Phase Transformation in Materials

Prof. Krishanu Biswas
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture - 23
Homogenous Nucleation

So, we are going to discuss today in the lecture more bout nucleation. I started this subject in a last part of the last lecture. So, as you know phase transformations are basically controlled by nucleation and growth. So, whenever a new phase forms for apparent phase, basically the starting point is the nucleation.

So, we will have a brief overview of nucleation, but at the same time I would like to tell that this will be little bit of overlap between solidification, which you are going to start at the beginning of the phase transformation different types of the phase transformation. So, solidification is; obviously, from this liquid to solid transformation. So, we are going to take examples of that to explain nucleation. And further more we are going to extend these things from a nucleation of a solid phase out of a solid.

So, I am going to discuss most of the things in the using the black board today. So, that you can understand nucleation is basically more of a mathematical way to understand than of physical significance. Physically it means that we form a solid phase form a parent liquid solid phase. It can be also for vapor, but normally we do not discuss this transformation from vapor to solid, we always like to discuss from either liquid to solid or solid to a solid.

So, whenever you know a solid phase forms from a liquid first thing, we understand we need to understand what is the driving force for it is formation although we have discussed in detail about the thermodynamics of these transformations, but it is better we put it in a proper foundation. So, I am going to take a liquid to solid transformation and explain you why driving force will arise, and what are the condition in which driving force will be available.

So, let us go back to board and see how we can use the thermodynamics formalism to explain the origin of driving force.

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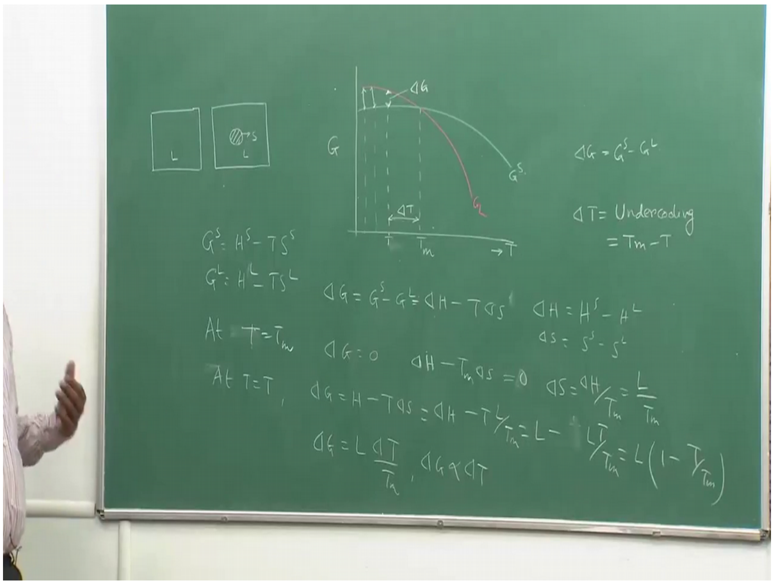

As you know suppose if I consider a box containing liquid. And suppose after under certain, condition experimental condition a solid phase forms in the liquid. So, the question is that why at all this solid phase form from this liquid. Why does the driving force separates formation? This actually origin it is form the free energy of solid and liquid phases. So, if I plot free energy of a pure solid or liquid as a function of temperature, then the free energy curves actually will look like this. Suppose this is for the liquid this we write GL and this is for the solid.

So, therefore, at the melting temperature these 2 curves will has to cross over because at the melting temperature they will have this same free energy otherwise there will be no coexistence of these 2 phases. So, because at the melting temperature these 2 free energies cross over, therefore, the delta G which is the difference of the free energies of the solid or liquid, this has to be S solid and liquid. So, if I write down GS minus GL that difference is 0 at the melting temperature because the values of this GS and GL are same at the melting temperature. So, as we go from, actually go away from the Tm towards higher temperature or if we go in that is if you decrease the temperature from Tm to lower there is always say a gap between free energy curves.

Now, these 2 free energy curves are telling relative positions of the free energy of solids and liquid. So, therefore, all if when I cool this, liquid to a certain temperature below the melting temperature, I see there is a gap and that gap is nothing but difference of free energies of solid and liquid which is available to the system to create to have phase transformation. At this temperature difference between melting temperature and any temperature is to which we have cool down the liquid is known as undercooling.

So, therefore, these terms we must remember this T delta T is known as undercooling in the literature and that is defined as Tm minus T. Because T is always less than Tm and above the melting temperature that is the driving force for the solid to melt down. So, as we are discussing solid phase forming out of a liquid. So, we know should now discuss the things happening about the melting temperature.

So, as you clearly see as I cool more and more the liquid or driving force increase from this value to this value or even this value to this value slowly. So, higher the undercooling more is the driving force, as you clearly see as you increase the delta T further driving force is increasing. Now can you just calculate the driving force in terms of undercooling in case of solidification? That is evident from this picture that as we increase the undercooling the driving force increases, but what is the scaling role law how the delta T actually affects exactly in terms of mathematical equations the undercooling well.

As you know GS is given by this equation we have already discussed a lot where S superscript stands for the solid GL is the liquid free energy where l stands for the liquid. So, therefore, difference is delta H which is nothing but GS minus GL that is nothing but delta H or we can write down actually S minus l T delta S, where delta H is nothing but H S minus H l and delta S is S, S minus S L. Remember that these H is the enthalpy and S is the entropy T is the absolute temperature.

Therefore, I can write down at the melting temperature at the melting temperature or a Tm a T equal to Tm that delta G is basically. It will be 0 because at the melting temperature these 2 free energies will be same. Thus, I can write down delta H minus Tm minus delta S to be equal to 0 right. So, that is gives me that delta S is equal delta H by Tm and you know at the melting temperature the heat which is evolved which is correspond to enthalpy change is nothing but the enthalpy latten state of melting. So, therefore, I can write down this is l by Tm.

So, now I can actually do reverse mathematics to find out at temp any temperature T going to be T what is a value of delta g. So, the delta G is nothing but delta H minus T delta s. So, I can write down the delta H minus T and replace this delta S by l divided by Tm and at the; obviously, here the solidification the latent heat of solidification or latent heat is evolved. So, therefore, delta H is must be equal to latent heat here. So, I can write down T l by T m. So, So, therefore, it is equal to l 1 minus T by Tm. As you do if you the mathematics properly delta H becomes delta G becomes actually l delta T by T m.

So, as you clearly see the delta G is proportional to delta T, directly because l is a constant and melting temperature is constant for a particular system. So, more is the higher is the delta T value higher is the value of delta g. So, as you undercool the liquid more there will be more amount of delta G available to us or for the system to transform. So, that is the main driving force for the solidification to happen. Now I say I said with the beginning thus this liquid to solid transformation has 2 parts one is the nucleation of the solid and another one is the growth of the solid.

So, nucleation is what we are going to discussing today. So, this driving force is which is available to the system will be used to create this nucleus or nuclei rather in the liquid. And there is then the nuclei will grow to form the whole solid that is the basic approach, we use. So how we can use this expression which is the available free energy to get some idea about the nucleation of this phase?

Now, as if I look at it little bit different way, initially I have a complete liquid you see here is the complete liquid. Then then what happened a solid very tiny small piece of solid has formed in the liquid and because of that there is a interface between solid and liquid remember solid, I have drawn like hatch lines will be crystalline in nature on the other hand liquid is a complete random structure. And because of that the structural difference of these 2 even if there is no chemistry difference for the pure metals this will lead to a interface between these 2 phases.

And this interface because of what you have to existence in the in this space will have certain energy. Because it has a broken bonds at the interface that is we have discussed a lot about these things in the few lectures previously. So, interface because of the broken bonds between the solid and the liquid there will be interfacial energy. And because it is relative of the broken bonds the interface there will be positive energy of the energy of the system. And this energy must be provided by the system or by this kind of free energy available to the system to form the stable form of nuclei that is the idea. So, how do we do it in terms of mathematically?

Let us suppose I have which is the case I have a spherical nucleus form in the liquid which is normally we always conceived because that is makes the mathematics much easier, but may not be the always case nucleus may be of a different shapes does not matter, if I have a solid nucleus formed in the liquid or let us suppose solid piece of a small tiny embryo which is formed in the liquid which is not yet becomes nucleus. And this solid has a radius of r if it has radius of r, the total free energy of the system total free energy of the system is nothing but a volume free energy change.

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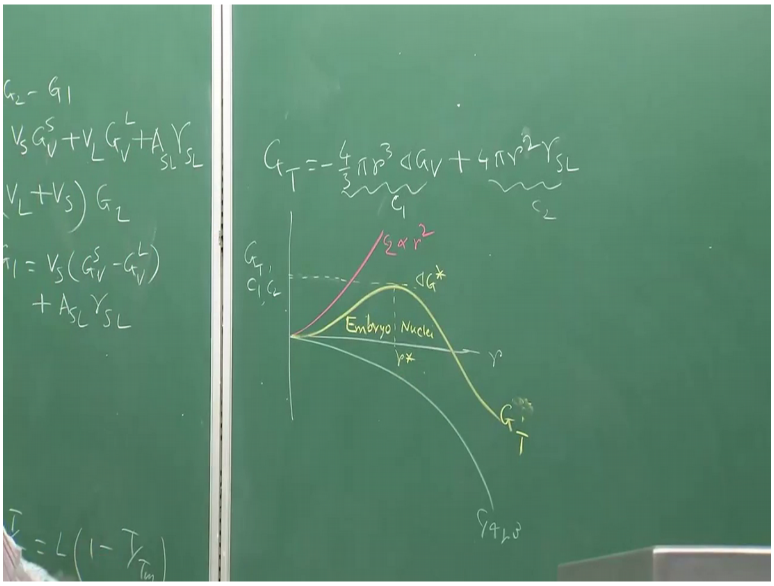

Because of the solid to liquid formation that is because of these solid and liquid transformation happens at a certain level of undercooling. There is free energy change because of that. So, that is volume free energy is nothing but equivalent to 4 third pi r cube delta G V that we always write why because the volume of these is basically spherical nucleus is 4 third pi r cube, where r is the radius and the G V is the free energy available to the system.

And this always we write down minus, why because this free energy you see here is the difference between a liquid and solid this free energy is basically, what is basically negative because (Refer Time: 13:21) difference between solid minus liquid that is what I have written solid minus liquid because solid has lower free energy than the liquid. And this is all you know this liquid is negative solid is positive here written. So, therefore, delta G V will be negative sign and this is must be added with the free energy of the interface. And we know that free energy of the interface is equal to gamma S l multiplied by the surface area and this surface area is fourth of 4 pi r square, of a sphere for a particular sphere of radius r surface it is 4 pi r square. And it has to be multiplied with interfacial energy. So, if unit interfacial energy is equal to gamma S l so; that means, this is equal to area multiplied by S l or let us do it in a little bit different way.

Let us suppose before we go back to the equation, we can actually get a let us suppose these has a free energy of G 1 this has a free energy of G 2. Therefore, if I write down properly here, let me just take out all these things before we go back into that.

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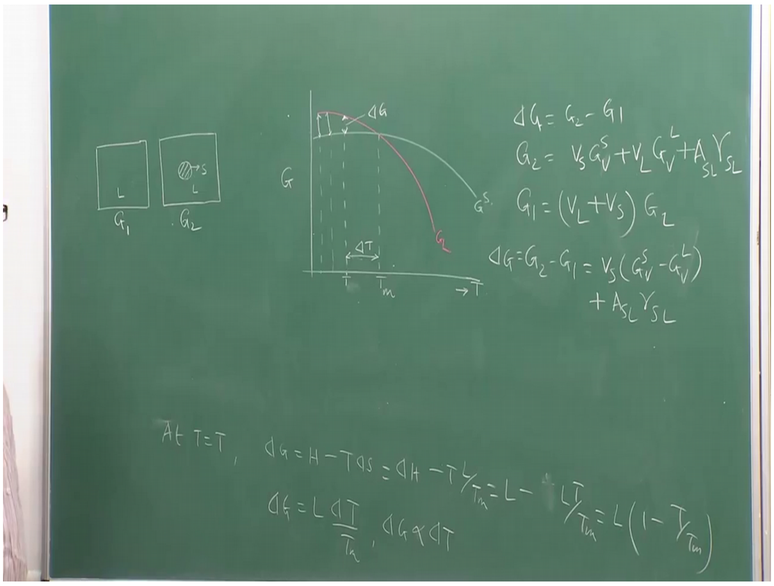

So, therefore, the free energy of the difference between this configuration is G 2 minus G 1. Now what is G 2 equal to G 2 is equal to V S solid; obviously, free energy of the solid, we can write this is volume is for V l G V l that is free energy of the liquid plus the surface area between solid and liquid multiplied by gamma S l. So, therefore, G 2 we has free energy of the liquid multiplied by the volume of the liquid free energy of the solid multiplied by the volume of the solid plus this interfacial area into interfacial energy. And what is G 1 equal to G 1 is equal to again same thing V l GL because G 1 has only what only liquid plus, but this is not the correct why because the volume of solid plus liquid was the complete volume of the of the liquid. Remember that this is a complete volume. So, this was this form. So, therefore, this has come out. So, this must be subtracted or added if I have to do G 1.

So, now, if I look at it completely G 2 minus G 1 is what this is, again GL V l will get cancel. So, therefore, I will write down V S into G 2 is GS V minus GS l plus a S l gamma S l. I am write I try this is what we get if we do the profound mathematics. So, that is the total free energy of the sys free energy difference of these 2 configurations. So, now, what I have done and these I will write down G t. So, what I have done is same thing in this equation, I have assumed this particular species we just form out of solid other liquid is nothing but spherical steps. So, if a spherical steps then I write down these delta G V is this solid (Refer Time: 16:57) liquid.

Therefore, this will be negative as you see here solid minus liquid this is a negative. And V S basically fourth of pi r cube that is a volume of the solid species similarly area plus area is 4 pi r square multiplied by this solid liquid interfacial energy. So, if you do completely mathematical way that is what you get. So, that is my total energy of this total energy of this solid we just formed because of solid we just formed out of a liquid.

Now, if I simply plot this equation, remember this equation has basically a single parameter r dependent. If we assume that gamma S l is isotropic and constant and assume delta G V is also a constant a fixed temperature. So, if I plot that equation here below let me just plot it here. So, what I am plotting here is this, is x axis is r y axis is G T and 3 things I am pointing G T. This one let us suppose this one is c 1 and this one c 2. This c 1 comma c 2 all of them, I am plotting on this plot in different colors for your understanding and all is a function of r as you clearly see all of them are function of r at a fixed temperature. So, let us first plot c 2, c 2 is basically r square dependent. What is the meaning of r square dependent basically r square is nothing but a parabolic? So, this will look like this c 2 is proportional to r square. What about c 1? C 1 is basically r cube dependent. And so therefore, if I plot c 1 this will look like this c 1 is proportional to r cube.

And now if I if you see G T is, what G T is a summation of these 2 terms? Summation of this term and this term. First one is c 2 is basically in positive term which is proportional to r square c 1 is propor negative term proportional to r cube. You know if I add these 2 up this will look like this. So, that is basically G T, G T subscript T is you if you do if I do that simple what do I see? If look at this curve which is interest curve actually this is basically genesis of homogenous nucleation in the solid in the liquid of a solid phase. So, as you see here, I have for small value also far the total free energy of the system will increase that is because for more values of r the c 2 term dominates, c 1 is much lower than c 2 therefore, the G T the total free energy increases.

Ok, but again for very large values of r the c 1 terms dominates that is what you can see here it is dropping very fast or very large values of r. So, because of that again the curve will go down curve will go down means the value will go down. So, therefore, in between first there is a rise because of small values occur, then there is a decrease of the total free energy of the system as a r increases.

So, in between there is a maximum value and this maximum value we always term as a critical value, what is known as r star in the literature all of you have read these things. So, r star is; what is nothing but critical value of r at which this peak happens. So, first of all this plot tells you the nucleation is a barrier or a statistical barrier dependent phenomenon here. The atoms needs to cross a barrier to become a nucleus r star is known as critical value of r, below which everything is known as embryo only when one extra atom either 2 r star the system will reduce energy and it will form nucleus, that is why I written nuclei.

So, r star is basically known as a critical value of the syst of the G T approximate to G T. So, therefore, the G T value for this is known as delta G star which is nothing but the critical value of G T. And that it tells you that the every system whether it is a solid liquid gas or whatever whenever there is a solid phase forming from the liquid or vapor or solid say syst the formation of nucleus from this from the parent phase (Refer Time: 22:20) is basically a various dependent phenomenon. And this is activation control rather because the system has to pass over this barrier cross over this barrier, or reach the size of these critical size of this species more than r star at least one atomic star, than the r star to become a nucleus. And then only we can go further because further as we increase the value of r the free energy of the system will keep on decrease and that is good for the system because we want low energy of the system all free energy of the system always.

Now, that is the basically physical under physical aspects of that. Now simply whatever time I have in next 2 3 minutes I can simply take this equation and do some mathematics also here. So, as you know this is peak value corresponding to r star. So, peak value means maximum.

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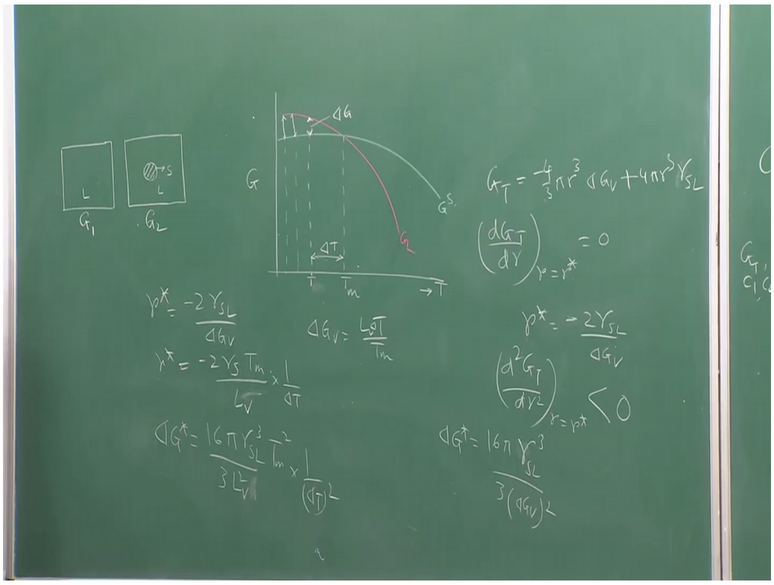

That means, if I want to find out r star from this equation, I should apply the condition of maximization of this equation right because that is the value of maximization. So, if I do that the condition from maximization is G T by d r, r, r is equal to r star to be equal to 0 and if you do the mathematics properly very simple. So, r star will be minus twice gamma S l divided by delta G V. Thus understandable that this is 4 third pi this will be it will be 8 pi r square, and suppose 8 8 pi r. So, 2 it will come and then r star is basically twice G V. And similarly if you want to cross check that these value of r star will lead to second condition to be satisfied this is a maximum. So, therefore, this will be less than 0. Similarly, what these r star value we can find out what is the barrier, activation control barrier that will be equal to 16 by pi, pi gamma S l cube y 3 delta G V square. So; obviously, these are all simple equations you can derive yourself in your note book.

Now, r star must be converted in terms of undercooling as you know delta G is basically, I know delta G V for solidification is what it is a latent heat delta T by pi T m. So, therefore, I can get twice gamma S l, Tm l delta T the latent heat is negative. We considered because heat evolved in solidification. So, that is why this negative will get canceled. And then r star will become a positive value. Similarly G star is equal to 16 pi comma S l cube divided by 3 and delta G V square. So, therefore, this is l square delta T l square Tm square 1 by delta T square, see if I know the undercooling if I know the melting temperature in the latent heat this latent heat is basically per unit per volume that is why it is better to write volume remember that this is not per mole this is per volume.

Therefore, if I know the delta T undercooling for a particular experiment, I can calculate what is the r star what is G star normally r star is couple of nano meters sizes is about 2200 atoms and G star is the critical barrier which can be very small actually 10 to the minus 15 to minus 18 or 20 joule per cluster this is very low value. So, in your assignments problems you will find how to use these equations to find out different values.

So, remember in the next lecture, that is what I am going to discuss when I am talking about solid to liquid transformation a liquid to solid transformations all thing I am assuming is what this interface between solid and liquid correct. And because liquid is a in basically cannot take up when shear.

So, I the any volume change because of solidification it is very clear the solid will have will be more closed pack structure in the liquid. So, because it is a more closed pack structure the volume unit volume of solid and liquid will be differ the densities of solid and liquid are not same. So, because of that there is a volume change and this volume change in a liquid to solid transformation will not affect anything in the liquid, because liquid is basically cannot take up any shear.

Therefore, if and if there is a strain or there is a stress applied because of dissolving change for the solid to liquid this can be easily accommodated in the liquid that is very simple, but suppose instead I have a solid phase coming out from a solid; that means, a solid nucleus forming in a solid inside a solid. Then there will be some single value volume change and this volume change will lead to stress at the interface. And this stress is or other strain actually elastic strain will be available will be leading to deform the matrix or the parent phase elastically. And these strains will have effect in the value of the delta r G, and r star and delta G star that we see in the next lecture.