this. Because this is the solid where surface is bounded by this plane this plane and this plane. So therefore, we need we can not only considered 2 dimensional surface like this we need to consider these once also which are perpendicular or these once to the perpendicular to the surface. So, that is why we need to calculate total number of bonds broken.

And as I said if these plane might be 1 1 1, but this planes may not be, this plane will be different types of planes. So, that is why we need to consider in general is view, and generalize view says the total number of bonds is basically bond broken is basically perpendicular number of bond bonds which are perpendicular to the surface, perpendicular surface this surface is or parallel to the surfaces. I am not doing mathematics you can do that this actually this mathematics are not difficult. If you do the proper calculations total number of bonds will be equal to cos theta by a square, which a perpendicular broken into the perpendicular directions. If I have the theta is the angle which is use the surfaces making with the bulk.

And similarly it is sin theta by a square for the parallel ones. So that means, what we have a cos theta plus sin theta by a square. Remember it is always put mod on sin theta, because sin theta can be theta can be more than 90 degrees and then it can be negative. That is why, but it cannot be negative bonds broken cannot be negative here suppose that is why always put a mod. So, then what actually happens then total surface energy is equal to n in multiplied by the epsilon by 2. And here n become cos theta plus sin to the by 2 a square or rather is becomes cos theta plus sin theta multiplied by epsilon by 2 a square.

Now that means, for interface energy is a function of theta means. It is also function of the A is basically is the distance between the 2 planes, and that is the inter interfacing depending on whichever plane actually that also you can change depending on the planes also, but we have consider average value of A and epsilon is the average ponds energy. So now, if I plot ESV versus theta that is what new probably you can do that in A 2 dimensional space, you can see basically it. So, a cusp very clearly; something goes increase and decrease. And cusps and at 90 minus 90 plus 90 the so, a sin is mod a minus 90 plus 90, and 0 the craps as very low values.

Basically these correspond to the low index planes. Low index planes like 1 1 1 or even 1 1 0 will have lower interfacial energy compare to the irrational planes or planes which are high index. Suppose let us say 3 3 1 2 2 1 or many other planes such like that. So therefore, these cusps has minimum or minimum points and these points are very important. Because these are the points in which surface of surface will be represents will be lowest. Therefore, if the system also decreases total energy system, which is equal to G equal to G 0 plus A gamma; the planes which will be bound the surfaces must be the ones which has the lowest energies because A and gamma will be than lowest gamma is low means A gamma will be low.

So, that is see basically main conclusion of such a kind of analysis for the solid vapor interface conclusion is that. There are cusps in the free energy in surface free energy plots, and this cusps has minimum points and certain value of theta.
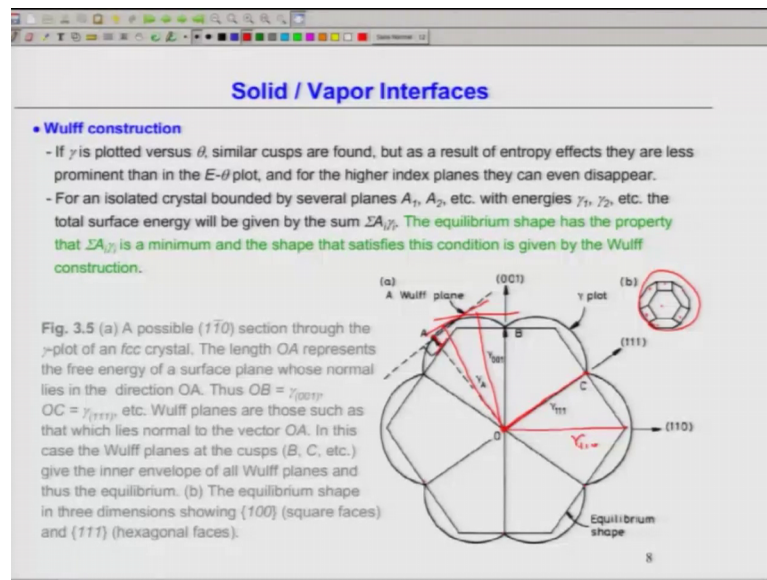
Now, how we can do that in a if I consider a complete crystal. Suppose the crystal is such a kind of complex steps you see here, can I do with do with a very simple way very simpler means very logical way. Well what I can do I can actually get you know gamma as a function of theta for all the cusps. All the cusps means all the surfaces. This is bounded by many surfaces is see here these, these, these, these, these so many surfaces.

When is surfaces I can do the similar analysis. And I can find out the surface energy interfacial energy between solid and vapor as a function of theta for each of there is surfaces, and I can plot that this the outside plot you see here is the 2 dimensional plots remember now that is why 3 d 2 d plots all though the crystal is 3 d. So, it is A 2 d plot just to make you see that you understand things you can always make A 3 d plot that is not a bring difficult, but you request little bit more calculations.

So, that is the 3 dimensional this is the cusps you see here the cusps and minimum points here. You can see here the minimum points are see outside envelop. Now and that is what is known as inverse the plot is the interfacial energy solid vapor interfacial energy. For the highest index planes they can even actually you can see let us assume. Suppose you have isolated crystal which is bounded by many planes that is what is shown on these between these picture. And this planes are different surface energy areas A 1, A 2, A 3 and depend surface energy is that is gamma 1 gamma 2 gamma 3. So, total energy is

equal to summation of that A 1 gamma, 1 A 2 gamma, 2 A 3 gamma 3; that means, it is summation of A i gamma i.

Equilibrium says say full of the property. That is the very important thing which you to understand. Equilibrium say then you steps which will be in the minimum energy say. You will have the property that this summation is minimum, and the set the satisfy this condition is given by what is known as Wulff condition, all construction rather. So, the actually it says you that you must control, you must not control, you must select the planes of the crystal bounding surface of the crystal such that the total gamma A is minimum. I know one can do it mathematically, that is not very difficult task also. Nowadays even with the (Refer Time: 25:50) computers you can easily do that. But it is better actually do it by geometrically. And that is what is done by Wulff what Wulff said. Let us do that suppose this is my cusps, what I do? I this is my center of the crystal or center of these plot not the crystal sorry center of this plot, this is where.

Now, what I do? I comes with the point on this cusps suppose this point is A. So, if I join this point A and this you know center point O. Let us join by dotted line, and then I do one thing I simply draw a tangent to that. So that means, I see you see sorry normal to the not a tangent. I do a normal to this cusps at this point you can see this is what is the that normal; obviously, normal is what, this is this is my this is my direction. And then I put a 90 degree 9 with respect to that. So, if I do that that is becomes my Wulff plane. You can clearly see if I task posed is here that is what it is. So, on each of this points I can do that. I can draw another line here and I can do that. I can do another line here I can do that. This is what is done, correct?

So, on the whole this gamma plot that is inverse is theta plot. Now once I do that the inner envelope what will be forming, in the envelope will be like this what is shown here is what is your equilibrium crystals say. That is what is huge construction say tells you, but it assumes one thing; that means, the interfacial energy of this planes is parallel is proportional to these length of the normal. Length of this length I have drawn per O to a this length is what is proportional to the interfacial energy. That is what is inherent assumptions, this is written here. So, here over C C is here you see here O C O C C is here O C is equal to gamma 1 1 1. Why because this point cross met to 1 1 1 plane there is a minimum point of the cusps that is must be 1 1 1 plane.

So, this distance is proportional to 1 1 1 surface energies now this is 1 1 0s this distance will be proportional to 1 1 0 gamma 1 1 0. That is why you can calculate you can actually get a ratio of the free energy surface energies of each of these planes. So, that is actually let us stop with here. So, that is the way actually solid vapor interfaces are deal dealt with. Now in the next what I am going to do with little bit different ok.

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So, this is shown here again. And must better way, basically same thing is shown here in a bigger picture not a different thing.

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Now, in the next class what I am going to do is I am going talk about grain boundaries. That is solid vapor interfacial energy is why this is the easiest thing to understand. You have a solid and you have a vapor around it, but if I have 2 grains solid and solid, same chemistry what is the type of interfaces it can develop.

That we will deal in the next lecture.