Basic Statistical Mechanics
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Lecture – 40
Nucleation Part 3: Kinetics of Nucleation, Classical Nucleation Theory, Heterogeneous Nucleation

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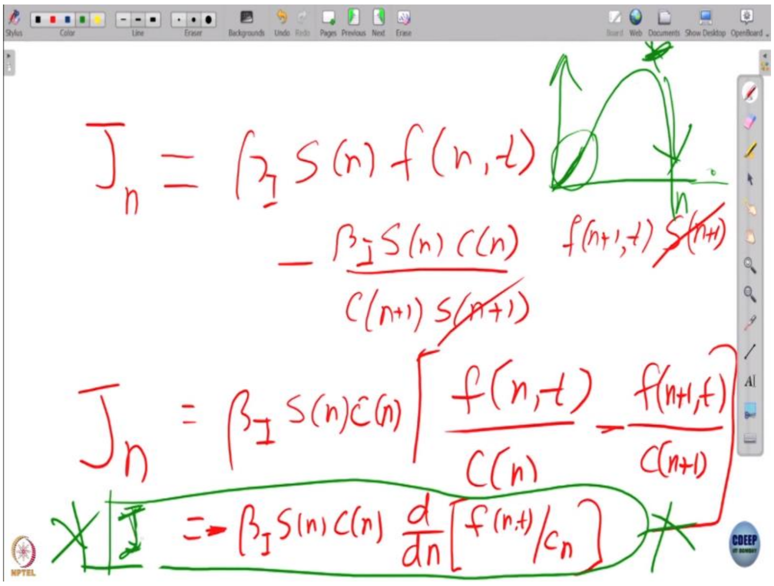

$$J_n = \beta_I S(n) f(n,t) - \beta_I S(n) C(n) \frac{f(n+1,t)\,\cancel{S(n+1)}}{C(n+1)\,\cancel{S(n+1)}}$$

$$J_n = \beta_I S(n) C(n) \left[\frac{f(n,t)}{C(n)} - \frac{f(n+1,t)}{C(n+1)} \right]$$

$$\boxed{J = -\beta_I S(n) C(n) \frac{d}{dn}\left[f(n,t)/C_n \right]}$$

So, now we are going to get somewhere. So, we have derived this beautiful equation

$$J_n = -\beta S(n) C(n) \frac{d}{dn}\left[\frac{f(n,t)}{c(n)} \right]$$

Now they are very interesting thing to look into. Now if I have against n I am using the corner because I need to talk of this equation quite a bit now. This is my free and landscape. Okay and this is my critical thing. Now here at small n, near n=1, at the limit and in this scale when n is very large could be of the something of 200 or 300 typically.

Then these region particles are trying to go and come back and there is enough of them. So this is the region it is like equilibrium. So when I go to the limit in going to 0, you know I am entitled to going to 0. Because I you know and I am made it continuous. Actually it does not go below n=1. But that does not make any difference, whether I go to 1 or 0 do not make any difference.

So, n going to 0 f(n)/C(n) goes to 1. However, when n goes to infinity that means n goes to infinity means here all the way there is nothing there. Okay before that I have the maximum after maximum. It just goes downhill. So n going to infinity it is quantity event is 0. Okay this is third is the most important thing. In a steady state when there is a flow of train that is what I said flow of train I again appeal to you remember that the train is going in front of you and one after another compartments are coming in one after another in regular interval. Train has constant velocity and speed. What does it mean?

That means our case what is happening That means compartment at (n – 1), the next compartment is n, the next compartment is (n + 1). There is a steady state flow. What does it mean? That means J is independent of n. Now I have this wonderful expression. Now J is independent of n. So what do I know? I know the limits. So I immediately now write down.

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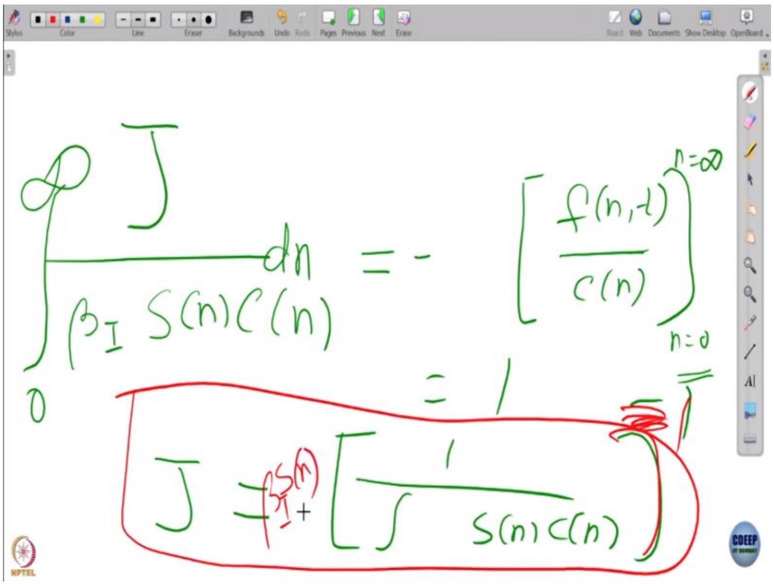

Now I can do an integration because I know the limits. So I do the integration 0 to infinity. Okay so I bring d here. I bring dn here and then I do this integration 0 to infinity. At infinity it is 0 and at n equal to 0 a infinity f(n,t) at that limit. So is there is a d here. So it just goes these become evaluate at n = 0 and n equal to infinity. Now n equal to infinity is 0 and n = 0 f(n) = C(n).

Okay so I just and this is a minus in front that because in wall limit. I just get 1. Okay so then I get the beautiful relation

$$J = \beta_I \left[\int_0^\infty \frac{dn}{S(n)c(n)} \right]^{-1}$$

I am almost there. Now so this is - 1 in bracket - 1. So that means my beta I and beta I and S(n) because they are in a denominator of denominator they comes out.

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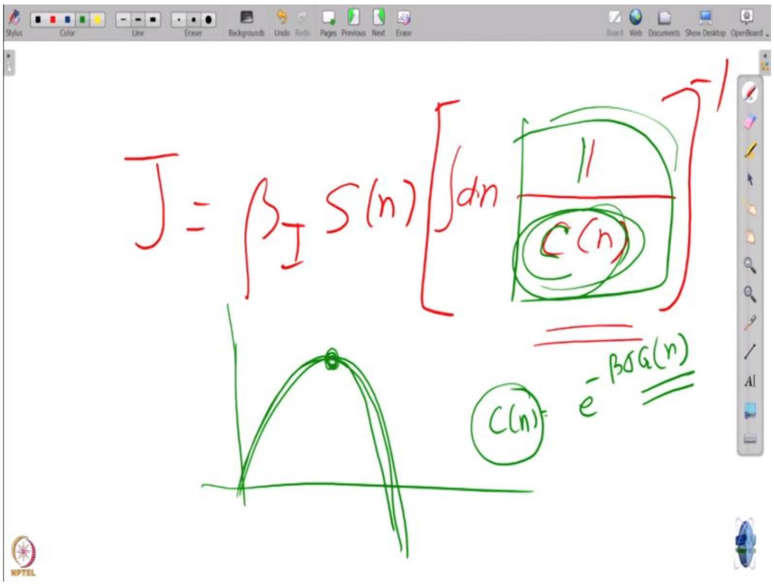

$$J = \beta_I S(n)\left[\int dn \frac{1}{C(n)}\right]^{-1}$$

$$C(n) = e^{-\beta\Delta G(n)}$$

So now I have the following expression. Right so I have to evaluate this thing. Now let us do little bit. So we have done the main thing. We have little faster rate. I will go now.

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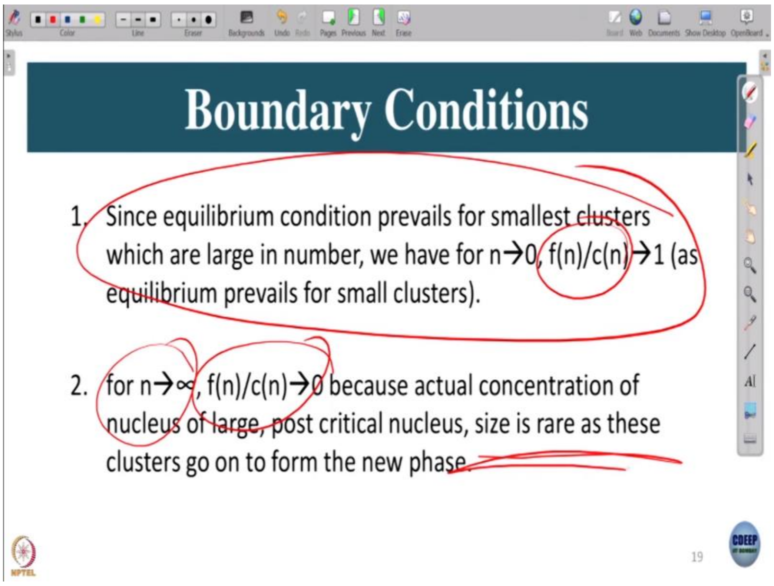

Boundary Conditions

1. Since equilibrium condition prevails for smallest clusters which are large in number, we have for n→0, f(n)/c(n)→1 (as equilibrium prevails for small clusters).
2. for n→∞, f(n)/c(n)→0 because actual concentration of nucleus of large, post critical nucleus, size is rare as these clusters go on to form the new phase.

So this is the thing I said since the equilibrium prevails for smallest clusters. Thus, f(n)/c(n) goes to 1. But when n goes to infinity this goes to 0 because of actual combat post critical size is rare actually not rare. It is not there then.

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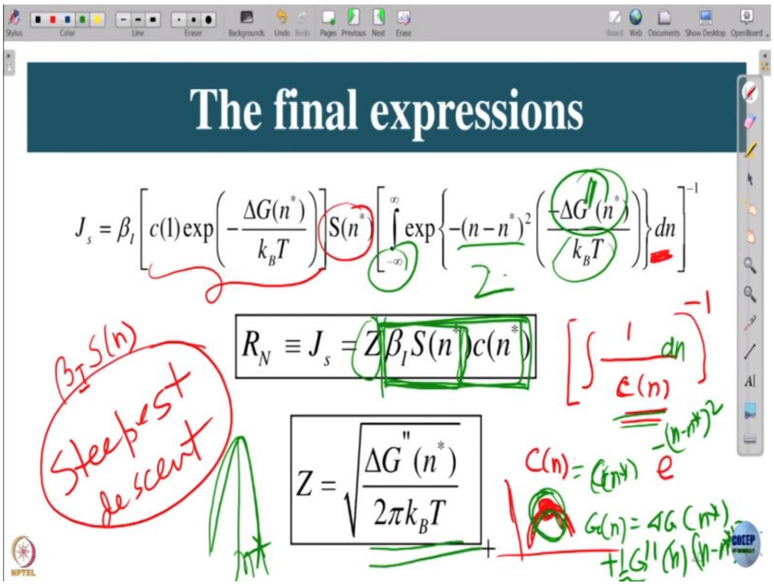

The final expressions

$$J_s = \beta_I\left[c(1)\exp\left(-\frac{\Delta G(n^*)}{k_B T}\right)\right] S(n^*)\left[\int_{-\infty}^{\infty}\exp\left\{-(n-n^*)^2\left(\frac{\Delta G''(n^*)}{k_B T}\right)\right\}dn\right]^{-1}$$

$$\boxed{R_N \equiv J_s = Z\beta_I S(n^*)c(n^*)}$$

$$\boxed{Z = \sqrt{\frac{\Delta G''(n^*)}{2\pi k_B T}}}$$

So now I have to calculate the rate. Now what do I do? So this is my C(n) this is beta S(n). Okay now I need, remember, I need the J at the critical cluster. So S(n) become a S(n*) or S(n$_c$) and then I have to evaluate this integral now and so important thing to assume that this is minus note that this particular integral that I have to do these integral that I have to do this is 0 to infinity. But I will come to it - 1 to + infinity.

Then I write C(n) the - 1 is there C(n) is

$$C(n) = C(0)\exp\left[-\Delta G(n)/k_B T\right]$$

I say okay I want population here. So because I have an integration to do. So I now say this I write C(n) but the; because this is a method called the method of steepest descent or many other goes by the Laplace’s formula. Many methods so basic idea is that around here C(n) is very small in this region. In this region C(n) is very small then that is the it is in denominator. So in the integral over the n these quantity here it dominates.

And so then I say okay C is I can now consider a only a small region around here. So the way I would do that then I will say. Okay C(n) is the C(n*) and then these are harmonic. I assume it to be harmonic and I write the fluctuation here the n minus n star square and then I need to do the double derivative because this I expand the ΔG(n) here as

$$\Delta G(n) \approx \Delta G(n^*) + \frac{(n-n^*)^2}{2}\Delta G''(n^*)$$

Okay so that is then by two and by k_BT is here then it becomes this. Let us explain this again. The little tricky I have to do the integral. So I have to do this integral. This integral I am going to do and these integral I use the following property. That the C(n) is very small here and this is the smallest C(n) in this landscape which is C(n) is $\exp\left[-\beta\Delta G(n)\right]$ and by Boltzmann distribution and this is maximum this ΔG(n) is maximum is ΔG(n) is maximum means C(n) is minimum.

So in this integration C(n) is minimum here. So 1 - C(n) is maximum here. Okay this is I am saying it is used again and again. So C(n) is very rare in a barrier top. So one over C(n) peaks and so it is enough in this integration to take care of the region near the maximum. That because of this advantage that we are taking. That the advantage that C(n) is this quantity is minimum. So 1 over C(n) is maximum.

We expand it in a harmonic thing and this is the second derivative and then this is a Gaussian. So I can now do this integration completely. So everything before I have done that I have the beta Sn so beta Sn and 1 - 1 of C(n*) that will come up. So that is so this Sn beta. Yes, in my earlier peak C(n*) coming because I am making approximation C(n) C(n*) then the Gaussian.

So that inverse that come from so this is fully documented by me I know Z is a leftover of the integration and that integration I can do because these Gaussian function now. Okay so minus infinity to plus infinity I can make it also 0 to ∞. I do not care because there is a these integration shows you sharply fit the function. It is so sharply peaked that I can always make it to -∞ without any loss -∞ as it is given here. Then this integration is just $\sqrt{(2\pi/a)}$ and the Gaussian integral and that gives now the ΔG^2. 2 is there when the $2\pi k_BT$.

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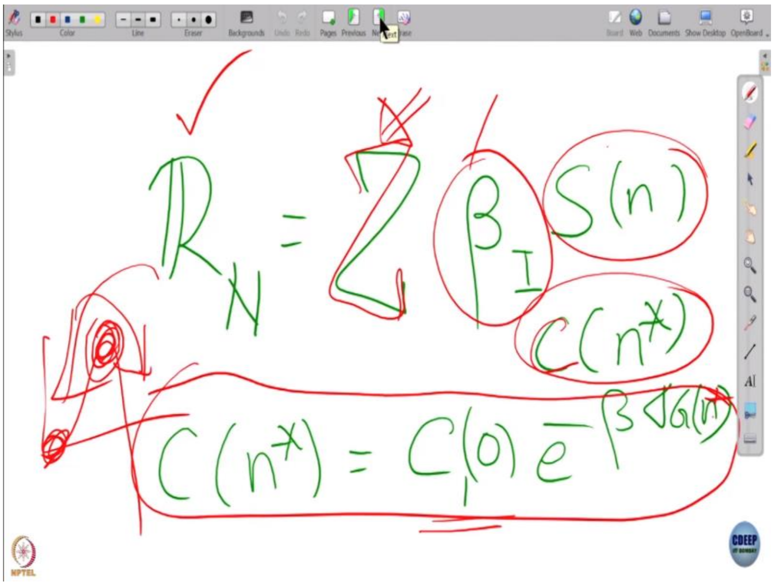

So I now get this beautiful expression. The rate of nucleation so everything is determined I have now. I have rate of nucleation is given by

$\mathbb{R}_N = \mathbb{Z}\beta_I S(n)C(n^*)$

The rate of infringement β_I that comes from kinetic theory surface area and the critical concentration that has to be there. We know that and it is reproduced beautifully. And C(n*) is given by Boltzmann's constant. The concentration of monomer because I start here and go there. This is the monomer and this is the n*. So that is given by n*. My probability of being here is given by this expression.

And my infringement surface giving that and these vary as Ludovic factor is called the non-equilibrium effects that take into account of going the both ways these exactly we do in chemical kinetics. We call we sometimes called that small cost equation approach. And they all these things happen very similar time and this is exactly what is Kramer's theory also of chemical kinetics very well known theory of chemical kinetics that will do little bit hopefully someday.

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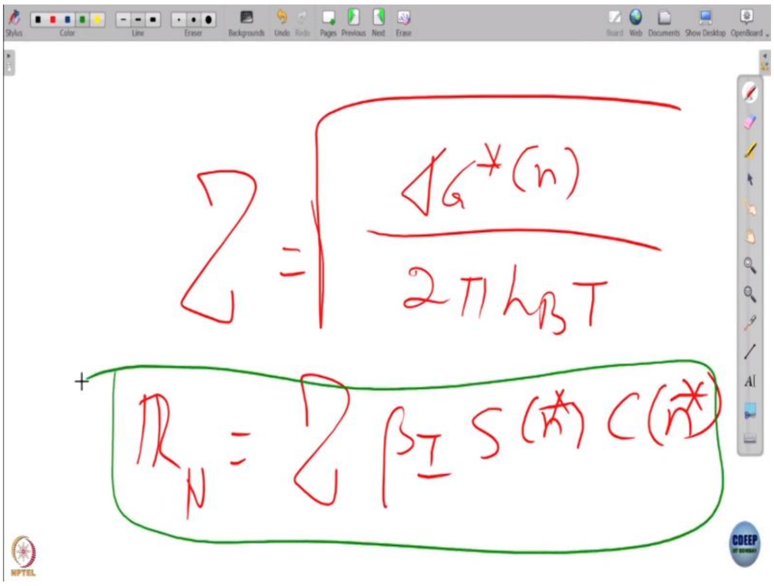

$$\mathbb{Z} = \sqrt{\frac{\Delta G^{*}(n)}{2\pi k_B T}}$$

$$\boxed{R_N = \mathbb{Z}\,\beta_I\, S(n^{*})\, C(n^{*})}$$

So now what is Zelda($\mathbb{Z}$)? Zelda is this beautiful expression. Let me write down that.

$$\mathbb{Z} = \sqrt{\frac{\Delta G''(n^{*})}{2\pi k_B T}}$$

And rate is Zelda factor impinge main surface ratio C(n*). This is the rate of rate of nucleation. The reason I did it in detail in such great detail and more detail is given in the book and of course I think you what I need here a little bit more straightforward than what is given in the book.

Big book is little bit writing some more detailed stakes and little bit more talking has been done which is not necessary. So basically these summarize the whole thing is that we did a calculation of the rate of barrier crossing. You know is very standard thing in chemical kinetics and many other things but $\mathbb{Z}$ did it without knowing anything. But I do no, the same times molecules carried this barrier lesson linear. Indeed, Michaelis-Menten and all these things all in the same time the same thing and this very general approach.

The formula of these two by k_BT root over these things is essentially goes as Laplace's formula. And so a few more comments we have done.

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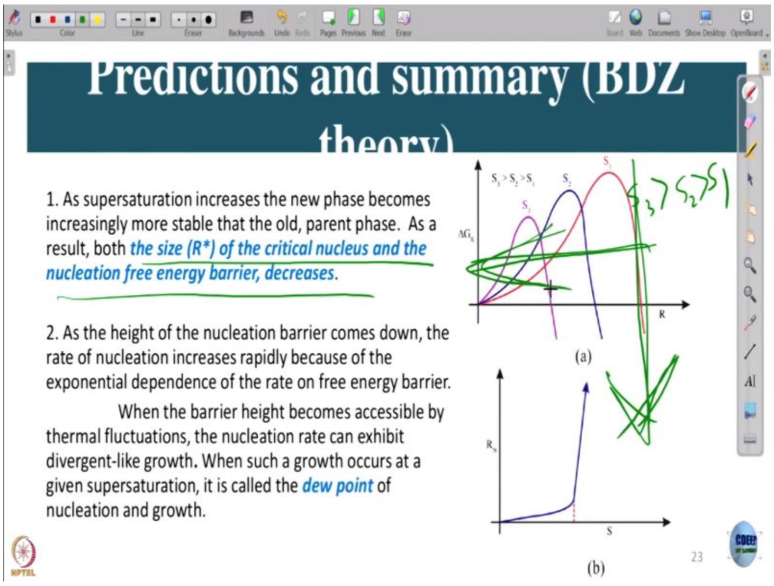

Predictions and summary (BDZ theory)

1. As supersaturation increases the new phase becomes increasingly more stable that the old, parent phase. As a result, both *the size (R*) of the critical nucleus and the nucleation free energy barrier, decreases*.

2. As the height of the nucleation barrier comes down, the rate of nucleation increases rapidly because of the exponential dependence of the rate on free energy barrier. When the barrier height becomes accessible by thermal fluctuations, the nucleation rate can exhibit divergent-like growth. When such a growth occurs at a given supersaturation, it is called the *dew point* of nucleation and growth.

So this is what I was talking about the temperature dependence. A very strongly temperature-dependent phenomena these super saturate. These sometimes it is not just a temperature but pressure and super saturation that means you increase the pressure you see nucleation. That is a way to see the nucleation in a cloud chamber and these are the different super saturation. The super saturation S3 is more than S2 than S1 and then when the super saturation increases, the size of the nucleus comes down and barrier comes down so activation free energy decreases.

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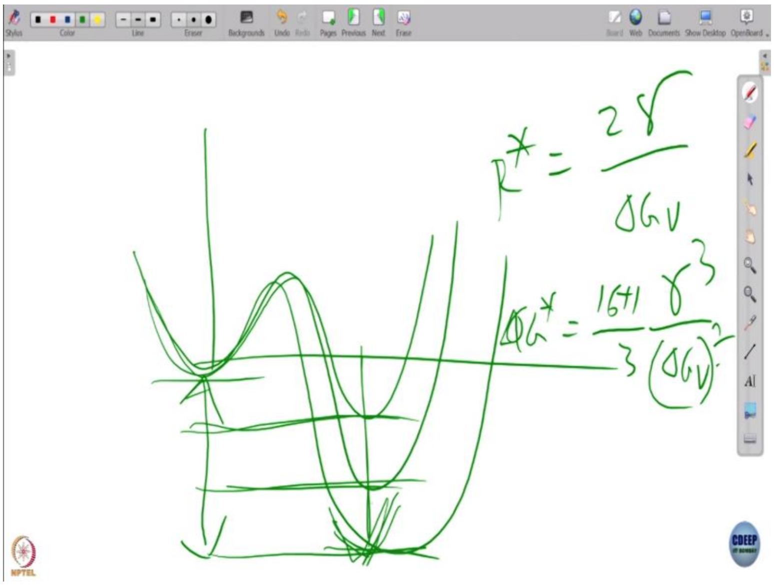

$$R^* = \frac{2\gamma}{\Delta G_V}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_V)^2}$$

The reason is that if you transfer into free energy landscape then what is happening is that as we increase the super saturation then these ΔG_v which is ΔG_v this quantity is increasing. As this quantity is increasing then R* is decreasing and $\Delta G*$ is also changing.

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma^3}{\Delta G_v{}^2}$$

But this is changing much faster. So as we increase super saturation or in lower temperature. We will call it increase super cooling like water. Instead of 0^{o}C I am going to -10 ^{o}C to -8 ^{o}C.

This you can say - 5 - 10 - 20 below the freezing and then the barrier comes down as I said and the size comes down. Then what is really interesting you find that nothing is doing. You go on suddenly it becomes explosive like it is shown here. The rate of nucleation suddenly increases because the barrier has to come down to a level where thermal fluctuations can access it and that exactly happens. So this is the picture very important picture of the nucleation theory.

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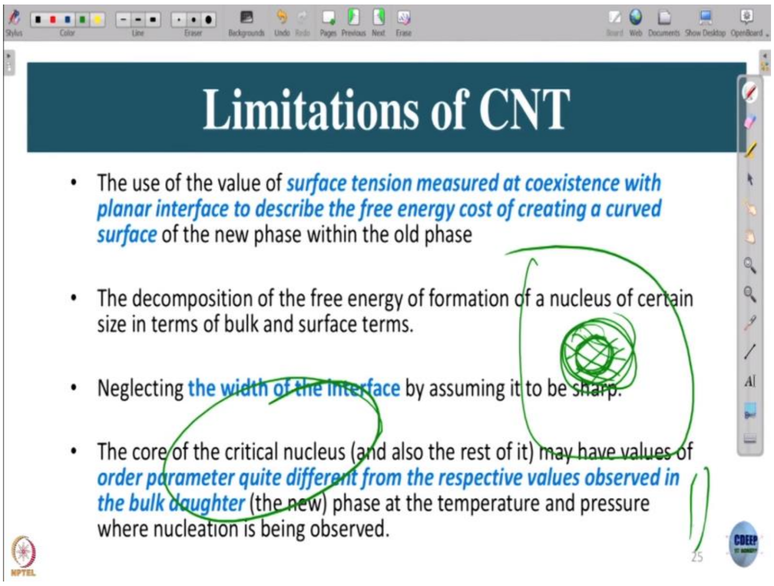

Limitations of CNT

- The use of the value of *surface tension measured at coexistence with planar interface to describe the free energy cost of creating a curved surface* of the new phase within the old phase
- The decomposition of the free energy of formation of a nucleus of certain size in terms of bulk and surface terms.
- Neglecting *the width of the interface* by assuming it to be sharp.
- The core of the critical nucleus (and also the rest of it) may have values of *order parameter quite different from the respective values observed in the bulk daughter* (the new) phase at the temperature and pressure where nucleation is being observed.

Next is that as both runs between bulk phase and surface known for several systems notably for water and many other systems a quantity variation across it is possible. And it is there are certain limitations. There are very detailed things like the surface tension we are using is that for coexistence. But we are using it in out of equilibrium. So there is certain limitation there. Then we assume it as a sphere that is a limitation there and many times they are little elliptical simulations have showed.

And then core nucleus is liquid like but surface nucleation we are assuming this is short boundary and core is that of the new phase. And these the old phase that is not quite like that because this is some extent it is cold like but then there is a diffuse region and that is also an important thing that we have not discussed and that is done by theory called data and density functional theory of expression. That we can do only when we do the density functional theory which I will explain little bit density functional theory later when you do the integral theory.

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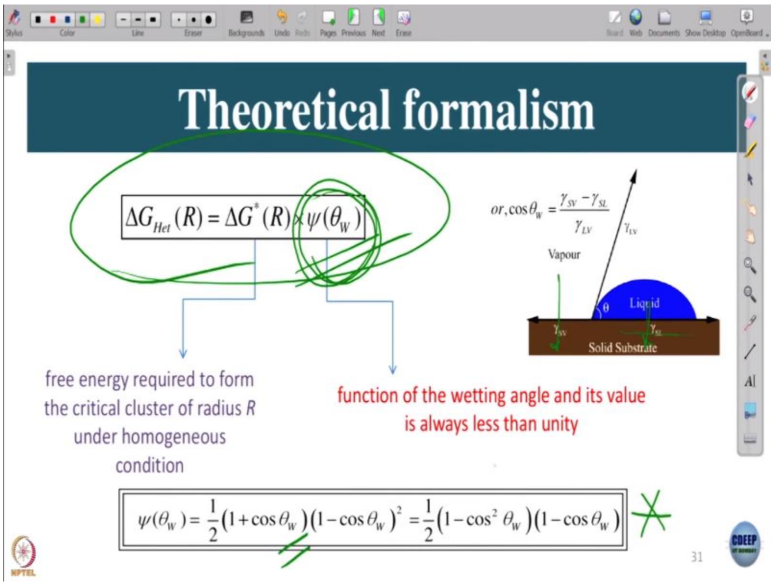

Theoretical formalism

$$\Delta G_{Het}(R) = \Delta G^{*}(R) \times \psi(\theta_W)$$

free energy required to form the critical cluster of radius *R* under homogeneous condition

function of the wetting angle and its value is always less than unity

$$or, \cos\theta_W = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

$$\psi(\theta_W) = \frac{1}{2}(1+\cos\theta_W)(1-\cos\theta_W)^2 = \frac{1}{2}(1-\cos^2\theta_W)(1-\cos\theta_W)$$

And there is this beautiful problem. Heterogeneous nucleation and that heterogeneous nucleation is described like that you are on a surface. The basic idea is that surface tension of the; you reduce the exposure of the liquid to the old new phase to the old phase. And the surface tension of these could be much less and as a result you get a free energy barrier that is the original nucleus which is the barrier gets substantially reduced and the amount it gets reduced is a quantity $\psi(\theta_W)$ which is that is given by

$$\psi(\theta_W) = \frac{1}{2}(1+\cos\theta_W)(1-\cos\theta_W)^2 = \frac{1}{2}(1-\cos^2\theta_W)(1-\cos\theta_W)$$

I am not going to derive it is rather long derivation. But θ_W is determined by

$$\cos\theta_W = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

The surface tension of and these surface tension and that is the expression that is given.

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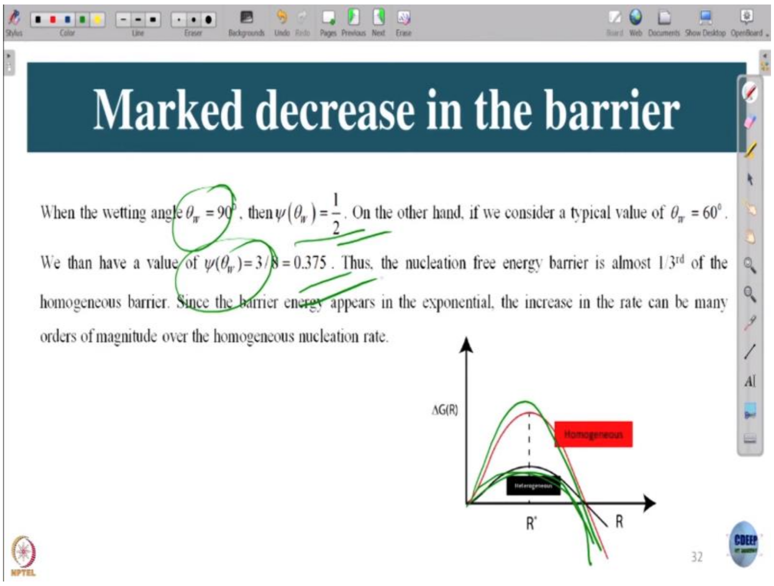

Marked decrease in the barrier

When the wetting angle $\theta_w = 90^0$, then $\psi(\theta_w) = \frac{1}{2}$. On the other hand, if we consider a typical value of $\theta_w = 60^0$. We than have a value of $\psi(\theta_w) = 3/8 = 0.375$. Thus, the nucleation free energy barrier is almost 1/3rd of the homogeneous barrier. Since the barrier energy appears in the exponential, the increase in the rate can be many orders of magnitude over the homogeneous nucleation rate.

So that this heterogeneous nucleation barrier comes down. This is homogeneous nucleation. But to describe it a heterogeneous nucleation you need over homogeneous nucleation and so that expression is not given here. But it kind of said that if the angle is 90 then barrier becomes half. If it is 3/8 then barrier becomes much less 0.375. So this is an important thing and there are some many other things which we would be describing later. So we will start next a little bit of Ostwald step rule then we go over to some other aspects of statistical mechanics and that will be in the next class.