Phase Transformation in Materials
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Lecture – 24
Homogenous Nucleation (cont.)

In the last lecture I gave you some mathematical formalism of the homogenous nucleation how a solid nucleus can form a liquid and in that case how we can deal with in thermo dynamical manner. Now, as I said in the last part of my last lecture that the whenever a solid phase forms out of a solid or the inside a solid rather like a product solid phase forming inside a parent solid phase there is a extra aspect we need to consider, the extra thing is the straining of the parent phase and how we can deal with it that is what we are going to see it now.

As we know we can simply write down the equation in terms of free energies again, but strain basically is a volume energy term strain is always proportional to the volume of a surrounding parent phase. So, let me go back and explain you with detail manner.

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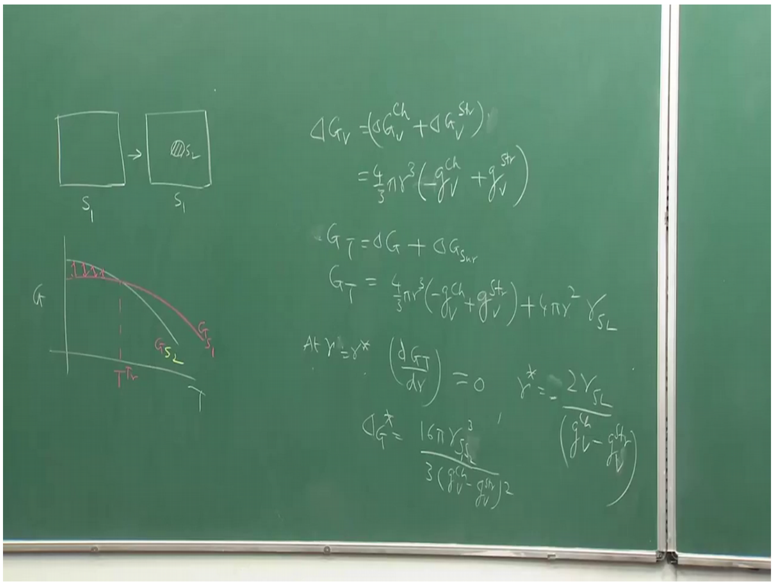

Suppose, if I have a solid is a complete solid S 1 and I formed or the system forms a new solid S 2 inside S 1 and so therefore, as a solid phase is forming out from another solid phase the densities of these 2 solids may not be equal why because it dependencies depends on how the atoms are packed; that means, density depends on crystal structure of these 2 phases.

So, as densities are may not be equivalent if it is equivalent is fine it may not be equal then what will happen? Because of these density difference there is a volume change; that means, volume of S 2 which has formed out of S 1 may be higher may be lower does not matter there will be volume change. So, because of volume change there will be elastic stress acting at the interface and this elastic stress will lead to straining of the solid S 1. So, therefore, this must be taken into consider.

How we can taken into consider? We can always assume the volume energy term has 2 parts - one which is a chemical free energy term and another one is basically strain free energy term. What is chemical free energy term? Chemical free energy is the free energy because of difference in the structure of these 2 solid phases and chemistry that is the chemical part; obviously, basically is a chemistry part that is we have seen. If I plot the free energies bulk free energies of these 2 phases S 1 and S 2 the difference of these 2, difference of these 2 phases will be difference of these 2 free energies will be equal to the chemical part.

So, if I say S 1 and S 2 this is the transformation pressure as you clearly see as a transformation temperature S 2 is more stable and below S 1 is more stable correct. So, therefore, this is S 2 and this is S 1 free energy curves or rather I can write down G S 2, G S 1. So, the difference chemical free energy is nothing, but this difference between the 2 free energy curves, but strain free energy is also volumetric term that must be considered that is also proportional to the volume.

So, what I can write down? I can write down these is equal to 4 pi r cube this is the volume total free energy this must be equal to volume rather plus basically sorry this multiplied by G volumes ch I am writing down a small g volume small g and that is what we can write down. So, these are the values of the free energy per unit volume remember that is why we written G volume. Now, we can do the same maths we can always write down this as a negative because this value is negative as we see here, but the strain free energy term is always positive.

So, you can do the same mathematics again the total free energy is equal to delta g v plus delta G because of the surface energy. So, that is the surface energy term. So, I can write down the free energy term. So, I can write down this as 4 third pi r cube minus g v ch plus v v strain plus 4 pi r square gamma S l that is my total free energy system. So now, is simple, now actually to find out at r is equal to r star at what is the d G T by d r is equal to 0. So now, one simply do the maths. So, it is basically it will come same thing. So, r star will be minus twice gamma S l g v minus g v ch sorry this is strain.

What is actually happening is that because of the presence of strain energy total free energy of the system available free energy of the system is getting reduced is a free energy available to the system that is getting reduced by the free energy because of the strain. So, therefore, r star value will increase. That means, the critical nucleus size will be higher when we have a strain in the matrix as you see here this value is going down r star will increase correct.

So, that is the main thing in a solid therefore, in a solid to solid transformations critical nuclei or critical size nuclei embryo or rather which will become nucleus later on size bigger than solid to liquid transformation that is the major conclusion you can draw here. And this is very important because will see in our examples, in our examples means in your different types of phase solid to solid transformation that this is a strong aspect strain will be present inherently in many of the phase solid to solid phase transformations.

Similarly, one can calculate G star again G star is also delta G star nothing will change much in the numerator, but this one will change g v ch minus g v strain whole square that is how it will change nothing else will change. So, therefore, again the critical value critical height will also decrease because this has decreased here if this will be solid solid sorry not liquid gamma solid solid or rather gamma 1 S 2 and because this value is getting reduced so therefore, delta G will increase again here also the critical area will increase. So, these are the things happens when you transform something from solid to solid.

Remember the most of the transformations which you will study in our cases basically solid to solid. So, therefore, if you really want to do the mathematics properly you need to calculate what is this free energy change because of the strain and this free energy can be calculated depending on different types of interfaces. If the interface is coherent there is no strain energy there will be complete coherence there will be no strain energy, but if interface is like a coherency strain is involved, coherency strain means the atomic bonds are little bit distorted, but still the atoms are perfectly bonded with each other, but the bonds are angles are distorted this will lead to strain.

Or you can also have a permanent strain because of dislocation dislocations can be formed at the interface to create a semi coherent interface that can lead to permanent strain or in case of incoherent interface strain energy is pretty high because that there are lot of distortion of the atomic bonds of the interfaces. So, this value is going to change depending on that the type of interface is developed as you can clearly see the nucleation of the phase is strongly depended on the type of interfaces we have in the solid solid.

So, we can actually take case by case that is there in the book in the basically it is second book is there more many examples are given where you can by Professor Jena and Prof Chaturvedy book in phase transformation in materials there are lots of examples are givens or how to take care of these strain part to calculate the free energy change, both the chemical free energy or strain free energy change how to calculate there are lot of examples are given. In case you have the book you can actually solve this problems and get a fair amount of idea how to take care of different interfaces.

Now in the next 10 minutes or so I am going to talk about rate of nucleation. See remember how fast the nucleation happen that will dictate how for the sort by the transformation will take place. So, fastness depends on the rate of nucleation; that means, if I have a ice and I want to put in deep freezer I would like it to be frozen in say couple of hours that is what is we observe really. So, that is what I am talking about it how fast something can solidify depends on the nucleation rate; obviously, it will also depends on the growth rate, but nucleation rate is first and foremost things in doing that. How do I we actually discuss that? That is there in the book in a very detailed manner, but I am not going to discuss in you know very title manner because it is not possible actually frankly speaking how the nucleation actually happens in a liquid.

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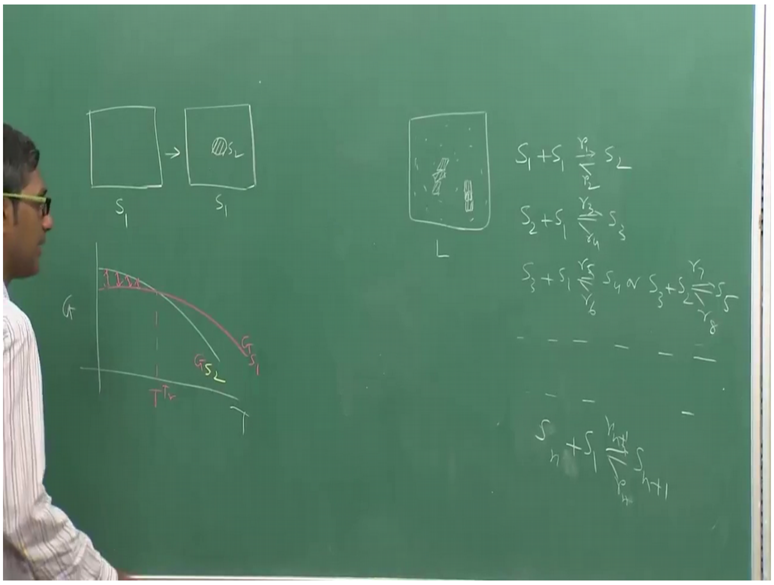

If I have liquid again I am considering liquid because that is easy there are atoms in a whole liquid and whenever few atoms comes together they form a that I have given in the last 2 last lecture that form a cluster and this clusters join together like this or they can join in many other configurations they can join like that also, in many ways and then become a critical size nucleus. So, therefore, in specifically if I want to calculate rate I need to calculate how this clusters are joining suppose I have a mono atomic clusters mono atom means single atom initially 2 mono atomic clusters join together form a diatomic cluster and I should need to k now rate of this reaction that is suppose rate of this reaction is forward reaction is r 1 and r 2 is the backward reactions. So, therefore, the resultant of that will tell me what is the how many of this clusters with 2 atoms will form.

Similarly, S 2 plus S 1 can lead to S 3 S 3 plus S 1 can lead to S 4 or S 3 plus S 2 can lead to S 5 and each of this reaction will have reaction constant. So, similarly so on I can write down and in my critical size nucleus contains n plus 1 atoms suppose; that means S n plus S 1 giving to S n plus 1. Finally, if I want to calculate rate of this nucleation I need to consider a complete chain form this to this, but that is very cumbersome job that is can be done actually that is people have done and as a part of many of this certification courses I will be teach it by this we are not going to discuss that in the literature in class. That is going to take lot of time and also it requires many many mathematical approaches to be discussed.

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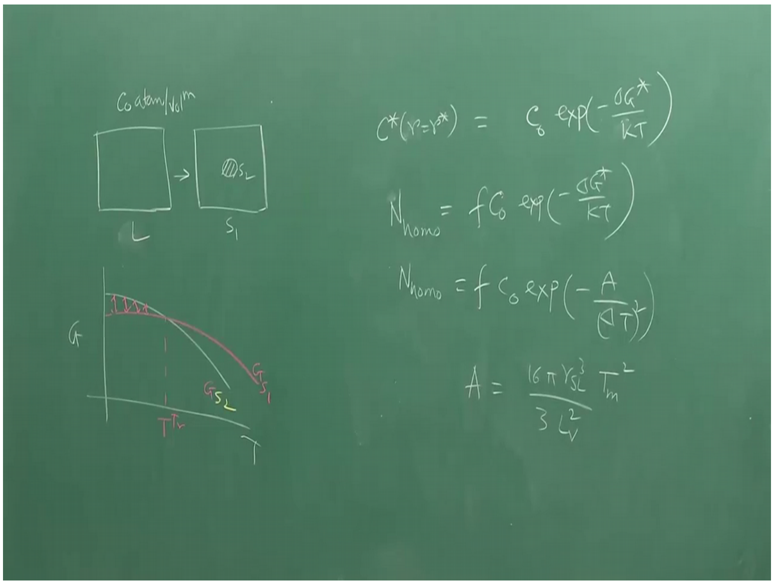

$$C^*(r=r^*) = C_0 \exp\left(-\frac{\Delta G^*}{KT}\right)$$

$$N_{homo} = f C_0 \exp\left(-\frac{\Delta G^*}{KT}\right)$$

$$N_{homo} = f C_0 \exp\left(-\frac{A}{(\Delta T)^2}\right)$$

$$A = \frac{16\pi \gamma_{SL}^3 T_m^2}{3 L_V^2}$$

So, a simplicity let me just tell you that suppose I have liquid again here liquid and I have C 0 atoms (Refer Time: 14:29) for unit volume right yes, I think its reformative volume yes. Now what is the probability that this critical size nucleus that we have seen r star number of nucleus or number of clusters of r star will be formed that is probability is equal to; obviously, this is must be equal to must be proportional to that. But it will also must be proportional to C 0 because initial number of clusters initial number of atoms are the once which will we start the reactions I have I have given you the reactions chain right. The first and foremost thing is S 1 plus S 2 S 1 plus S 1 going to S 2. So, S 1 is nothing, but number of monoatomic clusters; that means, number of atoms present in the liquid, so that is the factor.

Now obviously, if I want to make a nucleus I need to add all your one extra atom right if I the moment r star become r star plus one then it is become a complete its it is a nucleus it is no longer embryo I have a given you that in the last class. So, because all, so that that to happen I need to add only one atom and this addition will depends upon the frequency, frequency of vibration or frequency of collision right. So, I can write down that the homogenous nucleation rate is basically this equal to f C 0 exponential minus delta G star by KT. That f is that frequency vibration frequency collision frequency you can talk many things it depends on vibration frequency depends on the activation energy also because atoms from the liquid we are going to join the solids.

So, therefore, they need to cross an activation barrier that active why they need to cross activation remember in the liquids atoms will have certain potential because liquid atoms are like random they are moving. So, therefore, there is a definite interaction between and the interaction defined as a potential, potential means potential well you can actually draw the energy the potential energy is a function of distance. So, that is the way potential well that potential will tell you the potential energy.

On the other hand solid that this is different right the interaction between the atoms are more stronger and they are actually nicely present in this solid lattice because of this the solid atoms the solid will have different potential and these potential differences will give will be reason for activation energy that potential difference the atom has to cross over to reach from a liquid to solid. So, therefore, f this frequency is most of strong function of the activation available activation requires and activation basically comes with thermal energy part the fire with thermal energy is what is providing it is the energy to cross over that activation potential. So, therefore, S depends on f depends on these aspects these 2 aspects, initially the vibration frequency of the atoms on the activation barrier.

Now, as you know delta G star I also know so therefore, I can write down this one it will be C 0 exponential minus A by delta T square or delta T let me see its will be delta T square it looks like yes this delta T square because delta G star we have seen its 16 pi gamma SL cube 3 this is T m square 1 by T delta T square into L v square. So, that is why actually it is this is A is nothing, but this term. So, it is simply I can write down A is nothing, but A is equal to this.

As you clearly see that homogenous nucleation rate is a strong function of undercool again higher the undercooling higher is the undercool at the nucleation rate. That is because this is in the exponential term this is a basically very funny things f and C 0 are constant most of the cases we have assumed. They are not dependent on the undercooling although they will be actually actual sense, but we assumed for the sake of this is a phase this is a pre exponential term in the books you will find many of the simple books this has this is a pre exponential term is a value obtained 38 39 or 40. On the other hand this term which is the exponential term is has a minus inside the exponential structure and A is a constant why because gamma S l is a constant T m is melting temperature is constant latent heat is a constant. So, therefore, it is basically 1 constant divided by delta T square. And that is that is nothing, but that is nothing, but a funny function.

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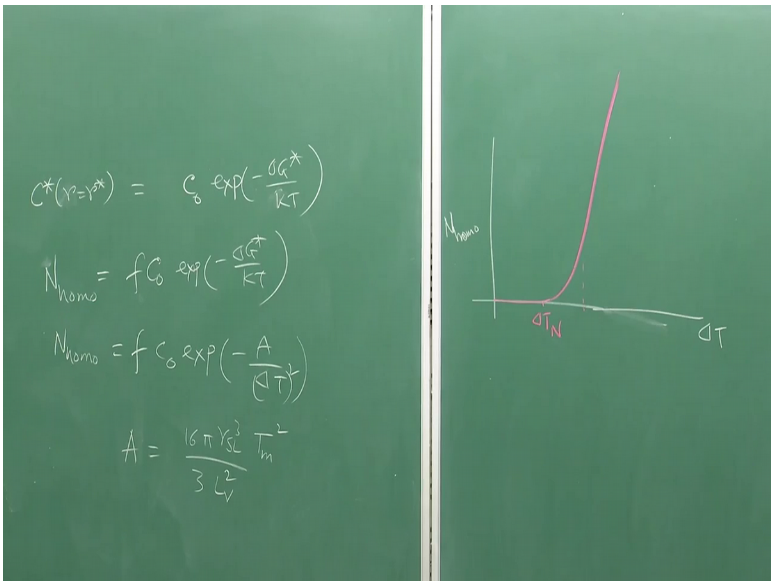

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If I plot that, if I plot n homogenous homo versus delta T there will be no nucleation will have certain value and above this value is a exponential of nucleation will happen. Why? Because this exponential term looks like this because this is a minus remember because it is a minus there is explosion of nucleation and within a small window of nuclea delta T all that nucleation will happen in the liquid.

So, that is what is the how the nucleation rate will depend on the undercooling. So, actually if I will continue the discussion further in the next lecture also about heterogeneous nucleation where will bring in more concepts, so that you understand things better and clearly in phase transformation whether it is a liquid to solid solid to solid or vapor to solid important aspect nucleation and growth especially nucleation is a undercooling. Level of undercooling is what dictates the available energies to the for the system to transformation for transformation.

So; that means, what; that means, all the mathematical formalism which you have seen so far equations they are strongly dependent on delta T either directly proportional with delta T or inversely proportional to delta T or is inversely proportional to delta T square we have seen that. That is mainly because delta T actually plays delta T provides us the driving force or the force for the transformation or the force for the atoms to transform for one parent phase to a product phase that is why. And we can actually bring in different levels of mathematical concept to make you understand how actually all these transformations actually happen all this in a nucleation happens in different way.

So, homogenous nucleation as I said is ideal situation ideal situation means what it does not actually happened in the real sense and that is why we always want to know or (Refer Time: 22:41) with rather one would want to know what happens heterogeneous nucleation because that is more close to the real problems.

In reality we always certify a liquid in a container and container will walls will have certain amount of impurities present either in terms of oxides or in terms of a gas bubble or in a terms of a pure surface like we say (Refer Time: 23:04) mold there will be no normal oxide, but there will be the solid surface. But they will all act as a nucleint that may help in nucleation process and all this formalism needs to be then modified, but to modify this we need to have a basic fundamental very clear and that is the reason in the books or even lectures we are always start with homogenous nucleation and explain all these phenomenon or phenomena in a manner so that you understand. And it helps also for the both you and also instructor to develop a theory in a regular manner.

So, we will see in the next class how we can deal heterogeneous nucleation.