Basic Statistical Mechanics
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Lecture – 41
Nucleation Part 4: Ostwald Step Rule

Okay. Welcome back and we are continuing on phase transition and after doing Landau theory of phase transition and general classification of phase transition. We went on to Landau theory we free energy landscape we started on a very important area of phase transition which is not fully covered in books and courses of statistical mechanics but which are of paramountly important and that is the formation of new phase and this is known as nucleation.

Nucleation has become of huge importance in recent times because of emergence of nanoscience and nanomaterials as an important area of research. It was always important nucleation because of formation of solids on liquids or droplets in the from gas liquid droplets in the atmosphere so nucleation, much of the nucleation study was done by the chemical engineers.

And were also interested in the formation of the bubbles, cavity inside hot liquid was has to do with corrosion and many others things so nucleation always but of late last 15 years or so it has become a excessively important subject, can we discuss in nucleation that how there is a barrier, barrier comes because although the new phase is more stable that is one of the prime condition of the formation of the new phase when nucleation, the new phase must be more stable thermodynamically.

So it will have a lower free energy then the old phase. Otherwise nucleation cannot be achieved, the reason it cannot take place nucleation because when you form a new phase inside then there is a large penalty for surface tension so bubble must grow or the new phase must grow by fluctuation the embryo of new phase of the nucleus of new phase must grow so that, it can out way the energy cost and penalty cost because of the surface tension.

So we work out this equation,

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

Then starting that we take the derivative and find out position of maximum, which is called Becker-Doring theory. So Becker-Doring theory gave you the free energy barrier and the size of nucleus in just two parameters, which is ΔG_v and the surface tension ΔG_v is the free energy per unit volume between the old and the new tree.

And good and that has been exceedingly popular. And in any, any books of nano materials. So it is something you start you Becker-Doring theory of nucleation is the first thing. So we often see that the formation of a new phrase is thermodynamically controlled or kind of controlled those languages very much come from the Becker-Doring theory that going to so many times the phrase that forms is not thermodynamically stable phase but it is the kinetically accessible phase way of thinking about the formation of a new phase.

Is particularly important in so for example, like zeolites in zeolites which are huge number of zeolites like, you start before your site in your calcimite and then many other things and going ultimately to quartz. So there are 10 zeolite phases and if you able to hi-tech by, the paradoxical result is that when you are starting at high temperature, then it is the quartz most stable place that forms.

But at low temperature, it is the least stable form that my Faujasite forms from the salt of aluminosilicate. These wonderful diversity and then of course there are many drugs and pharmaceutical industry, and then these drugs are polymorphic means that they can exist in many different solid traces and what is really interesting that some of these solid phrases biologically active or can act as a medicine but the many other is have no activity.

So that is why when you keep it dropped for a long time it tablet many times it goes to a different polymorphic form and it becomes useless. So the presence of multiple solid faces of the same material and even of the same competition like in quartz what is the number of water molecules are changing. But other than that there is composition of aluminosilicate. Another case is ice, ice is known forming some 18 different phases starting with ice 1 h, ice 1 c, and ice 2, 3, 4, 5, 6, 7, 8, 9 all the way.

So these different ices you know are formed at different thermodynamic conditions, but they are saying they are from water H_2O. So how to understand all these different things and so these statistical mechanics allow you to do statistical mechanics allows to ask you a question and answered. What are the phases about when form in what condition and often the study of them from nucleation is kind of difficult because you need to look at surface tension.

Even if you know, the ΔG_v the free energy gap between them surface tension is not always accessible, like surface tension in calcimite is a very tough thing to ask for an experimentalist. However long time ago, there was a beautiful work done by great Ostwald or sometimes called the father physical chemistry Wilhelm Ostwald, who lived in during the period which is shown here (1853-1932).

This is one year, and he did many, many, many things huge amount of work in chemical kinetics then in the face transition, Ostwald ripening, Ostwald step rule, both are important in the context of creation and formation of the new phases. Today as a natural consequence to the equation we do the Ostwald step rule. And this is actually the step rule, which is you put in. So succinctly is the following. The formation of the things is not determined by its absolute stability and but by closeness of the growing phase to the parent phase.

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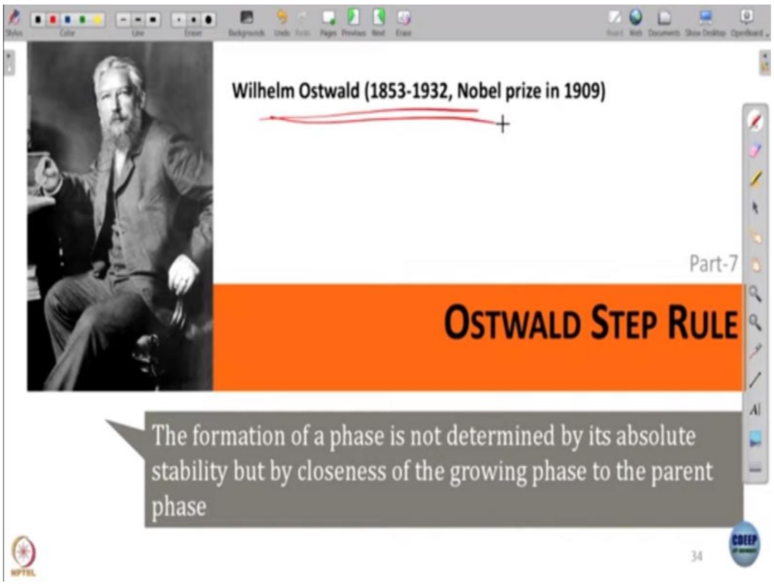

Wilhelm Ostwald (1853-1932, Nobel prize in 1909)

Part-7

OSTWALD STEP RULE

The formation of a phase is not determined by its absolute stability but by closeness of the growing phase to the parent phase

This such a clear statement So he is saying, if I start from a salt, there is not the quartz which is formed it is Faujasite, it will go to Calcimite and many, many such examples that are now coming out in Nature and Science like the big, big papers that people are like titanate not just Zeolites, then phosphates and they form multiple solid forms and they all of then obey

Ostwald step rule when Ostwald formulate the rule and somebody will come to him and say okay these solid does not follow your rule.

He would say go and look carefully. Even his statement was that even if seems like then the closest phrase has not formed. That means the closest phase did form and disappeared. So if you will be careful you will be able to detect the close form. This became a very big industry and it is called disappearance of polymorphs. It turns out the understanding of Ostwald step rule took us to very profound results on random Ising model or the number disordered systems.

And it forms a beautiful bridge from many, many fascinating areas of science. Some of them I will just be able to just touch the surface but I want to tell you about this rule and this beautiful consequence of many, many consequences that the rule ask. So let me take it from the very beginning or at the very outset that the closeness of the growing phase is in turn out to correct and to what extent Ostwald understood it I do not know.

What did that has to do with the surface tension if I have two phases or three phases of ABC and two B and C is close to B and far from A then one can show the surface tension between A and B is much less than, the A and C. So we have learnt in nucleation we have a barrier is

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

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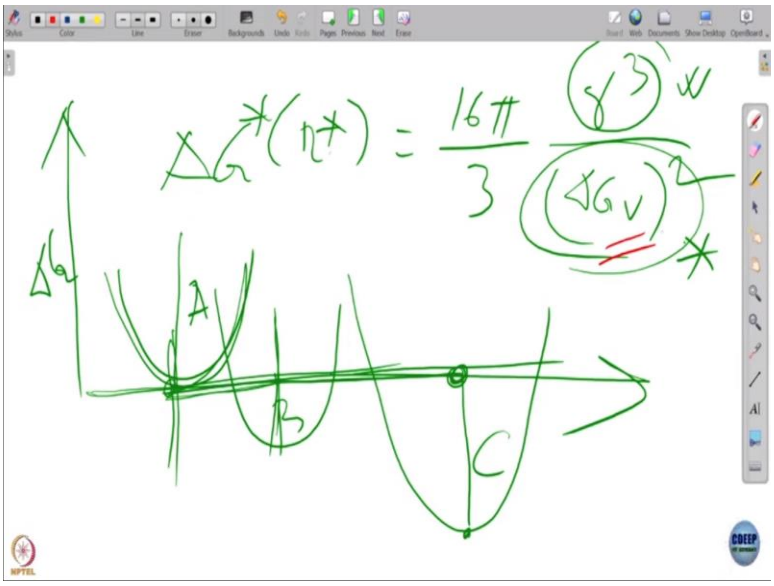

And let me write it down. There are two things. Now we have 3 phases A, B, and C. So let us see A as original phase. Now there is a phase in between. You know what, in order to form it has been more stable than the A is with these far from that is a state more stable C now I have plotted against the ordered parameter which is actually measure of the closeness.

Now A and B are close to each other but C is more stable but if A has to go to C it has to create embryo, which is very far from the A. Now, look at this barrier then γ^3, gamma is a surface tension what Ostwald did not have the Becker-Doring theory. So he did not know whether he know surface tension and when he saw that he do not have it as expression but he correctly guessed that when it is to closeness then A is close to B.

In our language now will translate is that surface tension between A and B is less. So γ comes with the cube and the ΔG comes with this square. This is of course not as trivial as I am telling this there is much more because it will depend on the value of ΔG_v and gamma. But surface tension between A and B is much less than surface tension between A and C. So now there is a balance between the two how big is the free energy gap and how different is this surface tension. So this is what determines for Ostwald step rule. Is it routinely used in things will let us go through a little bit more on that.

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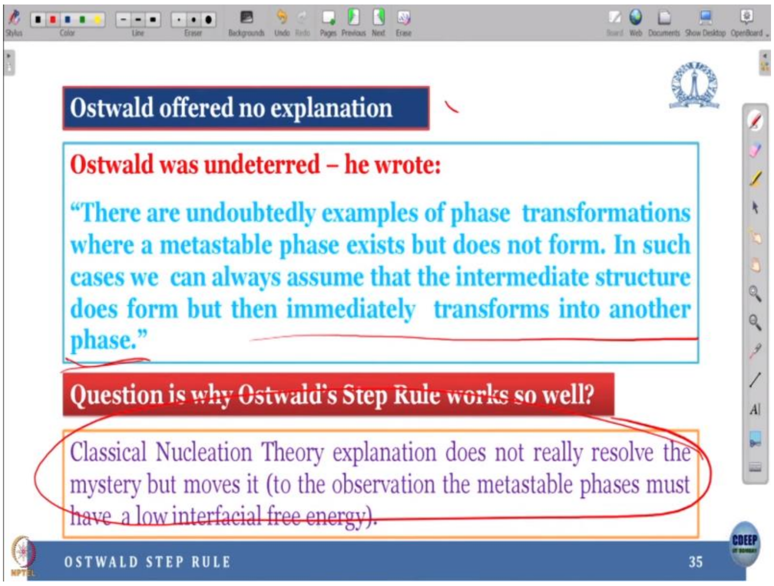

Ostwald offered no explanation

Ostwald was undeterred – he wrote:

"There are undoubtedly examples of phase transformations where a metastable phase exists but does not form. In such cases we can always assume that the intermediate structure does form but then immediately transforms into another phase."

Question is why Ostwald's Step Rule works so well?

Classical Nucleation Theory explanation does not really resolve the mystery but moves it (to the observation the metastable phases must have a low interfacial free energy).

So Ostwald was when people say you will do is not working he had a fantastic a lot of other very smart men Ostwald for no explanation. He has just stated it his experiment observation he offered no explanation and now comes when people used to come and tell him he said undoubtedly examples of phase transformation where a metastable phase exists but does not formed in such cases we can always assume that the intermediate structure does form.

But then immediately transforms in on the phase. This is amazing. So this is classical nucleation theory, which partly explains it. It does not fully explain, but moves it to the interfacial free energy I said but then comes the difficult task of relating the surface tension to the statement of closeness. Okay. How can we now relate the surface tension to the outer parameter. That is the question We will not do a full job but we will do a part job.

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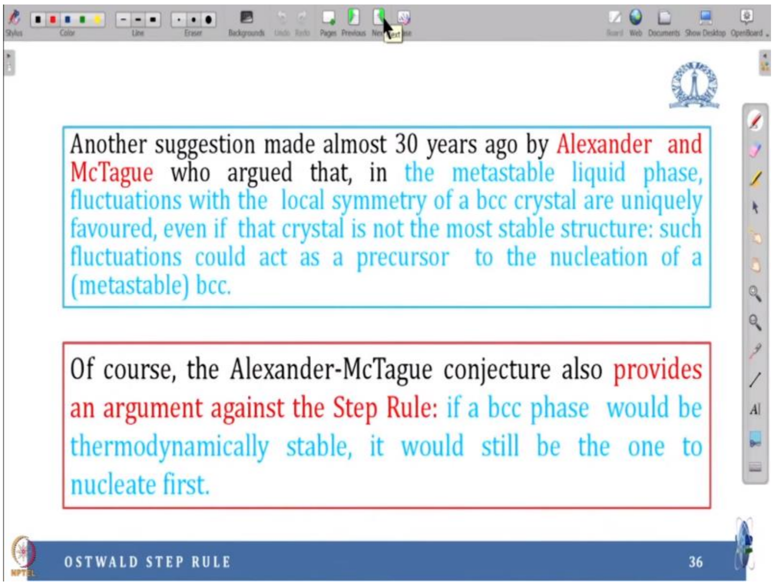

Another suggestion made almost 30 years ago by Alexander and McTague who argued that, in the metastable liquid phase, fluctuations with the local symmetry of a bcc crystal are uniquely favoured, even if that crystal is not the most stable structure: such fluctuations could act as a precursor to the nucleation of a (metastable) bcc.

Of course, the Alexander-McTague conjecture also provides an argument against the Step Rule: if a bcc phase would be thermodynamically stable, it would still be the one to nucleate first.

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Now there are many others that says that the meta stable liquid phase fluctuation with the local symmetry undoubtedly favoured and if the crystal not more stable than it could be cuts and all these good act as precursor and all these things we do not need to go into that right now. So here you see two examples. That very much is a form of the course material and it is discussed in my book or Alexander McTague.

I do not have in the book, but here comes these, zeolites for, from the salt aluminosilicates and it goes to Faujasite and then to calcimite. Finally it goes to most dense phase that most stable phase that is the quartz and there is another beautiful example that came out in few year ago in nature physics in lithium ferrous phosphate and it is now because of the enormous improvement in electro-microscopy and almost time-domain electron microscope.

You can detect all the intermediate States that actually Ostwald spoke off. So in lithium ferrous phosphate one could see in something like in couple of one hour or two hour or may be a day or two that you can see that this salt of lithium ferrous phosphate it goes through all the phases and ultimately the most stable form dense form forms It is just amazing exactly at Ostwald predicted and free energy diagram, they do not want to say we want that.

I just drew a two page ago. They go, that is how it goes from one. This is the one which is closest to in closeness quote Ostwald that forms fast, which would be these ones, then forms this one then these one, which is this one, then forms this one, which is this one and finally stable can still form, which is this one. So one sees in real world, the verification of Ostwald step rule one by one, and here in zeolite.

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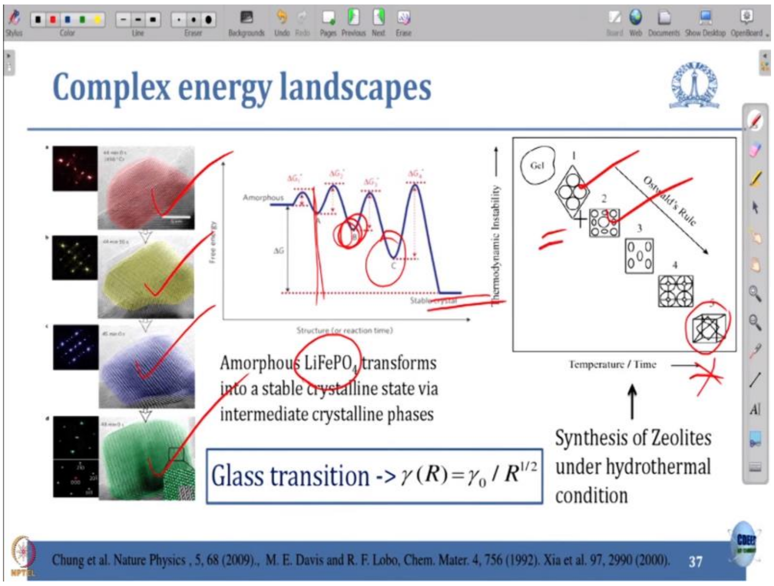

Complex energy landscapes

Amorphous $LiFePO_4$ transforms into a stable crystalline state via intermediate crystalline phases

Glass transition -> $\gamma(R)=\gamma_0/R^{1/2}$

Synthesis of Zeolites under hydrothermal condition

Chung et al. Nature Physics , 5, 68 (2009)., M. E. Davis and R. F. Lobo, Chem. Mater. 4, 756 (1992). Xia et al. 97, 2990 (2000).

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You also see what happens in zeolite with low temperature. Then you find the Faujasite, then calcimite. However, in high temperature again you do not see, but you are, you just see this one because if you follow Ostwald in this forms, but it transforms itself through succession of intermediate States and goes over to the quartz.

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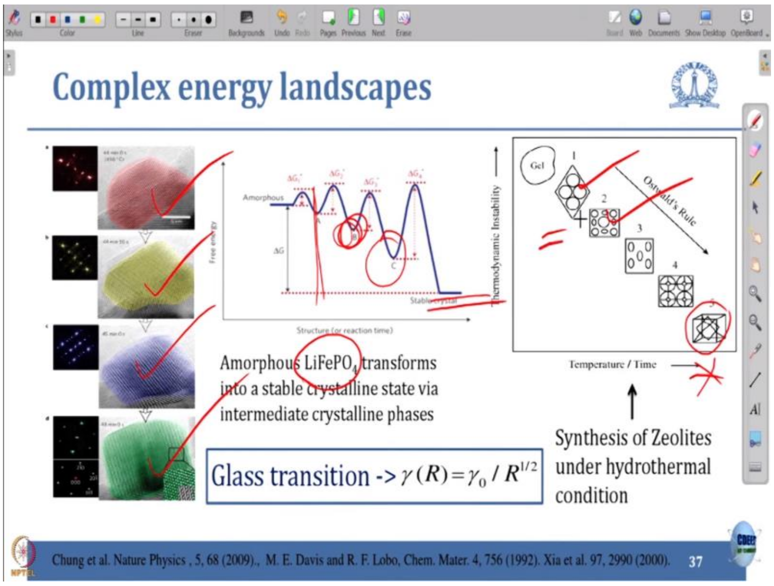

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Okay So how do we do this this is kind of interesting and rather complicated theory but we will go to that But for that let me consider the following condition that I have a metastable state then I have to I have melt which is metastable state final then we have a two metastable statemetastable one and metastable two and then I have finally stable solid very similar to what we saw in the so this picture from the nature of physics and the sentiment, and the picture that are drawn here is very, very similar.

And then one wants to calculate how the surface tension going to be here. And the way this calculation goes is the following and I will not go to the detail calculation but let me do this.

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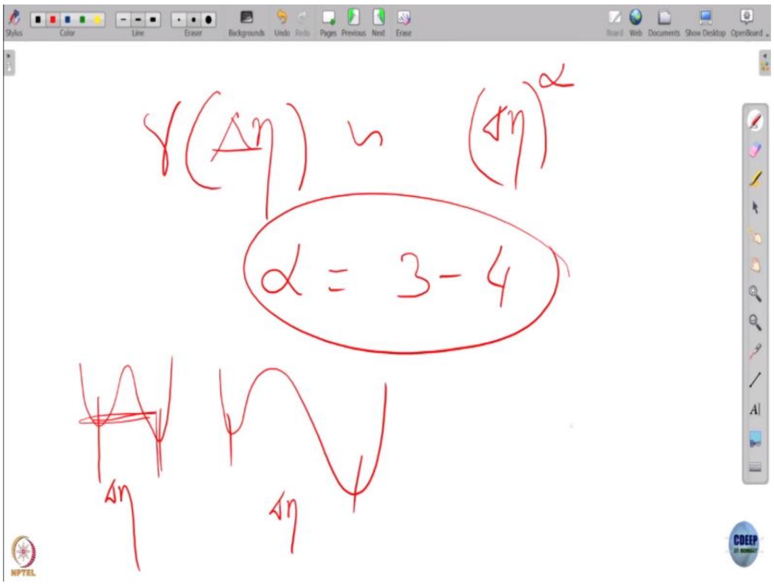

$\gamma(\Delta\eta) \sim (\Delta\eta)^{\alpha}$

$\boxed{\alpha = 3-4}$

One finds that if I have the if I plot these multiple phases and multiple surface tension, then surface tension as a function of order of parameter difference within the two goes as $(\Delta\eta)^{\alpha}$, and $\alpha \sim 3-4$ that means if you have one thing like that. And other things like that, then surface dimension of these because the order of parameter is this much difference is $\Delta\eta$ this much.

And all $\Delta\eta$ Then these will have a much, much larger surface tension. How do you calculate that way to calculate is actually goes through very interesting and I will be discussing.

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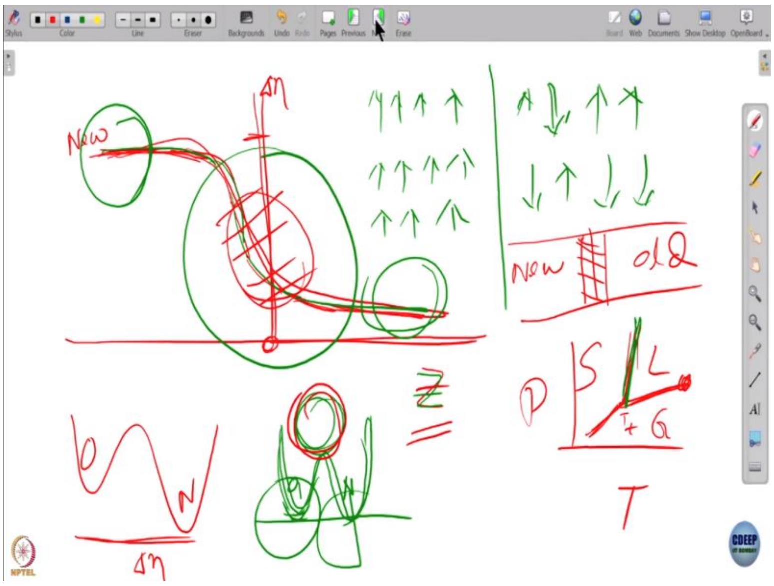

Probably and then it will be the more quantitative way one does is the following. I consider the old phase let us see the new phase and these old phase and let us see this is the arbitrary inter phase I have So I got new year and old here and remember surface equilibrium property because that means when surface tension is when two phases coexists. So under this condition I now try to find out how the order of parameter varies and that one can do by using that one case but you do not need that right now, but we have to understand.

So this is the order parameter $\Delta\eta$, and this is the minima and these old and these other way around, but it does not matter what, this is the difference. So I checked up the order of old phase as 0 and then it becomes just like land out. It becomes 0. Now if I plot it then what happens That this is becoming like that. Now, what is the meaning of surface tension? So this is order parameter profile? I call it order parameter profile.

It goes from here. Then in this region. It falls from the new to the old close to this. Now very interesting what is the meaning of surface tension? Remember surface tension at equilibrium is the equilibrium phenomena. So surface tension happens in the coexistence like in the pressure temperature plan. This is the critical point, this is the triple point and this is liquid solid and gas. So, these line are the coexistence lines.

And, surface tension is the define at the coexistence along this line. And, another coexistence free energy is same. Okay. Let us go a little bit more thinking. So, let me now draw free energy is the same. Okay. So these two faces are the two same energy, old and new. Now, they are at coexistence like here. So, let us old new. So, only free energy when the system is here which, is here the free energy at the chemical potential is the same energy is here because they are at coexistence.

Then they are co existence. That coexistence is here. However, in order to bring an old and new together, in order to create a interface I have to go through these regions of all the parameters. So, but it has the order parameters values are intermediate. Order parameters are neither this one which is this one neither this one which is this one but is in between. So, the certain amount of phase ahs to be in this region.

If can think in terms of spin, then there is the region in which all spins are up. All that ferromagnetic fields and then you have which is disordered. So, there is a completely; Now in between it will be a region, if I have to put an interface in between there is a region where there is a partly order. That would seek the system in this region. So, that is this region. But this is high energy region, high field energy.

And, as a result you have to spend extra energy. And the extra energy that you have to spend is surface tension. So, this is the definition of surface tension which is not told in most of the young writer text books or even in books that they do not even explain that the reason of the surface tension at a molecular there is a molecular level of understanding in the surface tension which is because a part of the material has to be the intermediate order parameters values. Now, very interesting comes now.

What is the next thing now? If I have a interface between these then I have to now understand the system always minimizes the external energy spin. So, the system tries to minimize amount of material in this intermediary period. So, it acts make it narrower. So, there is now competition between one is in the exact place. So you are looking at two dimension. One is really special dimension z and the dimension is out of parameter.

So, one wants to do that, when one wants to derive free energy expression which takes into account the free energy of the system as the function of the about the parameter as it travels this things. Plus, the extra energy cost of creating this thing and creating such a great n and that is the thing we are going describe now little bit.

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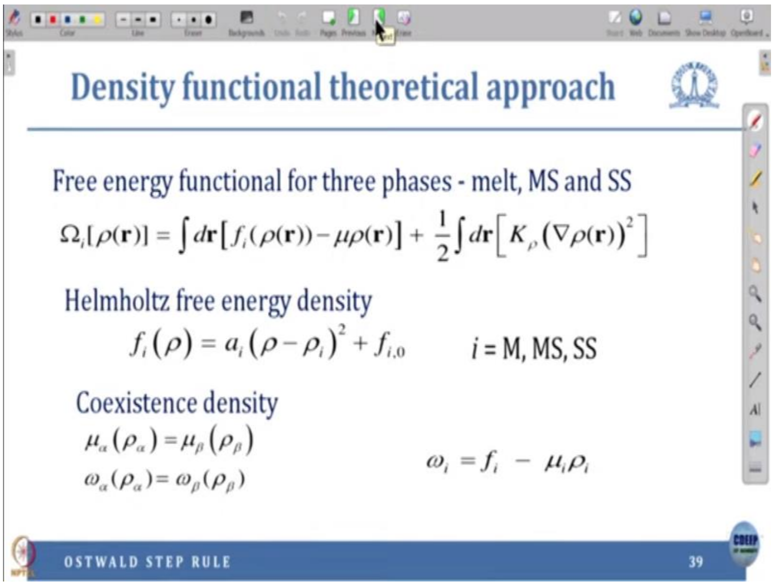

Density functional theoretical approach

Free energy functional for three phases - melt, MS and SS

$$\Omega_i[\rho(\mathbf{r})] = \int d\mathbf{r}[f_i(\rho(\mathbf{r})) - \mu\rho(\mathbf{r})] + \frac{1}{2}\int d\mathbf{r}\left[K_\rho(\nabla\rho(\mathbf{r}))^2\right]$$

Helmholtz free energy density

$$f_i(\rho) = a_i(\rho-\rho_i)^2 + f_{i,0} \qquad i = \mathrm{M, MS, SS}$$

Coexistence density

$$\mu_\alpha(\rho_\alpha) = \mu_\beta(\rho_\beta)$$

$$\omega_\alpha(\rho_\alpha) = \omega_\beta(\rho_\beta) \qquad \omega_i = f_i - \mu_i\rho_i$$

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So, this is a we are not going to go into very much detail into it. But I just want to tell you if density like gas liquid density is the parameter then it has the following kind of things. One is the free energy at the given position and then other is the gradient term, this term. That means how sharp you are varying. If you are varying very sharp, then you have to pay an energy. But if you make it wider you have to pay an energy here.

$$\Omega[\rho(\mathbf{r})] = \int d\mathbf{r}\left[f[\rho(\mathbf{r})] - \mu\rho(\mathbf{r})\right] + \frac{1}{2}\int d\mathbf{r}\left[K_\rho[\nabla\rho(\mathbf{r})]^2\right]$$

So, these two competitions. Then one wants to make it narrow, interface narrow. But the other one making it a narrow putting these 2 opposite faces next to each other that also do not like and so that is the square gradient and we call this square gradient term. There is a term and this term is free energy this energy. So these are the two things with the condition that is free energy or chemical potential. The chemical potential or the α and β are the same and then we minimize this.

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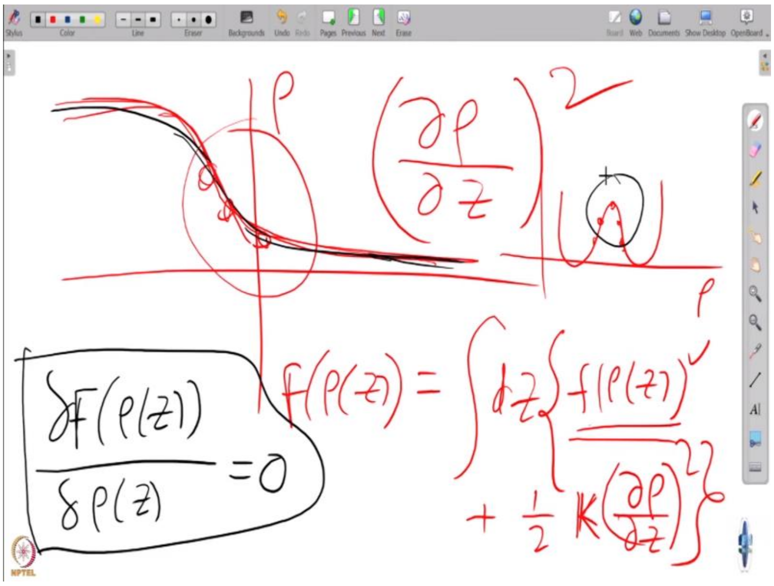

So, important thing to know is in any interface you are trying to make this narrow in order to minimize the amount here but in order to make it narrow you can make it too narrow then you have to pay energy in terms of in square gradient terms because if you had it too fast the you have to pay because you are making the density change very, very shapely and that system does not like because system does not like fluctuation.

As I told you all these density terms are harmonic. They are quantatic in the density. So, it does not like then what happens that the packaging in the inter molecular interactions are putting molecules next to each other that becomes very difficult. So, this extra term, so in addition so you are basically saying okay free energy of these kinds of a terms, two terms y integrate over the dz have a term of free energy as a function of ρ(z).

This is at a very point. What is the free energy? I called that a van der Waals term. And then you have to do. So you have one term which is a van der Waals term which is just picks up what is the values of free energy at that z. So, this comes from this thing. So, this ρ as z is changing. ρ is changing and as the ρ is changing is it climbing up. So, this van der Waals and how sharp it is varying that i said the is the kind of spin constant of the system.

So, this is the quantity. Now what you do, you listen carefully because this is something very neat and very clean and very simple. Just very new or quite new to students. So, now what one does one minimize the free energy cost with respect to the. So this is the functional derivation means derivative of function of a function. Here you do that then you get this solve this equation with these free energy functional then you output this is ρ(z).

And once you have the ρ(z) you put it back in the free energy and you get the excess of free energy and excess free energy is the substantial. So now we know how to do these things. We know how to think about it. That when so there is very interesting thing. If you make these very huge difference in order parameter then you have to make these region under broad because there is a very large variation and then you are facing regions which is very high region here. So, as a result of that the nucleation barrier goes up.

So, while Becker-Doring theory with Zeldovich correction tells you that how to under nucleation. It does not really tell you the basic essence why surface tension behaves the way it behaves. It does not connect to Oswald step tool. But these logic which Ostwald have in the back of his mind because he offered no explanation but lot of work in the last 10-15 years that people begins to put things together.

Work out these beautiful theories as the theory goes on the name of this particular free energy functional I have written down is goes by the name Ginzburg–Landau energy function. It is such a noble things. Let me write down. Critical phenomena is based on free energy functional.

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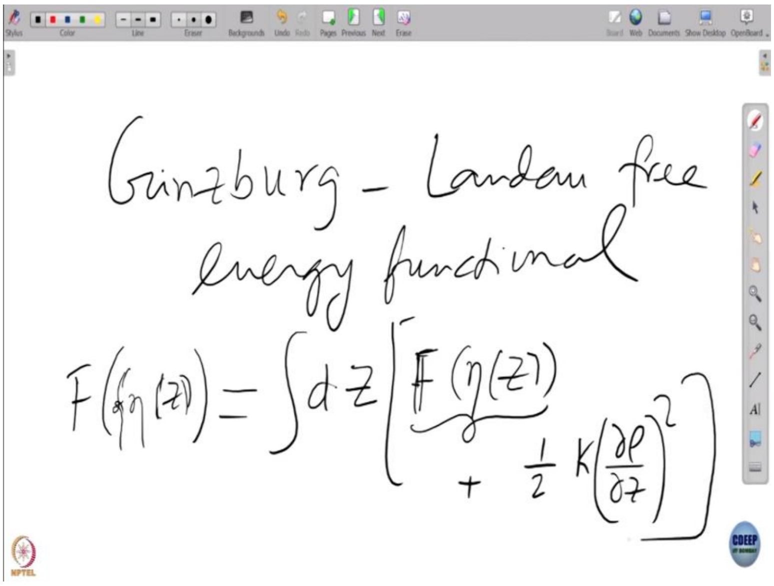

Ginzburg – Landau free energy functional

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

So this is; That is what I wrote down here. Actually we do more in terms of a general just one-dimensional, three dimensional also and actually three dimensional is the one you generally see but I just scattered it to for my own need here and this is to be understood as the free energy varying. So, pick Z then that Z give you van der Waals parameter and then you and put it in Landau of energy function and then you have this Ginzburg–Landau energy functional.

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

In many different forms it comes in many different areas of natural science.

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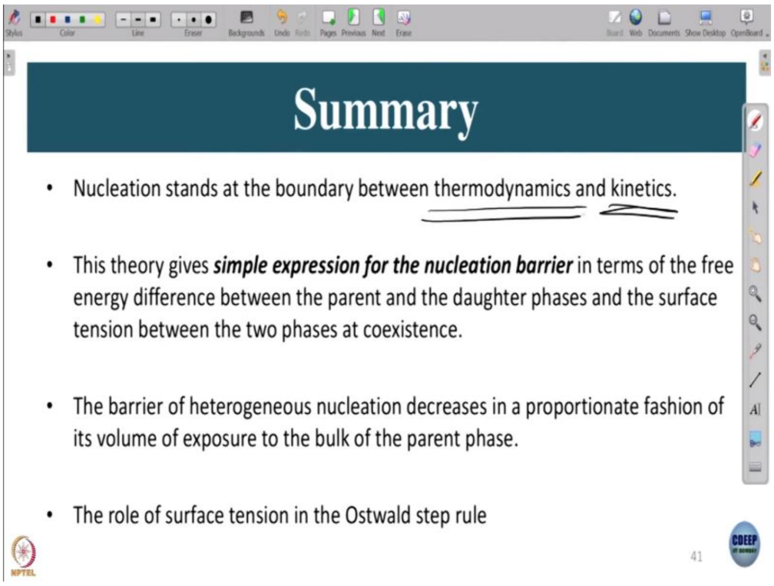

Summary

- Nucleation stands at the boundary between thermodynamics and kinetics.
- This theory gives ***simple expression for the nucleation barrier*** in terms of the free energy difference between the parent and the daughter phases and the surface tension between the two phases at coexistence.
- The barrier of heterogeneous nucleation decreases in a proportionate fashion of its volume of exposure to the bulk of the parent phase.
- The role of surface tension in the Ostwald step rule

Okay there are certain says to nucleation stand to the boundary between thermodynamics and kinetics; So it is a very nice slide. Let us go through that. This is really very interesting. The nucleation stand at the boundary between thermodynamics and kinetics because we are calculating the rate but we are going from thermodynamics. We really did not do much of kinetics as such except in Zeldovich. The theory gives simple nucleation by terms of energy difference of the parent and daughter phase and surface tension Becker-Doring theory. Then we say the role of surface tension in the Ostwald step rule. That is a very nice thing.

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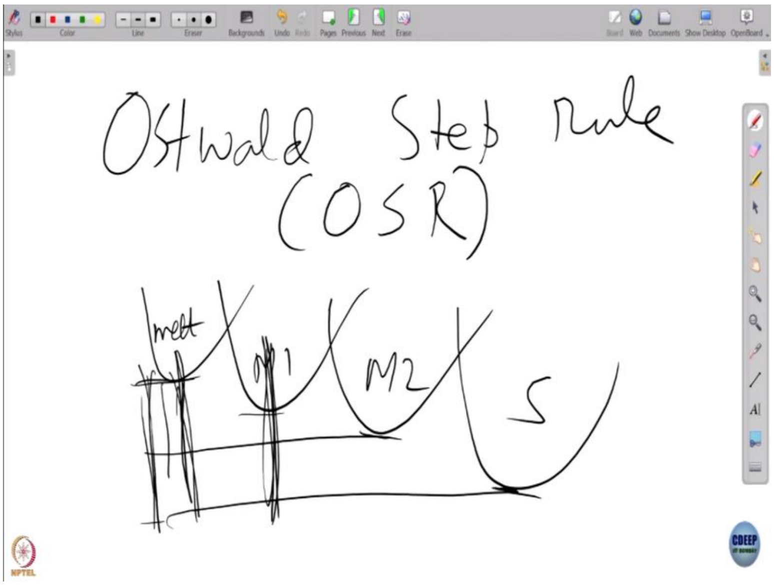

So Ostwald step rule then tells you often called as OSR that tells you yes when we have situation like that then this is the melt. Metastable 1, metastable 2 and stays as solid phase. Then how it forms depends very much not just on the depth not just on the gap but also because the location of the surface tension. So, when people try to talk of the stability as if they face formation of the phases is given by the stability, they talk of this free energy gap. But what people do not talk of account into add a stroke went it out as this one.

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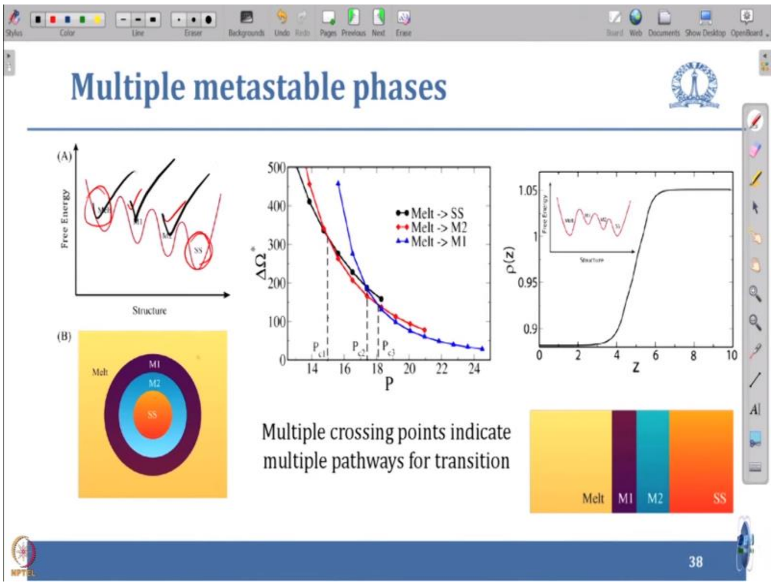

Multiple metastable phases

Multiple crossing points indicate multiple pathways for transition

So this is the kind of thing on experiments that you see the stable solid is sounded by the coating of the metastable tool as this one. And metastable one as this one and finally outside. So, this like for example when you from i did not go along Alexander-McTague paper that often you see excessive forming solids is coated my BCC. That because BCC phase is closer density and order to the liquid.

Remember if i have hard sphere then liquid typical density in dimensional is unit number density is multiplied by the cube if the diameter that you called row sigma cube. That is about 0.5 for liquid then it becomes 0.68 for BCC and 0.78 for FCC. These are close packs. So, when following from liquid then it is suppose to go to BCC first. Then within BCC embryo these are not the universally valid picture but reasonably close to it.

Then within the BCC, FCC forms. That is what Alexander McTague said and, this again connect with Ostwald step rule that from the melt least stable that is what Ostwald said, least stable but which is closest to the in symmetry in order parameter in density that closet to the melt will first from. From that something else grow. So, this is a particular but this is the not only the course but hopefully informative.

This is a bread and butter in material science by the people first gave the information. Since it is the new material and one still struggles to crystallize the one phase and having some understanding would help to figure out what is going on into this fascinating rather emerging new field. Kind of borderline between chemistry physics and material science and we take a great importance into this thing of. Okay, so I think we stop here for Ostwald step rules and we will do something else very similar to this in the next lecture. Thank you.