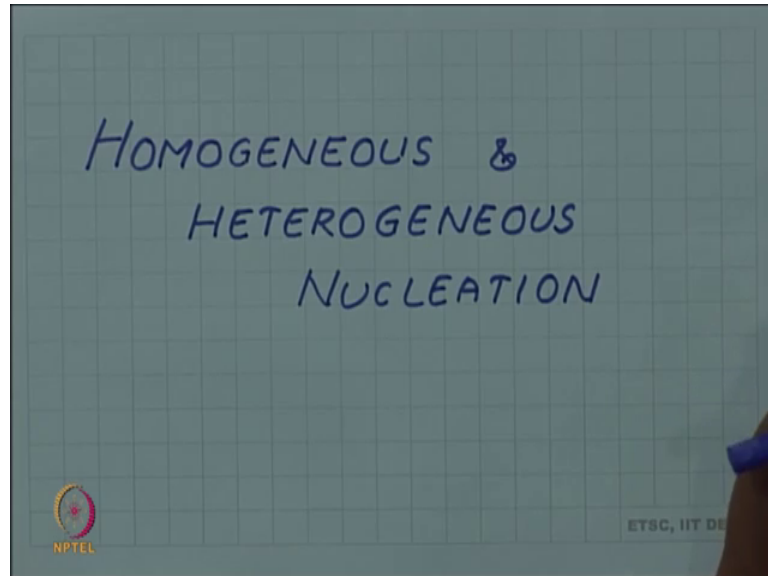


**Introduction to Materials Science and Engineering**  
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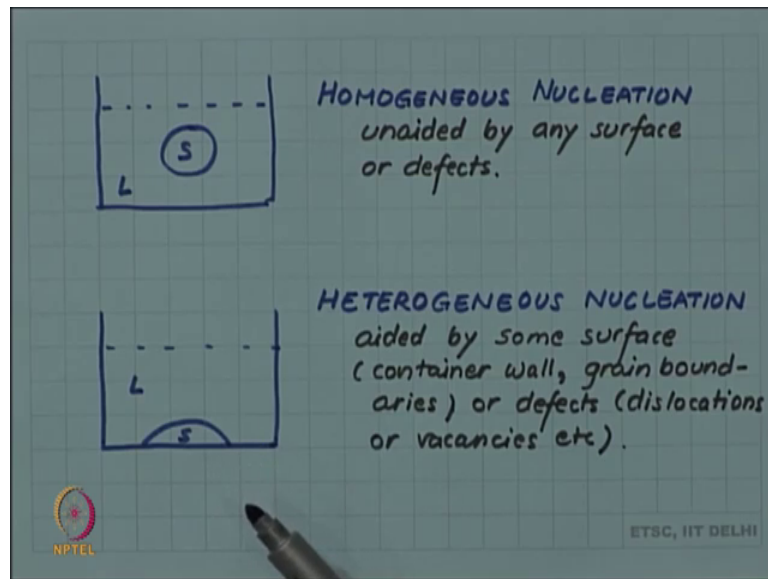
**Lecture - 94**  
**Homogeneous and heterogeneous nucleation**

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We are discussing the topic of phase transformation, and we discussed nucleation in particular. There are 2 kinds of nucleation, homogeneous and heterogeneous nucleation. I did not mention this before, but let us discuss this.

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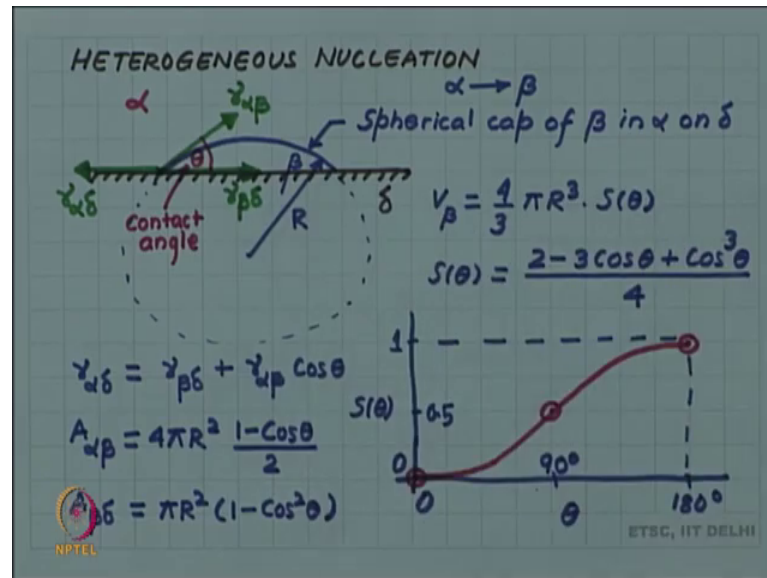
What we have been discussing till now is the like the formation of a solid nucleus inside a liquid. This is an example of homogeneous nucleation.

We didn't use this adjective before. We were simply calling it nucleation, but this is an example of homogeneous nucleation, which essentially means a nucleation unaided by any surface or defect. We took this up, because it is mathematically simpler to analyze; however, in reality this is a quite unlikely situation, a more likely situation for nucleation to happen particularly in the case of freezing is that nucleation will happen at the container wall. So, the solid may form at the wall of the container, this kind of nucleation is called heterogeneous nucleation.

Heterogeneous nucleation, the this kind of nucleation is aided by some surface, for example, like in this example container wall, or in case of solids it can be grain boundaries, or it can be other defects, such as dislocations or vacancies. So, this kind of nucleation is called heterogeneous nucleation, and it is a more common kind of nucleation, mostly for example, in this situation or itself you can see in case of solidification it is quite likely that nucleus will form at the container wall rather than totally inside the liquid.

So, homogeneous nucleation is a nice simple situation, easy to analyze mathematically, and in study in laboratory situations can be created such that we have homogeneous nucleation. But most practical nucleation situations are heterogeneous nucleation. So, let us look at heterogeneous nucleation in little bit detail.

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Just like we analyzed homogeneous nucleation in terms of energy, let us do a similar analysis for heterogeneous nucleation. Let me assume some sort of container wall or substrate over which there is some phase, some phase alpha, and let me call the substrate itself delta. And in alpha a nucleus of beta forms. Alpha is transforming in beta on the surface of delta.

So, that is why it is a heterogeneous nucleation, and in particular again just like we simplified the geometry of the problem in homogeneous nucleation by considering the spherical nucleus, here again we are simplifying the geometry by considering a spherical cap nucleus. So, essentially, we are saying that beta is forming a spherical cap, this spherical cap of beta in alpha on delta. So, we by spherical cap, I mean, that this surface the alpha beta surface is spherical, and I have tried to draw the entire sphere here. So, you can see that this sphere is cut by the surface of delta. So, only a small portion of the sphere and that is what it is spherical cap is acting as the nucleus. I show the centre of the sphere and the radius as R.

Now, 3 kinds of interfaces are involved here, and they are meeting at a junction like this. So, you have for example, the alpha beta interface, and I am showing the surface tensions by these arrows. So, this is gamma, alpha, beta this is another surface between beta and delta. So, this I write as gamma beta delta, and you have the surface between alpha and delta, which I write as gamma alpha delta. Since, these 3 these 3 surface

tensions are locally in balance at this point, we can write an equilibrium condition for these surface energy in terms of  $\gamma_{\alpha\beta}$ . If I take the horizontal component, then  $\gamma_{\alpha\beta}$  will be equal to  $\gamma_{\beta\delta} + \gamma_{\alpha\beta} \cos \theta$ . Where  $\theta$  is this angle here also known as the contact angle.

Now to carry on our analysis, we need the volume and surface area of this spherical cap. This can be easily derived using calculus we do not do that here we just write the result, but I encourage you to go ahead and try to derive this using calculus  $\frac{4}{3} \pi R^3$ . So, the volume of this nucleus which I am calling  $V_{\beta}$  is  $\frac{4}{3} \pi R^3$  which is the volume of the sphere times a factor depending on  $\theta$ . You can see that the way we have cut depending on where we cut the  $\theta$  will change, and correspondingly the volume will change. So,  $s_{\theta}$  will; obviously, vary from 0 to 1.

So, when you derive this, you will get the form of  $s_{\theta}$  also let me write that. So,  $s_{\theta}$  is  $\frac{2 - 3 \cos \theta + \cos^3 \theta}{4}$ . This function, let us plot  $s_{\theta}$ , 1 this is 0.5, this is 0 and the contact angle  $\theta$  varies between 0, 180 degree. So, if you look at this function, it will be 0 at  $\theta$  is equal to 0. It will be 0.5 at  $\theta$  is equal to 90 degree, and will be 1, at  $\theta$  is equal to 1. At  $\theta$  is equal to 180 degree, it will be one at  $\theta$  is equal to 180 degree.

And in between it takes a sigmoidal shape something like this. The volume of the spherical cap depending upon the contact angle can be any fraction of the volume of the full sphere, and that fraction is given by this  $s_{\theta}$  which depends upon the contact angle in this way.

We also require the surface area of this spherical cap so that that is the interface between  $\alpha$  and  $\beta$ . So, that area I call  $A_{\alpha\beta}$ , and that can be shown to be  $4 \pi R^2 \frac{1 - \cos \theta}{2}$ . And similarly, I require the area between  $\beta$  and  $\delta$ , that is the base circular base on which the spherical cap is sitting, that circular base on which the spherical cap is sitting a  $\beta\delta$  is  $\pi R^2 (1 - \cos^2 \theta)$ . So, we have all the geometrical parameter the volume of the spherical cap, the curved surface area of the spherical cap  $A_{\alpha\beta}$  and the horizontal base the circular base a  $\beta\delta$  in terms of  $R$  and  $\theta$  the radius of the sphere and the contact angle  $\theta$ .

So, with this we can take our next step of developing the energetics.

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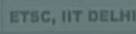
$$\Delta G_f^{het} = V_\beta(G_\beta - G_\alpha) + A_{\alpha\beta}\gamma_{\alpha\beta} + A_{\beta\delta}\gamma_{\beta\delta} - A_{\alpha\delta}\gamma_{\alpha\delta}$$

$G_\beta - G_\alpha \equiv \Delta G_v$

$= f(R, \theta)$

$$\frac{\partial \Delta G_f^{het}}{\partial R} = 0 \text{ at } R = R_{het}^*$$

$$\rightarrow R_{het}^* = - \frac{2\gamma_{\alpha\beta}}{\Delta G_v} = R_{hom}^*$$

$$V_{het}^* = V_{hom}^* \cdot S(\theta)$$



So, recall that we had we can write the energy of formation for the heterogeneous nucleation; for the heterogeneous nucleus that will be volume of the nucleus which is  $V_\beta$  times the free energy per unit volume of beta, minus the free energy per unit volume of alpha. Again, we are assuming that there is no volume change between beta and alpha. So, the same volume of alpha transformed into beta. So, we generated so much of free energy  $V_\beta G_\beta$  into  $G_\beta$ , but we lost we lost  $V_\beta G_\alpha$  into  $G_\alpha$ . This is the volume energy term, then we have surface energy terms and now there are 3 different kinds of surface energy terms as you saw. So, we have  $A_{\alpha\beta}$ , that is the curved surface of the nucleus that is the surface  $A_{\alpha\beta}$  times surface energy per unit area of alpha beta surface.

So,  $A_{\alpha\beta}$  gamma alpha beta. We also form the base of the nucleus which is a beta delta gamma beta delta but then when we created this surface, recall that when we created this beta delta surface due to nucleation. Before nucleation, the same surface was alpha delta, because alpha was filling this entire space. So, the amount of area which we created for beta delta, same amount of area was removed from alpha delta.

So, let me not write this as alpha delta let me to keep writing this as beta delta only because the area is the same, but the surface energy is alpha delta so, this is an important. So, recall that in homogeneous nucleation, the volume energy was the driving force so,

here also volume energy is the driving force and there the surface energy was barrier to nucleation.

Here also surface energy is barrier to nucleation, but one surface term since it is getting deleted, since it is being removed this surface term also acts like a driving force there is an additional driving force in terms of surface. Energy because nucleation is happening on a surface so, that particular part of the surface is getting removed from the system. So, this is the energy expression, and if you if you recall we have we have all these terms  $V$   $\beta$   $k$   $\alpha$   $\beta$  and  $\Delta G$  in terms of  $R$  and  $\theta$ .

So, we can express that so, this is a function of  $R$  and  $\theta$ , and we can again think of the variation of  $\Delta G$  as a function of  $R$ . So, we will find that this variation again is somewhat similar to the homogenous nucleation. And we can get the critical nucleus size by a similar condition that  $\Delta G$  heterogeneous by  $dR$  is equal to 0 at  $R$  is equal to  $R^*$ .

So, when you express all these as a function of  $R$   $\theta$  by substituting those expressions which we derived in the previous slide. So, and then differentiate you can find the critical radius for heterogeneous nucleation, and rather interestingly when you will do this algebra I am not doing it here, leaving this as an exercise for you, but you can do that and convince yourself that this  $R^*$  heterogeneous at which this differential coefficient is 0 turns out to be  $\frac{-2\gamma\alpha\beta}{\Delta G_V}$ .  $\Delta G_V$  is again this term here,  $G_\beta - G_\alpha$   $\Delta G_V$ , change in volumetric free energy change in free energy per unit volume when the transformation happens from  $\alpha$  to  $\beta$ .

So, final minus initial that is  $\Delta G_V$ . So, if you look at this expression, you see that this critical radius for heterogeneous nucleation turns out to be exactly the same what we had found for homogeneous nucleation. There we were thinking in terms of solid and liquid so that was  $\gamma_{sl}$ , but in a more general case, it will be  $\gamma_{\alpha\beta}$ .

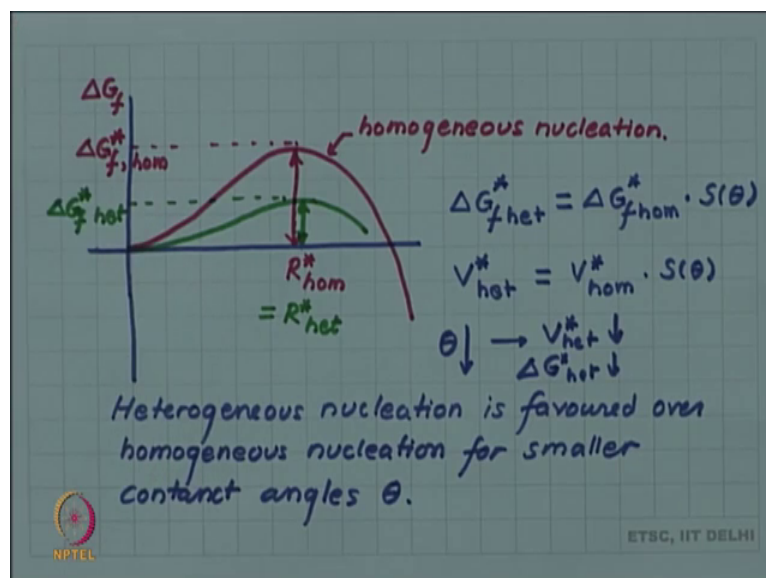
So, the critical radius for heterogeneous nucleation is exactly the same as critical radius for homogeneous nucleation; however, there is still a difference, because recall that in homogeneous nucleation the entire ball the entire is sphere of radius  $R$  was the nucleus. But in this case only a part of the sphere is the nucleus. So, still although the radius appears to be the same the volume of the 2 nuclei will not be the same.

So, if we look at it in terms of volume then we find the volume for heterogeneous nucleation is not equal to volume for homogeneous nucleation, it is different by the same factor  $s_{\theta}$  which we had derived in the since; obviously, since you have derived this expression  $V_{\beta}$  is  $4/3 \pi R^3 s_{\theta}$ , and this was the volume of the entire sphere, and  $s_{\theta}$  was the factor by which volume of the beta was different from the volume of the sphere.

So, that same  $s_{\theta}$  will be true for the volume of critical nucleus also. So, the volume of critical nucleus will be smaller than for heterogeneous nucleation will be smaller than volume for the homogeneous nucleation by this factor  $s_{\theta}$ . And since  $s_{\theta}$  is always less than 1 except for  $\theta$  is equal to 180 degree.

So, depending on  $\theta$  is the contact angle. So, it smaller is the contact angle smaller will be the volume of heterogeneous nucleation. And you can see that the point that for nucleation we have to assemble, so many atoms in the form of a new phase and that is the that is the initial difficulty of nucleation. So, is smaller is the volume, or smaller is the number of atoms which we have to assemble, easier will be the nucleation process. So, if  $s_{\theta}$  is much small, if the contact angle is small  $s_{\theta}$  will be small. And then the volume of heterogeneous nucleus will be correspondingly smaller than the volume for homogeneous nucleation and thus heterogeneous nucleation will be easier.

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We can try to draw this recall that in homogeneous nucleation, we got a curve of the shape for  $\Delta G$  vs  $r$  the maximum. We can call that as  $\Delta G^*$ . Your radius corresponding to that is  $r^*$ ; let me call this  $r^*$  homogeneous so, this is for homogeneous nucleation. If I superimpose the curve for heterogeneous nucleation in the same, we found that  $r^*$  is the same. So, for heterogeneous nucleation also we will get the maximum at the same value or heterogeneous. This were  $\Delta G^*$  for homogeneous, and as we saw  $r^*$  was the same.

So, this is same as so, you can think of this energy initially the energy of the system has to increase. So, this is a kind of energy barrier for the nucleation, and this energy barrier for nucleation, also will be lower for heterogeneous nucleation, then for the homogeneous nucleation, and if you derive the expressions for these this will turn out to be. Again, smaller by the same factor  $\cos \theta$  which we have been using for the volume. So,  $\Delta G^*$  for heterogeneous is  $\Delta G^*$  homogeneous times the same factor  $\cos \theta$ . And we have already seen that  $V^*$  for heterogeneous,  $V^*$  for homogeneous times  $\cos \theta$ . So, smaller is the contact angle, a smaller is  $\cos \theta$  and a smaller is the volume of heterogeneous nucleus.

So, you have to assemble lesser number of atoms to form the heterogeneous nucleus. Similarly, the energy barrier for nucleation that extra energy which is required for nucleation is also less for heterogeneous nucleus by the same factor; so, both these fact aid heterogeneous nucleation; so, a heterogeneous nucleation is favoured nucleation for smaller contact angles  $\theta$ . So, a smaller is  $\theta$  as  $\theta$  decreases both  $V^*$  heterogeneous and  $\Delta G^*$  heterogeneous both of these decrease this is what in physical term, smaller is  $\theta$  we say that better is the wetting. So, if the nucleus wets the substrate or the wall on which it is forming then heterogeneous nucleation will be favoured.