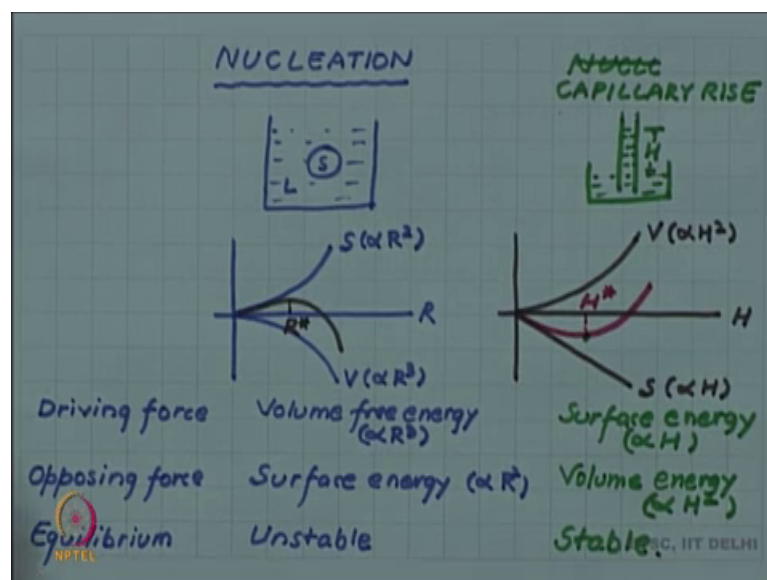


Introduction to Materials Science and Engineering
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Lecture - 91
Nucleation and capillary rise

We are discussing phase transformation and in particular we discussed Nucleation. In this video let us compare this nucleation process to another familiar phenomenon capillary rise, nucleation may not be so, familiar to you before this, but most students have some familiarity with capillary rise. So, it is interesting to compare the two processes.

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So, we have seen in nucleation that if we allow, if we consider a ball of solid forming inside liquid, then the energetic is such that we have we have a negative term, which is the driving force and that comes from the volume free energy, V and it is proportional to R cube and is negative, but then there is a barrier to nucleation. If this was the only case nucleation could have happened right from beginning at any given radius, but there is a barrier to this nucleation and that comes in terms of the surface energy and the surface energy term is positive and is proportional to R square.

So, a competition between these two, then gives us a total energy curve, which initially goes up and then comes down so, that we have a critical radius R^* for nucleation this

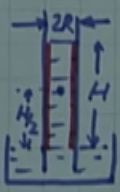
we have discussed. So, we see here that if we try to write the various competing energies in this. So, there is a driving force which is the volume free energy and, this is proportional to R cube. But there is also an opposing or a barrier, barrier term let us call it opposing force. There is a surface energy and, this is proportional to R square. And since R star corresponds to the maximum in the energy curve. So, we can consider this to be an equilibrium, but the nature of equilibrium is unstable equilibrium because, you have maximum of energy.

So, the nature of the equilibrium is unstable, if the if the critical nucleus of radius R star loses a few atom and radius decreases, then it will keep on decreasing. So, as to reduce the free energy and it will dissolve. If few atoms join such as the radius increases, then it will keep on increasing and will increase its radius. So, R star is an unstable equilibrium because, either if it decreases or increases it will not come back to the equilibrium position, it will keep deviating from that location.

Now, this whole thing can be compared, similarly related phenomena happens in capillary rise. So, if you look at capillary rise. So, if you dip a tub, you are all familiar with this phenomenon, then in the tube the liquid rises and it rises to some height let us call that H. Now, if you study or if you look at the energetics of this capillary rise phenomenon, it has it is very interesting and interesting similarity with nucleation.

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CAPILLARY RISE (ENERGETICS)



acceleration due to gravity

$$\Delta E_H = +\pi R^2 H \rho g H/2 + 2\pi R H \gamma_{GL} - 2\pi R H \gamma_{GA}$$

Density of liquid

γ_{GL} = Energy per unit area of the glass/liquid interface.

γ_{GA} = Energy per unit area of the glass/air interface.

$\Delta E_H = \frac{1}{2}\pi R^2 \rho g H^2 - 2\pi R H (\gamma_{GA} - \gamma_{GL})$

+ve -ve if $\gamma_{GA} > \gamma_{GL}$

driving force.

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So, let us look at that let us look at capillary rise on the basis of energy energetic. So, let us have a tube and, this is the height H of liquid column in the capillary tube. Now, if we want to write out the energy terms just like we did for nucleation. So, we want to we want to write down, what is the change in energy ΔE for the formation of a liquid column of height H .

If you see the potential energy of the liquid is actually rising. So, this cannot be the driving force it is actually an opposing term. So, let us first write down that. So, the potential energy of this liquid column, we can write in terms of the volume. So, let us say that the diameter of the tube is $2R$ radius being R so, the volume of this liquid column is $\pi R^2 H$. And if I multiply that by the density of the liquid, then I get the mass and mass times the gravitational acceleration g and times the height.

Now, the relevant height here is the height of the centre of gravity, which is just half of the total height, we multiply this by H by 2 . So, this term is there and this is a positive term because, energy will increase the potential energy will increase. So, the question is why will then a capillary rise happen, if the potential energy of the system is increasing. So, there should be the driving this cannot be the driving force, the driving force should be some other decreasing term.

So, what is decreasing? So, we can see here that there is things happening at the interface or the surface and we have to take care of that. So, if you look at that at the tube surface, then you find that initially there was a glass air interface, which has now been replaced by a glass liquid interface.

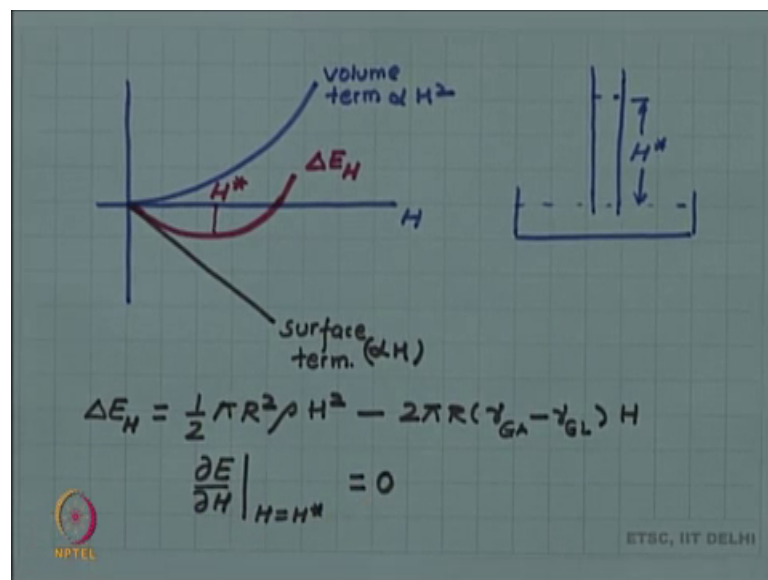
So, we have two more energy terms here, we have one more additional positive term and that is if you look at the cylindrical surface area. So, that is $2\pi R H$ is the surface area, times surface energy per unit area of the glass liquid interface. This has this is a further additional energy term and this is also positive.

So, this can also not be a driving force, but you can see to create this glass liquid interface the original glass air interface was replaced. So, this energy decreases, you have γ_{GL} of the interface and you will have γ_{GA} , which is the same quantity for the glass air interface. And it is this negative term which will act as the driving force for capillary rise.

So, this will be the driving force. So, let us write that expression. (Refer Time: 12:22)
 This is positive, this is positive. So, it cannot be their driving force, this can be negative or positive depending on the second term can be negative or positive depending on the sign of $\gamma_G A$ minus $\gamma_G L$.

If $\gamma_G A$ is greater than $\gamma_G L$; So, if the original glass air interface is having higher energy and is being replaced by glass liquid interface which is having lower energy, then this term will be positive and this whole term will then be negative and will be a driving force negative, if $\gamma_G A$ is greater than $\gamma_G L$ and capillary rise will happen.

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So, let us now plot these energy term in the same way like we had done for the nucleation exercise. So, we plot it as a function of the height and we can see that we have we have a positive term, which is proportional to we have a positive term which is proportional to H square. So, this and this depends on the volume. So, let us write this a volume term and is proportional to H square.

We also have we will have a negative term, which is proportional to H we have a negative term and this is the surface term and is proportional to H . And if you combine the two, then you can see that any initial slope of the H square curve is 0 whereas, initial slope of the surface term is constant. So, initially the surface term will be dominant and the curve will pull down, but gradually the H square term will start dominating and the

curve will go up. So, you will have a minimum in the total energy. So, this is your delta E H and that minimum will correspond to the equilibrium height of capillary rise.

So, when so as the liquid column rises, as the liquid column rises in the tube, the energy initially decreases, but then it reaches an equilibrium height and, that will be the equilibrium height beyond that if it wants to increase the free energy again will keep increasing.

So, just like we did for nucleation and found the critical radius we can do the same thing here, for the capillary rise and find the height equilibrium height of the capillary right. So, we have this term. So, for minimum we will need the condition to be 0. So, if all you have to do is to differentiate this expression.

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$$\frac{1}{2} \pi R^2 \rho g (2H^*) - 2 \pi R (\gamma_{GA} - \gamma_{GL}) (1) = 0$$

$$H^* = \frac{2(\gamma_{GA} - \gamma_{GL})}{\rho g R}$$

R. Prasad "On Capillary Rise and Nucleation"
Journal of Chemical Education
Vol. 85, No. 10, Oct 2008, 1389.

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So, we differentiate and then we find half pi R square rho H square differentiates as 2 H minus 2 pi R gamma G A minus gamma G L H differentiates as 1, and at the equilibrium height H star this quantity will be 0. So, you can cancel terms here. So, you can quickly find the equilibrium height H star as 2 gamma G A gamma G L divided by I missed G term here, there was a G term here, rho g R.

So, we can now complete our analogy with nucleation. So, if we bring it here now, we see that we have a similar energetic curve for capillary rise only thing is that the role of surface and volume term now changes. So, it is now the volume term because, that is the

potential energy which is increasing. So, the volume term is the opposing term and that is proportional to H^2 and the surface term is the driving force and is proportional to H and, the net curve goes through a minimum giving you equilibrium capillary height.

So, if you then complete these columns in the driving, driving force now is the surface energy term. The surface energy drives capillary rise because, there is a reduction in surface energy and this is proportional to H opposing force, now is the volume energy, which is the gravitational potential energy of the liquid column. And this is proportional to H^2 and you again have a equilibrium, but now you have the minimum of energy at the equilibrium. So, this is a stable equilibrium.

So, that completes the analogy between nucleation and capillary rise. If you want to see the details, this available in a article which I wrote. The details of this comparison is available in this article.