Heat Treatment and Surface Hardening (Part–1)
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Lecture Number 28
Maximum nucleation rate for heterogeneous nucleation

See in the last lecture we were talking about the critical undercooling and for nucleation for a measurable nucleation rate and the undercooling required at which the nucleation rate is maximum. And we had estimated that for nucleation of ice in water the critical undercooling required for homogeneous nucleation of ice is of the order of 42 degrees below its melting point.

Now our everyday experience tells us something else, that ice very easily forms at our homes in our refrigerators at a very low undercooling. The undercooling could be low as 5 or 6 degrees or even in some cases 15 degrees. So how does that happen indication of that has already been given to you in an earlier lecture by professor Mondal, that homogeneous nucleation could be difficult however nucleation can also take place through the heterogeneous route.

And heterogeneous nucleation you have already learned where a nuclei forms on another substrate for example a mould wall in solidification it could form on impurities, inside the material or inside the liquid. And an example of how it forms just to recall what has been done earlier.

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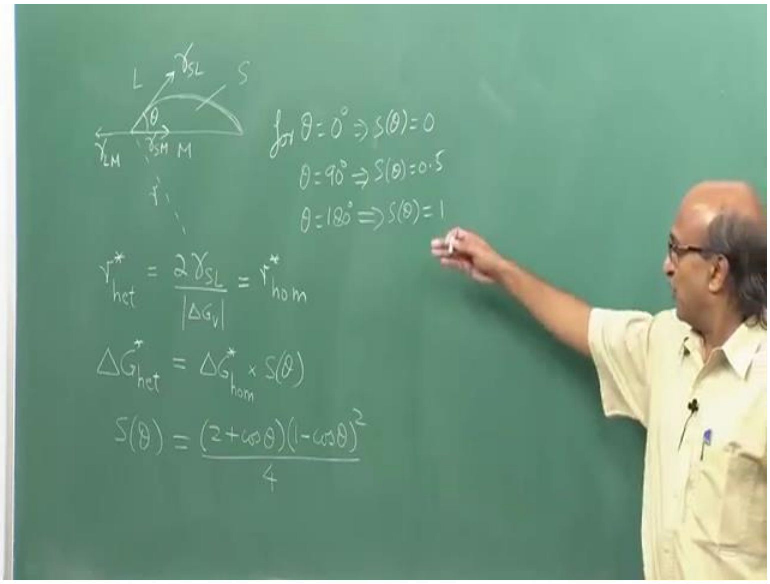

Instead of a spherical nucleus forming now on an on a foreign surface. For example a mould wall a spherical cap forms rather than a sphere in the case of homogeneous nucleation. So this is my spherical cap of a certain radius r and if I look at the surfaces involved here. This is my mould wall, this is the solid that forms and out here is the liquid. As a result the surfaces that are involved that is a surface tension between the solid nucleus and the mould wall gamma SM. There is a surface tension between the liquid and the mould wall gamma LM and then there is of course the interfacial surface energy between the solid liquid interface gamma SL.

Now what would be the exact shape of this nucleus would (wo) would be determined by the balance of all of these surface tensions and once you balance them one will find that there is certain angle theta which is called the contact angle. So depending on now on the value of theta the shape of the nucleus is determined whether it is going to be a very thin spherical cap or it is going to be a sphere or it is going to be a semicircular shape.

Now when we do we determine what is the critical size for such a nucleus one gets exactly the same expression as one got for homogeneous nucleation. So for critical size of the heterogeneous nucleus one simply gets two times gamma SL upon delta GV, which we had found the same expression for homogeneous nucleation as well the critical size. Similarly delta G star heterogeneous that is the free energy of the critical size nucleus at this case is also related to the homogeneous free energy in the case of the homogeneous nucleus of critical size delta G star hat is equal to delta G star homogeneous multiplied by a shape factor S theta.

And the shape factor S theta was also determined in an earlier lecture which is 2+Cos theta times 1-Cos theta square upon 4. So clearly the magnitude of the energy barrier delta G star het is going to be a very strong function of theta. And let just quickly see a few theta values. For example for theta is equal to 0 degrees S theta is equal to 0, what this means is that the barrier completely disappears.

There is no energy here required and nucleation would occur very easily. For theta is equal to 90 degrees if I plug into this equation I will get S theta to be equal to half. So the energy barrier then in this case is half the energy hill in the case of homogeneous nucleation. For theta is equal to 180 degrees S theta is equal to 1. Basically we have reduced it down to the heterogeneous case what do this theta value mean, theta is equal to 0 degrees essentially means that the surface is completely wetted the external for example the mould wall is completely wetted by the liquid.

For theta is equal to 90 degrees the wettability reduces, for theta is equal to 180 degrees it becomes non wettable. So therefore existence of let us say a substrate or a impurity particle which is non wettable would have no effect on the nucleation and the nucleation rate.

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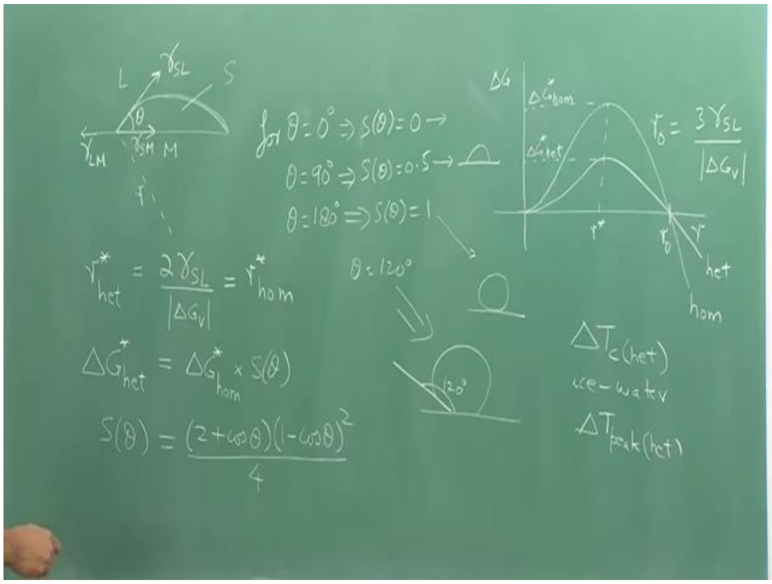

Now let us look at it if I plot delta G versus size of the nucleus for the homogeneous case we have seen that the plot is like this with the critical size r star and delta G star homogeneous as the critical free energy of the critical size. So this is the homogeneous case. In the case of heterogeneous nucleation the energy hill or the barrier or the height comes down so this becomes delta G star hat and this curve is for the heterogeneous nucleation. So the point to be noted is that the size for the two nuclei are the same whether r star for heterogeneous or homogeneous. But and they also meet at the same point where delta G0 and that size we had earlier denoted as r0. And in fact this r0 is going to be 3 times gamma SL upon delta GV.

You can compare this with r star which was 2 gamma SL upon delta GV. This one is 3 gamma SL upon delta GV for both homogeneous as well as the heterogeneous case. If I look at the shape of the nuclei for the different this thing, this completely spreads out so it is a flat no shape. This would give me a semicircular nucleus and this of course even though the substrate is there it produces a complete sphere.

In between 90 degrees and 180 degrees for example theta is equal to 120 degrees the shape of the nucleus that forms on the substrate could be something like this where the angle this angle is 120 degrees. So really heterogeneous nucleation would help us when theta is more than 90 degrees. And in fact closer it is to 30 degrees easier it would be for nucleation to start. Infact this thing is used while casting inoculants are added to produce lots of nuclei to produce fine gain structure.

So if you can produce large amount of nuclei in the belt then you can produce fine grained structures. Now let us do a little bit of a calculation now as to what would be the critical undercooling for the heterogeneous case and compare it with that we had obtained in the earlier lecture for the homogeneous nucleation. So we will do it for the system of ice water system again so that we are able to compare with what we have done earlier.

Similarly I would also like to look at peak what at what undercooling the peak in nucleation is there and compare it with the case of homogeneous nucleation. So let us do this quick calculation.

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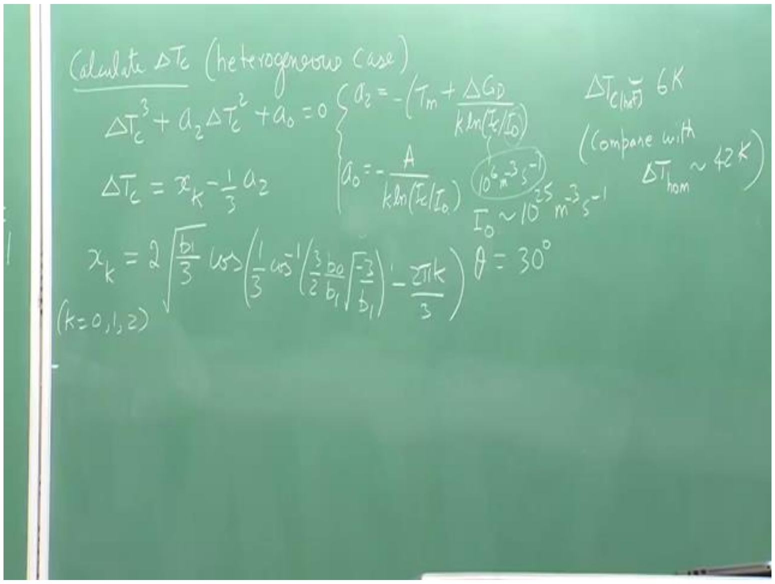

Calculate ΔT_c (heterogeneous case)

$$\Delta T_c^3 + a_2 \Delta T_c^2 + a_0 = 0 \quad \begin{cases} a_2 = -\left(T_m + \dfrac{\Delta G_D}{k\ln(I_c/I_0)}\right) \\ a_0 = -\dfrac{A}{k\ln(I_c/I_0)} \end{cases}$$

$$\boxed{10^6 m^{-3} s^{-1}}$$

$$I_0 \sim 10^{25} m^{-3} s^{-1}$$

$$\Delta T_c = x_k - \frac{1}{3} a_2$$

$$x_k = 2\sqrt{\frac{b_1}{3}} \cos\left(\frac{1}{3}\cos^{-1}\left(\frac{3}{2}\frac{b_0}{b_1}\sqrt{\frac{-3}{b_1}}\right) - \frac{2\pi k}{3}\right)$$

$(k = 0, 1, 2)$

$\theta = 30°$

$\Delta T_{c(het)} \simeq 6K$

(Compare with $\Delta T_{hom} \sim 42K$)

So first let us calculate delta TC, the critical undercooling at which measurable nucleation takes place. Heterogeneous calculate delta this for the heterogeneous case. If you recall we had written this cubic delta TC cube, well delta TC is the critical undercooling, a2 delta TC square + a0 is equal to 0. Earlier I had written I think delta T but now I am just simply writing delta TC it is the same thing, where a2 is equal to – Tm + delta GD upon Kln IC upon Inot, where IC is the critical nucleation rate or the measurable nucleation rate which we have been taking as 10 to power 6 per meter cube per second inverse.

Inot will talk about a little later wha what should be the value of I0. Similarly if I look at a0 this is the constant A upon Kln(IC upon I0) and the constant A is also you can go back to the earlier lecture that this is going to it is a function of the change in enthalpy change in the undercooling etc.

Then to solve this we had said that we can do this substitution delta TC is equal to xK minus one third a2 and xK is equal to 2 square root b1 by 3 Cos(1 by 3 Cos inverse (3 by 2 b0 upon b1 square root -3 upon b1) this bracket close let me just remove this from here and write it a little up and here I will let me complete this, this is something I had written in the last lecture so you can just go back to this lecture.

For this is for K equals 0, 1, and 2. And we pick out that value of K, for which ff which is of , which is a feasible value for delta TC. Now when I do this calculation for ice water system we already know what the values for various quantities in that in terms of the solid liquid interface energy, in terms of the enthalpy change, etc. Those values are already been done several times.

I will take I0 what is now I0, I0 as you recall is a function of the density of nucleation sites the lattice vibration frequency. It is a function of the number of atoms that are surrounding a critical nucleus. And it is also a function of probability of a successful jump. Now I0 everything else is same but in the case of heterogeneous nucleation the nucleation site the site density would be quite different from the homogeneous nucleation case.

In the case of the homogeneous nucleation we had basically taken every atom as a site for as a site of nucleation. Here it is going to be dependent on what is the density of the heterogeneous site. So let us assume value which is quite particle in many cases that Inot is 10 to power 25 per meter cube per second. So with I0 is this with IC is this, this is the measurable nucleation rate this is what I0 is substituting it in this view obtain a critical undercooling of abb approximately 6 degrees kelvin.

That is 6 degrees below the melting point or 6 degrees below 0 degree centigrade. Compare this, so this is for the heterogeneous case and here I forgot to mention that the the the sites on which ice was is would nucleate the contact angle with that theta has been taken as 30 degrees. So it is a very wettable site it is what we can call in case of water as a hydrophilic site.

Compare this with our calculation in the previous lecture so compare with delta T homogeneous as the order of 42 K. Huge difference when you have a heterogeneous sites available. From an undercooling of 42 K we go down to an undercooling of 6 K and that is why ice forms very easily in our refrigerator. A similar calculation one can also do for the at what undercooling the peak in the nucleation occurs.

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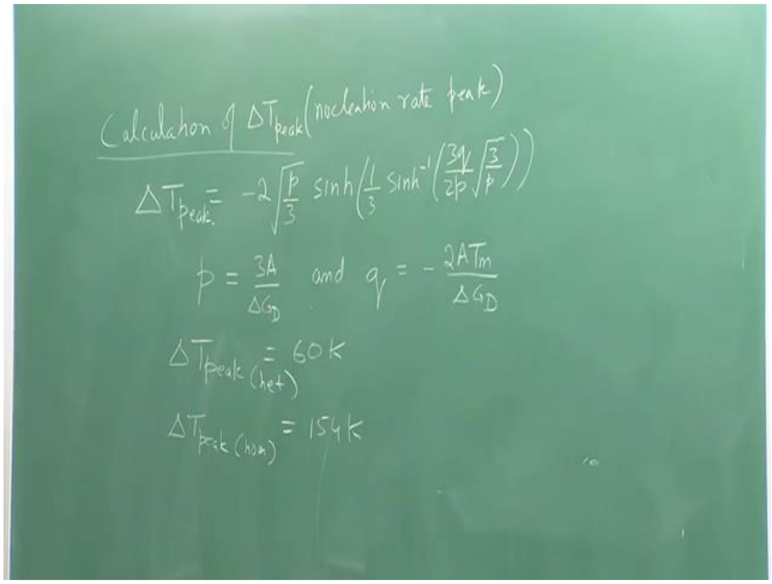

Calculation of ΔT_{peak} (nucleation rate peak)

$$\Delta T_{peak} = -2\sqrt{\frac{p}{3}} \sinh\left(\frac{1}{3}\sinh^{-1}\left(\frac{3q}{2p}\sqrt{\frac{3}{p}}\right)\right)$$

$$p = \frac{3A}{\Delta G_D} \quad \text{and} \quad q = -\frac{2AT_m}{\Delta G_D}$$

$$\Delta T_{peak\,(het)} = 60\,K$$

$$\Delta T_{peak\,(hom)} = 154\,K$$

And in order to do that let me just write down the relation for that as well. So calculation of delta T sub p (nucleation rate peak) or a maxima in the nucleation rate. So if I do this delta T sub p can be written as -2 square root of p by 3 Sin hyperbolic let me write this as peak so that one does not confuse this p with this p so 2 square root p by 3 Sin hyperbolic 1 by 3 Sin hyperbolic inverse 3q upon 2p square root 3 upon p.

Where p is 3A upon delta GD and q is -2ATm upon delta GD we plug in the various values for the ice water system and one gets the value for the peak in undercooling at peak in nucleation rate at an undercooling delta T peak as the order of 60 kelvin. So we get a so essentially from 6 kelvin onwards nucleation rapidly increases beyond 6 K it reaches a peak at 60 K and beyond which it will start to drop.

So this is for heterogeneous and just to compare it delta T peak from previous lecture in the homogeneous case we have obtained a value of the order of 154 K. So everything has been shifted to higher temperatures closer to the transformation temperature for the case of heterogeneous nucleation in the nucleation of ice where the contact angle has been taken to be 30 degrees.

Now what I will do very quickly is I will just go back to my spreadsheet and let us see how these curves shift when we introduce heterogeneous sites.

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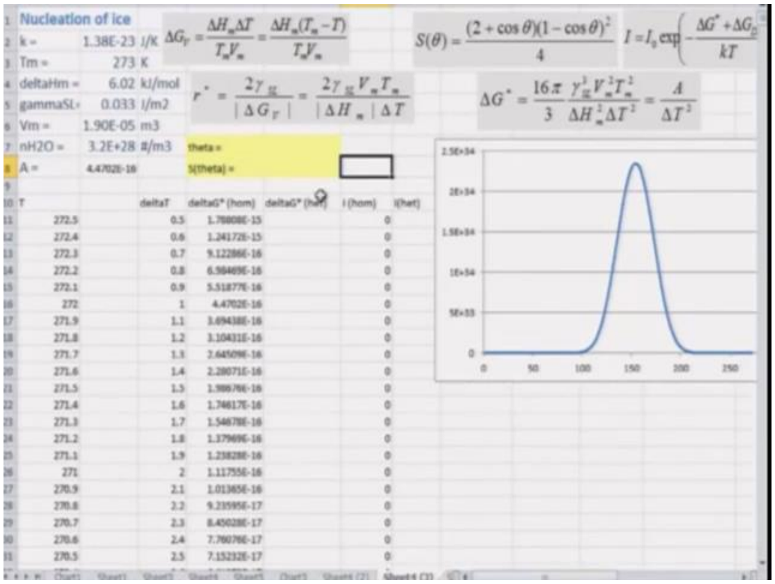

Nucleation of ice

k = 1.38E-23 J/K
Tm = 273 K
deltaHm = 6.02 kJ/mol
gammaSL= 0.033 J/m2
Vm = 1.90E-05 m3
nH2O = 3.2E+28 #/m3
A = 4.4702E-16

theta =
S(theta) =

$$\Delta G_V = \frac{\Delta H_m \Delta T}{T_m V_m} = \frac{\Delta H_m (T_m - T)}{T_m V_m}$$

$$r^* = \frac{2\gamma_{SL}}{|\Delta G_V|} = \frac{2\gamma_{SL} V_m T_m}{|\Delta H_m| \Delta T}$$

$$S(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

$$I = I_0 \exp\left(-\frac{\Delta G^* + \Delta G_D}{kT}\right)$$

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma_{SL}^3 V_m^2 T_m^2}{\Delta H_m^2 \Delta T^2} = \frac{A}{\Delta T^2}$$

T	deltaT	deltaG* (hom)	deltaG* (het)	I (hom)	I(het)
272.5	0.5	1.78808E-15		0	
272.4	0.6	1.24172E-15		0	
272.3	0.7	9.12286E-16		0	
272.2	0.8	6.98469E-16		0	
272.1	0.9	5.51877E-16		0	
272	1	4.4702E-16		0	
271.9	1.1	3.69438E-16		0	
271.8	1.2	3.10431E-16		0	
271.7	1.3	2.64509E-16		0	
271.6	1.4	2.28071E-16		0	
271.5	1.5	1.98676E-16		0	
271.4	1.6	1.74617E-16		0	
271.3	1.7	1.54678E-16		0	
271.2	1.8	1.37969E-16		0	
271.1	1.9	1.23828E-16		0	
271	2	1.11755E-16		0	
270.9	2.1	1.01365E-16		0	
270.8	2.2	9.23595E-17		0	
270.7	2.3	8.45028E-17		0	
270.6	2.4	7.76076E-17		0	
270.5	2.5	7.15232E-17		0	

So this is what you are seeing right now in the spread sheet is what was done in the last lecture and we are just continuing from there the last lecture for different values of undercooling delta T in this column C we had calculated the critical free energy for the homogeneous nuclei of critical size and we had calculated the nucleation rate I homogenous in column F.

Now in we want to compute the variation of the nucleation rate for the for the heterogeneous case how it varies as a function of undercooling delta T. So in order to calculate I het, let us first calculate delta G star heterogeneous which means I need to first get the shape factor for a given value of theta. So let us say that we have been just now on the board we did for 30 degree, so let us keep our angle to be 30 degrees.

For which let us calculate the shape factor S theta here so here I will write down the formula for S S theta which is given as well over here right at the top here. So S theta is equal to 2+Cosine of theta which is in cell E7. But I will have to convert this into radiance which means I must multiply by pi divided by 180 that will convert this into radiance so this is 2+Cos theta multiplied by +Cos theta the bracket outer bracket also has to be closed multiplied by 1-Cos theta square.

So let me open another bracket 1-Cos, I write again theta in cell E7 multiplied by pi divided by 180 brackets closed this outer bracket closed then square the ter whole term and another bracket closed and then whole thing divided by 4. I guess I made a mistake in somewhere in the brackets so I I will just have a look at that expression again let me just write this equation again, ok.

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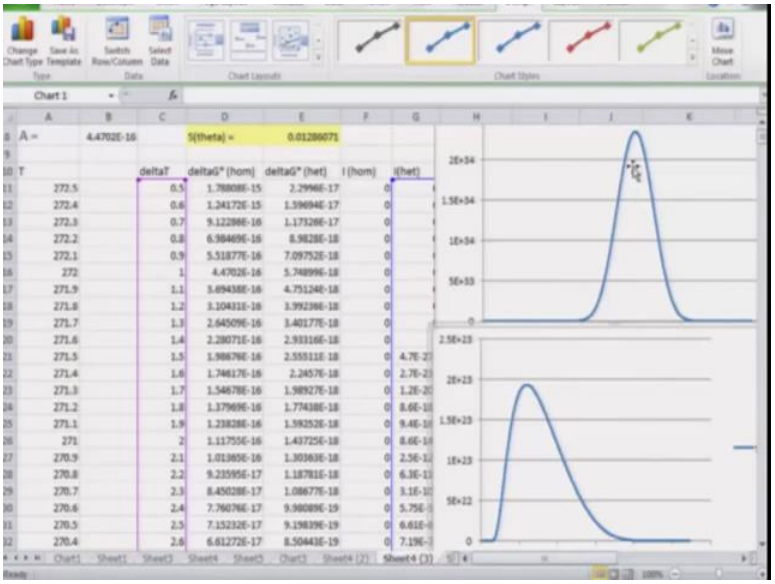

	A	B	C	D	E	F	G
8	A =	4.4702E-16		S(theta) =	0.01286071		
9							
10	T		deltaT	deltaG* (hom)	deltaG* (het)	I (hom)	I(het)
11	272.5		0.5	1.78808E-15	2.2996E-17	0	
12	272.4		0.6	1.24172E-15	1.59694E-17	0	
13	272.3		0.7	9.12288E-16	1.17328E-17	0	
14	272.2		0.8	6.98469E-16	8.9828E-18	0	
15	272.1		0.9	5.51877E-16	7.09752E-18	0	
16	272		1	4.47026E-16	5.74899E-18	0	
17	271.9		1.1	3.69438E-16	4.75124E-18	0	
18	271.8		1.2	3.10431E-16	3.99236E-18	0	
19	271.7		1.3	2.64509E-16	3.40177E-18	0	
20	271.6		1.4	2.28071E-16	2.93316E-18	0	
21	271.5		1.5	1.98676E-16	2.55511E-18	0	4.7E-2
22	271.4		1.6	1.74617E-16	2.2457E-18	0	2.7E-2
23	271.3		1.7	1.54678E-16	1.98927E-18	0	1.2E-2
24	271.2		1.8	1.37969E-16	1.77438E-18	0	8.6E-1
25	271.1		1.9	1.23828E-16	1.59252E-18	0	9.4E-1
26	271		2	1.11755E-16	1.43725E-18	0	8.6E-1
27	270.9		2.1	1.01365E-16	1.30363E-18	0	2.5E-1
28	270.8		2.2	9.23595E-17	1.18781E-18	0	6.3E-1
29	270.7		2.3	8.45028E-17	1.08677E-18	0	3.1E-1
30	270.6		2.4	7.76076E-17	9.98089E-19	0	5.75E-
31	270.5		2.5	7.15232E-17	9.19839E-19	0	6.61E-
32	270.4		2.6	6.61272E-17	8.50443E-19	0	7.19E-

I made some mistake earlier, now I got the answer here for 30 degrees I get a shape factor of point 01 if I change it to 90 just confirm whether this is correct or not for 90 I should get point 5, well I do get point 5. For 0 I should get 0, for 180 I should get 1 correct so go back to 30 degrees. Now to calculate the free energy for the critical size heterogeneous nucleus.

Well we take the value of the homogeneous nucleus so write the formula equal to so I take the value from cell D11 further free energy of the homogeneous nucleus multiplied by the shape factor I multiply by this and then I put dollar signs everywhere to anchor this so that when I copy this formula E8 will remain as E8. which contain the value of the shape factor.

And now I simply copy this down the column copy go down the column all the way down. So this is going all the way down and pasting it. So I got now the free energy for the critical size nucleus and on your left is the free energy for the homogeneous nucleus at different undercoolings. And you can see clearly see that the free energy for the heterogeneous nucleus of critical size is lower than that of the homogeneous nucleus for the same undercooling.

Now I calculate the nucleation rate for the heterogeneous nucleation so what I will do is I will copy some of the stuff from the homogeneous nucleation and then edit that formula. I just highlight this I will copy this formula as it is and then I will edit it for various terms for example let me take Inot here for the homogeneous case it is 10 to the power 42, let me take it as 10 to power 25.

Then instead of D11 which is the which the free energy for the homogeneous nucleation I change this to E11 to take the value from this cell and everything else is a same A11 the temperature or transformation remains the same, so that is it. I enter and I will get a value for heterogeneous nucleation you is partially hidden but it is again showing 0 as in the case of homogeneous let me just copy this and then we will look at the values.

So here we have now values nucleation rate for different undercoolings in this column and let me also plot this let us have a look at it how these values show up. So I go to insert go to scatter plot, let me move this here and select data add X values are undercooling select this. Similarly select now the column for the nucleation rate which is I het, this is selected, ok. Let me go up where hopefully the plot should be there and I have the plot here let me try to put as much of it is possible.

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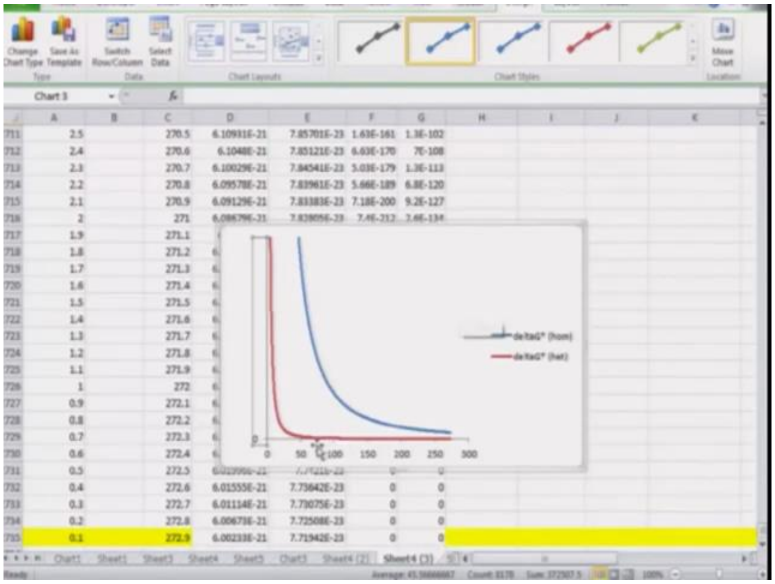

So you can now see both cases you can see that the peak has shifted to the left infact the entire curve have shifted to the left. This is for the homogeneous case and this is for the heterogeneous case. The peak has shifted to if I just go around here somewhat is showing around 55 and that is what we had computed just now as a peak.

If I look at the critical undercooling here let me just go down here and just see where do I get a nucleation rate of the order of 10 to power 6. This is where in between 6.3, 6.4 that is what we had just now computed on the board that the critical undercooling is of the order of 6 kelvin. So this is how this is shifted and very quickly one last thing before I end this lecture let us also have a look at the critical free energy or the free energy for the critical nucleus for both homogeneous and heterogeneous plotted at the same graph just to see how different they are.

So let me just pick out these three columns and go to insert go to scatter plot and plot this so it has plotted but the scale I will have to change to be able to see this graph clearly. So let me change this Y Y axis and reduce the scale over there. The scale is too big to show both the things properly let me change this to a much smaller value to let us say instead of 10 to power -15 I will change it to 10 to power -19.

And let us just see we can now see that the blue curve is for the way the free energy for the critical nucleus changes with undercooling here which is represented on the X axis and the red curve is for the heterogeneous case. And you can clearly see that for a given undercooling the energy barrier in the heterogeneous case here is much smaller than in the case for the (blu) for the homogeneous nucleation.

For example at 50 K the barrier is only this much while homogenous barrier is several orders of magnitude higher. Infact if you will notice if I go up here, let us say around we had computed an undercooling of critical undercooling of about 6 K and let us just have a look at what is the order of magnitude for the free energy.

It is of the order of 10 to power -19 as you can see where the curser is for the heterogeneous case it is a much couple of orders of magnitude higher in the case of homogeneous. So nothing happens in the case of homogeneous. If I go to 42 K which was a critical undercooling for the homogenous (nucl) nucleus. You would find that you get the same amount of free energy for the case of homogenous nucleation at 42 K as the undercooling. With this I stop here for this lecture, thank you.