Basic Statistical Mechanics
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Lecture – 38
Nucleation Part 1: Introduction, Thermodynamics of Nucleation

Okay, welcome back and good morning wherever you are or good afternoon again, so we discussed in the last class; review a little bit of phase transition, then I talked about 2 things I left out and not in great detail but students should know about them is the sol-gel transition which is a very common chemical industrial phenomena and percolation which is again very, very common in electrical engineering and these things.

Percolation is very commonly natural, well as I said in sand bed and many, many other places flow of water is dictated by percolation and then we talked about the Landau theory, the Landau's great free energy landscape picture of phenomena and then we talked about that first order phase transition is where you have a meta stability as given by hysteresis for given by the fact that you know, we all call that, we all say that water freezes into ice at 0 °C or go below 0 °C but that does not quite happen.

If you have a very pure water, you can make it a droplet, so that no impurity is there, then that remains in the liquid water till -40 °C, mercury and gallium you can supercool to about minus, you know below the melting by the freezing point, 50 °C or 60 °C, even in upstairs in clouds, the water, the temperature has to go down, before they really cloud; the droplets form.

And this is what is already in my Van der Waals theory, kind of Van der Waals loop and we know in meta stability in magnetic systems, you switch the field in the other direction but nothing happens, the spins still point; magnetic moment still point in up in the old direction, you have to turn your filed quite a bit before they turn around, so meta stability means that system is trapped in a minima free energy minima.

And that can be explained very easily from Landau's picture that in the first order phase transition, the old minima remains so even though new minima, deeper minima, deeper minimum has appeared, the system does not know how to go around, it does not know even, that probably knows that there is a new way of doing it but it does not know but what happen, system always undergoing fluctuations.

And these fluctuations is a way of exploring the thing and as we discussed in the thermodynamics that these fluctuations must be positive for a system to be stable that is why specific heat stability, specific heat greater than 0 is a condition of thermodynamic stability, isothermal compressibility positive is the condition of mechanical stability essentially, these fluctuations are we consider in a stable system, the fluctuations around a harmonic surface.

So, free energy can be that is why the; how does it come because it was a probability of a fluctuation of energy that is a Gaussian, $P(\delta E) \sim Ae^{-\frac{(\Delta \mathrm{E})^2}{C_V}}$.

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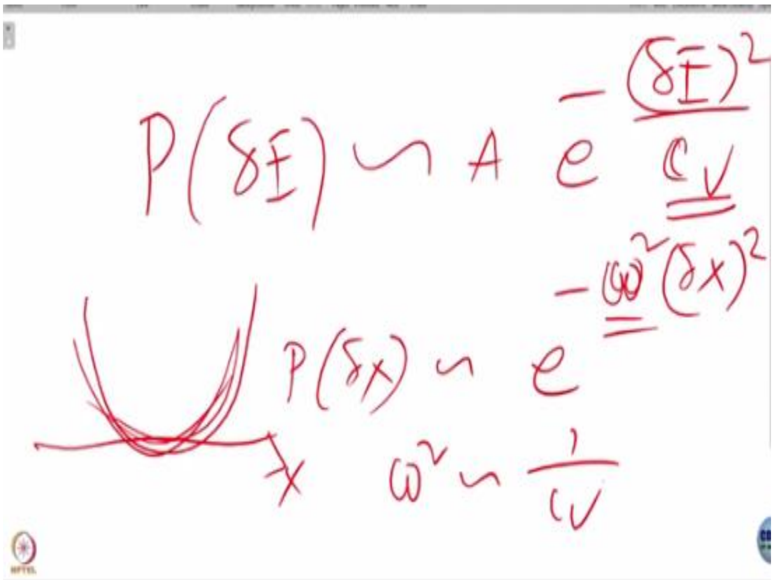

So, if I talk of a fluctuation δE, then that goes as $Ae^{-\frac{(\delta \mathrm{E})^2}{C_V}}$, so if I have a harmonic thing, then this CV is fluctuating then what is the probability of fluctuation; δX, if this is X, then it is again $e^{-\omega^2 (\delta X)^2}$, so ω^2 now you compare the 2, the frequency is C_V; $1/C_V$, so ω^2 is $1/C_V$.

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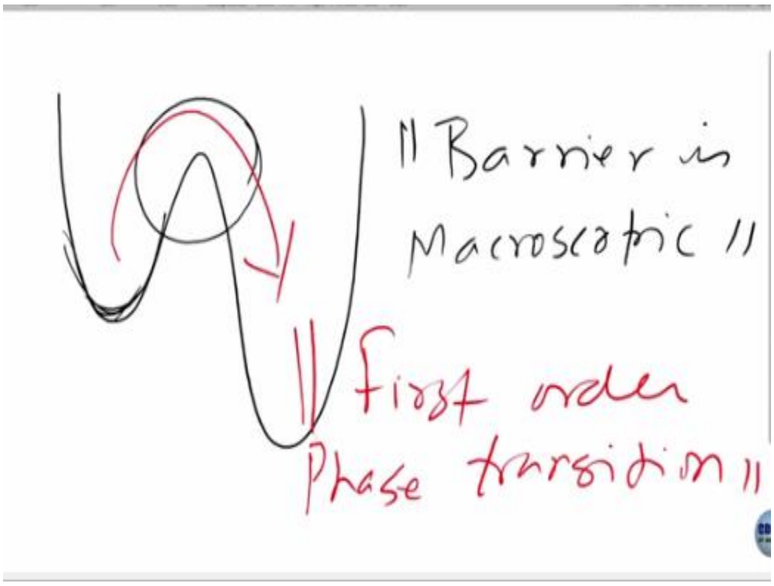

So, this a system stable system is in a bound in a harmonic surface, so right now what we are having then, we are having this kind of situation, this is harmonic but this barrier is large, the barrier is a macroscopic, so barrier is macroscopic, very important. So, how does the system go then from here to here, this is the question. In second order phase transition, it does not arise, second order phase transition does not have metastability.

It has just large and giant fluctuations appear with the divergence of compressibility and specific heat and you suddenly gate these systems split into 2 okay, order and disorder like in magnetic transition, you have ordered state and disorder state and a system choose between one of the 2, system choose between sorry, up spin and down spin and that is a beautiful phenomena called spontaneous symmetry breaking but we were not going to to that right now, we are going to do first order phase transition.

So, this is the first order phase transition, we will do second order more detail later but something extremely important to a physical chemist and to nanomaterial synthesis of more importance of late, now into material scientist and to physical chemist or in the department of solid state and structural chemistry or the next moving department of Chemical Engineering is very, very important that one understands the nucleation phenomena.

And this is something I can tell you a small story, once I was visiting Japan and I get talk and I was in first time and I was not comfortable with Japanese food and I was very hungry after the my talk, lecture, so there is one Indian student who was my ex-student, I was; not my own

PhD student but he is the student of another faculty member, he was very eager, send me many mails he wants to see me.

So, I remember it because after the talk I was very tired and he took me to his; I did a long talk, in Japan sometimes we did 2 hours lecture, I went to at 6 o clock, I went to his office and I told him first before you talk, you give me some food, so he gave me a couple of banana but then he was so told me sir, I wanted to see you because you saved my life I said how, he said you taught that course on nucleation and spinodal decomposition.

And here when I came they were doing something on a surface which was actually a nucleation and they did not know anything about it and so but I knew from your class, so I could explain the, experimental phenomena to them, the formation of islands and then there is a percolation and all these things and they are extremely, extremely happy and the first paper that I could read with; write within a short time in Japan.

But this guy was so; so then I realize that this guy was doing a surface scientist, so all the critical phenomena, critical exponent renormalization group you teach them, it is not useful to bulk majority of material scientists and to physical chemists or organic chemist but nucleation is very important because nucleation is more important than critical phenomena to these group of people.

Because they face that all the time a physical chemist, this is an experimental physical chemist, so that I always the pre-empt, I before getting critical phenomena, any other things I teach nucleation and I want students to learn nucleation, this is a beautiful phenomena okay.

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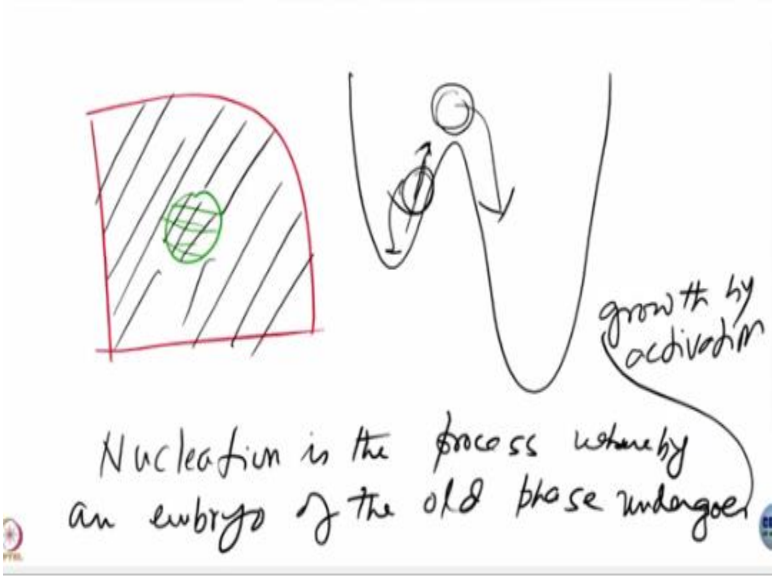

Nucleation is the process whereby
an embryo of the old phase undergoes

So, now how did the nucleation, then what happens actually in this system, when you have this phase, my old phase, in that old phase, the way it goes over to new phase is that a small embryo forms, so these embryo is a nuclei, that is a nucleus of the new phase and that tries to grow, so in this landscape this is somewhere here. So, this guy tries to grow by fluctuation is a spontaneous fluctuation.

And it go then, it comes down again, then again goes finally, it goes here and it goes over and then there is an explosive growth, so the process or the phenomena of an embryo growing into a metastable phase is nucleation, so nucleation is the process; let me write down, whereby an embryo of the old phase undergoes growth by activation and this is spontaneous, it has activation energy and we will now calculate the activation energy.

So, this is the nucleation, so when a first order phase transition happens not by any kind of big large scale fluctuation but this small fluctuation that goes, so the system is destroyed from within, from inside the system is destroyed and new phase comes up, that is how ice melts that is how water goes into ice or water droplets form, all the first order phase transitions or if you have a magnetic transition but in the presence of magnetic field, then you this again this, some localized spins get ordered from the disordered system.

And if you have spin on the up side, then up spins will get clustered together and they form a nucleus or an embryo and then that embryo melt and go but finally it will grow, they are growing in many places but one of them will grow and reach to the critical; these critical size and then it goes over to the other phase, so that is the phenomena we will describe now in a little bit more detail, okay.

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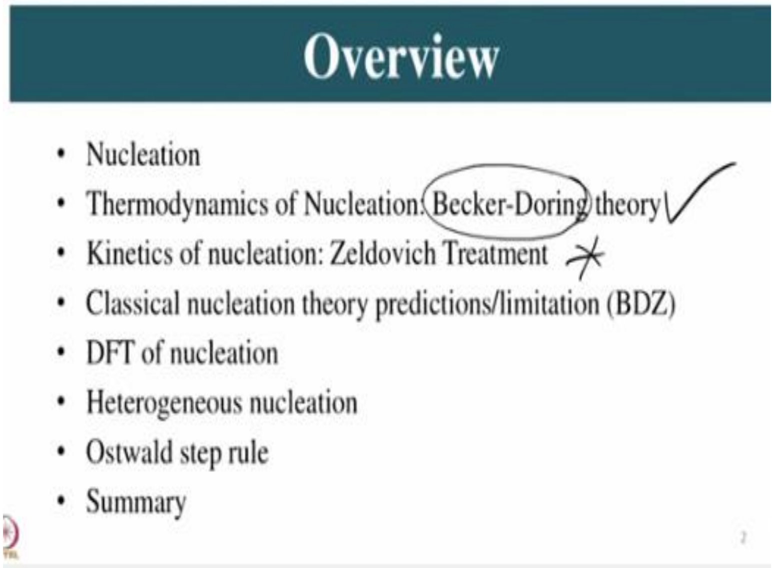

Overview

- Nucleation
- Thermodynamics of Nucleation: Becker-Doring theory
- Kinetics of nucleation: Zeldovich Treatment
- Classical nucleation theory predictions/limitation (BDZ)
- DFT of nucleation
- Heterogeneous nucleation
- Ostwald step rule
- Summary

So, we will now do the following thing that we will do nucleation, I described already thermodynamics of nucleation and the Becker Doring theory, then we will do something, it is a very, very nice things which is Zeldovich treatment of the correction of Becker Doring, by the way the Becker Doring is an extremely important thing, this is the thing which is described in many cases, physical chemist might know, Lindemann thing then you know, enzyme kinetics, Michaelis Menten and all these things they are all very similar things, they are connected to each other.

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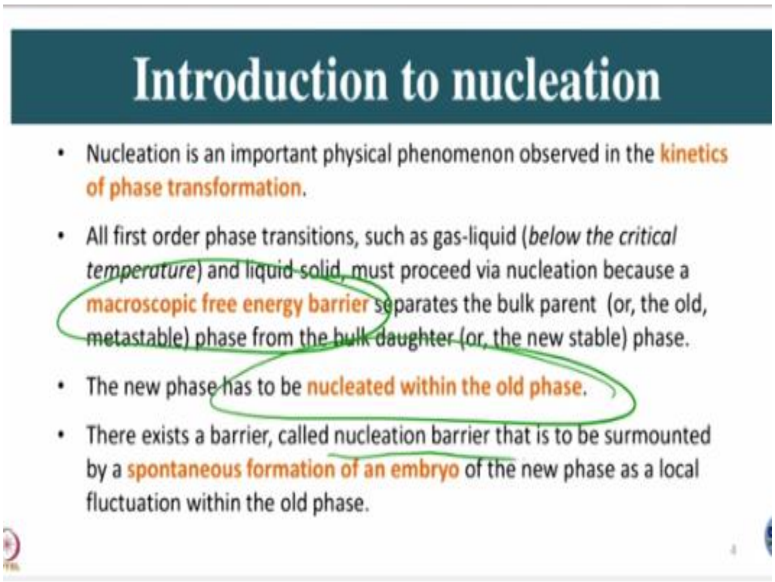

Introduction to nucleation

- Nucleation is an important physical phenomenon observed in the kinetics of phase transformation.
- All first order phase transitions, such as gas-liquid (*below the critical temperature*) and liquid-solid, must proceed via nucleation because a macroscopic free energy barrier separates the bulk parent (or, the old, metastable) phase from the bulk daughter (or, the new stable) phase.
- The new phase has to be nucleated within the old phase.
- There exists a barrier, called nucleation barrier that is to be surmounted by a spontaneous formation of an embryo of the new phase as a local fluctuation within the old phase.

So, someday if I can get time, I will talk about that okay, so then classical prediction limitations and all these things we will do, so let us start, then the nucleation okay, is the phenomenon observed in the large kinetics and phase transitions and it is from within, so there it must proceed via nucleation because a macroscopic free energy barrier, it cannot these I have already told, this barrier is macroscopic it cannot go, otherwise so it must from inside.

So, nucleated for new phase has to be nucleated within the old phase that I said and these they are; however, these process itself has a barrier and that is a nuclear barrier and does a beautiful physics and that is called nucleation barrier and that is the one we will now going to consider okay.

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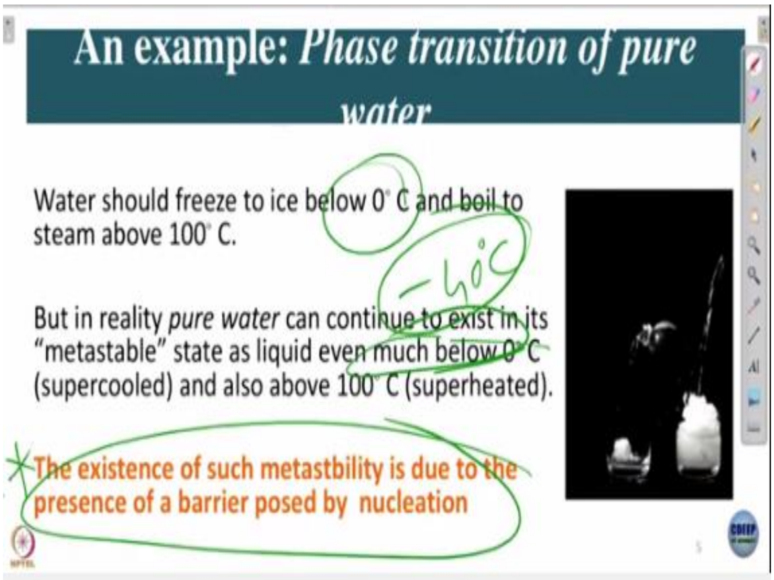

An example: *Phase transition of pure water*

Water should freeze to ice below 0° C and boil to steam above 100° C.

−40°C

But in reality *pure water* can continue to exist in its "metastable" state as liquid even much below 0° C (supercooled) and also above 100° C (superheated).

* The existence of such metastbility is due to the presence of a barrier posed by nucleation

And then an example as I already said that water should freeze at 0 degree centigrade does not it is can be supercool to great, great much below, much below minus 40 degree centigrade, water remains water, water does not be pure, water does not freeze at 0 degree centigrade that because the embryo need sufficient driving force to grow, it does not grow, okay and this is the existence of meta stability is due to the; this is a beautiful sentence actually. This is all taken from our book that the existence of metastability due to the presence of barrier posed by nucleation.

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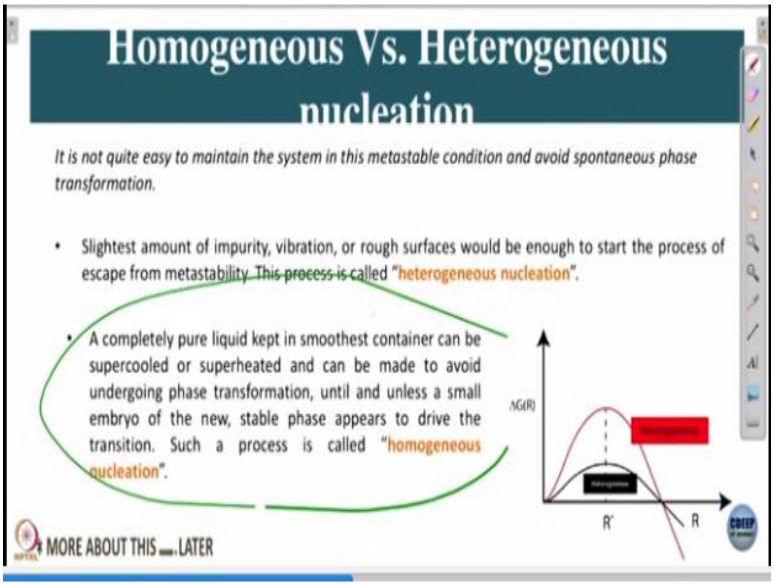

Homogeneous Vs. Heterogeneous nucleation

It is not quite easy to maintain the system in this metastable condition and avoid spontaneous phase transformation.

- Slightest amount of impurity, vibration, or rough surfaces would be enough to start the process of escape from metastability. This process is called "heterogeneous nucleation".
- A completely pure liquid kept in smoothest container can be supercooled or superheated and can be made to avoid undergoing phase transformation, until and unless a small embryo of the new, stable phase appears to drive the transition. Such a process is called "homogeneous nucleation".

MORE ABOUT THIS — LATER

Now, why pure water; pure water does not freeze below 40 degree, minus 40 °C, helium and sorry gallium and mercury does not they go 50, 60 °C below they are freezing, however you know in refrigerator ice forms you know, minus 5 degree centigrade, minus 3 °C, 10 °C, the reason is that if there are surfaces and there are lot of impurity so that is called heterogeneous nucleation.

Heterogeneous nucleation does not face that barrier and the way you do the heterogeneous nucleation of course, you have to do homogeneous nucleation first, then you include the surfaces and so that how regular nucleation takes place, okay. So, this is a completely smooth way and one interesting thing is that you are having a very; you might have done in physical chemist experiments, there you have super cooled it.

And you have the container below 0 °C, now you scratch it with and many of us have seen that or in liquid you scratch it with a rod, glass rod and you can see crystallites appearing, so the heterogeneous nucleation and this is because this is one of the telling and a great example of the role of surface tension and surface tension is something we want to study in this lecture later but right now, we defined surface tension as the energy required to create a surface.

So, if I have to create a surface of ice in water that is a different surface that requires extra energy that is energy surface tension quantitatively, it is defined at the energy required to create an unit area that you have grade in your high school even that surface tension but that same ice surface tension plays an extremely important role. Now, how we will go to do the theory and we are now going to that development of the theory, okay.

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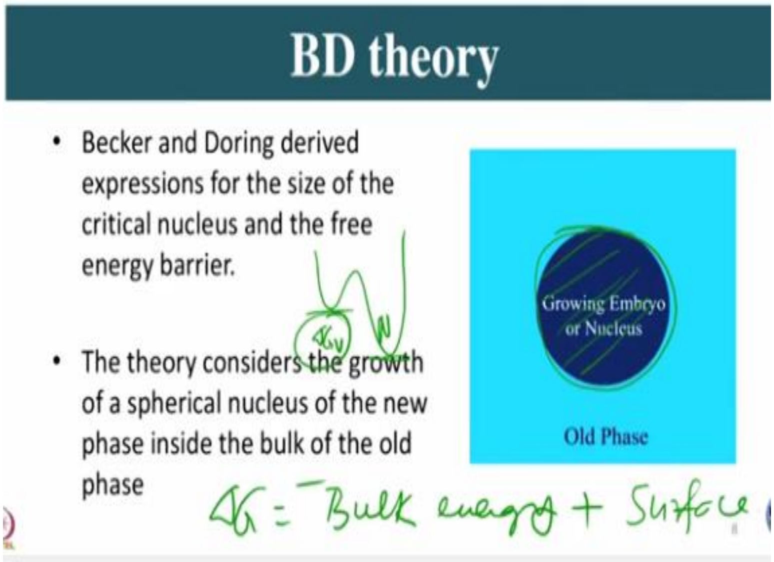

BD theory

- Becker and Doring derived expressions for the size of the critical nucleus and the free energy barrier.
- The theory considers the growth of a spherical nucleus of the new phase inside the bulk of the old phase

$\Delta G = -$ Bulk energy + Surface

So, the basic idea then that we have an embryo growing in this old phase, embryo of the new phase is trying to grow and we have to find out what is the energy okay, when I grow something then it gains energy because this the free energy landscape is like that, so this is the new phase, the embryo phase, so when it is here it gets free energy, it gets considerable of free energy, set free energy per unit volume, I define as ΔG_V, so it gains that energy.

However, it creates the surface and it has to pay for the surface, so total ΔG is then sum of bulk energy which is gain is minus negative plus then surface energy which is it has to pay, so these things and some of you might already willing to see what is there.

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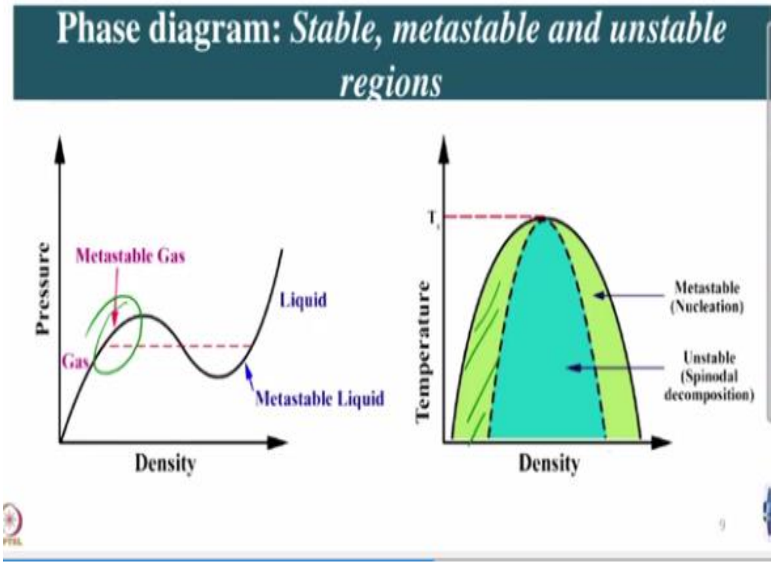

Phase diagram: *Stable, metastable and unstable regions*

So, these are metastable gas and in this case, this is metastability in temperature versus density and this is the critical point okay.

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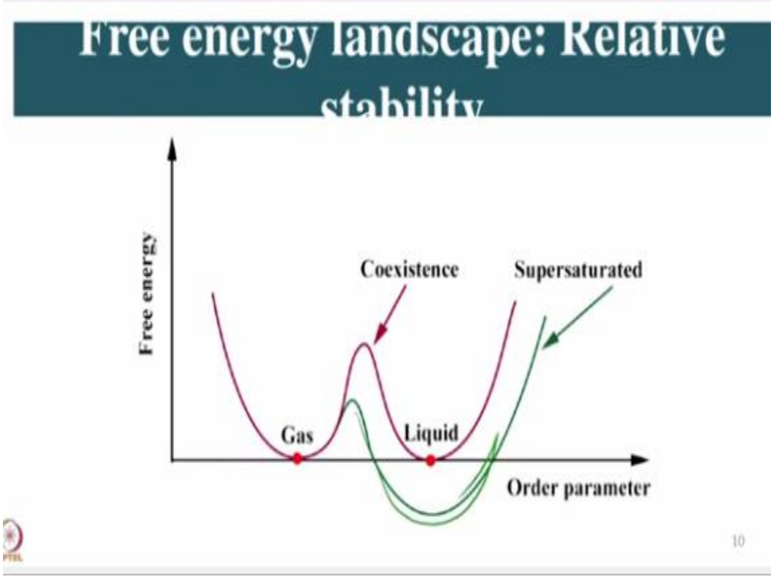

Free energy landscape: Relative stability

Now, so as we again and again saying if gas going to requite, then there is an coexistence but in order nucleation to take place, it must go down and I am now going to tell you why is that, okay.

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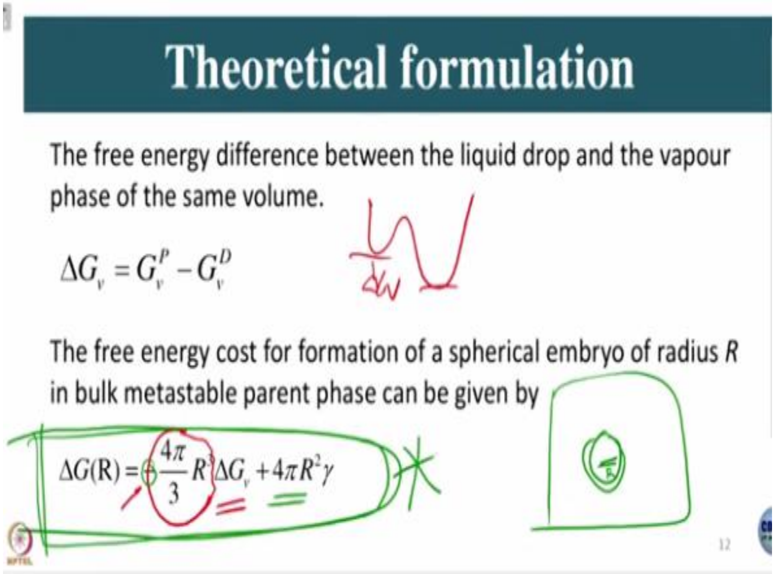

Theoretical formulation

The free energy difference between the liquid drop and the vapour phase of the same volume.

$$\Delta G_v = G_v^P - G_v^D$$

The free energy cost for formation of a spherical embryo of radius *R* in bulk metastable parent phase can be given by

$$\Delta G(R) = -\frac{4\pi}{3}R^3\Delta G_v + 4\pi R^2\gamma$$

So, basic equation is this is the equation okay, the basic equation is that if I want to create a nucleus of radius R in a old phase, then my volume is $\frac{4\pi}{3}R^3$, this is $\frac{4\pi}{3}R^3$ and then ΔG_v, this is a great thing and ΔG_v is the difference, this is the ΔG_v, so this is a gain, so this is negative in front, a gain this much, I gain, however I have to pay energy, so how much is the surface;

we know surface $4\pi R^2$ and γ is the energy per unit area, so 4π. So, this is the total amount of; so in order to create a fluctuation of size R, this is the energy that I have to pay, this is the total energy cost, energy gain and energy loss.

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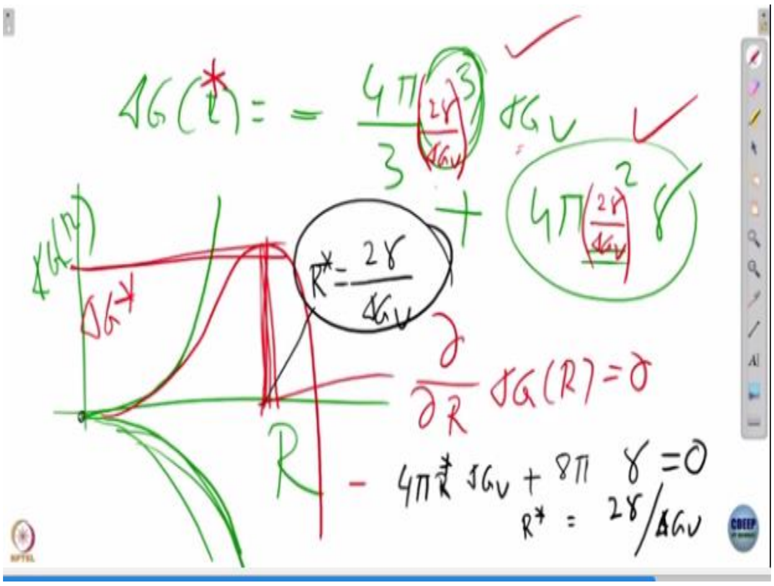

Now, what do I do okay, I go here and I ask for a new page okay, so let me now see ΔG(R), now one is energy gain and then how does do the loop; let us look at these, these are cube and these are square, so if I plot these ΔG(R), you can (()) (19:37) star, then this thing is negative 2 R cube, this thing is positive, okay. Now, surface tension is actually pretty large, so what happens these part wins in the beginning.

So, that is why you go up the hill and come down but if by some fluctuation it becomes large then it starts getting the advantage that this is larger because this R^3 okay, so then what happens as a combination of these 2, a maxima appears and this maximum, these maximum is very important thing in the language, this R* critical radius, this is the critical barrier.

So, in the folklore of phase transition, this is a very important diagram that is telling you how nucleation takes place, this is very important for nano material synthesis and every case, this one diagram called Becker Doring diagram that when I write free energy of creation, embryo of size R, then this has the structure, so again combination of 2 factors; one is negative rapidly becoming negative, other is positive and then you get that.

Then, how do I do that, then next thing of course and this is the critical radius R*, I have to find the expression of R* now and critical barrier, I have to find an expression of critical value okay, let me do that. How do I do that now? We have done it many, many times in this class already, we do $\frac{d}{dR}\Delta G(R)=0$, okay and what do I do now; I get, I do this.

So, I writing little big, I should write little small, so when I do that I get $-4\pi R^2\Delta G_V + 8\pi R\gamma = 0$, right. Now, one of them are is equal to 0 is the solution, part of the reason because this is the minimum, so R = 0 is the solution that is not the solution you want. So, we then divide by R, so these goes out and these become R, okay.

Now, these are now become my R*, yeah the other second solution is R* and that is now given by $R^* = \frac{2\gamma}{\Delta G_V}$, so these R*, this is the beautiful expression, so this is the radius; expression of the critical radius. Now, what I want to do; I want to put this value of R star into this, so now I want to do find this barrier, so now I put it, made it R* okay and I put $R^* = \frac{2\gamma}{\Delta G_V}$ to be here.

I will use the same excuse me but that will work out beautifully, so 2 gamma, cube and now I will put square okay, so now you get 8 and 32 by 3, here you get 16 by 3 and delta Gv; these ΔG_V cancels one of the ΔG_V here and you get gamma cube by delta Gv square back in the.

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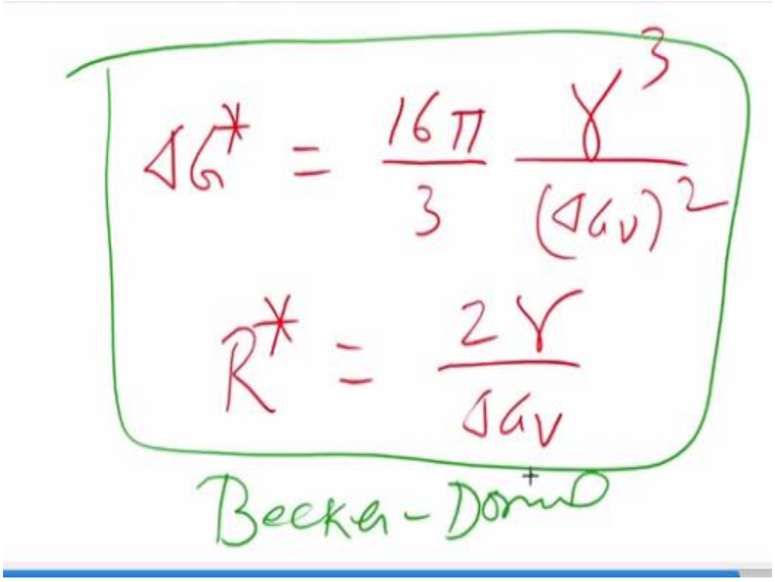

$$\Delta G^* = \frac{16\pi}{3}\frac{\gamma^3}{(\Delta G_V)^2}$$

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

So, now I get the following expression, so these are the 2 very important expressions, this theory of nucleation is called Becker Doring, let me tell you this also a theory was used in nuclear fusion and many, many across the condensed matter physics and chemistry, it is amazing important and beautiful things. So, basically what we have done; we have done a considered a combination of surface term and the bulk term and I just wrote down a very simple expression, surface tension is known, so ΔG_v is known.

Because I can calculate the free energy of the old and the new phase, I can come from the old phase and I can come from the new phase and I can calculate the free energy things, the standard free energy calculations, I can do that by theory of specific heat that is the way we set up the problems that I give you enthalpy, I give you specific heat and you calculate the free energy that can be done.

So, free energy of these phases are well known anyway, there have been many, many fittings also available to these things, so we know delta Gv, we know the surface tension and there are certain approximations and we will talk about that but since these stat mech course aim to for beginners essentially, we will probably minimize the criticism of a theory of the scale.

And we will discuss of course now but the; I want you to appreciate the generality of the concepts that are involved, it is very common generality and at the end of the day, we come out with certain beautiful expressions and which are very widely used, very, very widely used. So, when you say you hear the term nucleation is thermodynamically controlled or kinetically controlled, all these kind of a thing.

Then, you know many times what he is talking about nucleation that it follows the low barrier pathway, even though state is thermodynamically more stable that we will do now, another very beautiful thing we will do, just amazing important things, not usually covered in text books but we will do is the Ostwald step rule and extremely important in present day scenario of solid state synthesis.

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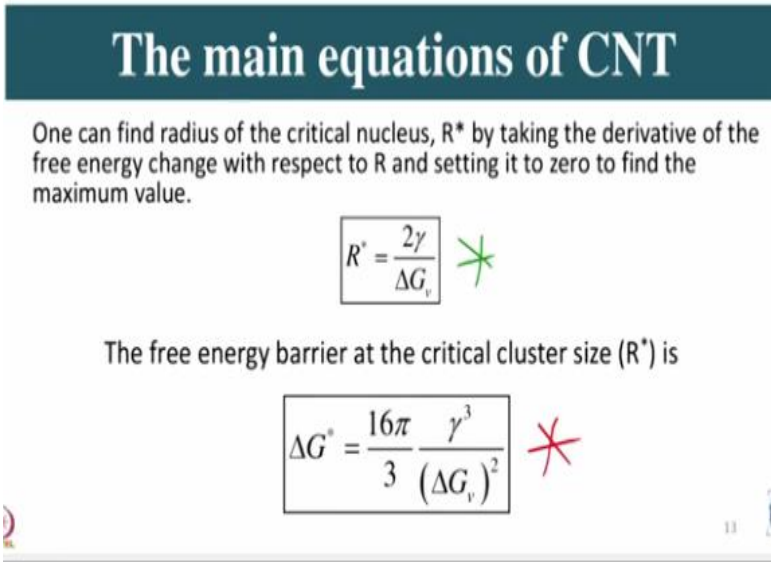

The main equations of CNT

One can find radius of the critical nucleus, R* by taking the derivative of the free energy change with respect to R and setting it to zero to find the maximum value.

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

The free energy barrier at the critical cluster size (R*) is

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

So, those thermodynamic control, kinetic control all these things that essentially we are talking of nucleation and so these are the 2 equations I just derived, so this is the size of the critical nucleus and this is the barrier of the you know, beautiful equation; $R^* = \frac{2\gamma}{\Delta G_V}$, we almost know this by memory, okay.

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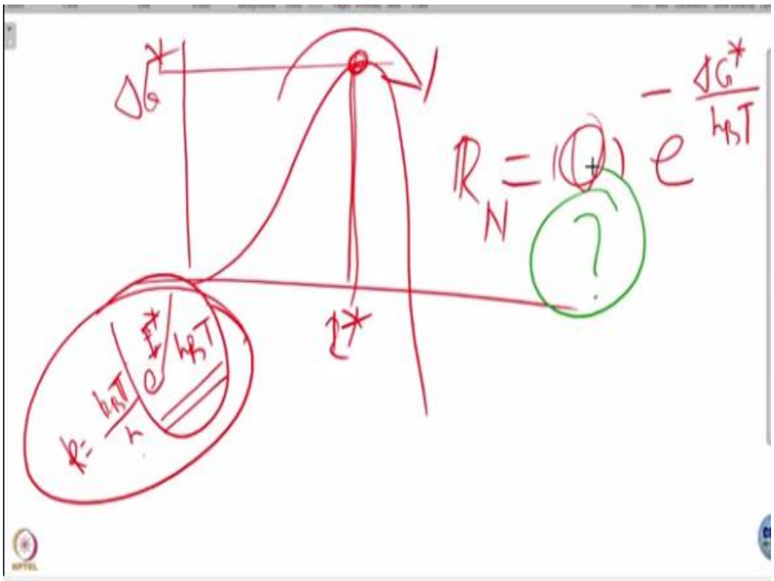

So, now how do I do that so, I have a situation like that and this is my free energy barrier ΔG*, R* now you ask me what is the rate, how do I calculate the rate of nucleation, RN, how do I calculate that, ask a chemist, that I have a barrier, I have to go out the barrier, the chemists will immediately say, I know there is a activation barrier, I know what is activation barrier, it is delta G star by k_BT, I know that okay, well and good.

Then, what is the P factor, so these part chemists will do, then the chemist will scratch his head, I am used to do transition state theory, if I have a barrier, I have a situation like that I write rate $k = \frac{k_B T}{h} e^{\frac{E*}{k_B T}}$. I know that this has been taught to me from school days that this is the rate of barrier crossing.

Can I do it here okay, so this is a Boltzmann factor, the weight of the probability that the particle is at the top that gives you this term that can be wrong, this has to be correct then but how do I get this term; I will do a chemical kinetics, little bit somewhere towards the end of our road because we take a bond and we say okay, the bond breaks and bond is a frequency ν and $h\nu$ and that is about thermal energy $k_B T$ and then say okay, μ is the frequency of breaking is $\frac{k_B T}{h}$ that is how we do it.

Then, how do I do it here; well we do in a way not too different, we will do in a way which is essentially follows this logic but in the process, we do something really extremely beautiful which is very much like chemical kinetics and it turns out what we do is a chemical kinetic, is a form of chemical kinetics and again, the guy who did it is a nuclear physicist, very famous nuclear physicist named Zeldovich.

And what he did here was essentially in the atomic bomb that same thing used in chain reaction and we will do exactly chain reaction and in fission and this beautiful stuff, so we will stop it here and in the next class we will be doing the Zeldovich correction and finish the nucleation theory.