Basic Statistical Mechanics
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Lecture – 39
Nucleation Part 2: Kinetics of Nucleation

Okay, welcome back, so in the last class we started on a beautiful subject of which goes on the kinetics of phase transition and but it is essentially, a thermodynamic treatment and we have included these in this course because of the generality in fact, phase transition itself, if you have noticed is quite general, it does not talk of any given system, it is applicable to all systems.

That means, I can I am talking on nucleation not just of gas liquid at the same break, I am talking of freezing, formation of ice nuclei melting, formation of water inside ice, I am talking of magnetic transition in the presence of a magnetic field when it is first order in the absence of magnetic field is a second order while the grand generality is appeals to some people.

This grand generality at the same time makes many people uncomfortable because people many times like to think in terms of specific system, specific examples but there are things where generality is extremely helpful and useful because you learn one thing you can apply to all different systems as I was telling, my ex-student in Japan, he learned these things in a class you know this nucleation and spinodal decomposition and he found; he is an experimental physical chemist not my own student but he was just taking the course. And he found it extremely helpful even now, he is so grateful whenever he comes to his Professor now in IIT Madras or IIT Chennai, whenever he comes to Bangalore, he make sure that he comes and sees me such is the reach of such a problem that you can apply to almost many, many disciplines okay.

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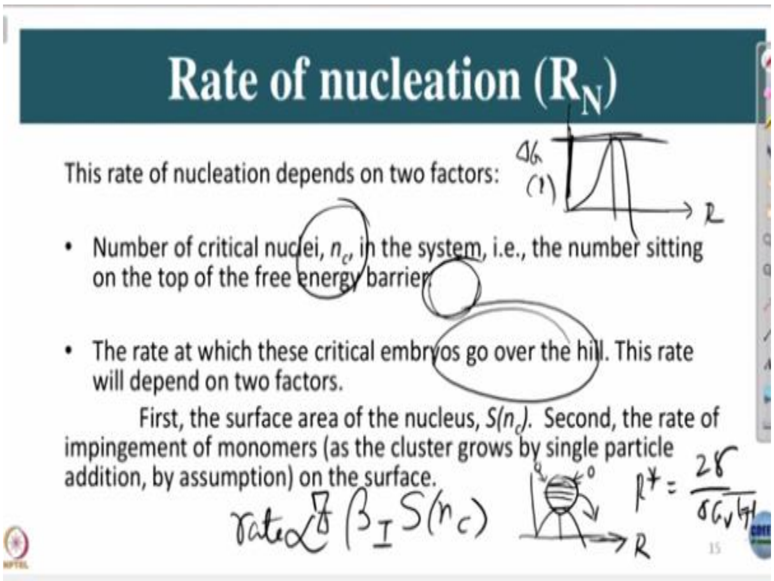

Rate of nucleation (R_N)

This rate of nucleation depends on two factors:

- Number of critical nuclei, n_c, in the system, i.e., the number sitting on the top of the free energy barrier.
- The rate at which these critical embryos go over the hill. This rate will depend on two factors.

First, the surface area of the nucleus, $S(n_c)$. Second, the rate of impingement of monomers (as the cluster grows by single particle addition, by assumption) on the surface.

rate $\propto \beta_I S(n_c)$

$R^* = \frac{2\gamma}{\delta G_v}$

So, now we are trying to get these thing going, so basic idea then is that we have this kind of a scenario and this is ΔG(R) and this is R and these are critical nucleus and we have to cross this barrier, I described the analogy with chemical kinetics where it is; we know how to do it, here we know partly because we know the probability of being in the top has to be Boltzmann e to the power minus ΔG* that we know.

But you do not know how to calculate the rate of going over, in chemical kinetics it is a bond breaking or twisting there we can write the detail motion of that molecule rotating or bond breaking but here we do not have that, so how do we get it? This was the one which was done by Zeldovich which as I told you, he is a nuclear physicist.

So, the way is now done is there 2 factors is the probability or number of critical, if you consider rate as a flow like water going through a pipe, the rate of water; we talk of rate of water flow similarly, a new phase is forming and from the old phase then if we can see that the rate as a time independent process, then how do I show, I will say okay, number of nucleus at the top, a critical nucleus; number of critical nuclei n_c.

And the that is I can find on the top of the barrier and then at the rate it will go over, so these I said is the same thing that we do in chemical kinetics this part and this part is the one that is non-trivial and I need to calculate that. So, if I now have a nucleus sitting here at the top then what would let it; if I have sitting on the top, a nucleus sitting in the top what will make it go over?

It will make it go over, if another particle comes and impinges on that so, I need a another more particles actually not 1, several but this is the radius R, so this is already a pretty macroscopic coordinate, so by changing r means several monomers is coming, so these monomers are going to impinge on this, the very, very interesting thing you know in many of examples, many problems, we get this quantity, I remember I passed a comprehensive at in Brown University because I could argue this one, this was the problem given in a comprehensive exam in PhD exam without telling us and during that time I did norm nucleation and but I could figure it out by using kinetic theory of gases that okay, the number of molecules that can pass, I realized that what could be; then I said okay we all done in Maxwell Boltzmann kinetic theory of gases that there is a unit area of a surface.

And the pressure is nothing but the molecules coming and colliding with it, what are the number of molecules colliding with it that is within certain parallel pipe, remember we draw the parallel pipe and okay these are the number of molecules in these and which has the velocity towards the wall, so the rate of impingement of monomers, it is very similar logic and on the surface.

But then also the surface area of the nucleus; larger the surface area more; now you may argue why I am taking different surface area because in different temperature, the size of the critical nucleus is different, remember $R^* = 2\gamma/\Delta G_V(T)$ and ΔG_V is temperature dependent, so as temperature becomes larger and larger and I will come to this little bit more detail now, maybe I could just do now and then come back because it is a very important thing, I had it in my last slide, I forgot it.

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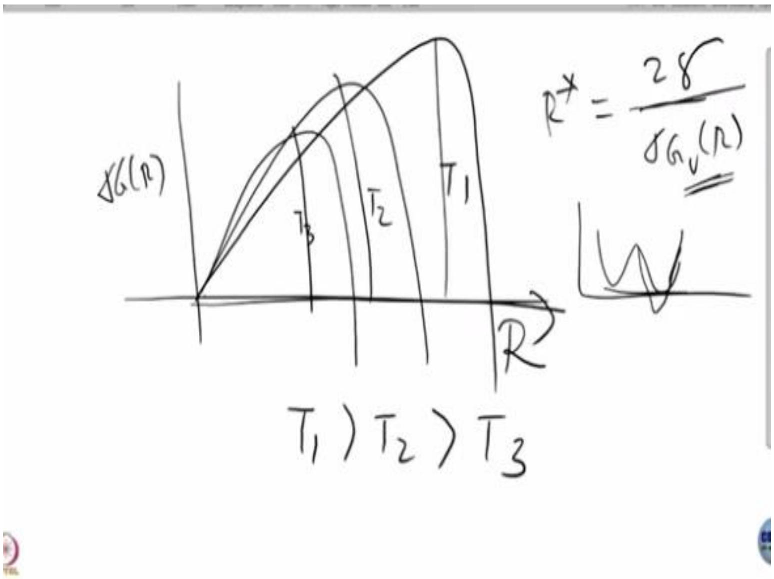

So, if I now, plot this $\Delta G(R)$ against R at different temperature, then I know γ is also temperature dependent surface tension but much weaker than this thing, $\Delta G_V(R)$ however when they are at equilibrium 2 phases; old and new, then this is 0, ΔG_V is 0, so R* is infinity. So, when I go little bit below then R* start decreasing but still can be very large, so I can consider the following situation that I can say okay, this is when it is large, it equals to coexistence, then it.

So, as I lower the temperature, so if it is T_3, T_2, T_1, then T is greater than T_2 greater than T_3, so barrier comes down, size becomes small as ΔG increases, so this is the reason why the surface area depends very strongly on temperature, then also depends from system to system because these temperature dependence and the free energy landscape completely varies, like if I talking of melting is different from that of freezing or more than that you know from gas liquid condensation that is what I wanted to tell.

So, this nucleus with the surface $S(n_c)$ sitting, so then I would be the rate would be proportional to the rate of impingement, let me call it β_I and $S(n_c)$ okay, so this should be proportional to that and then I need a rate to go over that I call Z.

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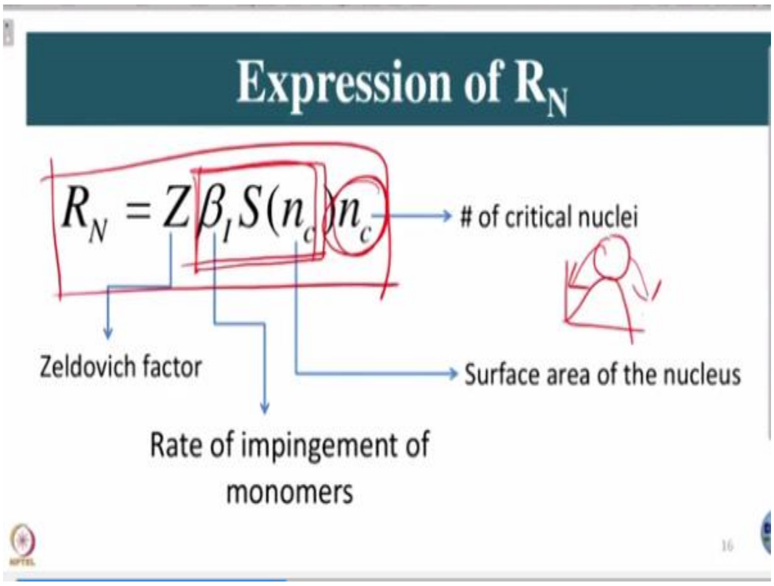

Expression of R_N

$$R_N = Z\beta_l S(n_c)n_c$$

\# of critical nuclei

Zeldovich factor

Surface area of the nucleus

Rate of impingement of monomers

Then, I can go now and write my; so this is the expression, so this is the probability of having a number of critical size nuclei that is the n_c, then this is the rate of impingement on the surface and then the probability, there is also a probability that during the every time, unit time, this β is the rate of impingement per unit time, per unit time which can also disappear, that means it can also come down here.

So, there is a non-equilibrium process and this is what brings it very close to chemical kinetics that I will discuss a little bit later, that effect that it can come down is included through these factors Z which is called Zeldovich factor. Now, we will go through the calculation and the calculation is a little complicated and but we have to live with it, this is one of the probably after our canonical ensemble calculations, this is the most detailed calculation that we will be doing. But we have to do that anyway and we will go through that with heroism, so this is the thing we have to calculate Z, how I calculate Z.

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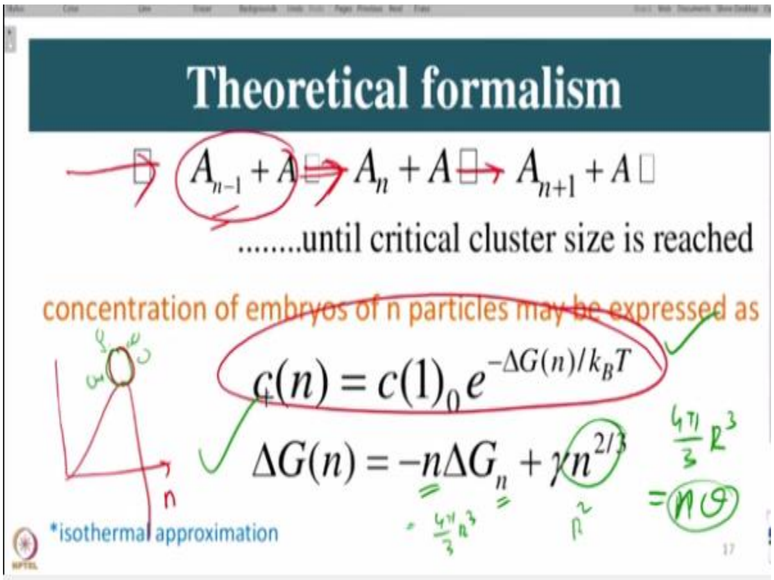

Theoretical formalism

$$\rightarrow A_{n-1} + A \rightarrow A_n + A \rightarrow A_{n+1} + A$$

........until critical cluster size is reached

concentration of embryos of n particles may be expressed as

$$c(n) = c(1)_0 e^{-\Delta G(n)/k_BT}$$

$$\Delta G(n) = -n\Delta G_n + \gamma n^{2/3}$$

*isothermal approximation

The way I calculate Z now is that I consider, as if a train is moving, so the growth of cluster is going like this, this can also, so I add 1, it goes there, then I add one more, A_{n-1} is becoming A, then A_{n+1}, it of course disappears that I will consider later, right now I am trying to set up a train and my aim is that just as we were in front of a; stood in front of a passing train, then this compartment after compartment going in front of you.

When the train moves in a steady state velocity, then what happens; each compartment comes to you at a regular interval, okay and that is a steady state. Steady state means just a flow of water in a steady state that means this is a time independent process, so I want to find a time independent rate, rate is always; when rate is a constant is a time independent, it gives a steady flow, completely independent, a time independence is equilibrium when nothing is happening, okay.

That is a; if I take a derivative of all the quantities, then at equilibrium then they are all 0, concentration, time derivative of concentration is 0 but here it is not, this is the next time independent thing that is steady state but it is not equilibrium, so we have to make a distinction between equilibrium time independent process and steady state time independent process.

I am going to do here that steady state because I want to study the rate, whenever I talk of a rate, it is a time independent is a steady state otherwise you do not have a rate, then we say time dependent rate that is a different thing altogether, okay. So, now I am going to calculate the flow as if a train, so however this quantity that I called c(n) that the this going over, I can write as Boltzmann, this equilibrium c(n) is an equilibrium concentration.

I now change my notation, I might change my notation from R dependence to N dependence that means because I want to talk of adding of impingement of particles on these things I and then growth I want to do in terms of number plane, the number of particles in the system, then I know there is one to one corresponding between radius. If I assume a sphere then volume into $4\pi R^3/3 = nv$, okay.

So that means, R scales as $n^{1/3}$ because this volume of one molecule of volume occupied by 1 molecule into a number of molecules in the cluster nv that has to be $4\pi R^3/3$, both have same dimension and volume okay, this is a trivial. If that is so, then I know this is $4\pi R^3/3$ per unit volume then that is nothing but proportional to n and that one volume I observed in n, so that because per volume and then v I multiply, so these become dimensionless, it is just but sorry, dimension of energy, energy per particle.

And now there is a surface term which is R^2, which is nothing but $n^{2/3}$ okay. So, my earlier expression $-4\pi R^3/3 + 4\pi R^2\gamma$ that becomes $-n\Delta G_n + \gamma n^{2/3}$. Why I am going to end the representation because I want to add the molecular picture; does not allow me a molecular picture, it allows the thermodynamic temperature.

Because I can; I could do the surface tension but now I add a molecular picture because I am adding molecules one by one and it is flowing and then I have the following ingredients, I have the Boltzmann distribution and I have conversion of ΔG $\gamma n^{2/3}$, okay.

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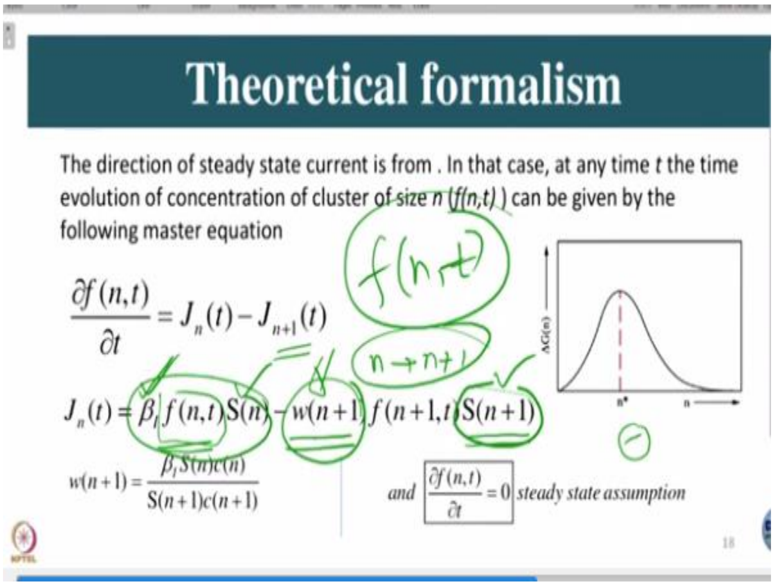

Theoretical formalism

The direction of steady state current is from . In that case, at any time *t* the time evolution of concentration of cluster of size *n* (*f(n,t)*) can be given by the following master equation

$$\frac{\partial f(n,t)}{\partial t} = J_n(t) - J_{n+1}(t)$$

$$J_n(t) = \beta_i f(n,t) S(n) - w(n+1) f(n+1,t) S(n+1)$$

$$w(n+1) = \frac{\beta_i S(n) c(n)}{S(n+1) c(n+1)}$$

and $\boxed{\frac{\partial f(n,t)}{\partial t} = 0}$ *steady state assumption*

Now, I want to see that how the; now I introduce a very important quantity that is f(n,t); f(n,t) is time dependent, this is the probability of having a particle a cluster in nucleus of n particles at a time t, okay. Now that thing is changing, it is changing because I have a flow and as a result of flow, that this guy is decaying by; I am just saying one-way flow now, if I do the equilibrium I would did both the two sides that I will do later, so these guy is changing because of that flow, the one-way flow very important, the one-way flow.

This is decreasing, because molecules are moving now, so then J_n - J_{n+1} that is the way this is changing, $J_n(t)$ I already wrote that is my impingement, time dependent probability into surface minus; now this is very interesting, now this is; this n+1 becoming n also and that is; so this is this $J_n(t)$, it is going to n to n+1 okay, so it is going to n to n+1 but it is on the other hand n+1 becoming n and n+1 becoming n by evaporating that is n+1.

So, if I consider this guy, then this guy is going on that but in the previous step it is going to these but on this enzyme, a part of that is in the flow, it is going at that rate but at the part of that is coming back, so I am just considering these process as I said, I am going to consider only these process and in this process, it is going by impingement but this also disappear by evaporation.

So, if amount going a, some amount is coming back here, now I can do also this case but doing 1 in enough for to get me the flow, so this is a forward and this is the backward, of that I have an estimate of the rate of impingement on a surface from kinetic theory of gases, as I told you the Maxwell, Boltzmann, $f_n(t)$ is a time dependent probability, very difficult thing, right now I will see that we do not need that, we need that if more difficult calculation.

So and I have the surface area of n and n particle, this is disappearing; evaporation also depends on the surface area clearly but so this I have a control, S(n) I know, S(n+1) I know surface, the surface of a sphere of radius R is $n^{2/3}$ I know that, I do not know what is w(n+1), these are very, very interesting condition here. How do I find w(n+1)?

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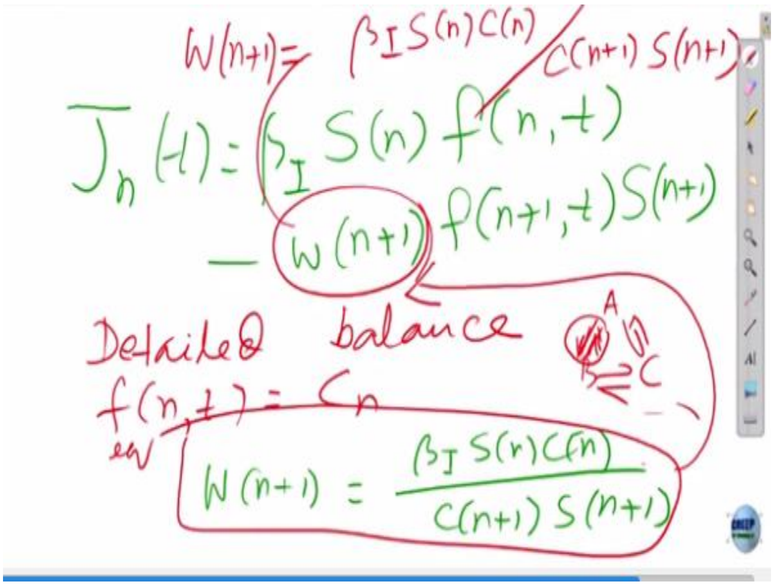

Now, there comes a very, very important quantity, let me get a page to explain that, so $J_n(t) = \beta_I S(n) f(n,t) - w(n+1) f(n+1,t) S(n+1)$. Now we use something I go back, I have to calculate this quantity and this is another beautiful thing that we use a lot in your chemical kinetics undergraduate we have use, is the principle of detailed balance, one of the most honour, most respectable, the principle called principle of detailed balance.

Onsager used it, generalized it and microscopically which in his famous 1932 paper or irreversible thermodynamics and he got Nobel Prize for that. Now, principle of detailed balance says that if I have now at equilibrium, I have to consider back and forth, steady state I got it flow, you have to make a distinction, so I have principle of detailed balance is a very strong statement.

It says that if you are at equilibrium then it is not enough to have a steady time independent but each state must be individually balanced that means, these state, there are number of particles going up in towards midway and must be same as A to B, so individual steps, this is the principle of detailed balance, so microscopic reversibility, extremely important that is the only condition that guarantees equilibrium.

So, equilibrium means flux is 0, no flux, it is everything is balanced but we are ultimately calculating a steady state, we are flying a flow but see how we are using equilibrium at the same time, this is exactly done many, many branch as I told you if you, enzyme catalysis, kinetics Michaelis Menten, then you have the Lindemann, famous chemical first order kinetics unimolecular dissociation reaction, everywhere this is use.

But it was initially first done by Zeldovich okay, now all of maybe, all of them have done independently but it is the same thing at least I am just mentioned 3 very famous theories but probably 10 theories uses this kind of logic that is why I like nucleation because it is being so much beautiful thing, so okay now $J_n=0$. If I put $J_n=0$ then what; that is equilibrium.

But I have already defined that C_n is the equilibrium distribution, so at equilibrium f(n,t) becomes time independent but at equilibrium; now I put $0=\beta_I S(n)c(n)-w(n+1)\,\mathrm{c}(n+1)S(n+1)$. So, what does it mean now; that means, I get w(n+1), so w(n+1), these quantity now become equal to $\frac{\beta_I S(n)\,\mathrm{c}(n)}{c(n+1)S(n+1)}$, so this is my w(n+1).

So, I have now by using the detailed balance, I got an expression for w(n+1), let me write this down clearly because I need it, so w(n); now what I going to do now; I am going to put these quantity into these equation, okay. So, I am going to this expression is going to be substituted in this one.

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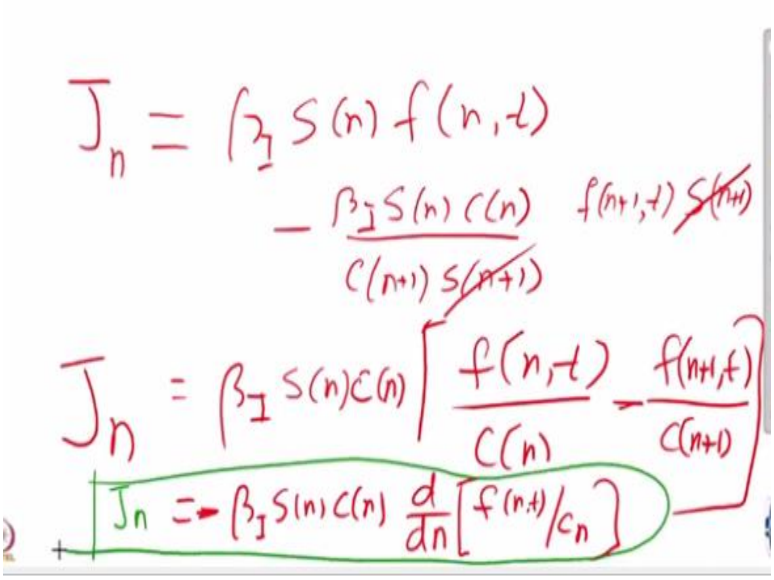

$$J_n = \beta_I S(n) f(n,t) - \frac{\beta_I S(n) C(n)}{C(n+1) \cancel{S(n+1)}} f(n+1,t) \cancel{S(n+1)}$$

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

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

Once I do that what do I get sorry, bear with me for a minute okay, so I got this now, now I noticed the following thing Sn plus, Sn plus get cancelled and I get β_I common, so I take $\beta_I S(n)$ out, I also take C(n) out common, then I get $\left[\frac{f(n,t)}{c(n)} - \frac{f(n+1,t)}{c(n+1)} \right]$, so I get for J(n) this expression, okay. Now, if you look at this expression what do you see; you see a beautiful thing, you see that this quantity, this f(n,t) and they are now, I can write it in the limit of large N, I can call it a time derivative. So, this thing can be written as because this f(n+1) is $-\beta_I S(n) c(n) \frac{d}{dn} \left[\frac{f(n,t)}{c(n)} \right]$, this beautiful thing.