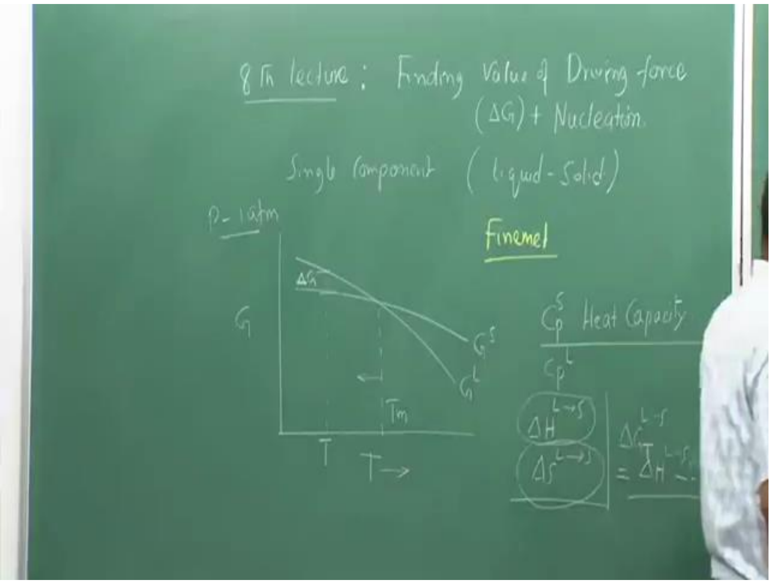
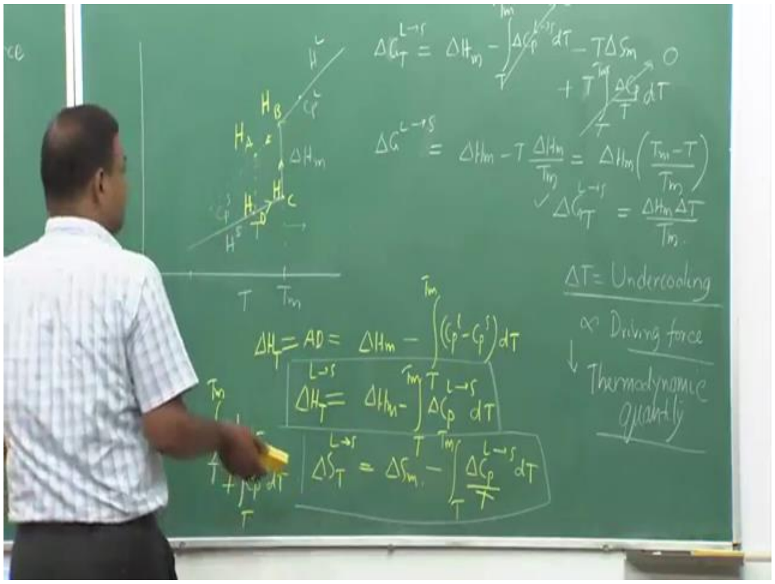
Heat Treatment and Surface Hardening (Part–1)
Professor Kallol Mondal
Professor Sandeep Sangal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur
Lecture Number 08
Finding Value of Driving force (deltaG) Nucleation Single Component (liquid-solid)

(Refer Slide Time: 00:15)



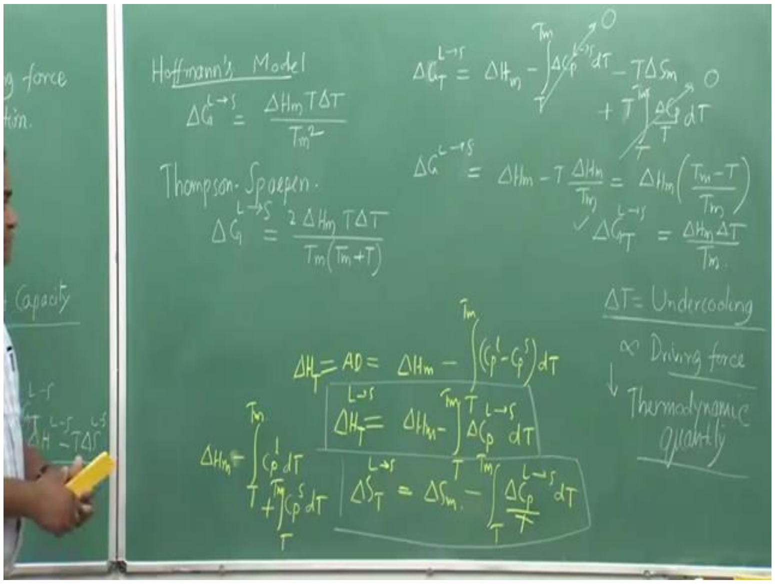


Let us begin eighth lecture and eighth lecture, we will be continuing our discussion on finding value of driving force and then we will start discussion on nucleation. Now in the last lecture, in the seventh lecture we have started from here and then gradually we have moved to this particular expression which is del Gt the temperature at any temperature below melting temperature if I try to find out driving force which is del G liquid to solid, I can express in terms of enthalpy of melting, melting temperature and del T which is the undercooling is nothing but the temperature where we try to find out del G is subtracted from melting temperature.

So all the parameters are known values and they are not complicated values, okay. So we get a very simple expression to find out del Gt. Now when we try to see this value let us see how it can be more defined? How it can be refined? Now we like to see the refinement in terms of more and more better and better approximation for del Cp liquid to solid, since in the beginning while coming to this particular expression, we assume that this values, these two this del Cp liquid to solid the difference in liquid Cp and solid Cp is zero, but that cannot be, so that is a very crude over simplified assumptions.

Now in order to get into more refine value of this, we need to spend almost about three, four lectures. But our intension is to get to the heat treatment part, our intension is to get to the TTT diagram as soon as possible after understanding the basics of thermodynamics we would be content with this, but before that we need to see whether we would be able to content with this particular simplified value. Now there are many people who worked on this particular, in this particular field in order to refine this value, for example there are people like Huffman, people like Thompson-Spaepen , people like professor Ram Chandran or professor B.S Murti, so those people have tried lot of other ways to refine this particular value.

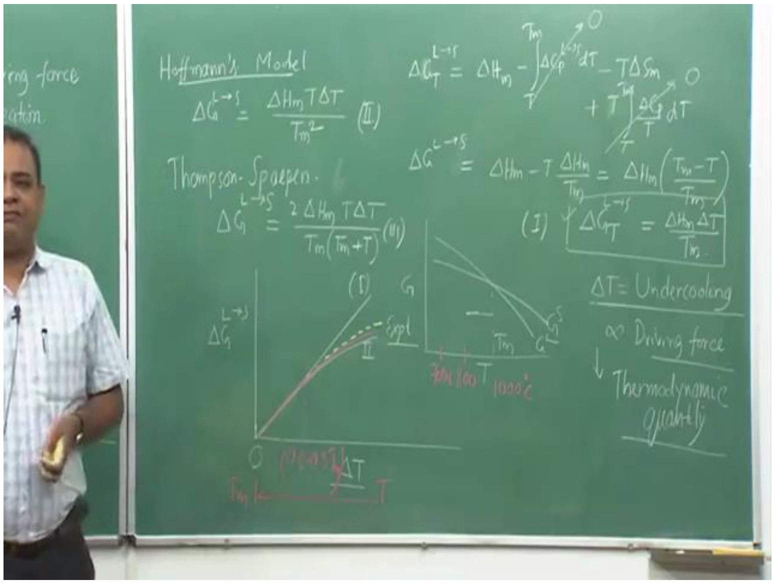
(Refer Slide Time: 04:00)



Now we just look at few simplify few refine expression. So the refined expression for example, if we consider Thomps Huffman, Huffman’s model, let us only look at the expression if I see the expression del G liquid to solid equal to del Hm T del T Tm square, so this is one of those famous expressions which takes more refine treatment to that particular the whole treatment would have seen. And there they have not considered del Cp to be zero, then there was Thomson-Spaepen where they say.

So more complicated expression, but if you see the beauty of those expressions, those are divide of del Cp they have assume some value which are, which is non-zero value and they have done treatment to this whole operation and then they have come up with a (moh) particular expression where you see everything again becomes a measureable, easily measureable quantity del Hm, T, de T is nothing but this del T which is the driving force Tm and here also those terms are common, but only thing is the basically are those expression is different.

(Refer Slide Time: 06:05)



Now if I try to see the variation, let us say, somehow I could calculate the Cp, del Cp which is experimentally found out value when we try to see the liquid to solid transformation I would get a plot where this is del G liquid to solid and this is del T, if we try to plot as a function of del T. Now if I try to see this expression, this expression since del Hm and Tm both are constant for a particular metal, I would get a straight line as a function of del T which is a straight line equation.

And this del T, here it is zero, what does it mean? It means if I try to replicate this same diagram here, this is Gs, this is Gl, then at this point T – Tm is zero, that means del T is zero as we go lower and lower temperature below m Tm, I have incremented del T. Now at the same, if I try to find out experimental variation of del G, if I could find the Cp of liquid as a function of undercooling, I would get a plot like this if I try to plot in terms of, the plot would be let us say something like this, this is my let us say this is my expression 1, this is my expression 2, this is my expression 3. So this is (experi) expression 1, this is experimental. Now if I try to plot this model values del G, the plot would be, if I try to plot this, this is expression 2 and if I try to plot this one, it could be like this. Now interestingly, the only noticeable thing is, until this, this temperature, all those refine calculated value and then also a crudely assumed value, they are matching.

And this value can extend up to 0.2 to 0.3 Tm, why zero what is, what does it mean 0.2 to 0.3 Tm? Let us say if this temperature is 1000 degree Celsius, melting temperature this should be 800 to 700 degree Celsius. So 300 to 200 degree difference below melting point I would get almost same value for del G, even if I use very simple approximation, rather going for that suggest and also you would later see that most of our practical values would be lying in this temperature range.

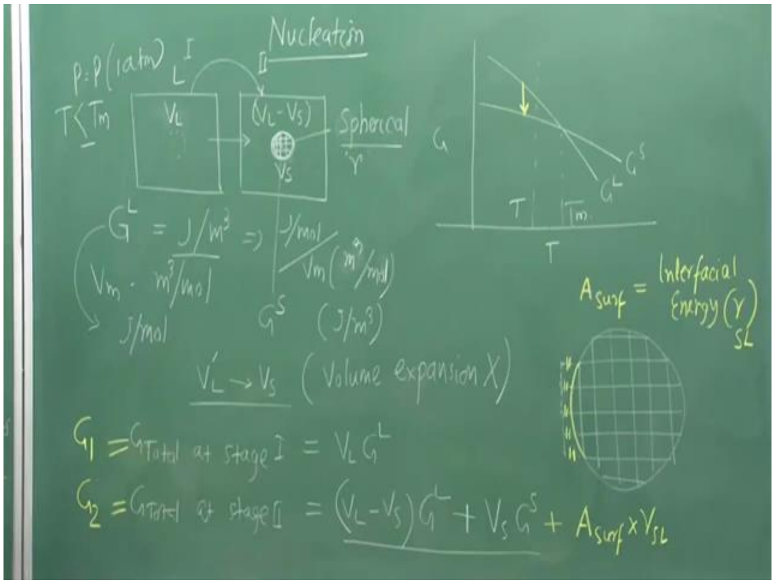
So if I try to plot in terms of temperature, so then this particular temperature which is zero is Tm, so within this range 200 to 300 degree Celsius range from Tm, below Tm we have most of the (experi) most of the reactions over, okay. So that means we do not need such kind complicated expressions, okay we are okay with a simplified expression since we are seeing that within the temperature range where I would be concentrating on would not make any difference even if we use very simplistic approach and engineering does not look at a very refine thing most of the cases.

It just takes a kind of value which would be useful for doing calculations and finding values which will be needed for getting a kind of range of properties specified for a particular application, okay. So we do not need those kind of complicated things, we will be okay with this. So that suggests that even if we take very very simple approximation some time those approximation would have a very very positive effect on our engineering problem solving, okay.

So I think we would be okay with this, we will also do some calculations later on considering this two things you would see that yes it does not make much of difference, okay of course if you go further below the temperature this will start making difference, but we do not need to go to that particular temperature zone, rather than we would be concentrating on this temperature, okay. So that is the contention of doing this particular thing, but of course there is a special importance given to this particular treatment, yes those have a very very scientific values because we do need to find sometimes the actual value what is there.

Now once we found out the driving force, now we need to see whether that driving force, how that driving force is going to affect the actual phase transformation. So now, once we finish discussion on finding value of driving force, let us get to the nucleation part, okay. Now when we talk about nucleation, now we would again consider single component system solid to liquid transformation and let us initially consider simple pure metal solidification, okay.

(Refer Slide Time: 13:10)



And when we do simple solid pure metal solidification, we can have I am just drawing the same plot again, temperature G, now let us say at this particular temperature, I have a solid, okay. So if we have this enclosure and let us say this is a close system at a particular pressure P, okay and which is nothing but 1 atmosphere and if it is at temperature T less than Tm, initially when I take that liquid to that particular temperature, everything is liquid. And let us say the volume of this particular enclosure is nv, nv sorry Vl.

Now in that particular enclosure I will have a situation, there I will form a nuclei which is a small I would say initially it can be considered as a kind of cluster where from liquid it transforms to solid of volume Vs, okay. And it could have different shapes, either it could have spherical shape, or it could have rectangular shape, or it could have cylindrical shape any shape is possible, okay. So initially let us say, let us assume that it is cylindrical, it is, spherical, let us say it is spherical.

So whenever we talk about spherical, so that means it is speri sphere and it will have a radius R, okay. Now that means at that temperature if we keep that liquid of volume Vl, it will make change due to solidification, it will form a solid of radius R and it will have spherical shape.

Now, so now this is a stage 1, this is stage 2 and if it is a liquid, then I can consider a some free energy value of liquid, okay, at that temperature and this free energy value would have unit as joule per meter cube.

Now how would we get this? Let us say if I know the Vm, which is meter cube per mole and initially if this is express in terms of joule per mole, I simply get this by joule per mole divided by Vm, which is mole per meter cube, sorry meter cube by mole. So then I would get joule per meter cube. So that means, it is a volumetric free energy and this also tells something, this volumetric free energy is coming from the volume of the material, so that means, it is considering the energy that is available from a particular volume of material.

Now similarly, if I have solid, so I can consider that is Gs, this is also the unit is joule per meter cube. Now I can calculate what would be the total free energy of this particular close volume, I can calculate the total free energy of this particular close volume and there interestingly the volume of liquid is now Vl – Vs because I have also taken consideration of a solid. And interestingly, I am considering that Vl to Vs whenever this transformation takes place, so let us say this is V prime so that means this volume of liquid, so this volume of liquid is converting to this volume of solid that time I do not consider any volume expansion is nil.

So that means I do not have any volume expansion. So that also makes my treatment easy, so all as we try to find out some try to see some assumption within within the rightness of that particular treatment we have to make those assumption in order to make things simple. So now if we assume that, then so actually my transformation is from this to this. So this is stage 1, this is stage 2 and if you see that stage 1 is entirely liquid, this line and stage 2 I have solid here at the same time some liquid.

Now if I try to find out what is the total free energy, total at stage 1 is equal to Vl Gl, similarly G total at stage 2 is equal to (Vl – Vs) Gl because this is the volume of liquid that is remaining to convert to solid plus this Vs into Gs, now question is does it end there? And another interesting thing this also tells because we are adding it up, the thermodynamic state function we are adding it up it also says that free energy is nothing but the extension properties. Now from there, we stop here, but would it stop here? Now there is one interesting part now, see whenever I am creating a solid as per our phase definition, I am seeing that in this particular (situa) cases everywhere the composition is same.

Here also the composition is same, but the structure is different here, structure is different here because whenever I try to see the solid, that means I am talking about the crystal in solid, so that means they have regular arrangements of atoms and whenever I am talking regular arrangement of atoms, that times there is an interface which separates the regular (inter) regular arrangement of atom zone from a random arrangement of atom zone if we consider liquid atoms are randomly distributed.

That times I do create an interface, fine. Now let us blow it up, this particular section, if I blow it up, this is my blowed part, the sphere. So I do draw all those lattice plains of a crystal, I have drawn those lattice plains. Now if I see and if it is a regular arrangements and if I consider that this length and this length is a two dimensional lattice, this length and this length both are same. Now at some point I do have missing part, for example this is not of the same length of this, so if I extend it then only I get a lattice, okay.

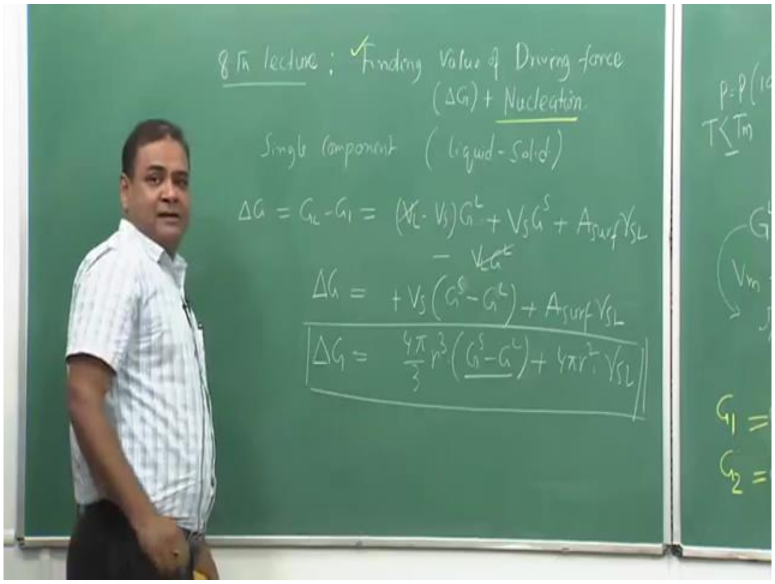
Similarly, here if I extend it then I will get a lattice, if I extend it then I will get a lattice, so these are form. Now here I have created the interface and we have said that the liquid atoms are random, so there is no regular arrangement of atoms over a three dimension in a long range distance. So that means at this place, so this one, this one, this one, this one and this one, see if we consider only this part, these lengths are breaking and whenever I break any arm, what does it mean? It means that I am exciting that particular region.

Now whenever I excite that particular region, that means I am increasing the energy of the system. So that means whenever I have an interface as if I can say that arms are broken and if arms are broken I enhanced the energy so it this particular line increases the system energy. If something increases a system energy, that we can consider as a positive energy, okay. And interestingly this difference in energy is a negative energy and the negative energy is always good because it goes down the energy hill and it talks about spontaneity, the process is possible.

But creating energy, or creating a kind of interface with a higher energy is not a spontaneous process, we are breaking it off, so that means this reacts against to this free energy lowering because it in purse positive energy and this particular energy, positive energy is around the interface and this interface (hais) having some area which is let us say Asurf, that means surface area, okay, and along that surface area, we have a energy and energy we call it interfacial energy, which is we call it gamma.

And this gamma is different than the gamma we consider in case of FCC. So in order to make difference with the gamma, FCC gamma in iron which is called austenite or FCC gamma in alpha aluminum which is nothing but the aluminum single phase alpha we put it as Sl in case of solid liquid. So that means, whenever I form a solid, I do create an interface and I do have interfacial energy which tries to increase the system energy, okay. So now here the story does not end, because since I have create an interface, I do have to consider the interface energy part, the total interfacial energy which is As into gamma Sl.

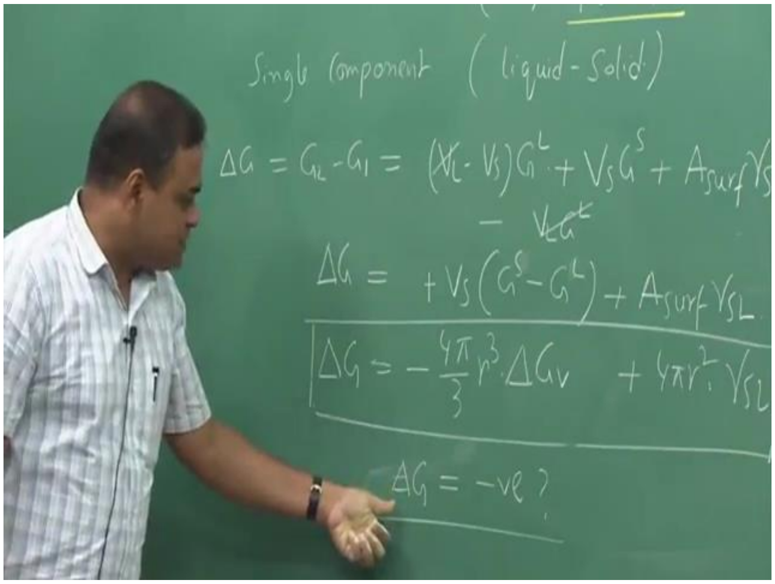
(Refer Slide Time: 27:05)



So that means, at stage 2 I have these many energy terms. Now if I consider to be G1 and this is G2 which is final this is initial, I can find out what is the difference in energy, okay. So in order to find that difference in energy, so del G which is the difference in G2 – G1 equal to (Vl – Vs) Gl + Vs Gs + A surf gamma Sl – Vl Gl. So then I would see that this term and this term goes out. Now this term and this term goes out, so I would be left with Vs – Gl – Gs or I can say Gs – Gl + Asurf gamma Sl. So this is del G of this, so now this is a very very important expression.

Now if we consider a spherical, spherical particle forming in the spherical solid forming in the liquid, this should be 4 pi 3 r cube (Gs – Gl) + 4 pi r square gamma Sl. Now this is extremely extremely important expression, and now you see this is what? This is nothing but del Gv, so this is 4 pi so I can convert this particular term.

(Refer Slide Time: 29:10)



I can write this particular term in the form of del Gv. And this del Gv, there is a negative term inherent to it I can take this negative term out. So this is my expression where I will be working on, rather we will see that from this we get an expression for the nucleation, okay.

So this is expression and also you see this del G is the difference between stage 1 and stage 2 and this del Gv is the difference between liquid to solid transformation. So that means this is my driving force and this whether, whether that solid would form or not because this is a positive energy, this is a negative energy finally where the system would go for this transformation would be decided by the negative value of this. So we finally have to see what we have to see whether del G going to negative value.

So that will tell me that whether transformation would actually take place or not, now we have to that whether del G, this del G goes to negative in order to (ham) have transformation. Because this tells me that there is a spontaneity but this term is acting against to this and this term has to (sup) over overcome this particular positive energy term, finally it will create the condition that whether del G is negative and that time we will have actual nucleation. Let us stop here, we will continue this discussion in our next couple of lectures. Thank you very much.