Basic Statistical Mechanics
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Lecture – 42
Spinodal Decomposition and Pattern Formation: Evolution of Structure through Dynamics (Part 1)

Okay welcome back we just finished studies of several chapters on phase transition which are all described in my book. But what I am trying to do here take you through several aspects and give you more of the physics and the physical picture. Many cases like we did in Zeldovich and or on the partition functions and many other cases be it on the Landau theory. We did the deep mathematics but we will do now again some mathematics.

But that is not be really because details of mechanics you can get in my book the statistical mechanics would be this book you can you can get it in all the chapters are there though what I am teaching not in the same chapter. Because I want to make it interesting, I want to make it engaging to students and I want to make it worthwhile for them they should know why they are studying you know I do not believe that one should study.

Because it is a course material one must have some amount of enjoyment I am not saying fully up to extent you can jump up and out but you should have some amount of involvement and some liking for the subject otherwise it will not stay with you and not only equation would not stay with you but physical picture to stay with you. Now coming with okay so we were doing Landau theory phase transition free energy functional.

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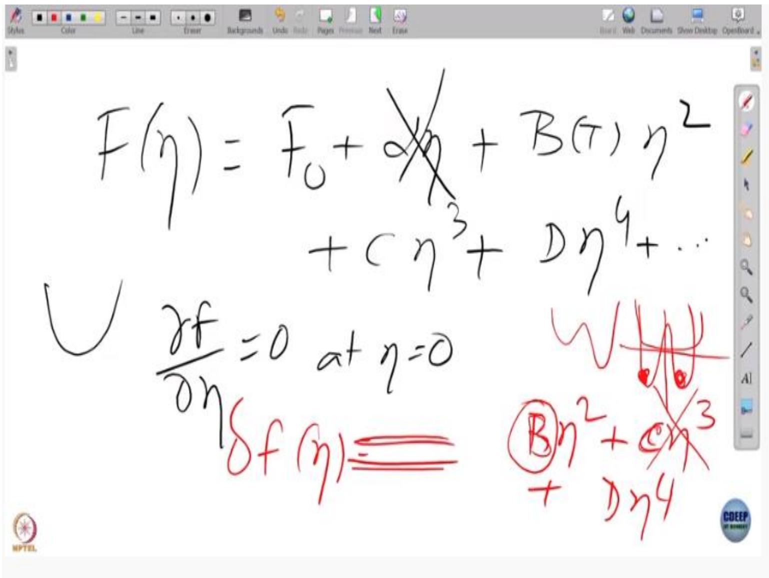

Landau wrote down the beautiful free energy functional

$$F\left(\eta\right) = F_0 + \alpha\eta + B(\mathrm{T})\eta^2 + C\eta^3 + ...$$

that if it is if F_0 which is eta = 0 of n eta then B like that and then since free energy has to be minimum then

$$\left.\frac{\partial F}{\partial \eta}\right|_{\eta=0} = 0$$

that immediately means this term disappears and then we are left with simpler things and that is

$$F\left(\eta\right) = F_0 + B(\mathrm{T})\eta^2 + C\eta^3 + ...$$

then this thing I can just remove for the time being and make this δF .

So then I have $B\eta^2$ and $C\eta^3$, and this is important temperature dependent term and for first order phase transition I need the asymmetry of metastability and hysteresis I need the C term. But for critical phenomena where I have a flat like that then it becomes like that, I do not need this term. So because of sparing because it has to be same here and there and they are equally displaced from origin, one is - and the +.

So no odd term can be there so then the free energy just written as square root of plus these sometimes we use for field theory and very common in field theory where these things are. So this was the Landau beautiful then one can go ahead and can get the entropy from here and one can get the I will do it again when I do to get even a little bit more we can get the entropy from here we can get this specific ability from here and these similar things but that I will do little bit more when I do critical phenomena.

Right now I am doing the first order kind of phase transition and similar things which are more we like we need it much more in physical chemistry materials chemistry. These Nucleation and the Ostwald step rule and similar things now we also did but now many of the phase transitions require the heterogeneity.

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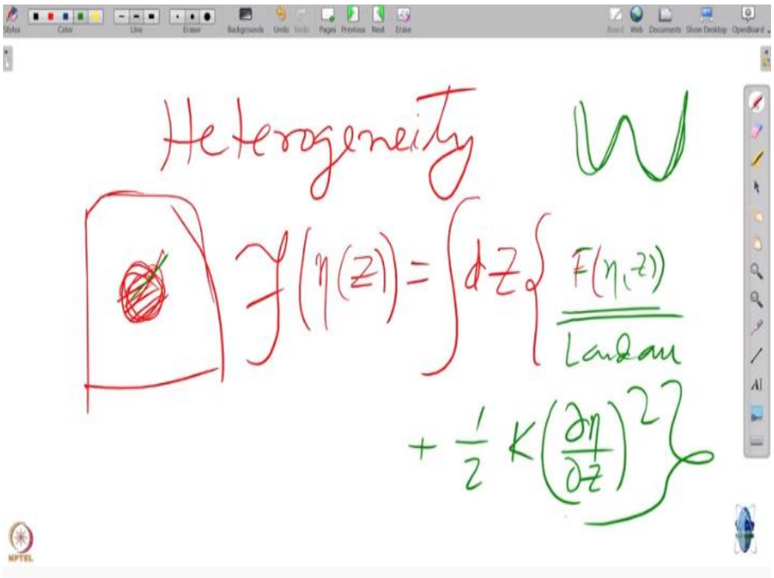

So there must be a homogeneous system must become heterogeneous because these we create an embryo; so there is error in any fluctuation from the new phase is a heterogeneous fluctuation. So there is a density fluctuation gas liquids are when gas goes to liquid suddenly a hugely more dense region comes and but when in chemical engineers rue for the cavity bubble forms inside a liquid boiling liquid and that is how it evaporates then you suddenly have a very low density region in a dense region.

So this is heterogeneity because this huge density change takes place at the surface as I go okay. So now so how do I describe that heterogeneity Landau clearly cannot describe the that heterogeneity because it has macroscopic density that is why Ginzburg Landau comes in this Ginzburg Landau appears okay if I have a order parameter or density as a function of Z then the way to get the free energy is you get the free energy as a function of Z okay these let me then as a function of Z.

These F is the Landau free energy so this is Landau however when I create the heterogeneity I have to describe that and that is done by using harmonic and these is which allows me to vary order parameter like this an order parameter in a gas liquid solid interface or nucleation then this is called the famous Ginzburg-Landau free energy function.

$$F\left[\eta(z)\right]=\int dz\left[F\left[\eta(z)\right]+\frac{1}{2}K\left(\frac{\partial\eta}{\partial z}\right)^{2}\right]$$

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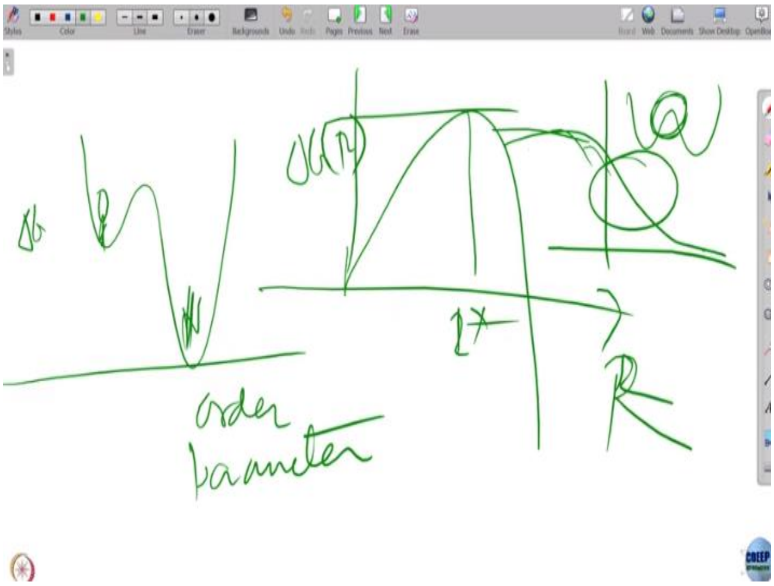

A nucleation what we do we said okay I have something like that, and this is the new one has to in create from the old one and then what do we do it will be a cut during and this is goes over a barrier comes like that okay. So this is the nucleation R* we did it R and this is ΔG_R okay it is ΔG as a function of order parameter. This order parameter and but this is a function of R.

So one has to be careful okay but now I am going to, so we have done nucleation we have done surface tension I described how one talks of surface tension. Because you create a surface it create a surface and then you go through the surface and creation of surface means you go through the an interface and this region is neither here not here surface tension always there equilibrium so free energy is the same.

So this region is rather in this unfavorable domain. So since it has to go to there is no other option and one phase to other phase has to create this interface and creation of interface has to put matter in the free energy last free energy barrier. Now the system tries to minimize the free energy and the way it minimize the free energy plays around with the profile. So, now you have to put in this thing that is what Landau does there is a variation with cost to energy.

And there is these putting in the unfavorable total cost to energy both costing you energy, but you have to minimize that and that gives you surface tension. So, that is why this is a statement you have always entered a in why raindrops are spherical because it minimizes this happens okay and so it is the same principle that is working there. So, now what do you have done till now we are going from one minima to another minima.

However, there is a large class of phenomena where something else happens like when a volcano erupts and pattern formation in nature; we see formation of patterns they go through completely different setup.

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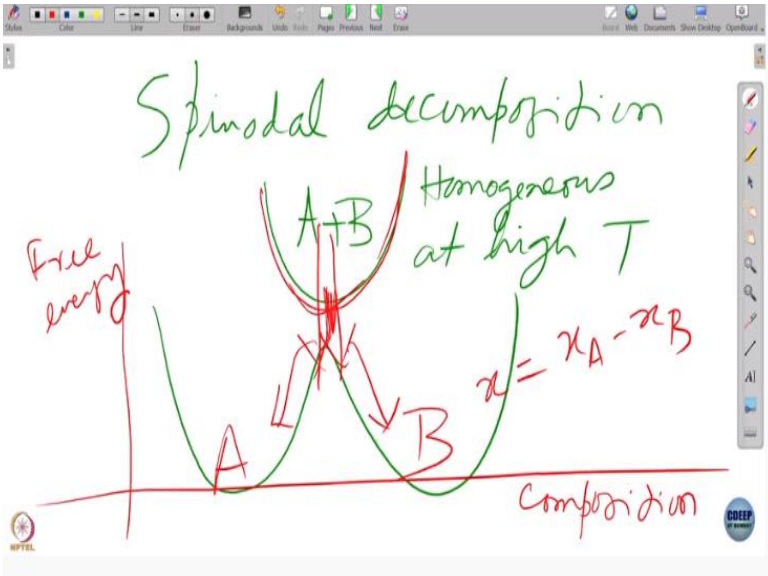

And this is the phenomena of spinodal decomposition. This is again it is a very famous and well-known subject in phase transition and in material science you know because this is something always taught in materials so meteorology departments. So, here what happens we consider the following thing we have a homogeneous space or high temperature homogeneous mixture of A and B homogeneous high temperature.

Now we suddenly coincide for example say we have a temperature scale temperature just one I want quick quench it very far I want to quench it to 0.1 and that happens see when you take the volcanic rocks you find that there are many of the volcanic rocks are beautiful pattern. Okay many of the patterns are because of this iron bearing salt and you find the stripes same stripes you find in zebra you find the same stripe many places in nature and the reason is that these are non-equilibrium processes.

So now I suddenly quench it but what happened at low temperature, low temperature these are homogeneous low temperature A and B phase separated. So, if A and B so A is with A and B is with B like you can do aluminum and manganese and that alloy it is a homogeneous mixture high temperature coincide if they phase separate. Now these are happening may be happening all in solid state so in high temperature they are disordered but if you go to low temperature they separate.

However, I do it suddenly so suddenly the system finds that it is put in this region. So these are free energy, and this is the maybe composition which is the order parameter here you should define that the composition is 0 when they are homogeneous so you can say it is $x_A - x_B$ is the composition order parameter 50 - 50 mixture. So completely mixed minimum here is where these quantity difference is 0 and is there a harmonic as we are describing again and again fluctuations are harmonic in the first order.

Because simply because the first derivative is 0 because it has to be minimum with respect to free energy, free energy has to be minimum based on the fluctuation that is the thing the first composition goes to 0. So first term the real the relevant term comes this harmonic term that means δx^2 okay then δx^3 could be there but for small fluctuation δx^3 is also not important because δx^3 is small.

So the initially it is always harmonic like that okay now they are low temperature their phase separated. So they are just like your coexistence I have been drawing all morning or our previous lectures, so this is A phase and this is B phase their phase separated. So A and B are phase separated and indeed now when I join something like that is very interesting thing going to happen the system now has to go into these phase and needs to go into this phase.

However, it is a homogeneous system at high temperature they are homogeneous A and B are mixed with each other. Now I am suddenly telling them to go phase separate and it starts to phase separate but is no nucleation there is a mass bulk phase separation. But phase separation in a which it was it finds zeros in free energy surface like the upper free energy surface it then suddenly finds in the lower free energy surface, but mass is conserved I cannot just destroy one A particle in place and then replace it by B particle.

Similarly, I cannot take a B particle from here and put it in A particle I cannot do that number is conserved. So I must do it in a progressive fashion moving around how do they move in such a dense thing they move by diffusion that is the only thing they must move it. So however these of diffusion, diffusion.

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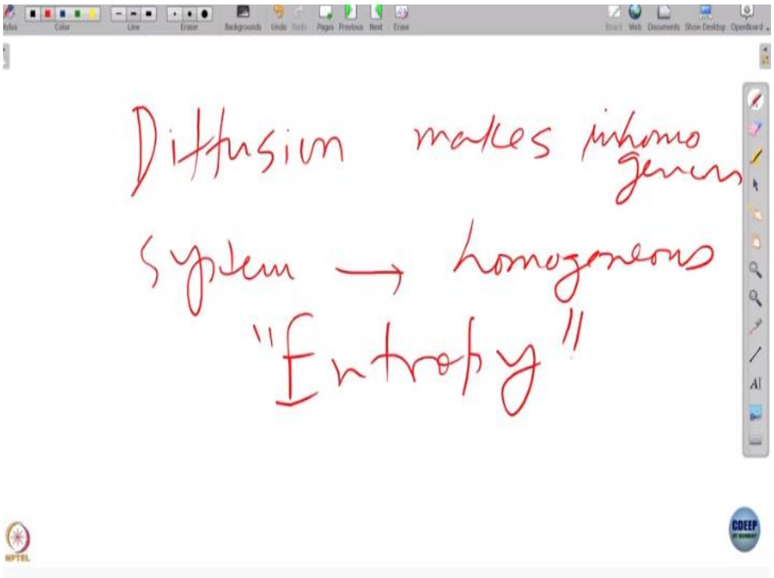

Usually diffusion makes in a homogenous system homogeneous that is what in diffusion is actually diffusion is very closely connected with entropy there is a relation between diffusion and entropy they are actually interval the actual semi relations diffusion increases entropy increases. So diffusion favors entropy, so you have an homogenous system which is lower entropy then diffusion makes them homogenous because entropy increases this is very easily understandable, very pictorial, and very although profound but very simple to understand.

However, now we are in a different situation we are now in a homogeneous system that homogeneous system has to become homogenous but with the diffusion. So, that is why this is sometimes called spinodal decomposition is called uphill diffusion. Let me give you some example now there because we are talking a lot.

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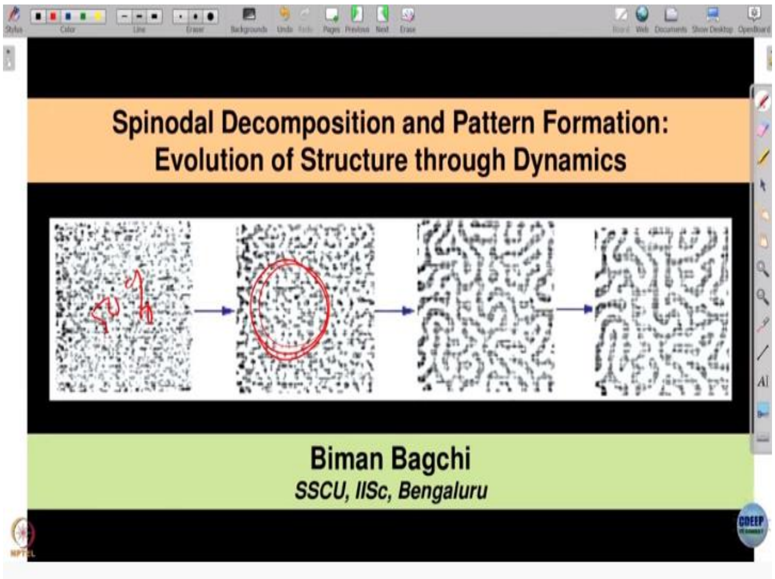

So this is an example of computer generated spinodal decomposition and the evolution of structure through dynamics. So at a high temperature A and B, I made one A may be white B may be black. So, they be a black and white, white is just empty, and blacks are these small squares so here is we are nearly almost 50% 50% and then I suddenly quench it then it starts to phase separate.

It is different from equation you can see is a large scale large amplitude phase separation scenario. So now it goes intermediate you can see in a nascent phase separation how does it do now A likes A, A wants to be with A that is what the free energy dictates, B wants to be with B that is what reality takes it. So now the nearby black ones they start forming chains and white ones they form chains.

So you start seeing the initial pattern formation then they move around more and blacks form and but they have to avoid each other and in the process they form this beautiful pattern which is called a spinodal pattern and this is what one sees in many cases in nature in a metallurgy in physics chemistry in any kind of things and in also in basic theory goes over almost to the animal world a very similar equations that we are going to use that is used.

So, the formation of this pattern and that can be experimentally study to X-ray and the X-ray will be excess scattering will pick out this pattern formation will pick out the emergence of the landscape and these length scale then shows as a peak in the X-ray structure factor.

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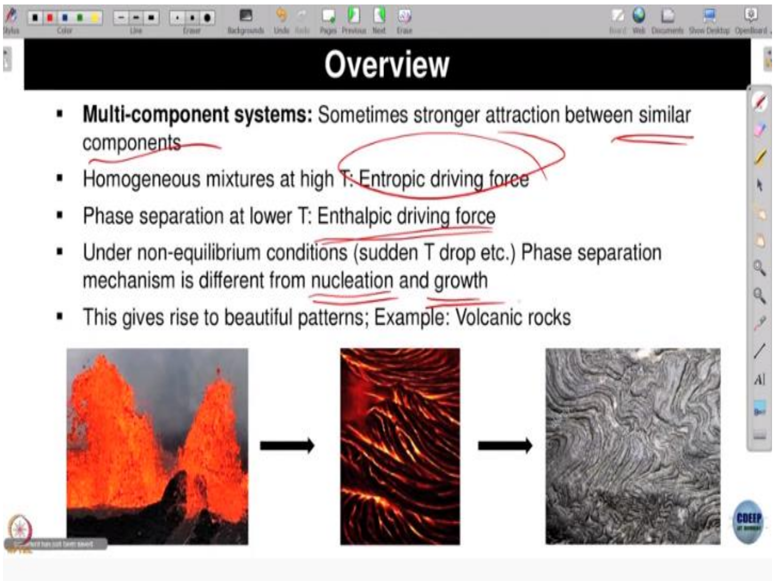

But there are many things like that these all multi stronger attraction between similar space component that A like A, B likes A then homogeneous mixture high temperature entropy dominates but suddenly quench loaded enthalpy that is a driving force and in non-equilibrium conditions or in temperature drop etc. Phase separation mechanism is different from nucleation and growth what we studied in the last lecture or so.

There is a nucleation before last two lectures nucleation and growth now it is different but it is nevertheless is a very well-known of phase separation and so there is this showing the volcano and the volcanic rocks that form and when the volcano takes place then after that it is just suddenly finds itself from something like 5,000 ^{o}C or something like that to room temperature you know to it degree centigrade for 5 ^{o}C.

And then these beautiful patterns in that form because a volcanic melt has many different components ferrous sulfate, sulfide is one of them and some zinc and other things are there and they like to be among themselves and so that is beautiful. So you can imagine always that here out of a homogeneous state we are getting any homogenous state so immediately one thing that comes to your mind.

Okay so this is the cleaning at the minimum okay to free energy minimum, but I have to separate them out. So the diffusion yes but there is also the surface tension play an important role because I have to create the surface there is no surface before now there is a surface so again. So surface is being created and many surface being created okay so surface tension going to play a very important role.

So system tries to avoid formation of surface but in this case there is no way but you can imagine what will happen in the low very long time these patterns will become thicker and thicker so slowly some islands will disappear like this island here these will disappear they will go into here and there and then these island will disappear these island will disappear. So there will be thickening or called coarsening ultimately in a very long time there will be phase separation just like one A and one B.

But that may take a very long time that is why even volcanic rocks from the million years before we still have the patterns and so this evolution takes place in time dependent and we will discuss them how do we understand that okay.

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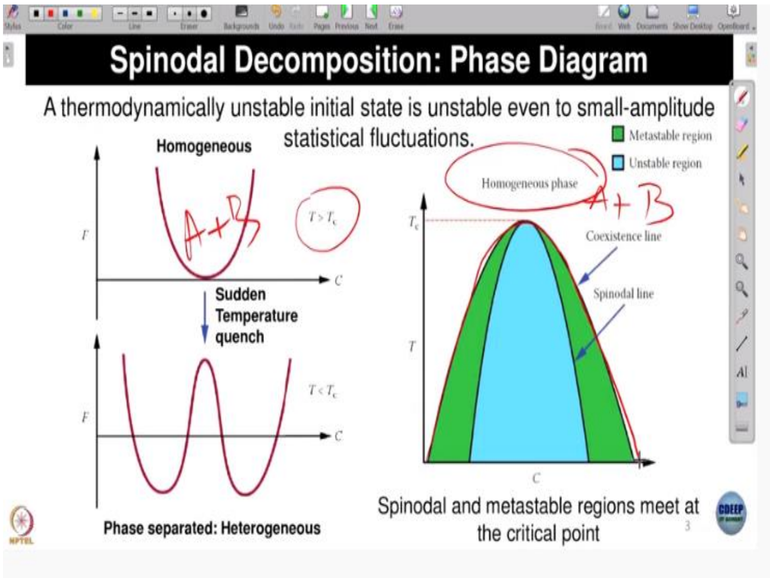

So this is what I just said a sudden temperature quench then A and B and these T much greater than homogeneous things then A + B here and then then we can also say that very important phase diagram in a binary mixture is a very common phase diagram you study in your Mechanical physical chemistry that if an A and B then homogeneous phase where A + B are here and then it is like as liquid then this is a phase and the boundary and then inside you remember the Lever rule and all these things then the phase separate like that.

But there is you quench it usually you see only this one but if you quench it then you get this is the spinodal line and that if form this somewhere here it forms and then there is an unstable region that we will discuss little bit now okay.

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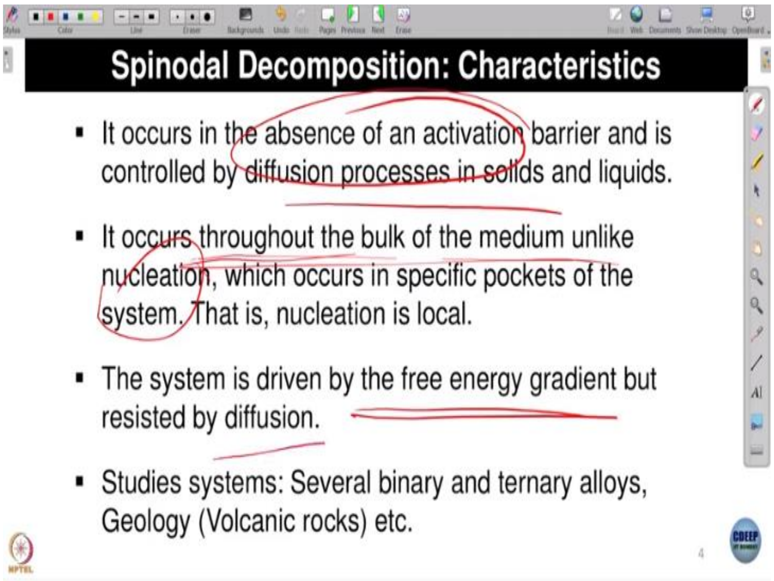

So important thing of Spinodal decomposition is very important in absence of an activation barrier and it is controlled by diffusion it is all through it is very important it occurs through all through the bulk it is not unlike nucleation which occurs in a local region so it is that is what we call is large amplitude phenomena it is almost everywhere in the system it is happening system is falling out of equilibrium and falling out of equilibrium in a really dramatic fashion. Then free energy radiant but is driven by the free energy gradient but resisted by diffusion so many system this thing is same I am repeating here.

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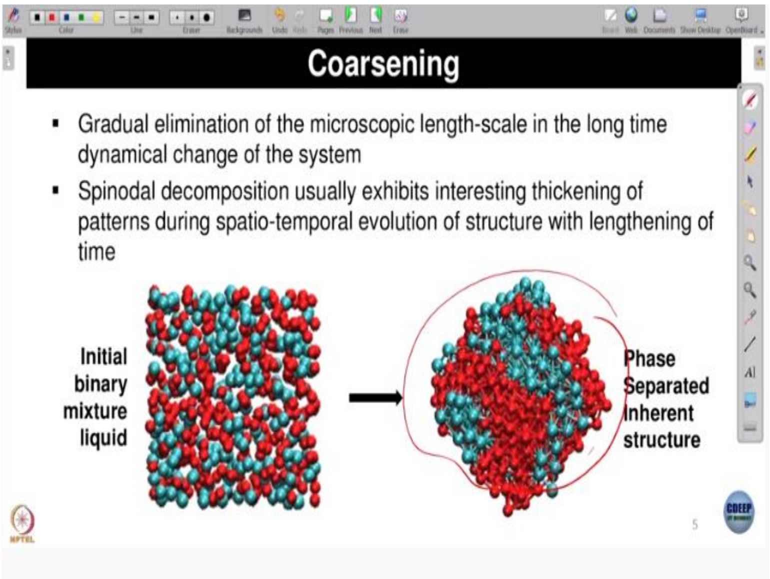

But I just show you one of the computer simulation results that you know in the binary mixture two spaces A and B blue and red and then you quench it and then in the long term and the quench it and then you remove some vibration then you find this beautiful pattern. So these guys are connected one and blue is connected below that like that, so it is just like the pattern I showed you that they form this beautiful pattern in that wind in a beautiful way and this is a pattern formation in a spinodal decomposition.

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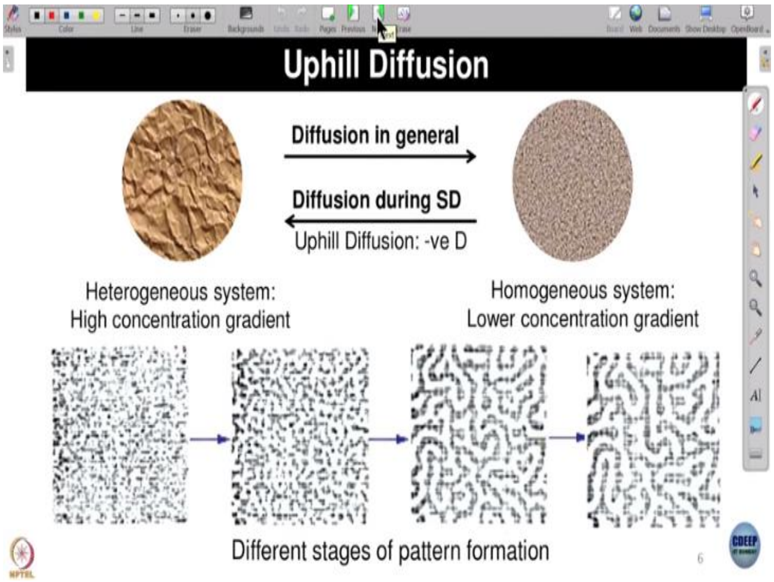

So, this is again the same thing different stages of pattern formation we showed here.

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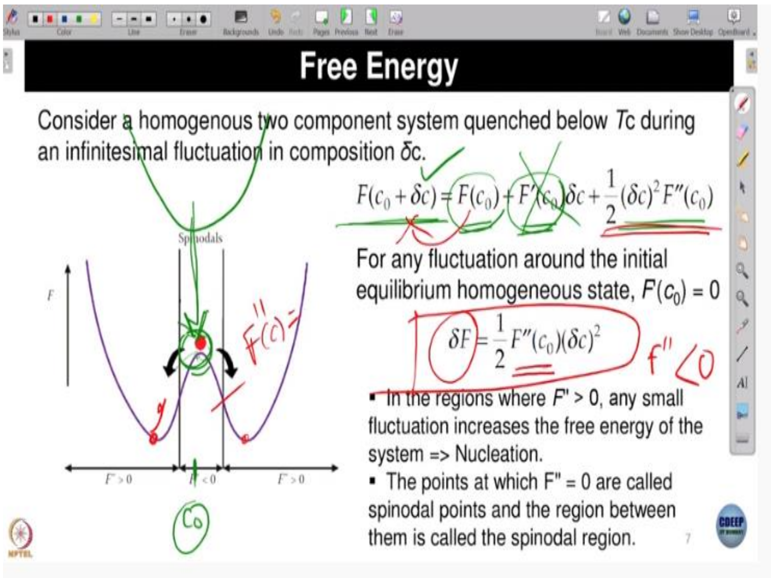

So now let us do the theory a little bit of theory I will not do a great deal but some amount of understanding with evolve again these are nothing but based on Landau theory and this very similar kind of thing we did make a drawing thing. But now the; you know back up doing although we have to go up now, we are coming down so free energy and all these beautiful things happening.

The one of the reason that I like to do this slow decomposition and nucleation because this is take you to a deeper understanding but there at the same time without too much difficult calculations but at the same time it is a beautiful physical insight that student gets and it is something which is a as I told you this is the same thing used in a very large number of cases and very nice okay.

So enough of that now let us see certain amount of little bit of equations that is say it is nothing but Landau again. So, I am now when initially when t= 0 I am here I from here I have dropped here I have dropped the red one is the guy I have dropped. Now that thing now is going to going to go into these direction and he is going to go this direction and I want to do the evolution okay.

Now so let me start with the free energy at the; this is c_0 this is my c_0. Now I want to say okay I want a small fluctuation in composition around this region. By the small fluctuation little bit on this direction or little bit on that direction any of the direction I have chosen the symmetric, so it does not matter. So now I expand it in a Landau expansion the Taylor expansion

$$F(c_0+\delta c)=F(c_0)+F'(c_0)\delta c+\frac{1}{2}(\delta c)^2 F''(c_0)$$

This is derivative first derivative value c_0 here that thing is maximum. So, this term goes to 0 and I again take to this part to here and call it δF these quantity is δF and then I have only this term left on the right hand side so this is my simple equation.

$$\delta F=\frac{1}{2}F''(c_0)(\delta c)^2$$

So if I do a small fluctuation now these are maximum so secondary where these quantity is - F’’< 0.

Then I am coming down, so they are two region in this region is small fluctuation decreases to energy but if I for ultimately reach here then small any small fluctuation increases energy. So here small fluctuations increases the energy free energy here small fluctuation decreases free energy. So it goes through a F’’>0 which is the condition of the minimum < 0 so in between there somewhere it must be 0 so somewhere here F’’(c) must be equal to 0.

So, this time where the F”(c) changes sign from negative to positive is an inflection point this is the point which is called the spinodal point that is where the corrector nature of force coming from free energy on the system changes and this is the called spinodal line is a fairly well-known terminology we use. But in the level of free energy it is described in terms of second derivative free energy and the function of the composition okay.

So when you did nucleation we went up like that and now in the slowly decomposition we are coming down from the free energy landscape how a simple free energy landscape is used by Landau describes such huge phenomena and that is why in physics community in unconscious matter science in general these kind of pictures are so admired. Because they give us, we invest so little and we get back so much in return.