Basic Statistical Mechanics
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Lecture – 43
Spinodal Decomposition and Pattern Formation Evaluation of Structures through Dynamics (Part 2)

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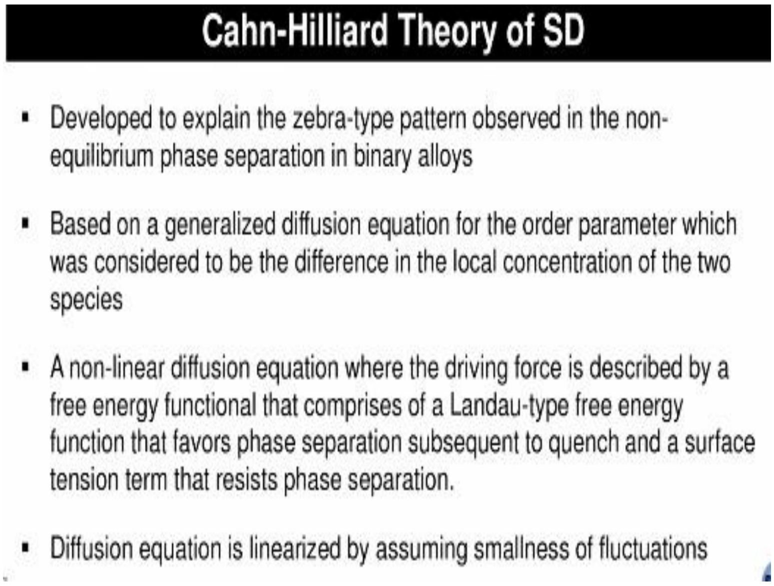

Cahn-Hilliard Theory of SD

- Developed to explain the zebra-type pattern observed in the non-equilibrium phase separation in binary alloys
- Based on a generalized diffusion equation for the order parameter which was considered to be the difference in the local concentration of the two species
- A non-linear diffusion equation where the driving force is described by a free energy functional that comprises of a Landau-type free energy function that favors phase separation subsequent to quench and a surface tension term that resists phase separation.
- Diffusion equation is linearized by assuming smallness of fluctuations

So this explain zebra type pattern in phase separation alloys and what we do now we just like what we did in nucleation in Zeldovich we write down a kind of diffusion equation kind of scenario and then we go into that and I will now this time I will describe little bit more of what do we mean by diffusion equation and this things develops little bit more detail.

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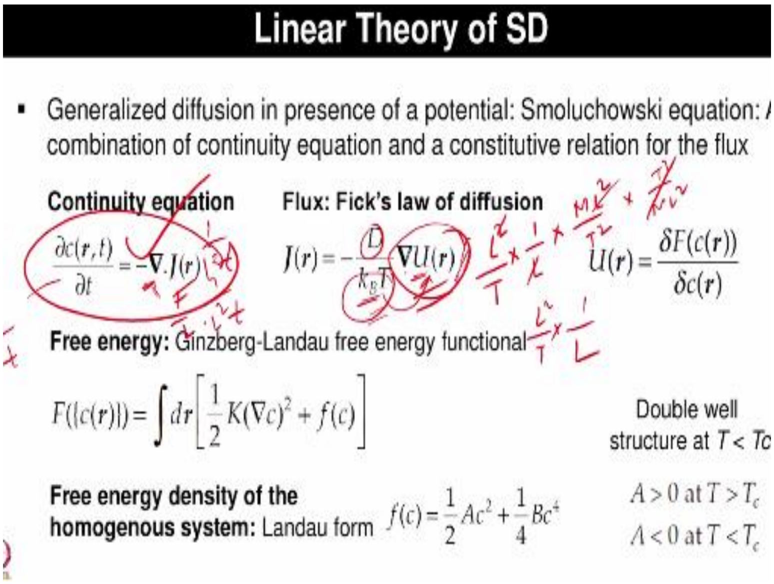

Linear Theory of SD

- Generalized diffusion in presence of a potential: Smoluchowski equation: A combination of continuity equation and a constitutive relation for the flux

Continuity equation

$$\frac{\partial c(r,t)}{\partial t} = -\nabla . J(r)$$

Flux: Fick's law of diffusion

$$J(r) = -\frac{D}{k_B T}\nabla U(r)$$

$$\frac{L^2}{T} \times \frac{1}{L} \times \frac{ML^2}{T^2}$$

$$U(r) = \frac{\delta F(c(r))}{\delta c(r)}$$

Free energy: Ginzberg-Landau free energy functional

$$\frac{L^2}{T} \times \frac{1}{L}$$

$$F(\{c(r)\}) = \int dr\left[\frac{1}{2}K(\nabla c)^2 + f(c)\right]$$

Double well structure at $T < Tc$

Free energy density of the homogenous system: Landau form

$$f(c) = \frac{1}{2}Ac^2 + \frac{1}{4}Bc^4$$

$A > 0$ at $T > T_c$
$A < 0$ at $T < T_c$

Now let us consider diffusion equation this you know from your undergraduate very, very well and it is actually just a part of tangible and statistical mechanics which we will do much more later, but we need a little bit of it here and this is very, very easy. This gradient this quantity gradient here is a 3 dimension it is 3 dimensional vector that means d/dx, d/dy, d/dz nothing to be here and J is the current term.

$$\frac{\partial c(\boldsymbol{r},t)}{\partial t} = -\nabla.\boldsymbol{J}(\boldsymbol{r})$$

So this is called conservation of mass that I take the derivative of position dependent composition and composition c is $x_A - x_B$ then this is just a statement of the continuity we will call it continuity equation the statement of law of conservation.

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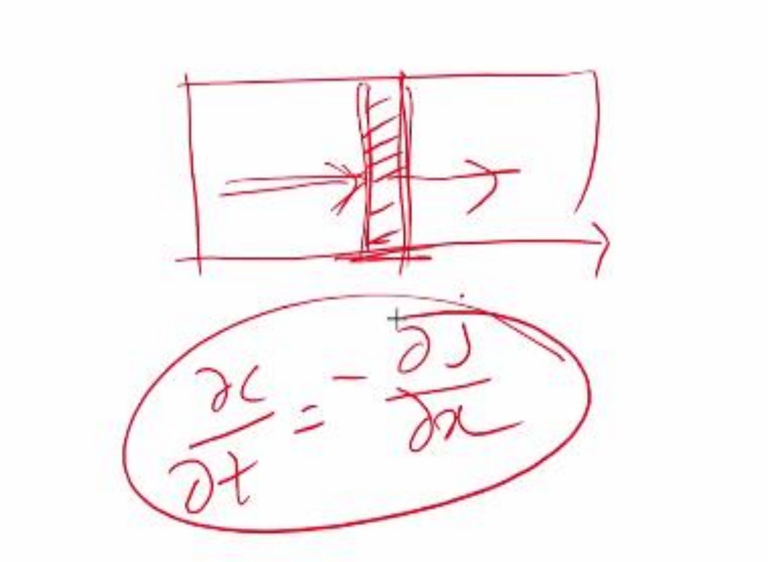

That means if I have a like that then I have taken area here then the particle coming there and I want to consider change what is happening here then the change inside will be the amount coming in and the amount going out and flux is J.

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$

because it is more going out it will be less. So this is nothing but the continuity equation and this is the one that we just describe it.

So this is the continuity equation just the conservation, but that means we essentially say particle cannot be created or particle cannot be destroyed so it is intimately connected with law of conservation, but continuity equation is a very, very simple thing and you might paste it in your undergraduate in electrochemistry chapter and kinetic theory chapter. Now we know one more thing this equation by itself is not complete because they are too unknown.

Now what is done is something is extremely nice which is called Fick's law.

$$\boldsymbol{J}(\boldsymbol{r}) = -\frac{D}{k_B T}\nabla U(\boldsymbol{r})$$

Remember what is Fick's law Fick's law is now this is an exact, but Fick's law is not exact but Fick's law is an assumption. Fick's law tells that the flux is derivative of chemical potential. So if there is more chemical potential then matters flows from large chemical potential to lower chemical potential.

Here I use 'U' as a chemical potential. So Fick's law is what you call constitutive relation, is an assumption and these assumption as one plays it is kind of with a linear regime that means small fluctuation regime will vary. So you can read these thing in Google, you can read these thing in Wikipedia, but these are very, very fundamental very, very nice things. So this is my chemical potential they are essentially saying matter close from large chemical potential, low chemical potential large free energy to no free energy.

$$U(\boldsymbol{r}) = \frac{\delta F(c(\boldsymbol{r}))}{\delta c(\boldsymbol{r})}$$

However, it flows with a rate and that rate is a diffusion D/ k_BT and k_BT is put in here you could have tested. It is because that k_BT can as well go in the chemical potential. So this is a dimension of energy, k_BT is dimension of energy so U/k_BT is dimensionless. This as you can see here is K comes because this is composition or concentration so this is L^3/T this flux is remember amount of matter per unit area per second right.

So flux is L^2/T. This is gradient so you get number per unit time per area so this $1/[L^2T]$ so gradient comes with 1/L so this $1/[L^3T]$ dimensional analysis. So now so this is $1/[L^2T]$ flux. Now this takes care of that and this is energy taking care of and this is $1/L^2$ and D is L^2 / T and so this is L^2/ T there is some interesting thing here so D is diffusion L^2/ T bear with me for a minute and 1/L.

And then it ML^2 /T^2 and that is then L, L goes then L^3 / T^3 , but I have a k_BT so again T^2 / $[ML^2]$ so that goes out and $1/L^2$ by L / T if this is composition then it is L / 2. So c is used as a composition difference in mole fraction. So c is used as a dimensionless quantity so if c is dimensionless quantity then flux is 1 / L and flux is number of particle by 1 / [L^2T]. This is 1/L^2 by T and this is 1/ L.

So I think there is something a bit screw up here, but we have to continue and I will fix it up sometime later that this things. So now we continue with now there is a issue either I am doing something wrong here most probably it is correct, but one of the notation used here probably is different from what I have in mind, but you can figure it out probably yourself. So now this is the but the rest of the things is okay this is continuity equation.

This is continuity equation and this is the flux this definition is correct and the chemical potential remember chemical potential is z is dA free energy by density that is the chemical potential. So here the chemical potential is exactly same thing here chemical potential is u chemical potential is I am sure derivative of free energy with respect to composition or concentration that so this is an exactly same thing as that, but this is functional because c this c is a which is c is.

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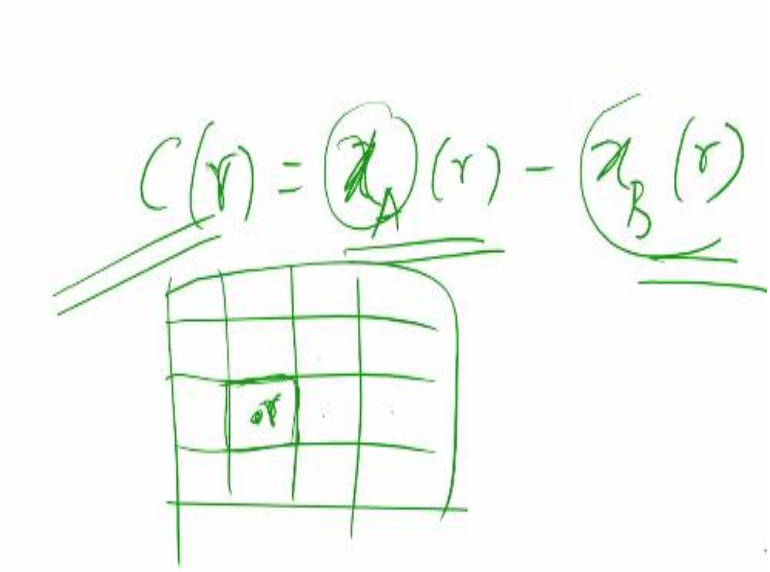

So

$$C(r) = x_A(r) - x_B(r)$$

And that is I think is my confusion so this is a mole fraction and this is a mole fraction of A it is mole fraction of B. So if I have the particle like that then I divide into grid I am saying something very, very interesting so please listen carefully. So then I choose one of them and I say this is my location r and in that old location now I find out why in this location it is r I find out what is the number of A molecules.

And what is number of B molecules so what is then that will give me the mole fraction so A molecules – B molecules so that is the composition C. So the way to consider decomposition dependent composition is to consider your system dividing to grid and then each grid you go you can make the grid very small, but do not make it too small so it does not contain they let it contain about 8 to 10 molecules then you can see.

So when they are 50-50 equal number of A and B then you will composition 0, but it varies from position to position and because of the environment that is being created and also because of fluctuations.

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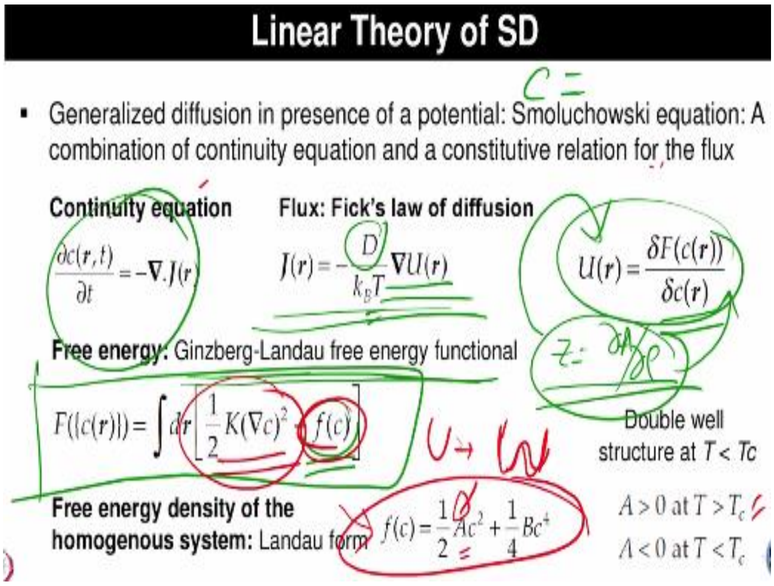

Linear Theory of SD

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$A < 0$ at $T < T_c$

So now so this is a definition of composition so when I take derivative of free energy with respect to composition that gives me chemical potential just like in thermodynamics. So Fick's law is driven Fick's law is diffusion gradient of chemical potential. This $k_B T$ might be the problem of the dimensional thing. Now exactly what I said before the free energy I am going to create in homogeneity now.

I am going to create the free energy really lot of fun now I am going to create form here the homogenous where in every grid my C is 0 from there now I am going to place where C is 1 and here n – 1 here. So I am going to create through this the heterogeneity and I already told you the way to describe heterogeneity is Ginzberg-Landau that I already told you that Ginzberg Landau allows you to get this free energy.

$$F\left(\{c(\boldsymbol{r})\}\right) = \int d\boldsymbol{r}\left[\frac{1}{2}K(\nabla c)^2 + f(c)\right]$$

This is free energy as a F(c) so F(c) this quantity is really lot of fun this quantity is this thing. So this is the thing F(c) now and this is the energy you have to pay in order to create a heterogeneity so this is surface tension term. So this is the Landau term which is a bear free energy and this is the surface tension term because I have to create surface. To create surface I have to pay energy and so combination of the two is a.

So now if I want to see the double well if I have to create the double well and I know how to create the double well and I know that is just Landau. Now the beauty of these things that I can create single well to double well by saying it is A > 0 then I have a single well that is a high temperature then I quench to low temperature when I quench to low temperature A becomes negative if A becomes negative and this changing that the single one like that become something like that. So that is a very clever way of doing. So I can now use Landau free energy into Ginzberg-Landau and I can do something very, very clever.

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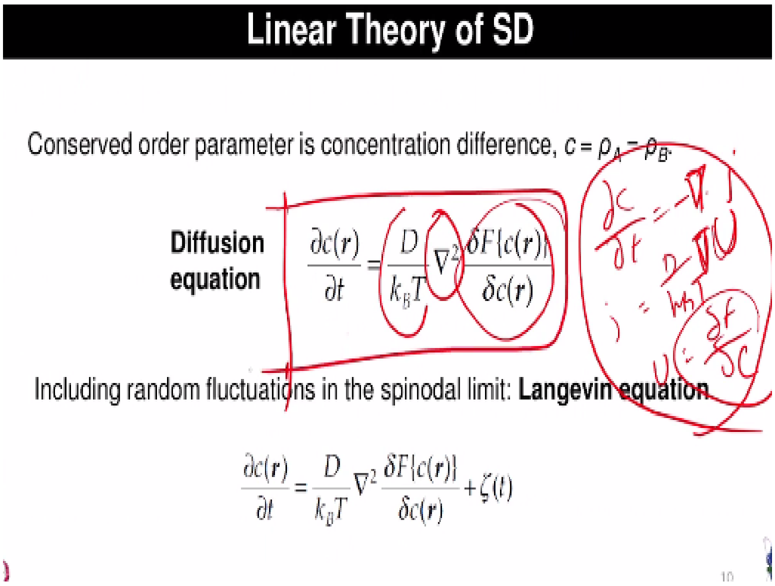

Linear Theory of SD

Conserved order parameter is concentration difference, $c = \rho_A - \rho_B$.

Diffusion equation $$\frac{\partial c(\boldsymbol{r})}{\partial t} = \frac{D}{k_B T}\nabla^2 \frac{\delta F\{c(\boldsymbol{r})\}}{\delta c(\boldsymbol{r})}$$

$$\frac{\partial c}{\partial t} = -\nabla J$$

$$j = \frac{D}{k_B T}\nabla U$$

$$U = \frac{\delta F}{\delta c}$$

Including random fluctuations in the spinodal limit: **Langevin equation**

$$\frac{\partial c(\boldsymbol{r})}{\partial t} = \frac{D}{k_B T}\nabla^2 \frac{\delta F\{c(\boldsymbol{r})\}}{\delta c(\boldsymbol{r})} + \zeta(t)$$

So I combine the diffusion equation. I have two things one flux term, another A term. One flux term remember when

$$\frac{\partial c(\boldsymbol{r},t)}{\partial t} = -\nabla .\boldsymbol{J}(\boldsymbol{r})$$

j term that is in terms of

$$\boldsymbol{J}(\boldsymbol{r}) = -\frac{D}{k_B T}\nabla U(\boldsymbol{r})$$

and then ‘U’ is in terms of

$$U(\boldsymbol{r}) = \frac{\delta F(c(\boldsymbol{r}))}{\delta c(\boldsymbol{r})}$$

this three things are combined here. So there is one del here another del here that gives del square D / k$_B$T comes out and the third part delta F del c over the chemical potential this term, so 3 ingredients.

$$\frac{\partial c(\boldsymbol{r})}{\partial t} = \frac{D}{k_B T}\nabla^2 \frac{\delta F\{c(\boldsymbol{r})\}}{\delta c(\boldsymbol{r})}$$

Now I can consider this equation in terms of the fluctuation, but that we can we do not need to do that we can work this equation this beautiful equation.

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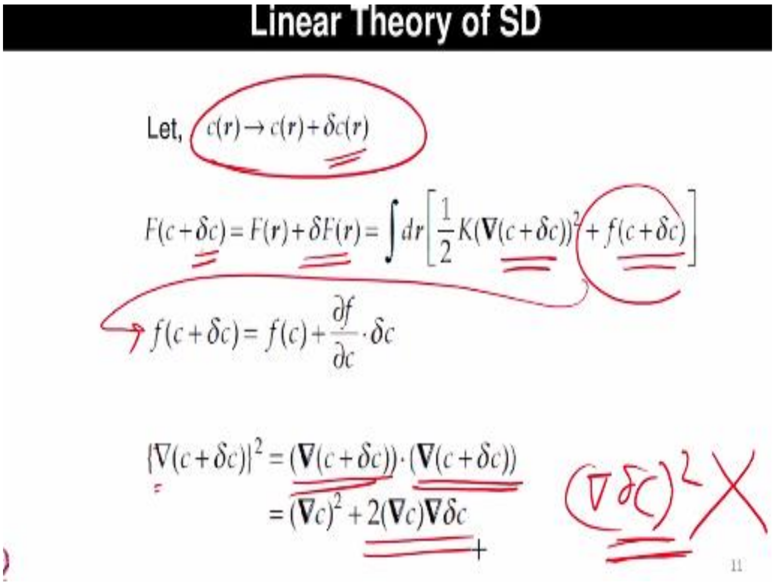

Linear Theory of SD

Let, $c(\boldsymbol{r}) \rightarrow c(\boldsymbol{r}) + \delta c(\boldsymbol{r})$

$$F(c+\delta c) = F(\boldsymbol{r}) + \delta F(\boldsymbol{r}) = \int d\boldsymbol{r}\left[\frac{1}{2}K(\boldsymbol{\nabla}(c+\delta c))^2 + f(c+\delta c)\right]$$

$$f(c+\delta c) = f(c) + \frac{\partial f}{\partial c}\cdot\delta c$$

$$|\nabla(c+\delta c)|^2 = (\boldsymbol{\nabla}(c+\delta c))\cdot(\boldsymbol{\nabla}(c+\delta c))$$
$$= (\boldsymbol{\nabla}c)^2 + 2(\boldsymbol{\nabla}c)\boldsymbol{\nabla}\delta c + \qquad \cancel{(\nabla \delta c)^2}$$

Now what do we do is the following we are almost done that we consider just like we did in nucleation exactly Zeldovich and all these things that we consider in infinitesimal fluctuations or position dependent composition.

$$c(\boldsymbol{r}) \rightarrow c(\boldsymbol{r}) + \delta c(\boldsymbol{r})$$

So I said there is a fluctuation delta c then I go back and I said okay Fc + delta c is Fc and I write Fc as a result of that fluctuation as a result of this fluctuation my free energy has undergone at a position r some small change.

$$F(c+\delta c) = F(\boldsymbol{r}) + \delta F(\boldsymbol{r}) = \int d\boldsymbol{r}\left[\frac{1}{2}K(\nabla(c+\delta c))^2 + f(c+\delta c)\right]$$

How do I do that now I go back my Ginzberg Landau and put in place cc + del c and here c + del c. Now this quantity I can do a Taylor expansion Fc + del c Fc + this is the first order expansion. Now and this quantity del c + del c square so I now going to do that grad c + delta c square. So now I multiply that means this since this is the vector this is delta has got delta c grad dot delta c.

$$f(c+\delta c) = f(c) + \frac{\partial f}{\partial c} \cdot \delta c$$

When I do that I get delta c dot grad c grad c grad c square and then grad delta c grad delta c square so delta c square is a small term so that is neglected because it is a non linear or quadric in fluctuation then 2 terms remains 2 delta c, delta c.

$$\begin{aligned} \{\nabla(c+\delta c)\}^2 &= (\nabla(c+\delta c)) \cdot (\nabla(c+\delta c)) \\ &= (\nabla c)^2 + 2(\nabla c)\nabla \delta c \end{aligned}$$

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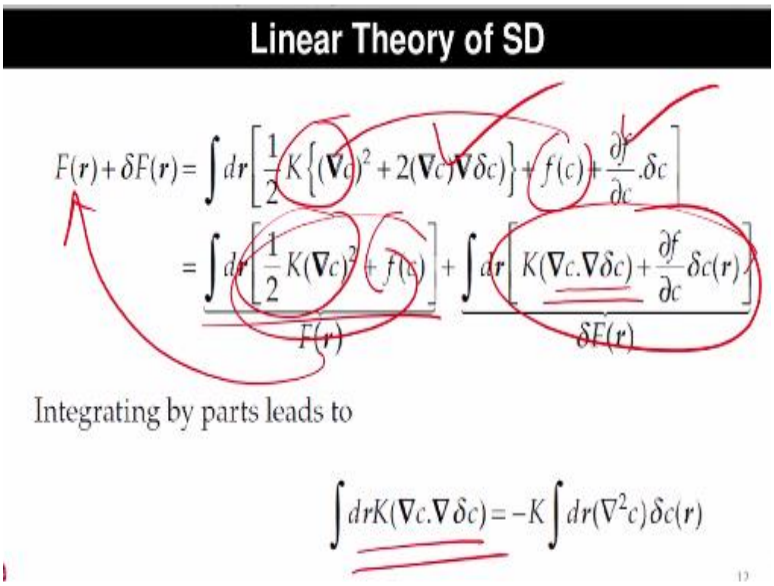

Linear Theory of SD

$$F(\mathbf{r}) + \delta F(\mathbf{r}) = \int d\mathbf{r} \left[\frac{1}{2} K \{ (\nabla c)^2 + 2(\nabla c)\nabla \delta c \} + f(c) + \frac{\partial f}{\partial c} . \delta c \right]$$

$$= \underbrace{\int d\mathbf{r} \left[\frac{1}{2} K(\nabla c)^2 + f(c) \right]}_{F(\mathbf{r})} + \underbrace{\int d\mathbf{r} \left[K(\nabla c . \nabla \delta c) + \frac{\partial f}{\partial c} \delta c(\mathbf{r}) \right]}_{\delta F(\mathbf{r})}$$

Integrating by parts leads to

$$\int d\mathbf{r} K(\nabla c . \nabla \delta c) = -K \int d\mathbf{r} (\nabla^2 c) \delta c(\mathbf{r})$$

So I can now go back and put all these things together and that is given here you know you put term then you realize that this term and this term this two can be combined to get Fr this quantity and I am left with this combined I am left with this term and this term which I collect here and then I integrate this by parts delta c delta c and I can get this term I integrate by parts I will get delta square c delta I got the linear thing out.

$$\begin{aligned} F(\mathbf{r}) + \delta F(\mathbf{r}) &= \int d\mathbf{r} \left[\frac{1}{2} K \{ (\nabla c)^2 + 2(\nabla c)\nabla \delta c \} + f(c) + \frac{\partial f}{\partial c} . \delta c \right] \\ &= \underbrace{\int d\mathbf{r} \left[\frac{1}{2} K(\nabla c)^2 + f(c) \right]}_{F(\mathbf{r})} + \underbrace{\int d\mathbf{r} \left[K(\nabla c . \nabla \delta c) + \frac{\partial f}{\partial c} \delta c(\mathbf{r}) \right]}_{\delta F(\mathbf{r})} \end{aligned}$$

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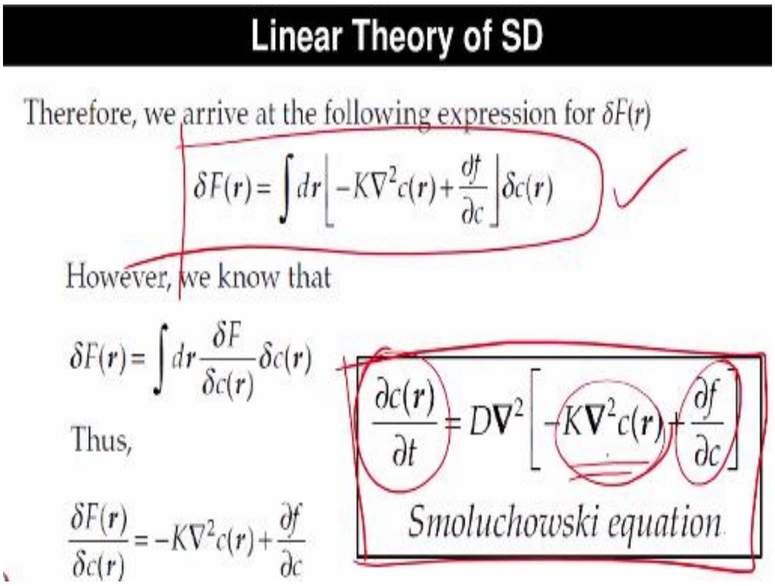

Linear Theory of SD

Therefore, we arrive at the following expression for $\delta F(r)$

$$\delta F(\mathbf{r}) = \int d\mathbf{r}\left[-K\nabla^2 c(\mathbf{r}) + \frac{\partial f}{\partial c}\right]\delta c(\mathbf{r})$$

However, we know that

$$\delta F(\mathbf{r}) = \int d\mathbf{r}\frac{\delta F}{\delta c(\mathbf{r})}\delta c(\mathbf{r})$$

Thus,

$$\frac{\delta F(\mathbf{r})}{\delta c(\mathbf{r})} = -K\nabla^2 c(\mathbf{r}) + \frac{\partial f}{\partial c}$$

$$\frac{\partial c(\mathbf{r})}{\partial t} = D\nabla^2\left[-K\nabla^2 c(\mathbf{r}) + \frac{\partial f}{\partial c}\right]$$

Smoluchowski equation

And then I do that I am going to get the following equation delta Fr is this quantity.

$$\delta F(\mathbf{r}) = \int d\mathbf{r}\left[-K\nabla^2 c(\mathbf{r}) + \frac{\partial f}{\partial c}\right]\delta c(\mathbf{r})$$

This is the one now I am going to use to find out my chemical potential and when I do that put it together this is equation one gets this Smoluchowski equation.

$$\frac{\partial c(\mathbf{r})}{\partial t} = D\nabla^2\left[-K\nabla^2 c(\mathbf{r}) + \frac{\partial f}{\partial c}\right]$$

Now the important thing is that with this equation given that look at this is not difficult at all it is just simple linear algebra the same thing you did in calculus.

But the important thing is now I have an equation for small fluctuation and that is of the following form there is diffusion second order term and the term dF/dc.

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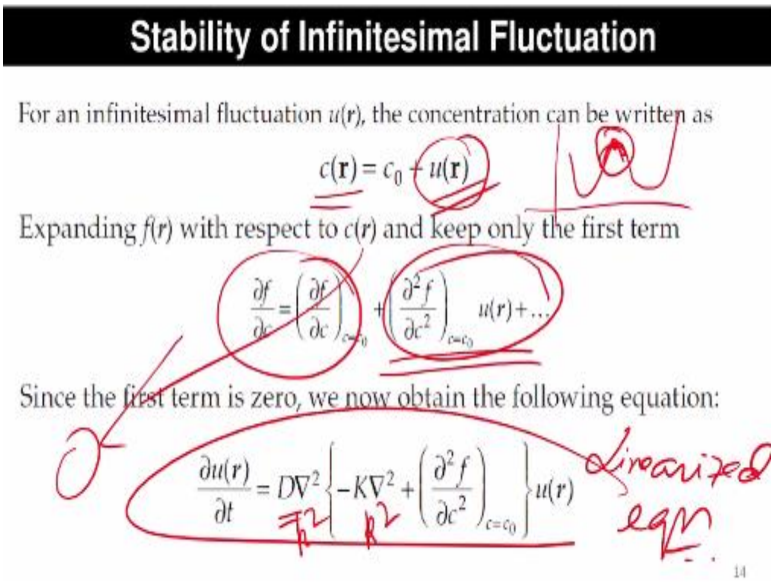

Stability of Infinitesimal Fluctuation

For an infinitesimal fluctuation $u(r)$, the concentration can be written as

$$c(\mathbf{r}) = c_0 + u(\mathbf{r})$$

Expanding $f(r)$ with respect to $c(r)$ and keep only the first term

$$\frac{\partial f}{\partial c} = \left(\frac{\partial f}{\partial c}\right)_{c=c_0} + \left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0} u(r) + \ldots$$

Since the first term is zero, we now obtain the following equation:

$$\frac{\partial u(r)}{\partial t} = D\nabla^2\left\{-K\nabla^2 + \left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0}\right\}u(r)$$

So in the next statement go and say okay I go back to original thing that this equation is a very powerful equation and lot of things can be done with equation, but we are not going to do that now we are doing something very simple we are going to do just here. So my fear my fluctuation I consider just announcing now little fluctuation here

$$c(\mathbf{r}) = c_0 + u(\mathbf{r})$$

this little fluctuation then I say

$$\frac{\partial f}{\partial c} = \left(\frac{\partial f}{\partial c}\right)_{c=c_0} + \left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0} u(\boldsymbol{r}) + \ldots..$$

And this of course we know is df/dc maximum is 0 so that goes to 0. I am left with this term. If I do that then I go back and put it back here this c_0 + u so it becomes du/dt so then I get

$$\frac{\partial u(\boldsymbol{r})}{\partial t} = D\nabla^2\left\{-K\nabla^2 + \left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0}\right\}u(\boldsymbol{r})$$

So this is the final equation what you call linearized equation and then something very, very nice to it. So with this equation now one very, very simple thing one can do is that we can say okay if I have the small fluctuation what happens to the fluctuation.

So this is my small fluctuation now is this fluctuation going to grow or the fluctuation going to decay. If fluctuation going to decay I am not going to get the phase separation or similar decomposition, but if the fluctuation grows then there is an instability and that when it happens one introduce a Fourier analysis and does Fourier space analysis here and one can show that if that because this equation is fully linear equation. I can do a Fourier transform this become Dk^2 this become small k^2 this k^2. So $k^2 + k^4$

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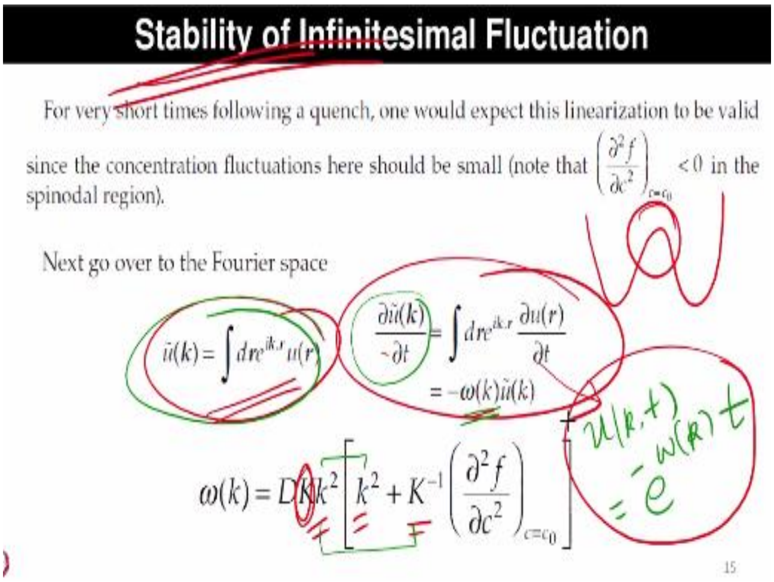

Stability of Infinitesimal Fluctuation

For very short times following a quench, one would expect this linearization to be valid since the concentration fluctuations here should be small (note that $\left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0} < 0$ in the spinodal region).

Next go over to the Fourier space

$$\tilde{u}(k) = \int dr e^{ik.r} u(r)$$

$$\frac{\partial \tilde{u}(k)}{\partial t} = \int dr e^{ik.r} \frac{\partial u(r)}{\partial t} = -\omega(k)\tilde{u}(k)$$

$$u(k,t) = e^{-\omega(k)t}$$

$$\omega(k) = DKk^2\left[k^2 + K^{-1}\left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0}\right]$$

And then you get this equation k^2 and k^2 k4 I take k^2 out and I just take the surface tension term come out. So in this small decomposition then we are talking of a small fluctuation in this initial we call linearized regime because u is very small and one of the way to study is kind of small fluctuations through a linearized equation like that is to go to Fourier space we call this a stability analysis.

So this stability analysis that we are doing here is a wonderful thing for stability of fluctuation recognizes the same thing as the stability of that we do in the free energy with the that means whenever you do a fluctuation if the energy increases as a result of fluctuation then the system is stable like if I here for example I give a small fluctuation if it stays then it is stable, but if it in a given like that marginal stability if it falls like that then that free energy decreases here in this case chemical energy.

In terms of fluctuation, free energy decrease then the system is not stable. So this is the way we talk even in thermodynamics the stability and instability just because we look into the first derivative and second derivative. The same thing we are doing here we already have a beautiful equation for the evolution of the small fluctuation here and I want to know what happens with small fluctuation.

And this equation here is going to tell me what will happen to the small fluctuation that equation already has a great character it has a surface tension term which resists building of heterogeneity and a free energy term which help in the phase separation because this term is coming from this term that help, but surface tension term as I said is by diffusion they do not like it.

They do not like creation of surface that is why it comes with a negative term and this two are opposite in sign they fight against each other and in that fight who wins? that is called a stability analysis and way to stability analysis is just introduce a Fourier. Why you do Fourier it is simply because this equation is linear equation it poised beautifully. So if I do Fourier transform in k square so this case go with this and k4 term.

So this case go with this and k4 go with that and that exactly what happens this k square and k4 term and this is the k square term. So now if I say okay my this quantity my fluctuation grows it grows or decays with this omega k so now I solve that I said okay u k t = e to the power – w kt. So this is my equation from this equation I did nothing. I said okay I will introduce this definition then I go back and do the Fourier transform.

$$\tilde{u}(\boldsymbol{k}) = \int d\boldsymbol{r} e^{i\boldsymbol{k}.\boldsymbol{r}} u(\boldsymbol{r})$$

I find du(k)/dt becomes omega k uk and then that omega k is given by this term.

$$\begin{aligned}\frac{\partial \tilde{u}(\boldsymbol{k})}{\partial t} &= \int d\boldsymbol{r} e^{i\boldsymbol{k}.\boldsymbol{r}} \frac{\partial u(\boldsymbol{r})}{\partial t} \\ &= -\omega(k)\tilde{u}(k)\end{aligned}$$

Now this equation means I have this solution.

$$\omega(k) = DKk^2\left[k^2 + K^{-1}\left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0}\right]$$

Now if on a fluctuation the fluctuation has to grow then omega k has to be negative if the fluctuation decays the omega k will be positive. It is very simple stability analysis that you probably have done in a stability analysis of differential equation in undergraduate those are little mathematics course.

They will have the stability analysis of a differential equation is very, very important thing for a differential equation whether it has a stable solution or not. Many solutions are neglected because they are not stable solutions. The same thing we are doing nothing very, very fancy.

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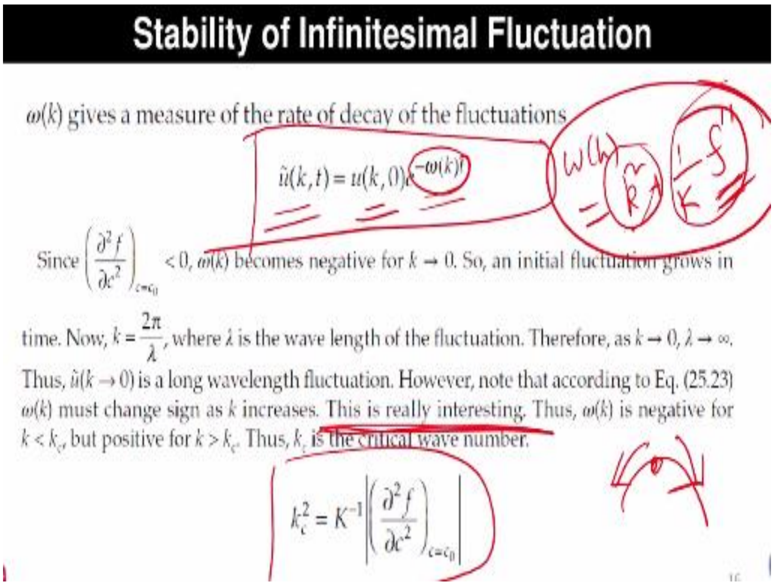

Stability of Infinitesimal Fluctuation

$\omega(k)$ gives a measure of the rate of decay of the fluctuations

$$\tilde{u}(k,t) = u(k,0)e^{-\omega(k)t}$$

Since $\left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0} < 0$, $\omega(k)$ becomes negative for $k \to 0$. So, an initial fluctuation grows in time. Now, $k = \frac{2\pi}{\lambda}$, where λ is the wave length of the fluctuation. Therefore, as $k \to 0$, $\lambda \to \infty$. Thus, $\tilde{u}(k \to 0)$ is a long wavelength fluctuation. However, note that according to Eq. (25.23) $\omega(k)$ must change sign as k increases. This is really interesting. Thus, $\omega(k)$ is negative for $k < k_c$, but positive for $k > k_c$. Thus, k_c is the critical wave number.

$$k_c^2 = K^{-1}\left|\left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0}\right|$$

So now at the end of the day I get the solution and omega k now is given by this thing. So this is a constant term not important so it is k square. So important thing is that

$$\omega(k) = k^2 + \frac{1}{k} f''$$

$$\tilde{u}(k,t) = u(k,0)e^{-\omega(k)t}$$

Now this quantity remember is negative because this is falling down this quantity is positive at function of k. Now there will be a k when so small k this is positive, but when so this quantity that is coming from here falling down.

So maximum second derivative is negative so sorry this is negative, but this is positive. So this is negative and this is positive so very small k this quantity is negative, but large K this become positive. So when I go to large K remember I have a negative sign in front of it so when a large K it becomes positive that means the fluctuations decay but at very small k this quantity wins and then omega k becomes negative.

$$k_c^2 = K^{-1}\left|\left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0}\right|$$

At omega k becomes negative I have a negative sign then these quantity becomes positive what means won infinitesimal fluctuations grow and there is a crossover this is the crossover. So below that old number fluctuations it is really interesting as I said here that below that old number fluctuations grow, but then large wave number fluctuation stable.

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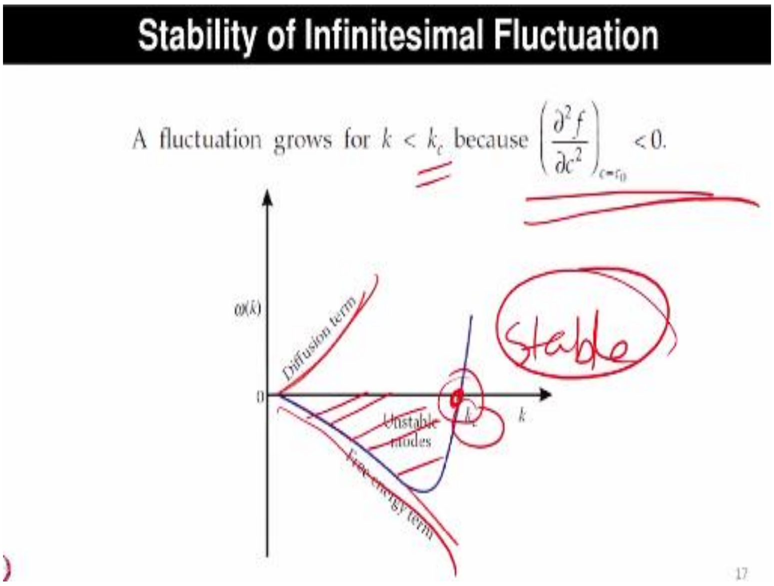

Stability of Infinitesimal Fluctuation

A fluctuation grows for $k < k_c$ because $\left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0} < 0$.

And this is exactly like our nucleation kind of thing there is a surface term is a diffusion term and there is a free energy term and so below that kc system is unstable, but above that it is stable because this quantity is negative. So this is the stability analysis and that explains the spinodal decomposition that why infinitesimal fluctuation can give rise to grow up the patterns and the patterns that grows, grows with the wave number kc.

Because this is where first time because you are not going to go very large scale fluctuation. You are doing local small fluctuation and you are trying to do local small fluctuations and you find your fluctuations just decay. However, suddenly you can have a fluctuation your particles B and A particles have brought together such that there is a fluctuation and certain size of A and certain size of B are there very much like nucleation.

So these A and B are now can be stable now. So that particular is a kc that magical wave number is the kc and in kc that pattern now suddenly is stabilized and then we know that is the pattern that can you call. How do you know that all these things we are telling is right or wrong.

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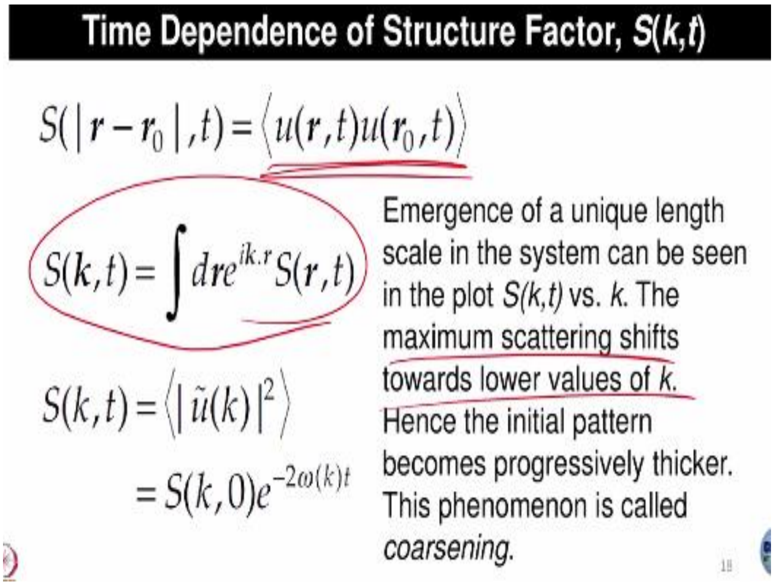

Time Dependence of Structure Factor, $S(k,t)$

$$S(|\boldsymbol{r}-\boldsymbol{r}_0|,t)=\langle u(\boldsymbol{r},t)u(\boldsymbol{r}_0,t)\rangle$$

$$\boxed{S(\boldsymbol{k},t)=\int d\boldsymbol{r}e^{ik.r}S(\boldsymbol{r},t)}$$

$$S(k,t)=\langle|\tilde{u}(k)|^2\rangle$$
$$=S(k,0)e^{-2\omega(k)t}$$

Emergence of a unique length scale in the system can be seen in the plot *S(k,t)* vs. *k*. The maximum scattering shifts towards lower values of *k*. Hence the initial pattern becomes progressively thicker. This phenomenon is called *coarsening*.

Well, people go and can calculate these fluctuation, fluctuation-collision function by scattering this is called structure factor. Just like we did wave number Fourier transform this is the structure factor that one gets by x-ray scattering or neutral scattering. So the maximum scattering occurs towards lower then what happens that one when do you get scattering. You do not get scattering for homogenous system you get scattering when there is homogeneity and because in order to scatter you have different regions of different density just like light scattering you need to have different reflective index.

$$S\left(\left|\boldsymbol{r}-\boldsymbol{r}_0\right|,t\right)=\langle u(\boldsymbol{r},t)u(\boldsymbol{r}_0,t)\rangle$$

$$S(\boldsymbol{k},t)=\int d\boldsymbol{r}e^{ik.r}S(\boldsymbol{r},t)$$

$$\begin{aligned}S(k,t)&=\left\langle\left|\tilde{u}(k)\right|^2\right\rangle\\&=S(k,0)e^{-2\omega(k)t}\end{aligned}$$

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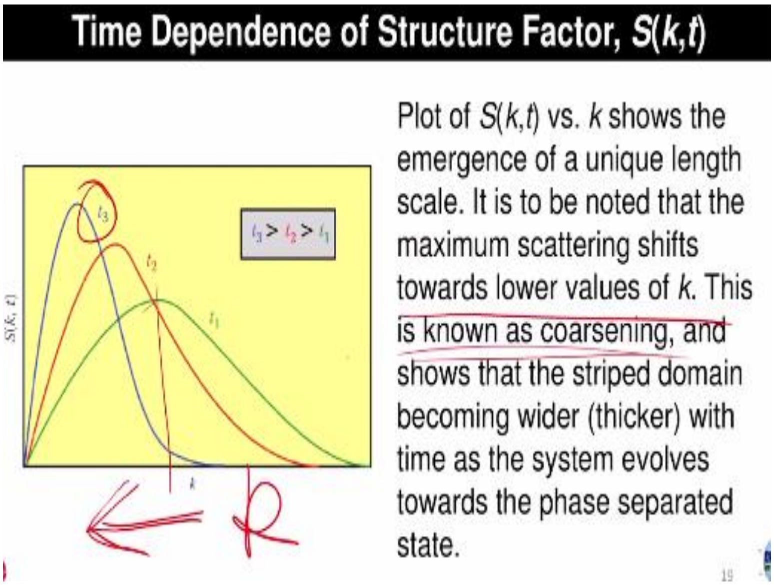

Time Dependence of Structure Factor, $S(k,t)$

Plot of $S(k,t)$ vs. k shows the emergence of a unique length scale. It is to be noted that the maximum scattering shifts towards lower values of k. This is known as coarsening, and shows that the striped domain becoming wider (thicker) with time as the system evolves towards the phase separated state.

And that exactly one sees in x-ray scattering that this pic and as this phase separation focuses, the pic is the manifestation of there in this region and this region move to a lower and lower k value this is k with time lower value that this is the longest time and that means what happens my patterns becoming thicker and thicker and phase separation is going on more and more.

So this scattering shifts towards lower value this is known as coarsening very important thing in phase transition language coarsening. So system is coarsening itself it evolves to a separate state. So I think this is the end of this phenomenon decomposition. To summarize that it is a wonderful subject to end the phase transition from the time being we are back with the critical phenomena later.

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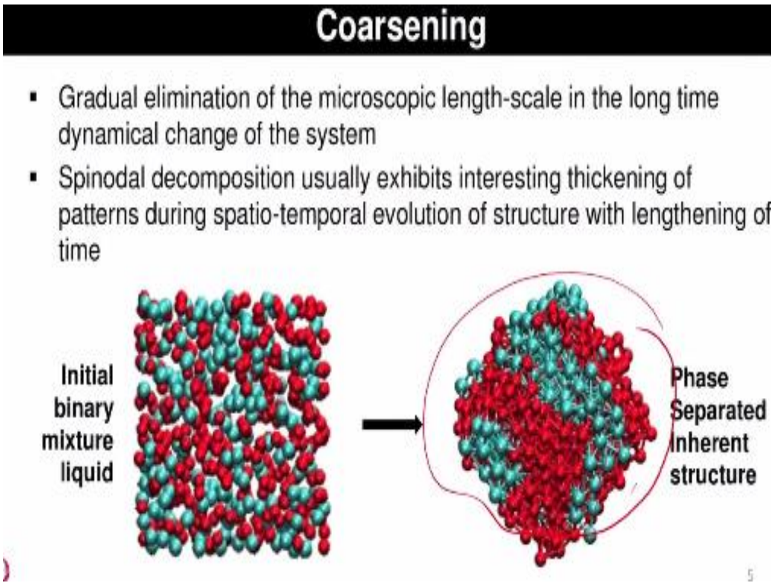

Coarsening

- Gradual elimination of the microscopic length-scale in the long time dynamical change of the system
- Spinodal decomposition usually exhibits interesting thickening of patterns during spatio-temporal evolution of structure with lengthening of time

And this is the kind of situation we are describing.

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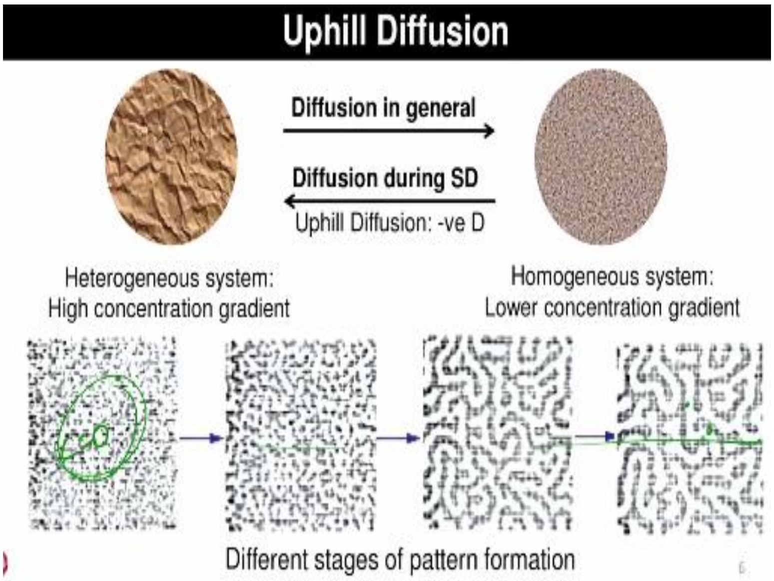

And this is the kind of coarsening behavior so this is very different from nucleation, but at the same time exceedingly common and popular and is not really taught in statistical mechanics courses, but as soon as we go in the realm of research, this is one of the first thing that we face just like nucleation and I think students should be prepared for this kind of things rather than knowing lot of equations and lot of partition function they are fine and they get us started, but they do not really give you to any interesting and important areas of research.

And do not allow you for example, such papers and other materials and other things where people will see nucleation thermodynamic control or kinetic control they are talking of Becker-Doring and Zeldovich they are talking spinodal decomposition, but this is it because I think student should read at the level or BSC or MSC this kind of things. So this is where we stop now and we will return soon with another dose of phase transition.

And then we go over to more mundane and more detail things of liquid state theory and more interacting systemizing model and phase transition and many, many other things at their life by how the binary mixtures, how to talk of surface tension and many other thing. Okay.