Heat Treatment and Surface Hardening (Part–1)

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Lecture Number 24

Nucleation Rate - 1

So in this lecture we will begin our analysis of nucleation rate and and to keep things simple, we will look to begin with nucleation rate in pure component systems.

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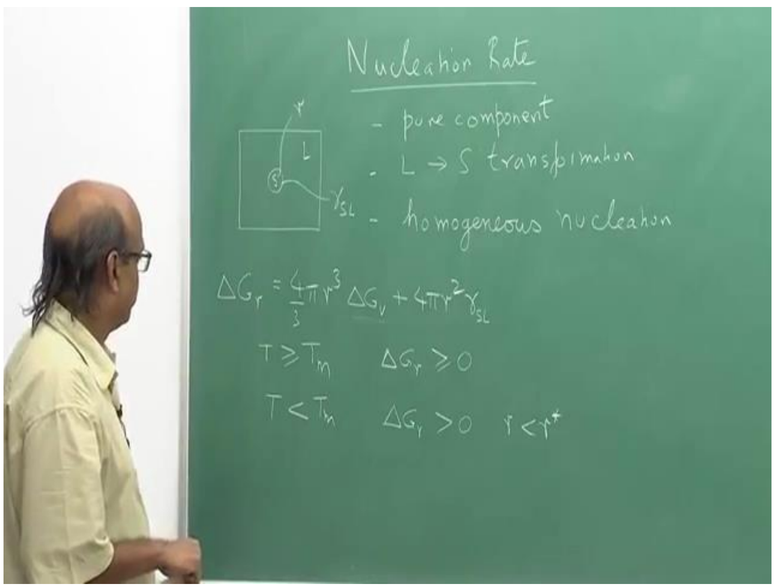

We will look nucleation rate in situations where a solid is nucleating, so we are looking at liquid to solid transformations such as nucleation of ice in water, nucleation of a or solidification of metals where a nucleation of a pure metal solid is taking place and we will look at nucleation rate concerned in this lecture with homogenous nucleation.

So homogenous nucleation as you have been told repeatedly that to begin with you have a liquid and a solid nucleates of a certain radius r and there is a associated with it a surface energy of the solid liquid interface gamma Sl and just to write down a couple of equations for reference the free energy change when a solid of radius r nucleates within the liquid is given by the volume of this nucleus 4 by 3 pi r cube multiplied by the change in the free energy of the bulk per unit volume delta Gv + the surface area of the nucleus 4 pi r square multiplied by the solid liquid interface energy gamma Sl.

I have just a little change that I have used the subscript r on the left hand side of this equation to show that the overall change in free energy is going to be a function of the size of the of the nucleus that is nucleated. So that I am calling it as delta Gr. If we examine this, let us first look at delta Gv we can look at for temperatures greater than or equal to the transformation (te) temperature or the melting point of the solid of the pure component. So T greater than or equal to Tm we would have that overall change in free energy whenever a nucleus forms or a cluster forms a cluster of atoms or cluster of molecules form delta Gr is going to be always be greater than or equal to 0.

In fact it will be equal to 0 only at T is when the temperature is equal to Tm or the transformation temperature, while for temperatures less than the transformation temperature so T less than Tm delta Gr would be greater than 0 for the size of the nucleus r less than r star, in fact we are only interested in analyzing the formation of a nucleus up to the critical size of the nucleus r star. So, in this kind of a situation what we are trying to say is that whenever there is a liquid at whatever temperature, there are always cluster of atoms or a cluster of molecules are coming together in a crystalline form which is the crystal structure of the solid.

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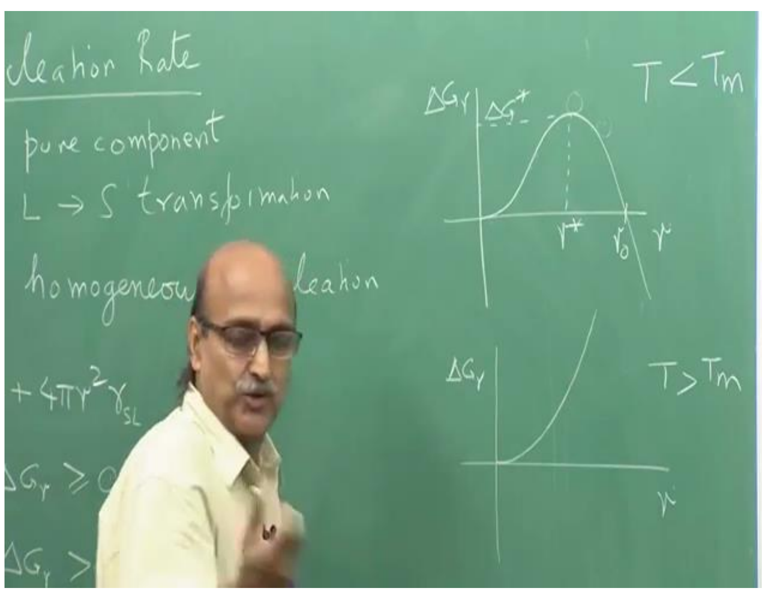

But depending on the temperature, that nucleus could be stable or unstable and that if you recall if I plot delta Gr versus r, I have a function like this or a curve like this where it goes through a peak which is the critical size of the nucleus and corresponding to critical size there is a critical free energy delta G star. Then there is a size if I can denote it as r0 beyond that the change in the free energy is negative. So if a nucleus is formed anywhere in this region, then that nucleus will be unstable and will be tend to dissolve back.

If the nucleus is formed in this region, then it becomes stable and becomes part of the solid. And if the nucleus is formed of a critical size, then that nucleus is what we call in unstable equilibrium and it can either fall back on left hand side and dissolve or it can go on the right hand side and become a stable solid. This is for temperatures less than Tm. For temperatures greater than Tm if I were to plot delta Gr versus r, then we would simply have a monotonically increasing change in free energy with just suggest that whatever nucleus forms will always be unstable and it will dissolve back.

Now how are these nuclei forming? They are just forming by chance when some atoms or molecules come together and they form a cluster which has a structure same as a solid if that nucleus is unstable in this situation or in this situation, then that nucleus will tend to dissolve back. Now the one question that one would like to address and that is, what kind of a density of nuclei I can expect for a given temperature and for a given size of the cluster.

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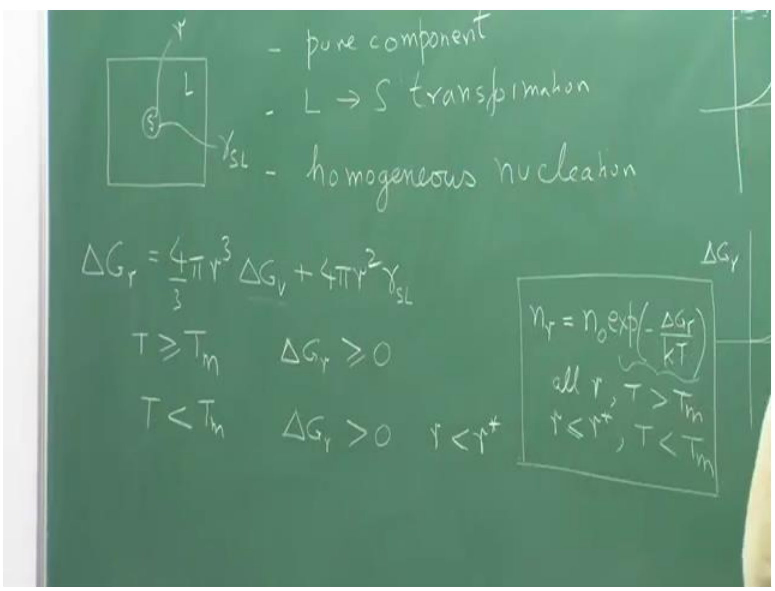

This is given by the Maxwell Boltzmann statistics and the relationship for this can be written like this that number of nuclei formed of size r nr in a unit volume is given by n0 total number of nucleating sites per unit volume multiplied by an exponential function of delta Gr which is exponential of minus delta Gr divided by kT. If I look at this expression, this exponential part is like a probability of a nucleus of size r forming.

This multiplied by number of such potential sites where such a nucleus can form gives you an estimate of the number of nucleus that one can expect in a unit volume. This relationship is valid for all r for temperatures greater than Tm, while it is valid for size less than or equal to the critical size for temperatures less than Tm. Now what I would like to do now is just to get an idea that given a system what kind of a density of nucleus one can expect for different size of nuclei at some given temperature.

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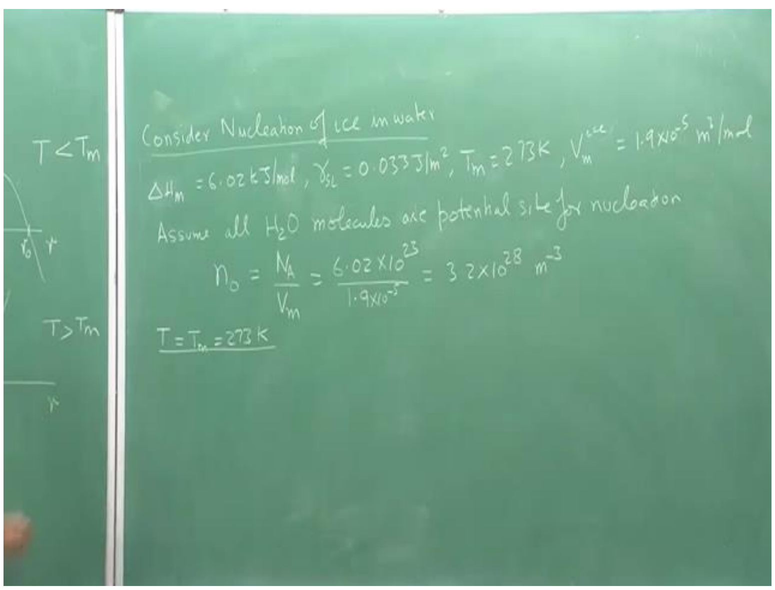

So let us take a system for this, so consider nucleation of ice in water, this I had also taken as an example in the earlier lecture. Let us I will just put down the relevant values the change in the free bulk free energy per unit volume is 6.02 kilo joules per meter cube. The interfacial free energy gamma Sl is equal to 0.033 joules per meter square of course Tm for water is 273 k or 0 degree centigrade. And the molar volume of ice is 1.9 into 10 to power minus 5 meter cube per mole, and this excuse me this should be delta Hm the change in enthalpy in fact per mole, so 6.02 kilo joules per mole.

Now let us assume that all H_2O molecules are potential site for nucleation, therefore the number of potential sites per unit volume n0 in this relationship can be written as the Avogadro number divided by the molar volume. So Avogadro number if I take as 6.02 to 10 to power 23 divided this by the molar volume with for ice which is 1.9 into 10 to power minus 5 meter cube per mole, this gives me 3.2 into 10 to power 28 potential nucleating sites per meter cube.

Now let us try and see what kind of estimates for nr, I get for different size of the nuclei nucleating at a specific temperature and let us also take consider this at the melting point itself. So let us take the temperature to be equal to Tm which is equal to 273 degrees kelvin. So at this temperature what I need to do? First I need to calculate the change in free energy for a given size of the nucleus r.

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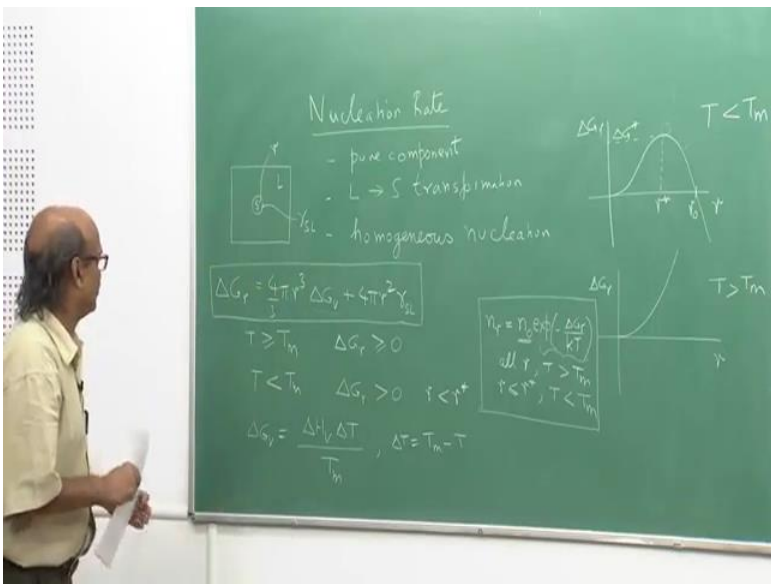

So delta Gr which is given by this relationship, but at the melting point delta Gv would be 0, remember that delta Gv is the change in enthalpy per unit volume delta Hv multiplied by delta T divided by Tm.

Since we are going to look at nucleation at the melting point itself 273 k which means delta T which is Tm minus T and hence delta T is zero, therefore delta Gv would be 0. So this term we need not consider and I can write delta Gr to be equal to then simply 4 pi r square gamma Sl.

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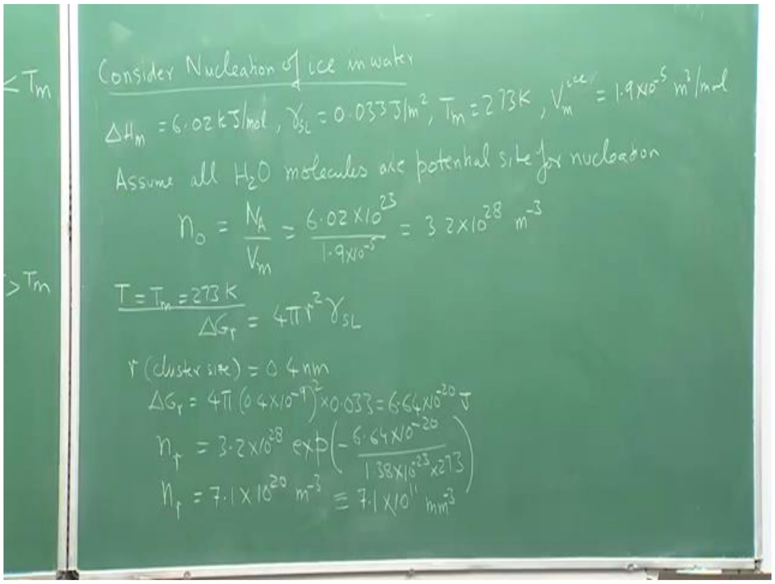

So let me consider now for example let us consider a nucleus or a cluster size to be 0.4 nanometers. So let us take r the cluster size of molecules of H2O this r to be equal to let us say 0.4 nanometers and let us see what kind of an estimate I will get for the expected number of nuclei to form at any instant in a unit volume.

So for this, first let us calculate for 0.4 nanometers delta Gr which is 4 pi times r which is 0.4 into 10 to power minus 9, to convert this to meters square multiply it by gamma Sl and gamma Sl is 0.033 joules per meter square, so 0.033 this gives me a value of 6.64 into 10 to power minus 20 joules. So using this, then nr the density of expected nuclei at this temperature of 273 k would be n0 which 3.2 into 10 to power 28 times the exponential coming from this relation minus delta Gr which is 6.64 into 10 to power minus 20 divided by kT which is 1.38 into 10 to power minus 23 joules per kelvin that is the Boltzmann constant k multiplied by the temperature which is 273.

If I solve this, I get nr to be 7.1 into 10 to power 20 nuclei in (met) in one meter cube of the liquid, let me write this per millimeter cube, so in 1 millimeter cube of the system I will have 7.1 I just have to multiply this by 10 to power minus 9 to give me 7.1 into 10 to power 11 per millimeter cube. So just in 1 millimeter cube of the system at a temperature of 273 k I can expect order of 10 to power 11 number of nuclei of size 0.4 nanometers.

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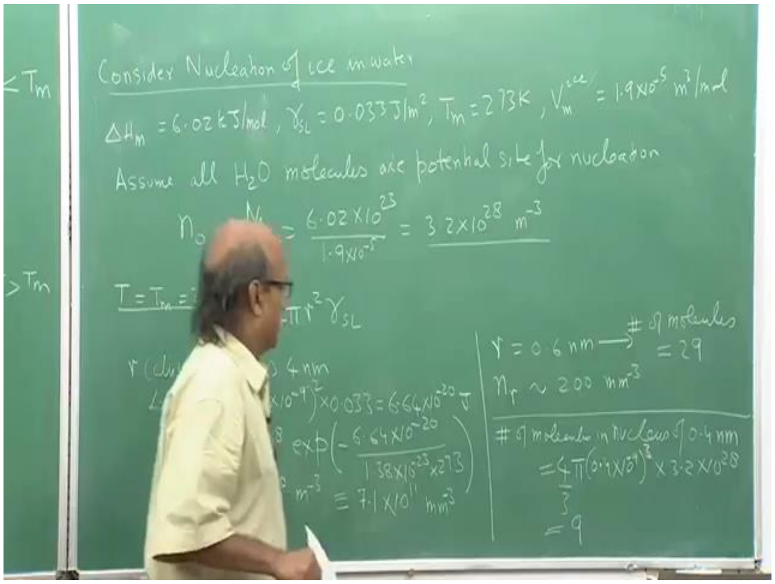

Now let us examine what would happen if I let us say try to find out how many nuclei I can expect if I change the size to 0.6 nanometers, so let us consider the size to be 0.6 nanometers, then if I go through this calculation again instead of 0.4 I will put 0.6 here and I get I will get some delta Gr, put that delta Gr in the exponential relationship for nr and compute, I will get nr to be the order of just 200 per millimeter cube. So 1just by a small change in the size of the nucleus from 0.4 nanometers to 0.6 nanometers the density of nucleus goes down from an order of magnitude of 10 to power 11 to just three orders of magnitude in 1 millimeter cube.

So this shows how sensitive the number of nuclei would be as a function of size. So in fact we can also calculate for example if I have 0.4 nanometer as a size, how many molecules of H2O do I expect in 0.4 nanometer radius nucleus. So if I calculate that so number molecules in nucleus of 0.4 nanometer radius that would be simply in fact I will leave this in a way a problem for you to workout the volume of the nucleus and multiply this by the number of molecules per unit volume. Now how many what is the number of molecules per unit volume? Well it is just an zero itself 3.2 into 10 to power 8 28 per meter cube.

So all I have to do then is simply multiply 4 pi 0.4 into 10 to power 9 square, this is the sorry 4 by 3 pi r cube, this is the volume of the nucleus multiplied by 3.2 into 10 to power 28 and this will give me the number of molecules s only nine. So there are only nine molecules in a nucleus whose size is 0.4 nanometers if I change the size to 0.6 nanometers in this case number of molecules in a nucleus turns out to be or the order of 29.

So all what we have seen here is that as the size is increasing, obviously the number of molecules have to go up which also means that for the nucleus of 0.4 nanometers only nine molecules have to come together to form a crystalline solid which is much more probable as compared to if 29 molecules have to come together to form a solid. Similarly if I increase the size even more, the number of molecules required to form that nucleus would be even more and hence the number of the probability would be even lower. So as the probability goes down, obviously the density of nuclei that we can expect would also reduce.

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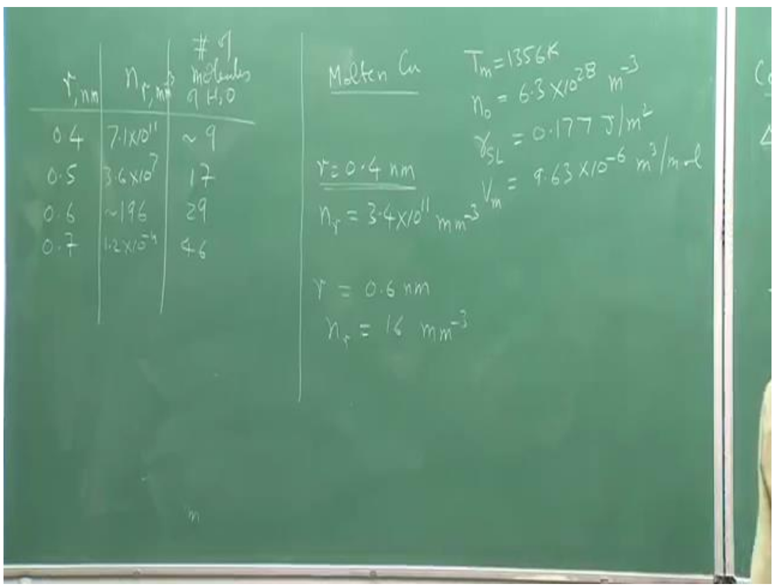

So if I just put down some numbers for you to look at for different size of the nuclei, so size nr and number of molecules of H2O r is in nanometers, this is per millimeter cube. So for 0.4 as we have seen nr is 7.1 into 10 to power 11 and or 9 molecules forming the nucleus, if I change the size to 0.5, this is 3.6 into 10 to power 7 17 molecules forming the (co) nucleus 0.6 as we have already calculated, it is the order of 196 29 molecules forming the nucleus, if I go to 0.7 nanometers size, then the size become or the nr the density becomes 1.2 into 10 to power minus 4 and 46 molecules coming together.

In this particular case, as you can see for 0.7 nanometers you will not find even one nucleus in one millimeter cube or the system. Of course if given enough time, a nucleus would eventually form, but it will take a much longer time and that would depend on at what rate the nuclei are forming. Just to put few more numbers, suppose I want to take molten copper.

For molten copper Tm is 1356 kelvin, n0 turns out to be 6.3 into 10 to power 28 potential sites per meter cube or so many number of copper atoms per meter cube gamma Sl is 0.177 joules per meter square and the molar volume is 9.63 into 10 to power minus 6 meter cube per mole. If I calculate let us say for r is equal 0.4 nanometers, then nr is 3.4 into 10 to power 11, for r equals 0.6 nanometers nr is only 16 in one again this is per millimeter cube.

So again, what we have done is we have shown one is the sensitivity of the number of nuclei that would be present for as a function of size, so as size increases the number of nuclei that are expected would rapidly reduce and this is going to play an important role when we consider in a next lecture the rate of nucleation in a quantitative manner, thank you.