Fundamentals of Materials Processing (Part–1)
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Lecture Number 06
Kinetics of Solidification (Heterogeneous)

Okay so we were discussing about ‘homogeneous nucleation’. Now one more thing we were, with respect to probability of nucleation is to talk in terms of nucleation rate; so today we will talk about nucleation rate. Okay so again we get back to the same equation.

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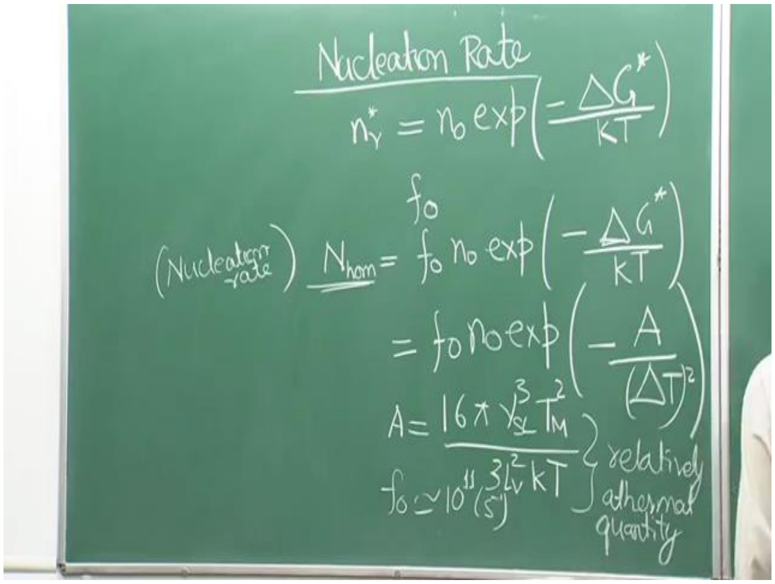

Let us say r star is the critical radius, and if we want to find how many clusters of those size are formed, or can be found, we can write it like this: nr, or actually let us make it nr star equal to n0, exp minus delta G star. Again when I say star, remember it is about the critical value. So this is r n star, meaning that number of clusters of that critical size, the r star value. Similarly, this delta G star is the free energy change for that critical radius, for the formation of that critical size radius, divided by KT.

Now this is the total number of clusters of critical size. If we add just one more atom to this, it will become solid, because now, it will have a free energy change or which is negative, meaning, the free energy will reduce. Hence, we have to just look at the frequency at which this can happen. Let us say that frequency is f0. Then, the nucleation rate, or N, since it is homogeneous, we can write N homogeneous equal to. This is nucleation rate for, under the condition that homogeneous nucleation is taking place. So this is what we are terming as; and this is the frequency, the frequency at which the atoms get attached to these nuclei, this critical nuclei which were found.

Now like we said earlier, that as soon as the size of this nuclei becomes larger than r star, it will become stable, it will get transformed from liquid to solid; and therefore, this is the frequency at which nucleation nucleus, the critical nucleus is becoming supersized, or above the critical size and hence it is becoming getting transformed into (solidif) into the solid. Now this rate of homogeneous nucleation, it can be rewritten if we expand the terms of delta G star, and then, you would see that it can be written like; you remember delta G star was inversely proportional to delta T, square of delta inversely proportional to square of delta T. So we have changed this delta G star into A, into a term like A divided by delta T square.

Now A also contains this 1 over KT term. Now why we have written it like this? Because A is, you can, if you want to look at the full form of A, it can be written like, or it can be given by this equation. Why we are writing it like this is because we are saying that this A is relatively athermal quantity. This A term is relatively athermal quantity. Now you would say there is a T term over here, then how come it is relatively or it is athermal? See that is where we are saying relatively. Now if you look at delta T, in with respect to that, T is actually athermal. Now let us say you are very close to delta T, sorry you are very close to TM, and you are just 1 degree below it; so TM, T is over here equal to TM minus 1. But delta t is equal to 1.

Now if you change this temperature to TM minus 2, so this has changed by a very minor quantity; but this has become twice, and therefore this if you take the square of it, this becomes 4. So if this whole quantity becomes 1 over 4, and therefore, this is a much more dominant term because we are looking only at delta T, and in that respect, this is a athermal quantity. Now this f0, what is this f0? This is f0 is a very, you can say complex in the sense that it is it depends on lot of other factors. So, in general, it is found that f0 is a of the order of 10 to the power 11 per second. So we will take this as a constant quantity and put it over here; and therefore, you have this f0, you have N0, you have this exponential term where A is a relatively athermal quantity, and delta T is the drop or the under-cooling, amount of under-cooling. So this is the overall equation for nucleation rate.

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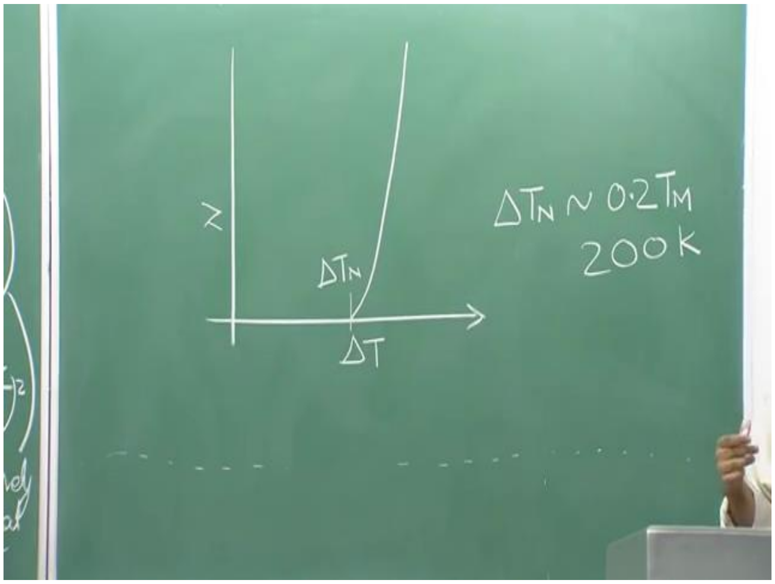

Now, if you try to plot it with respect to delta T, how will it look like? This, let us say this is the, on the x-axis we have delta T, and over here we have N, which is the nucleation rate. Then, it so happens that delta T; this is how the plot will look like; meaning, this nucleation, number of the (nu) the rate of nucleation the number of nucleus that becomes supersized or above the critical size, suddenly increases as you drop the under-cooling beyond this. So there is a critical value below which you will not see any amount of nucleation, and we saw that even earlier, which is, which what we termed as delta TN. But if you go beyond this critical under-cooling, or you decrease the temperature below this (delta) under-cooling, then suddenly there is explosion of nucleus, and you will see a lot of nuclei growing inside the material. So this is how the change in the nucleation rate takes place with respect to under-cooling.

Let us summarize. So in fact, nucleation rate explodes below this under-cooling. However, this under-cooling that we are talking about, we have not yet looked at the absolute quantity; what absolute, what is the absolute value for this. In general, this delta TN is approximately equal to 0 point 2 times TN. So if and most of the materials will have melting point somewhere of the order of thousand; we are talking about order, so we are looking at 200 Kelvin. So this is a very very large under-cooling that we are talking about. So it (req) for homogeneous nucleation, you require a very large under-cooling for the increase in the nuclei, or the point below which you will see a very large number of growth in the nucleus.

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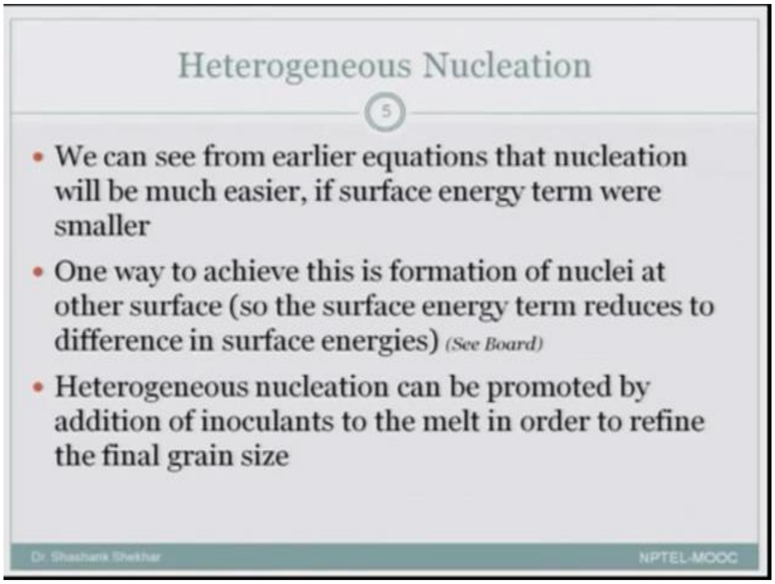

Heterogeneous Nucleation

- We can see from earlier equations that nucleation will be much easier, if surface energy term were smaller
- One way to achieve this is formation of nuclei at other surface (so the surface energy term reduces to difference in surface energies) *(See Board)*
- Heterogeneous nucleation can be promoted by addition of inoculants to the melt in order to refine the final grain size

So in practice what happens is that homogeneous nucleation is not so common. Then, what is so common? And here, it is here that we, and try to understand heterogeneous nucleation. Okay, so now at this point I will also invoke earlier point that that I made, where I said that the r star as well as delta G star are proportional to the surface energy term; in fact to the square and cube of the surface energy term; which means that if you increase the surface energy, if the r star value becomes very large, and we know from earlier that if r star becomes large, then probability decreases. On the other hand, if you decrease this gamma SL term, it means r star drops, delta G star drops, so probability of nucleation becomes large; and that is where heterogeneous nucleation comes into picture.

You can achieve heterogeneous nucleation in by changing this gamma SL term, the change in the surface energy. How do we get that? What we do is or (what) what actually the nature does is that it forms a surface at a place where there already was a surface; therefore, you are actually looking only at the difference in the surface energy. Let us look at this picture in a greater detail.

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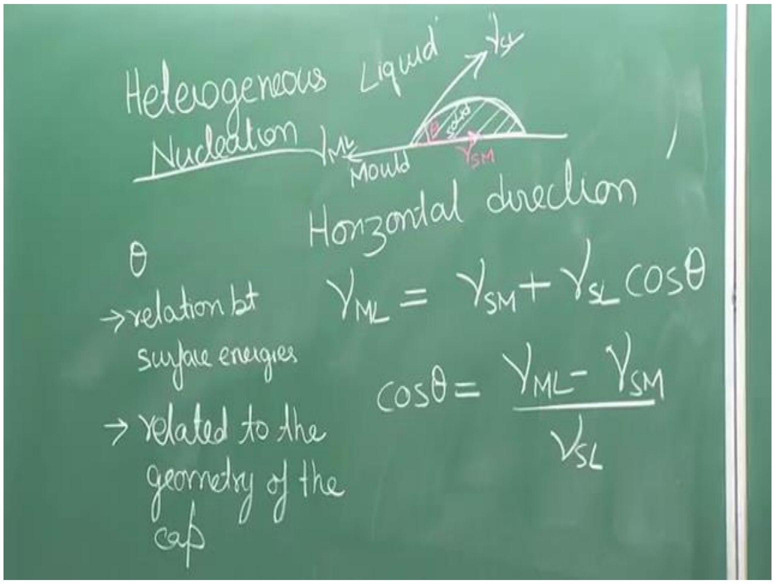

Heterogeneous Nucleation

Horizontal direction

$$\gamma_{ML} = \gamma_{SM} + \gamma_{SL}\cos\theta$$

$$\cos\theta = \frac{\gamma_{ML} - \gamma_{SM}}{\gamma_{SL}}$$

θ

→ relation bt surface energies

→ related to the geometry of the cap

So let us say this is mould, this is liquid. Mould is anything which is containing the liquid, or the material that has to be solidified, and this is where your liquid is. Now, there is a interface between liquid and mould, and whenever there is a interface, there will be energy associated with it. Now let us say, you form a solid over here; so this is our solid, newly formed solid. So what do we see? This, surface energy which existed earlier has now been replaced in effect by this new surface energy, this new surface; and therefore when we are looking at the surface energy terms, we are only looking at difference in the energy of the newly formed surface and what has (already) what has been taken away.

So because of this, we will see that heterogeneous nucleation becomes lot more probable and lot more you can say easy to form, or heterogeneous nucleation becomes the much more preferred route. Now, when we are looking at it, let us we will also have to formulate the equations. So let us look at it, if there is will be surface energy associated with this, which was also the surface that existed before the solid formed, and since it is between mould and liquid, we will denote it by term ML, gamma underscore ML. Now there is a new surface between solid and the liquid. So this surface, remember surface energy is also equal to the tension, surface tension. So here we are representing it as a tension which is a vector.

So this is the gamma solid liquid, which is represented by gamma SL, gamma subscript SL. And over here, we have a interface between solid and mould, which will be represented, since it is not very clearly visible, so let me draw it in red. So this is our gamma SM; and there is angle, included angle over here, which is given by theta. Now if we take, if we try to do a horizontal balance of forces, because these are, remember like I said, these are tensions. So in the horizontal, let us do it in the horizontal direction. Okay, so one thing I forgot to mention. So let me write it here; we are talking about now heterogeneous nucleation. So in the heterogeneous nucleation, we have this solid formed at one of the preferred sites. See this is not inside the solid, sorry not inside the liquid, it is at a preferred site, and what is that preferred site? It is this mould. So this solid has formed at the mould liquid interface, and in that sense it is not homogeneous; meaning it is not forming in a random way.

Now, to derive the equation for delta G star and r star, we are looking at the surface energy term. So we have three surface energy terms, gamma ML, gamma SL, and gamma SM, and since the contact angle is equal to theta, so, in the horizontal direction, we can say, gamma ML is equal to gamma SM plus gamma SL cos theta. Or in other words, we can write; so this is the cos theta term. Now, remember that this theta is representing now a relation between the three different surface energy terms; that is one thing; another thing theta is representing relation between. At the same time, we have assumed a shape which is a part of the sphere, okay? For simplicity you can say we have assumed this kind of shape.

So what is this shape? This is a part of the sphere. So this theta is also telling us what fraction of that sphere has actually, is actually seen over there. So this theta is also related to the geometry of the cap. And because theta is serving two purpose over here, it also makes our job easier and we can see that delta G star value which should be first written; so now we will try to formulate how the delta G term should look like, and then we will go on to how the delta G star can be obtained.

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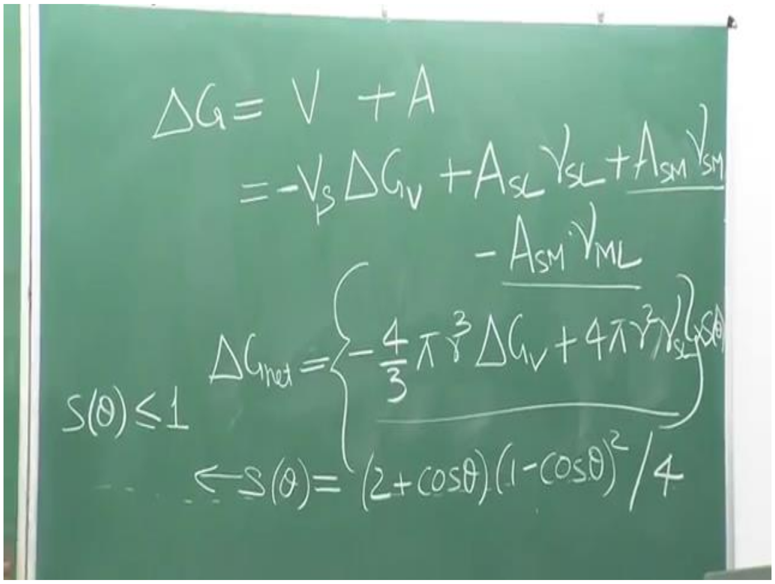

$$\Delta G = V + A$$

$$= -V_s \Delta G_v + A_{SL}\gamma_{SL} + \underline{A_{SM}\gamma_{SM}}$$

$$\underline{- A_{SM}\gamma_{ML}}$$

$$\Delta G_{net} = \left\{ -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \right\} S(\theta)$$

$$S(\theta) \leq 1$$

$$\leftarrow S(\theta) = (2+\cos\theta)(1-\cos\theta)^2/4$$

So if we are looking at delta G, again there will be a volumetric term, and there will be a area term. So remember this, volumetric term is what, the negative, or which reduces the overall energy and area term is what increases the energy. But over here, we have also gotten rid of some area, surface area. So energy associated with that (ener) that area has been taken off. So that will also come to reduce the overall free energy. And therefore, we will get equation of this form. See we have again added a negative negative sign over here, meaning although this delta GV itself should have been a negative quantity, but to make it, to make the mathematics simpler, we are assuming this is a positive quantity and to and since it is leading to reduction in energy, there is a negative term. So this overall quantity still remains negative.

Over here, ASL is the area of surface liquid which is this part. So this surface has been newly created, and therefore, it will add to the energy and the energy of this is gamma SL, so ASL times gamma SL. Second we have ASM term, which is this area. Now this is the area which was earlier occupied as by between the solid and the liquid. But now it is occupied between solid and the mould. So this new area has been created by taking away the interface between solid and liquid. So one quantity has been added, which is ASM times gamma SM, while the other quantity, which is ASM times gamma ML, has been taken off. So that is how you are getting all these terms.

Now, when you put in the geometry factor for VS, which is part of the sphere, which can be (ex) , which can be explained in terms of theta. Similarly, you can express gamma ML and gamma SM in terms of theta. You can you can find that this delta G for this heterogeneous nucleation reduces to a very simple equation like this. Times S theta. Okay. So there is a factor S which is a function of theta. Now let us look at this equation again. Delta G heterogeneous is this term, times overall this thing times this S of theta which is a function of theta. Now do you recall this value, this equation?

This equation is the same equation that we obtained for homogeneous nucleation. So this is really in a way affect very surprising in a way that we are able to get a equation which is very similar in form to what we obtained for homogeneous nucleation, the only difference is this term S theta. And it is possible because this theta is related in two different ways to the geometry that we discussed. One, it is able to relate the surface energy, and one it is, second it is also able to relate the geometry of the cap, meaning what fraction of the cap we are looking at. And, since we are talking about S theta, we can write what is this S theta; it is given by this equation.

Now if you look at the form of the equation, what can you say is the maximum value of S theta? If you try to find the maximum value, you would see that S theta will have a maximum value of 1, which means that in all the cases, S theta would be less than equal to 1. In fact, it will not even reach 1, it will always be less than 1. Again it will have a very interesting implication; we will look at it in just a moment. So that is the form of the equation, delta G heterogeneous; this is the overall change in energy. Okay.

We have, for some, for any radius r, we have not yet talked about the critical radius. And what do we need to do for critical radius? Remember we have to, we have to differentiate this equation with r. When you differentiate the equation with r and equate it to 0, which is equivalent to saying you are trying to find the maxima for this equation, you will be able to get r star value and when you put that r star value back into the equation, you get delta G star.

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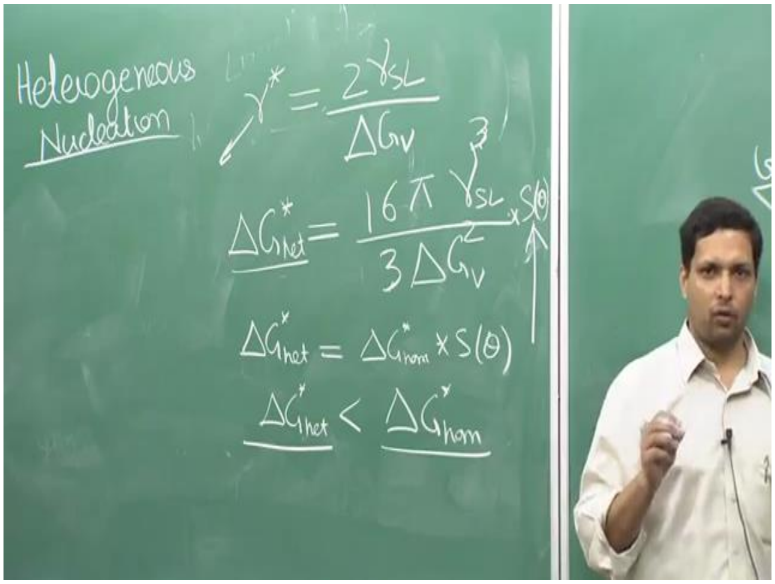

So, I will again without going into those mathematics, I will I will write down the final values. So r star value that you get, and delta G star; so these are the critical values. That was the overall change as a function of r. Now we are talking about the critical values. Okay. So again, let us look at these equations, r star and delta G star. What do you see? What we see is that r star that we obtain here is exactly same as we obtained for homogeneous nucleation. On the other hand, delta G star is just a little bit different, and what is that little bit different? It is just this S theta value. So it means, and what do we know, S theta value, S theta is value less than 1. It means that delta G star for heterogeneous reaction can be written as delta G star homogeneous nucleation times S theta.

And, in effect it means that delta G star heterogeneous is always less than delta G star homogeneous. So heterogeneous will always be smaller than delta G star homogeneous. Now you remember what do you want, you want smaller value of delta G, or you want a larger value of delta G for easy nucleation. You want a smaller value of delta G for easy nucleation. So it means that heterogeneous nucleation would be easier than homogeneous nucleation. And this will become even more clear when we look at the (value) plot of variation of delta G as a function of r for both homogeneous nucleation and heterogeneous nucleation.

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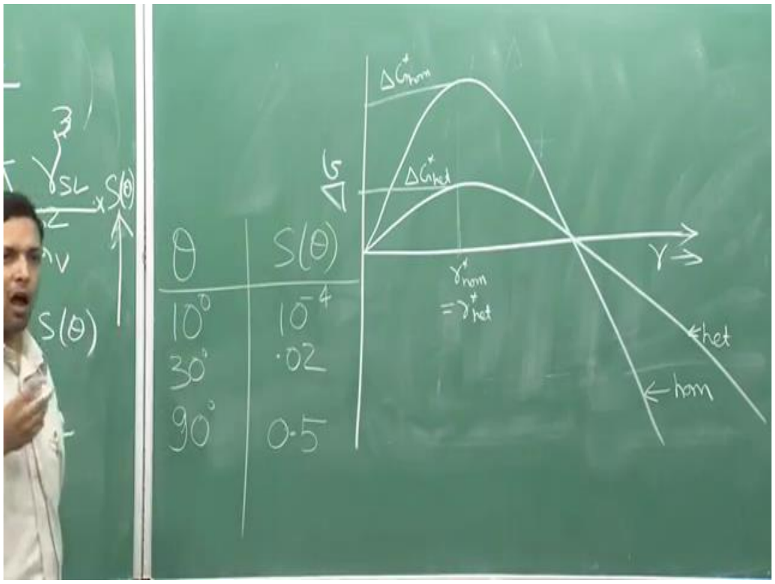

So this is our delta G, and this is r. Now if we plot, first let us plot for homogeneous; this is for the homogeneous, this is how delta G varies when you have only homogeneous nucleation; and this will be your r star for homogeneous, and this will be your delta G star for homogeneous nucleation. How will it change if everything else, that is delta T, the material, the liquid remains the same, but now you want to talk about heterogeneous nucleation. How are the things changing, with respect to free energy? The r star terms will not change, we know from this. This remains the same, r star is remains the two gamma SL divided by delta GV; all these quantities remain same, whether we are talking about homogeneous nucleation or heterogeneous nucleation. So this r star value will remain same, but delta G star value will decrease, it will become delta G star homogeneous times S theta.

Now we will look at exact value, what are the various values of S theta for different conditions. So, this will become; so this is the plot for heterogeneous nucleation. So this r star homogeneous is same as r star heterogeneous, and this is delta G star heterogeneous. So this is a much much smaller value of. But how much smaller? Let us remember S theta is just a function of theta. So let us look at some of the values of theta and the corresponding value of cos theta. If you take a very small value of theta, something like let us say 10 degrees, then you get S theta equal to 10 to power minus 4; it is a very very small value; meaning this will be 10 to the power minus 4 times of this. Very very small, somewhere like a flat line.

Now let us make this theta equal to 30 degrees. Then this becomes equal to point 02. It is still small, but not as small as it was for 10 degrees. Now let us make it 90 degrees. So this becomes 0 point 5. So even for very large, okay even before I say that, I should say that as theta becomes very very small, you get a much larger difference between homogeneous and heterogeneous nucleation. But even for very large theta values, like you see 90 as high as 90 degree; because the S theta term involves cos theta, so whether you increase beyond 90 degrees, it will not make a difference.

So if you are at 90 degrees, which is the maximum possible, you still have a factor of point 5. So your delta G will still be much smaller, half of delta G homogeneous. And you remember from the nucleation rate, this delta G term comes inside the exponential factors, so that will be still be a very, that will this small difference, just half point 5 difference will still lead to a very large difference in nucleation rate.

That we will look at in next class. So we will stop here, and we will continue from here about, discussing about the heterogeneous nucleation. Thank you.