Solid State Chemistry
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Lecture – 03
Crystallisation Kinetics

In the last class we learnt about the thermodynamics of solids. We learnt about how the Gibbs free energy of solids and liquids changes with temperature and when you are below the melting temperature the Gibbs free energy of the solid is lowest. So, we also learnt about phase diagrams; now today I am going to talk about crystallization kinetics. That is what is the rate of crystallization? What is the rate of solidification?

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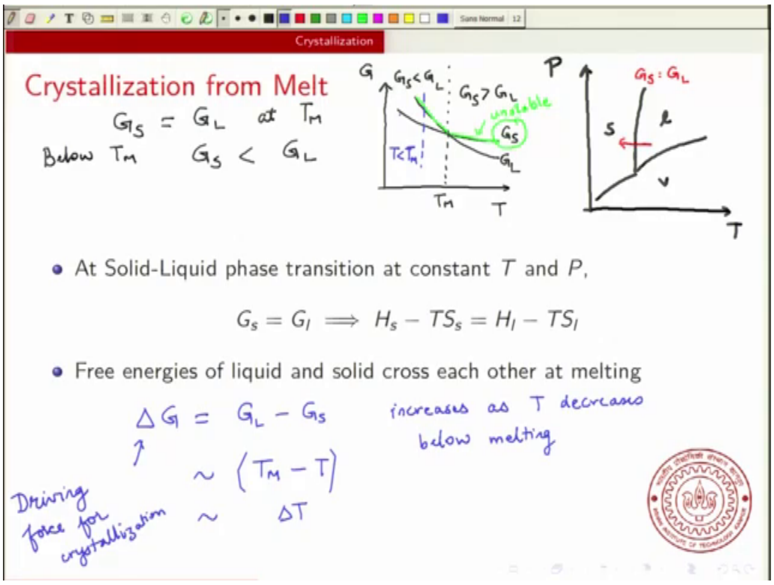

Crystallization

Crystallization from Melt

$G_S = G_L$ at T_M

Below T_M $G_S < G_L$

- At Solid-Liquid phase transition at constant T and P,

$$G_s = G_l \implies H_s - TS_s = H_l - TS_l$$

- Free energies of liquid and solid cross each other at melting

$\Delta G = G_L - G_S$ increases as T decreases below melting

$\sim (T_M - T)$

$\sim \Delta T$

Driving force for crystallization

Let us first just refresh what we learnt about the phase diagram. So, if we look at the; if you look at the pressure temperature phase diagram for any material then what we saw is that, there is a solid phase a liquid phase and a paper phase.

So, so this was the vapor this was a liquid and this was a solid. And what we said was that was that you can take that if you if you start at some point let us say you start in a liquid you start at some point here and you move towards this. You move in this direction that is you lower the temperature of the liquid. When the temperature of the low liquid becomes smaller than this temperature then the liquid will solidify. So, when the temperature of the liquid crosses this line then it will solidify ok. So, and what we say is that along this line we have the Gibbs free energy of the solid is equal to the Gibbs free energy of the liquid.

So, so along this line the anywhere on this line anywhere at this line corresponds to certain values of pressure and temperature. So, at those values you will have the Gibbs free energy of solid and liquid be the same. So, now we can see that the Gibbs free energy is a of the of the solid is equal to Gibbs free energy of liquid at may at the melting temperature.

And it should be kept in mind that the melting temperature depends on the pressure melting temperature at different pressures changes ok. Now below T M below the melting temperature the Gibbs free energy of solid is less than Gibbs free energy of liquid. So, the solid is a more stable phase below the melting temperature. So, now it should be kept in mind that below the melting temperature the liquid itself is not stable.

So, but if you imagine if you imagine as a function of temperature calculating the Gibbs free energy of the solid and the liquid ok. You will see them cross each other. So, you might see the Gibbs you might see that that this is the Gibbs free energy of the liquid this is a Gibbs free energy of the solid ok. And I am just imagining that if you had any material then typical curves for the Gibbs free energy as a function of temperature would look like this. So, the liquid would typically be higher than the solid at low temperature and it would go below the solid at higher temperatures where they cross this is the melting temperature. So, that is when the Gibbs free energy of the solid and the liquid are the same and it should be kept in mind that I am doing this whole thing at some fixed pressure.

So, as you can see herein this region clearly Gibbs free energy of the solid is greater than Gibbs free energy of the liquid here Gibbs free energy of the solid is less than Gibbs free energy of the liquid ok. This is the basic idea of crystallization. So, so you and what you should keep in mind is that the solid here is actually not stable ok. So, this is unstable and that is why its. So, so you will never actually see a solid. So, this is just a hypothetical state. So, so the solid in this region above the melting temperature is just a hypothetical state. So, what we mean really is that if you had a solid at this temperature then its free energy would be greater than that for a liquid. Similarly the liquid at this state is not is a is a hypothetical state ok. So, that is also unstable.

So, so what you again mean is that if you had a liquid below the melting temperature its free energy would be higher. Now well its a question now; obviously, you do not have a liquid below the melting temperature you do not have a solid above the melting temperature. So, what do these numbers really mean and you can think of them as some sort of model calculation.

So, you model a liquid and you try to extend its free energy below the melting temperature or then you would get these curves. Similarly if you model a solid and you x and you calculate its free energy and extend that model above the melting temperature you would gets some curve and this is representative of that.

So, these are purely representative cartoons and, but they illustrate one interesting point that that this free energy of solids and liquids they will typically cross each other at melting ok. And so and so, you can imagine that if you are at if you are at some temperature ok. So, suppose you are at some temperature below the melting melting point let us say let us say you are at you are at this temperature. So, you are at some T less than T T melting. So, at this T less than T melting as you go lower and lower then the difference in the free energies of the liquids and solid increases ok. So, you can see that delta G this is equal to G liquid minus G solid this delta G increases as T decreases below melting ok.

So, so as you take T lower and lower it becomes smaller and smaller and in fact, in fact you can say that this delta G will be will go as T M minus T. So, as this T becomes smaller it will go I mean it will keep increasing with this. So, it is an increasing function of how much lower than melting you are. So, this is the temperature below the melting. So, how much lower your temperature is that is than melting. So, if it is much lower than melting than this quantity will be large and this delta G will be large ok. So, you can think of this delta G this difference in free energy as a driving force towards crystallization in other words what we are saying is that the reason the.

So, reason the material crystallizes when your below this temperature is because delta G is greater than 0. And so and so if you want to imagine how fast it is crystallizing then you could easily imagine that there is a quantity like delta G, which tells you how much lower than the melting melting point you are and that tells you how fast it will crystallize ok. Now again the there is a difference because what we are interested in is the rate of crystallization.

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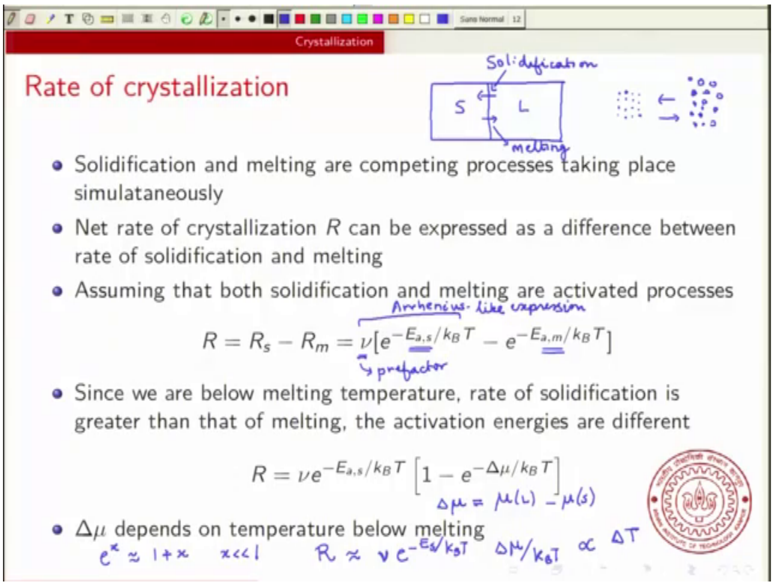

Rate of crystallization

- Solidification and melting are competing processes taking place simulataneously
- Net rate of crystallization R can be expressed as a difference between rate of solidification and melting
- Assuming that both solidification and melting are activated processes

$$R = R_s - R_m = \overbrace{\underset{\hookrightarrow \text{prefactor}}{\nu}[e^{-\underline{E_{a,s}}/k_B T} - e^{-\underline{\underline{E_{a,m}}}/k_B T}]}^{\text{Arrhenius-like expression}}$$

- Since we are below melting temperature, rate of solidification is greater than that of melting, the activation energies are different

$$R = \nu e^{-E_{a,s}/k_B T}\left[1 - e^{-\Delta\mu/k_B T}\right]$$

$$\Delta\mu = \mu(L) - \mu(s)$$

- $\Delta\mu$ depends on temperature below melting

$$e^x \approx 1 + x \quad x \ll 1 \qquad R \approx \nu e^{-E_s/k_BT}\,\Delta\mu/k_BT \propto \Delta T$$

So, so we are we are interested in actually the rate of crystallization and the rate of crystallization this is a question about the kinetics this is actually a question about kinetics of crystallization ok. So, what we say is that if you its probably best to show this through a little illustration. So, if you have a system and this side you have a solid and here you have a liquid ok. And this is just a you imagine that some part of the system has become a solid and some part has become a liquid ok.

Now what is happening is that some of this liquid is getting converted to solid and some of this solid is getting converted to liquid. So, the liquid freezing to solid and the solid melting to liquid are both taking place simultaneously. And so you have solidification and melting these are competing processes that are taking place simultaneously. And the net rate of crystallization is the difference between the rate of solidification and the rate of melting ok. So, you can write that the net rate of crystallization is the difference between the rate of solidification and the rate of melting.

So, that that clearly tells you how many what is the rate at which crystallization is taking place or the net rate of crystallization ok. Now we can ask a little more questions about what happens during crystallization ok. So, Let us take the case of solidification where the liquid is getting converted to solid. So, I will use a word solidification here fication and I will called this melting. So, during this solidification you have some atoms in the liquid which are in the liquid state. So, if you take your particles that are particles if there are atoms or molecules they are in the liquid state.

And what is happening is that suddenly a collection of particles they arrange themselves and they go to a solid state may go to some ordered lattice ok. You have a collection of particles that are suddenly arranging themselves and forming a solid a solid like ordered structure ok. Now in order for this to happen, these atoms have to execute certain motions ok. So, if you take any atom in a liquid typically it sees lot of atoms around it and it has to essentially push them a little bit.

So, that it arranges into the form of a solid ok. So, there is an activation energy going from this liquid state to this solid state if you look at the if you look at the actual process of solidification then it has to nudge all the things around. So, any atom or a group of atoms have to rearrange and there is some activation involved with that. So, you can say that the rate of solidification has some activation energy and that is given by E activation of solidification. So, s here stands for solidification. Similarly the rate of melting will also have some activation. So, if you have a solid and it has to become a liquid then these this solid has to break some of the bonds that it has and then it goes into a liquid so there is an activation for melting ok.

Now if you are below the, if you are below the melting temperature then the you can imagine that the activation energy for solidification will be smaller than that for melting in other words its harder to melt than to solidify ok. So, and that is the reason you form the crystal in the first place and again this is below the melting temperature. So, you can write this you can take this factor of E to the minus a s by k B T outside and you can write this as 1 minus E to the minus delta mu by k B T where delta mu is the chemical potential difference between the solid and the liquid ok. Now I should mention that the new this is a pre factor and this is a very typical kinetic expression for any activated process.

So, the first term if you look at it its a new multiplied by E to the minus a s by k B T this is an Arrhenius like expression ok. So, this whole thing is an Arrhenius like expression. And the reason we use an Arrhenius like expression is because we said that solidification is an activated process; that means, there is some activation energy involved with it.

Similarly melting is also consumed to be an Arrhenius like expression ok. So, we are assuming that melting is also an Arrhenius like expression with the same pre factor ok. So, the assumption the crucial assumption is at both solidification and melting are Arrhenius like processes and both of them have the same pre factor ok. And if you remember your elementary kinetics you learnt that this pre factor is related to some sort of frequency of oscillation.

So, it tells you how these atoms vibrate either in the either in the liquid or the solid. So, there is some fundamental vibration frequency which sets this pre factor ok. And in this simple picture we are just assuming that both of them are the same ok. Again I should emphasize that this is just one very simple way to look at the rate of crystallization it is a very generic way, but, it is a highly simplified expression.

Now so we can write this difference as in terms of delta mu where delta mu is essentially the free energy free energy of liquid minus free energy of solid or the molar free energy which is the give which is the chemical potential. So, the chemical potential of liquid minus solid and if you are below the melting temperature the liquid has a higher chemical potential than solid. So, delta mu is greater than 0 and so and so this is the rate ok.

And if you go to very very low temperatures if you go to very very low temperatures then the then the free energy of the chemical potential of liquid is much greater than that of solid ok. And so and so this quantity becomes very large or or this delta mu becomes large. And so E to the minus a large number goes to 0. So, the rate becomes just given by this rate is just given by this factor, but and if you are very close to the melting temperature if you are very close to the melting temperature then this quantity becomes very small ok. And you can do it you can do what is called a Taylor expansion you can use the fact that E to the E to the x approximately equal to 1 plus x for small x ok. So, when x is less than less than one. So, when x is very small then you can use such an expression.

So, so basically you can see that r ok. So, you have one minus E to the minus x. So, so that will just give you one minus E to the minus delta mu by k B T. So, this whole factor will just be approximately approximately. So, you have the nu E to the minus E s by k B T and you have a factor of delta mu by k B T ok. So, so in other words the rate is proportional to the chemical potential difference ok. And this is a very useful picture so it is so if you go back to what we said in the last slide we said that this difference in chemical potential the delta G which is G liquid minus G solid which is essentially the molar part of this difference is the is the chemical potential.

So, this is the driving force and in this simple picture we see that the rate for small temperatures is proportional to this to this to this quantity delta mu. And further you can analyze this and you can show that this rate is actually proportional to this delta T ok. How you can consider again for small temperatures you can show that this rate looks proportional to delta T ok. Now so this is the process of crystallization from a off from a melt or from a liquid. So, here you have a liquid and your and its converting to a solid.

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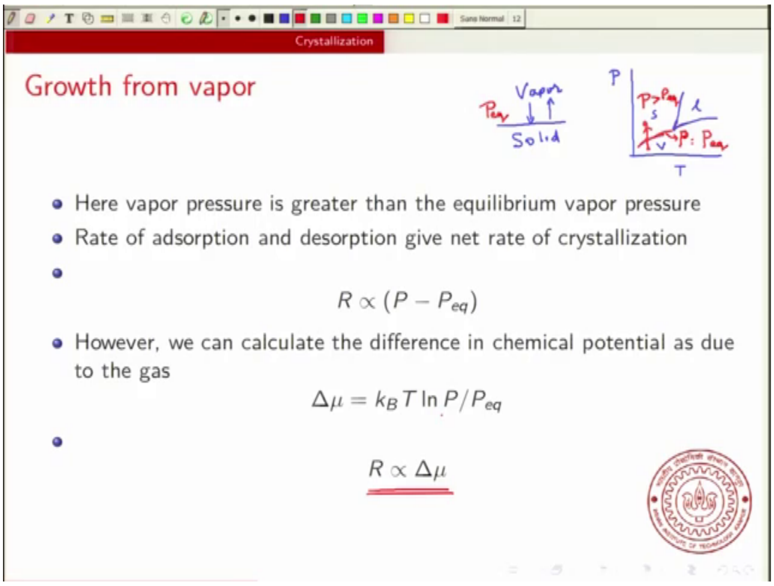

Growth from vapor

- Here vapor pressure is greater than the equilibrium vapor pressure
- Rate of adsorption and desorption give net rate of crystallization
- $$R \propto (P - P_{eq})$$
- However, we can calculate the difference in chemical potential as due to the gas $$\Delta\mu = k_B T \ln P/P_{eq}$$
- $$\underline{R \propto \Delta\mu}$$

You could also have crystallization from vapor the in the sense what you have is your crystal is growing because there is a vapor off the material ok. Now suppose you have a solid and you have a vapor above the solid ok. What we are looking at is your looking at a position from the vapor and you have and you have days option from the solid. So, so you have these two processes absorption of vapor onto the solid and desorption of solid onto the vapor.

Now again if we look at our, if we look at the phase diagram the P T phase diagram the liquid you have the solid you have the vapor ok. So, what we imagine is that you we are going in we are going like this in this case ok. So, so you imagine that you have a vapor at and this is typically at very low pressure and you increase the pressure and you will end up with a solid. So, in this case the vapor pressure is greater than the equilibrium vapor pressure.

So, if you have a solid and a vapor then there is always whenever you have a solid there is always some equilibrium vapor pressure. So, the vapor pressure is the pressure at equilibrium. So, you have a vapor of the same material as a solid that has some equilibrium pressure; that means, if you take any solid there will be some vapor on top of it and P equilibrium is the pressure of that vapor.

Now suppose the pressure of this vapor was much greater than P equilibrium ok. Then what would happen is some of the vapor would solidify and it would form the solid. So, you can work this out so the rate of absorption and desorption they it gives the net rate of crystallization. So, the net rate of crystallization in this case works out to be the difference between the rate of adsorption and the rate of desorption ok.

And I am not going to work this out in too much detail. But you can show from very generic arguments that the rate of crystallization should be proportional to the difference between the actual pressure of the vapor and the equilibrium vapor pressure. So, obviously, if the pressure is equal to the equilibrium vapor pressure then the solid and vapor are in equilibrium and there will be no crystallization.

But if the pressure of the vapor is greater than that of the of the equilibrium vapor pressure then the solid will crystallize ok. And you can again connect this to a chemical potential difference ok. Now when you go from when you go from a point that is let us say at along this line you have P S or P equal to P equilibrium.

So, the pressure is equal to the equilibrium vapor pressure and again the equilibrium vapor pressure depends on temperature. So, along this line this pressure is equal to the equilibrium vapor pressure. Now if you imagine looking at the difference in chemical potential between one state that is here and one state that is somewhere here. So, we are imagining that we are increasing the pressure we are putting P. So, in this region P is greater than P equilibrium and in the lower region P is less than P equilibrium.

So, up so on this line you have P equal to P equilibrium. So, right along its only along this little line that you have P equal to P equilibrium along this line above this line you have P is greater than P equilibrium below this line you have P less than P equilibrium ok. So, now you can calculate the difference in chemical potential between a solid and a liquid. Now the chemical put the as in terms of the pressure and. So, the so the difference in pressure between a gas at or the change in chemical potential is mainly due to the change in pressure of the gas because the solid the chemical potential of the solid is not really dependent on pressure.

So, the change in the change in chemical potential is only due to the change in gas and if you just use a ideal gas law then the difference in chemical potential between a gas at pressure P and a gas at pressure P equilibrium is given by this quantity ok. And in this case also the rate can be written as proportional to delta mu ok.

So, the rate works out to be proportional to approximately proportional to delta mu for pressures close to this P equilibrium ok. So, again we see that the driving or the rate of crystallization depends on this difference in chemical potential ok. And the difference in chemical potential can be calculated by the difference in pressure ok.

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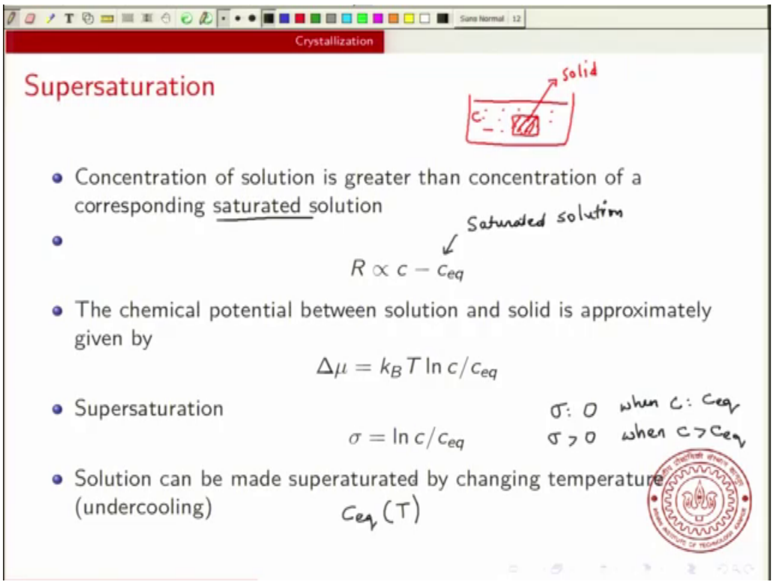

Crystallization

Supersaturation

- Concentration of solution is greater than concentration of a corresponding saturated solution
- $$R \propto c - c_{eq}$$
  Saturated solution
- The chemical potential between solution and solid is approximately given by
  $$\Delta\mu = k_B T \ln c/c_{eq}$$
- Supersaturation
  $$\sigma = \ln c/c_{eq}$$
  $\sigma : 0$ when $c : c_{eq}$
  $\sigma > 0$ when $c > c_{eq}$
- Solution can be made superaturated by changing temperature (undercooling)
  $c_{eq}(T)$

So, now the other common case that we consider is crystallization from a solution ok. So, here we are looking at crystallization from a solution and what during crystallization from solution what you have is you can imagine that you have a you have a solution and you have some part of a solid in that so this is a solid. Now if the concentration of the solution is c c is the concentration of the solution ok. Now in order for it to solidify the concentration of the solution has to be greater than the concentration of a saturated solution.

So, the saturated solution means that you cannot put any more of your of your solid in the solution without it crystallizing. So, the saturated solution is what is called the has a has a concentration of c equilibrium ok. So, this is your saturated solution so in other words in the saturated solution your crystal and your solution are in equilibrium ok. So, and so in this case the rate again you can work this out from various elementary theories this rate is now proportional to the difference in concentration of the solution and the equilibrium concentration.

So, the equilibrium concentration is basically the concentration of the saturated solution. So, how much the concentration of the solution is greater than that of the saturated solution. Now you know that you cannot make a solution more concentrated than a saturated solution. So, actually we say that. So, the crystallization will only take place when the solution is supersaturated. So, we call this super saturation which is saying that the concentration is actually greater than that of the saturated solution ok.

And in this case you can write the chemical potential difference between the solution in the solid is approximately given by k B T the natural log of concentration divided by the concentration of the saturated solution. And sometimes we defined a quantity called a super saturation which is this ln of c by c equilibrium and this super saturation is equal to zero when c equal to c equilibrium. So, sigma equal to 0 when c equal to c equilibrium and when c is greater than c equilibrium.

So, sigma equal to 0 when the concentration is equal to that of the saturated solution and sigma is greater than 0 when the concentration is greater than that of the saturated solution and again the you should remember that is not an equilibrium solution and that is why it crystallizes ok. Now so this idea of super saturation is quite interesting and what you can see is that the delta mu or the difference in chemical potential is proportional to this super saturation ok.

Now the solutions is now on a on a practical note how do you make a solution supersaturated how do you put more things how do you how do you have a solution whose concentration is greater than that of the saturated solution. One way in which this is done in practice is by actually changing the temperature. So, you have a solution you have a saturated solution and you suddenly cool it ok.

Now what happens is that is that when you cool it at a lower temperature your saturated solution concentration actually becomes lower ok. So, in other words c equilibrium is a function of temperature ok. It depends on temperature and c equilibrium at higher temperatures is higher and at lower temperatures is slower which makes sense that if you have if you have a higher temperature then you can dissolve more material if you have a lower.

So, the concentration of the saturated solution will be higher. So, suppose you suddenly lower the temperature then you are under cooling it you are you. So, you use the phrase under cooling which says that you are below the below the equilibrium temperature ok. And in that makes a solution supersaturated. So, it is again out of equilibrium ok.

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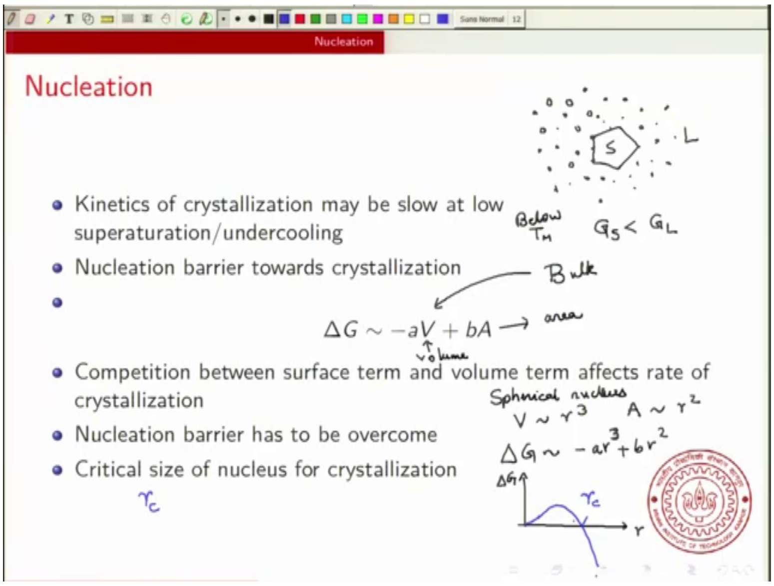

Nucleation

Nucleation

- Kinetics of crystallization may be slow at low superaturation/undercooling
- Nucleation barrier towards crystallization
-

$$\Delta G \sim -aV + bA$$

- Competition between surface term and volume term affects rate of crystallization
- Nucleation barrier has to be overcome
- Critical size of nucleus for crystallization

So, so this is one way of growing crystals from solution. Now one of the things that we see in practice is that your kinetics of the crystallization may be very slow at low super saturation or under cooling. So, let us say you have a solution and your super saturation is small; that means, you are just you have a concentration just slightly greater than the saturated solution then the kinetics of crystallization is often very slow.

And this is something that you have seen when you are when you do your chemistry labs whenever you are crystallizing some let us say you prepare some compound may be organic or inorganic compound and then you have it in a solution and you slow and you let the solution cool down and you wait for it to crystallize. And sometimes this crystallization is very slow ok. The reason crystallization is slow even though you are below the below the melting temperature is that there is something called a nucleation barrier towards crystallization ok.

So, so and how this arises is the following. So, if you have a let us take the case of a simple you have a liquid ok. You have a liquid and now in this whole liquid there is let us say a small part of the liquid somewhere here becomes a solid and I will just show some piece that has become a solid and you have liquid all around ok. So this is your liquid and you have a solid here.

Now if this solid is well so, we will say that if you look at and you are below the melting temperature. So, so we say that the Gibbs free energy of the solid is less than Gibbs free energy of the liquid so you are below TM ok. So, ideally. So, what you would expect is that the whole thing will become a crystal ok; however, when crystallization starts you start with a small piece becoming a crystal and then bigger and bigger crystals forming.

So, crystallization starts from a very small crystal which keeps growing ok. Now if you have a small crystal then it has a bulk which is a volume part and it has a surface part. Now the atoms or molecules that are on the surface they actually are not as coordinated as the atoms in the bulk. So, the atoms in the bulk are connected to all the other atoms that they are bonded to atoms on all sides, but the atoms on the surface they see a liquid on one side and they see a solid on the other. So, there is a tendency of these atoms to go into the liquid. In other words there is an interfacial energy associated. So, this interface between the solid and the liquid that actually costs some energy ok.

So, if you look at the free energy difference between the liquid and the solid ok. So, there is a term which is proportional to the volume term ok. So, you say that the bulk term ok. So, this is a bulk term ok. So, the bulk term; that means, the free energy of the solid is less than that of the liquid. So, if you have a bulk solid then it will have a lower free energy..

However, there is an energy cost to form this interface which is proportional to the area. So, this is your volume and there is a cost that is proportional to the area ok. Now it turns out that if you have a very small crystal ok. Then this area term dominates and actually the free energy for a small crystal becomes positive of course if you have a large crystal then the volume is much bigger than the area and so and so, the free energy will be negative and you will form a crystal ok.

So, what; that means, is that this free energy depends on the size of the crystallize. If you assume for example, that you have assuming spherical nucleus ok; so, this little piece of crystal is called a nucleus. So, if you assume that it is spherical then the volume goes as r cube this 4 by 3 pi r cube. So, in other words its proportional to r cube the area looks like 4 pi r square so it is proportional to r square ok. So, you have a free energy for crystallization that that goes like minus a r cube plus b r square some constant some constant times r cube and some constant times r square ok. Now if you plot this free energy difference as a function of R. What you will see is that when r is very small then the r square is much greater than r cube ok. So, so the r square term will be important when r is very small.

So, when r is very small it look like the r square s o and this is a positive term. So, the delta G will actually be positive ok, but of course, when r is very large then it then the r cubed term is much larger and it will it will change signs and will go like this that will become negative. So; that means, if you have this place where it crosses the size is called r c ok; that means, if you have a crystal if you have a small piece of crystal whose size is less than r c then the free energy performing that is actually positive. So, it is unstable. So, you have to grow a crystal that is larger than r c in order for the crystallization to be favorable and this phenomena is called nucleation because you have to nucleate a crystal that is at least rc. So, rc is the critical size for critical size of the nucleus for crystallization.

So, until you grow a critical nucleus of size rc you are crystallization will be very slow will not be favorable once you grow greater than rc and then the crystallization will be very rapid ok. So, so this is an example where the area term or the surface term actually does not favor crystallization whereas, the volume term favors crystallization and the net effect is to have a nucleation barrier. So, we say that the delta G has to overcome this barrier for crystallization in other words you have to keep growing all these very small crystals which actually increase the free energy until you grow a crystalline crystal that is large enough ok.

So, so initially until this critical nucleus is formed you have rate of crystallization is very slow and once you form this critical nucleus then the rate of crystallization as fast. And this is something that you have seen in some of your chemistry labs that initially the crystallization is very slow sometimes you shake it or you stir it and then the crystallization becomes fast ok.

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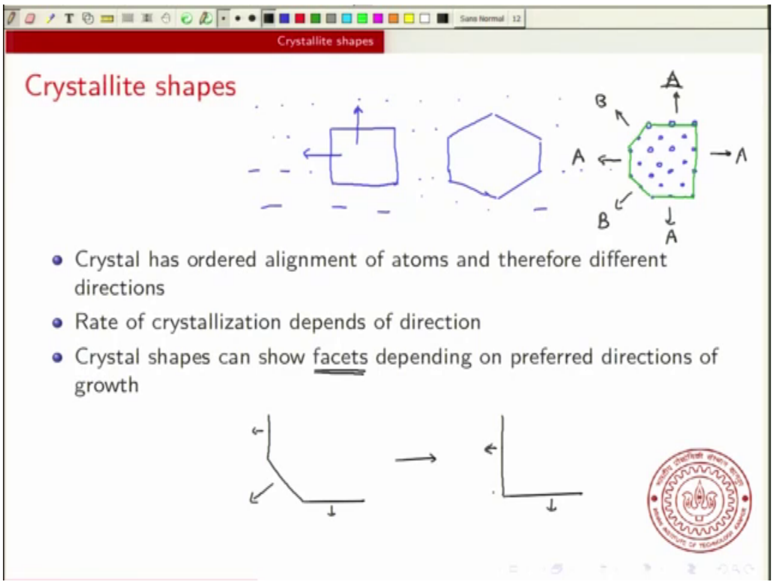

Crystallite shapes

- Crystal has ordered alignment of atoms and therefore different directions
- Rate of crystallization depends of direction
- Crystal shapes can show facets depending on preferred directions of growth

The last thing that I want to talk about today is the shape of crystals or more you can say the shape of crystallite that is so when I say crystallite I mean a piece of a crystal. So, if you are growing a crystal, then what is the shape is it is it like a cube or is it like a is it like a hexagon I mean these are really looking at three dimensional shapes ok. So, so you imagine objects ok. Is it is it an octahedron what is the shape of the crystal. Now what governs the shape of the crystal?

So, the shape of the crystal is basically telling you which directions the crystal is growing. So, so if you imagine if you imagine that you have a if you have a liquid all around you have the liquid around and end up and a small piece of the liquid has crystallized. So, you are looking at crystallization from melt. So, you have liquid all around and a small piece of it has become a crystal ok. Now the question is how does a crystal grow ok.

Now if you look inside the crystal then it has an ordered arrangement of atoms ok. So, so; that means, the atoms in the crystal are ordered in some in some way and therefore. So for example, if the atoms were ordered; ordered this way I will just take an example if the atoms are ordered in this way ok. And we just extend it a bit more and deliberately showing certain.

So, if you just imagine a centered square lattice and this is a piece of a centered square lattice, let me outline it by green color. This is a small piece of a crystal of this square lattice and just for illustration I am considering a 2 dimensional crystal, but you can do the same in three dimensions. What you see is that because of this ordered arrangement you see that this direction is different from this direction and this direction and this direction all these are different directions ok.

Now you can see that these two directions are actually equivalent in the sense that if you look at the atoms arrangement of atoms in this direction and this direction it is the same similarly these two directions are equivalent and these two directions are equivalent. However, if you take these two directions they are not equivalent similarly these two directions are not equivalent ok.

So, in other words due to the order or alignment of atoms the crystal has different directions. And now the question is if this piece of crystal is lying inside a liquid, then atoms will deposit on all sides ok. But there will be certain preferred phases in which in which the atoms will deposit faster ok. So, they might prefer to deposit on this phase ok. And so certain directions of the crystal will actually grow faster than certain other direction.

So, in other words the rate of crystallization depends on the direction. So, the crystallization might be faster along one direction and might be slower along the other direction. So, let us take this crystal again so let me call this direction as A and this direction as B ok. Now if the rate of growth is faster along B and slower along A and this is also I will I will I am just taking a square symmetry.

So, all all these directions are a now if the rate of growth is faster along b and slower along a then what will happen is that this b will move a lot faster and eventually and this a is moving a lot slower. So, A since B is moving a lot faster you will deposit these atoms and finally, you will end up you be will completely disappear. In other words this crystal if you have if you have something like this. So, its growing fast along this direction and slow all slowly along this these two directions ok.

Then eventually it will go to something like this and it will just grow along this direction. So, in other words the crystal will end up with a certain symmetry. So, so the shape of the final shape of the crystal that you get that or the crystallite that depends on which directions the growth is fast and which direction the growth is slow. So, this particular phenomena where certain phases of the crystal. So, when you grow this crystallite you get only you see only certain phases you do not see all the phases of the crystal you do not see it growing along you do not see other phases or.

So, so if you take any crystallite it has a very specific shape and these are called faceted this these phases of the crystal are referred to as facets and if you take any crystal. In fact, in here crystals of very very beautiful shapes that you that you can see it and I mean if you just search on the internet you will see you will see very nice pictures of crystals of different shapes ok.

And what I wanted to say here briefly is that the shape of the crystallite is really a function of which directions grow fast and which directions grow slow ok. There are other factors governing the equilibrium shapes of crystals which I would not talk about in this lecture. So, with this I will conclude the lecture for I will conclude this third lecture of the first week of this course.

Thank you.