Heat Treatment and Surface Hardening (Part–1)
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Lecture Number 22

Introduction to Kinetics of Phase Transformation

So in this lecture we are going to talk about kinetics of phase transformation.

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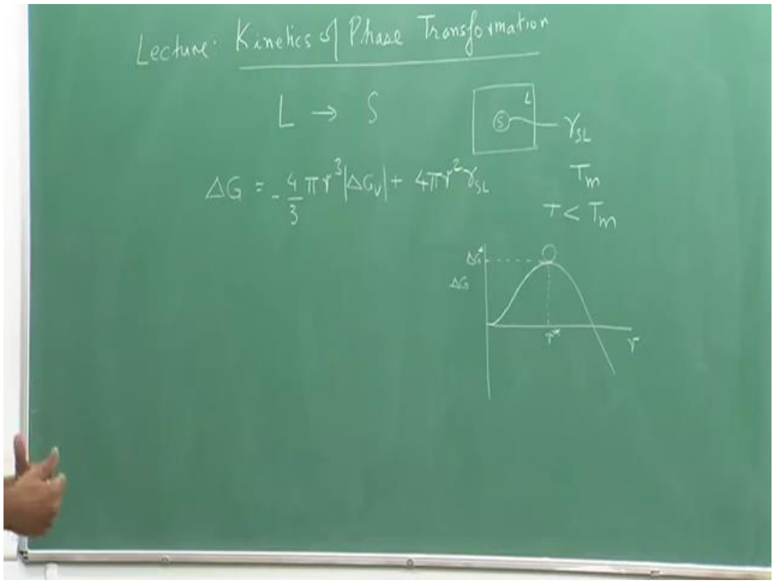

Lecture: Kinetics of Phase Transformation

$L \rightarrow S$

$$\Delta G = -\frac{4}{3}\pi r^3|\Delta G_v| + 4\pi r^2\gamma_{SL}$$

Professor Mandal had talked about the thermodynamics of phase transformation he had mentioned something about the kinetics of phase transformation, but now we are going to look into details of how a phase transformation takes place. In your earlier lectures by professor Mandal, he had talked about phase transformation starts with first nucleation and once a nuclei a critical size nuclei forms, it can grow and eventually the bulk phase transformation takes place.

So for example, if I if we consider liquid to solid transformation, so first in the liquid phase a solid nuclei must form before a phase transformation can take place. Now in the formation of this nuclei as professor Mandal was talking about in the earlier lectures, there is a critical size of nuclei that needs to form for it to become stable. The two factors that govern this are the change in the volumetric free energy of the nucleus and the surface energy of the solid liquid interface that is created gamma Sl. You have been introduced to this relationship in your earlier lectures that the overall change in the free energy is given by the change in the free energy produced by the transformation from a liquid state to the solid state a small volumetric region.

And let us say if this nucleus that forms is a spherical nucleus, then of radius r then its volume would be four by three pi r cube multiplied by the change in free energy per unit volume and an additional term due to the surface solid liquid surface that is created also comes in which is by the given by the surface area of the nucleus multiplied by the surface energy gamma Sl. In these two terms the transformation will take place or becomes feasible if delta G is less than 0. Now the surface or the interfacial solid liquid energy is always positive, so therefore the second term remains positive.

However, delta Gv would be negative if your if the temperature is below the transformation temperature, for example, if Tm is the transformation temperature for liquid to solid transformation, then delta Gv would be negative for T less than Tm. I can write this equation in slightly differently by taking the absolute value for delta Gv and putting a negative sign here to clearly indicate that the first term is negative. Now if a nucleus is very small, then the positive term would dominate over the negative term and overall change in free energy for creation of a nucleus of a small radius would actually be positive.

However, if the nucleus becomes much larger, then the negative term can dominate over the positive term. So as professor Mandol has already told you if I want to plot delta G versus the size of the nucleus or the radius of the spherical nucleus, then we get a curve like this showing that initially for small radius as we have positive delta G until it reaches a peak which is characterize by a value r star (indicat) indicating that this is the critical size nucleus and corresponding to this critical size is delta G star which is the size of the energy hill.

So for a nucleus to grow, it first a nucleus has to be generated over critical size and then if additional atoms add to it, then the nucleus size would be greater than r star and then after that this nucleus will simple grow down the energy hill and eventually the free energy would become negative. For all nuclei which are produced, which have which get created whose size is less than the critical size r star they will tend to dissolve back into the liquid, disappear back into the liquid.

So one of the critical things when we have to look at nucleation and what is the kinetics of nucleation because that is going to play an important role in the kinetics of phase transformation would be at what rate critical size nuclei would form and at how many of them would become super critical which would be greater than the critical size that would govern the nucleation rate. Once we know what the nucleation rate is, then this second mechanism would be that this super critical nucleus would begin to grow, so have to look at growth.

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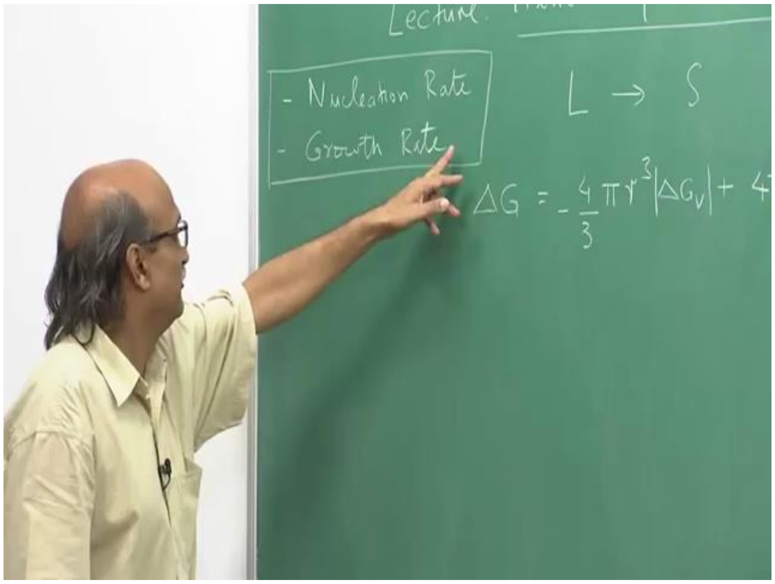

So therefore, in the kinetics of phase transformation we have to consider two factors nucleation rate and second, growth rate. So in order to fully understand the kinetics, we need to understand what would be the rate of nucleation, what would be the rate of growth both of them would have to be combined to give us the rate at which transformations would take place. It should be clear that if we if the nucleation rate is very small, the overall rate of transformation is also expected to be small, in fact it can happen that if you do not produce any nuclei, then no phase transformation can take place.

Depending on the conditions which would be in depending on at what temperature liquid to solid transformation is taking place, both the nucleation rate and the growth rate get controlled. For instance, we will see that we will see soon that if we are at temperatures close to the transformation temperature Tm but of course below the transformation temperature one will find that the nucleation rate would be very small. However, because of the high temperature the growth rate could be high.

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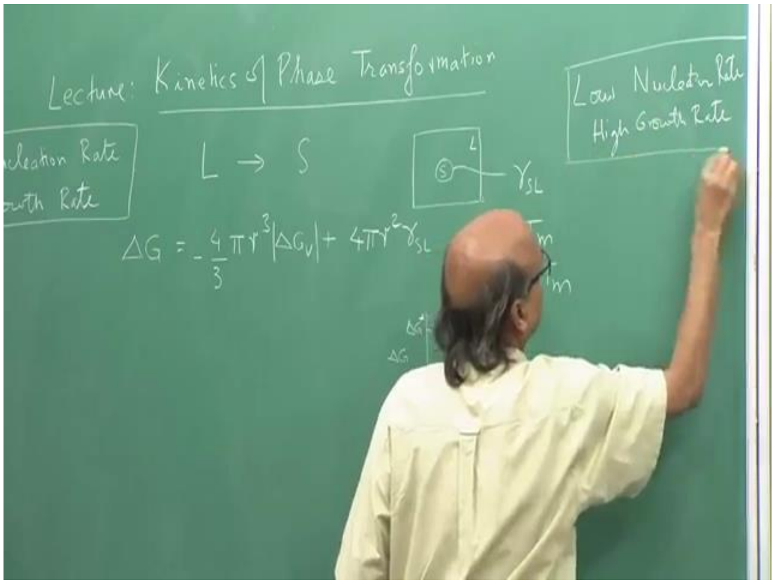

So you can have a situation where you have low nucleation rate and a high growth rate, this could be one kind of situation.

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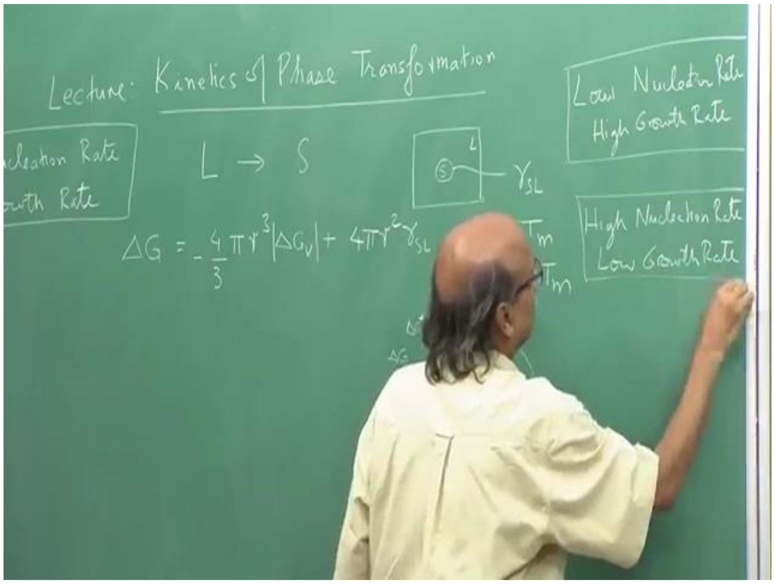

Another kind of situation could be you can have a high nucleation rate and a low growth rate. And of course you can have a whole range of situations in between these two conditions, you can have intermediate nucleation rate, intermediate growth rate etc. These are going to govern not only the rate at which the transformation is taking place, but it is also going they are also going to govern the scale of the microstructure, what is the size of the grains or the size of the particles that are eventually produced.

And in fact if these conditions determine the scale of the microstructure then in turn the material that in which you have let us say large grains, you have a different set of mechanical properties versus a material with small grains where you will have a different set of mechanical properties. So by controlling nucleation rate and growth rate we can then control the properties of the material in fact and that is one of the crucial reasons why we need to understand the kinetics of phase transformation in great depth.

Let me show you before I proceed, let me show you one let me show you a simulation in which how the scale of the microstructure gets determine depending on whether you have a low nucleation rate, high growth rate or high nucleation rate or low growth rate. So let us look this this is very simple simulation that is essentially developed in java and I will show you, but let me just first show you the simulation as it is, what it is showing?

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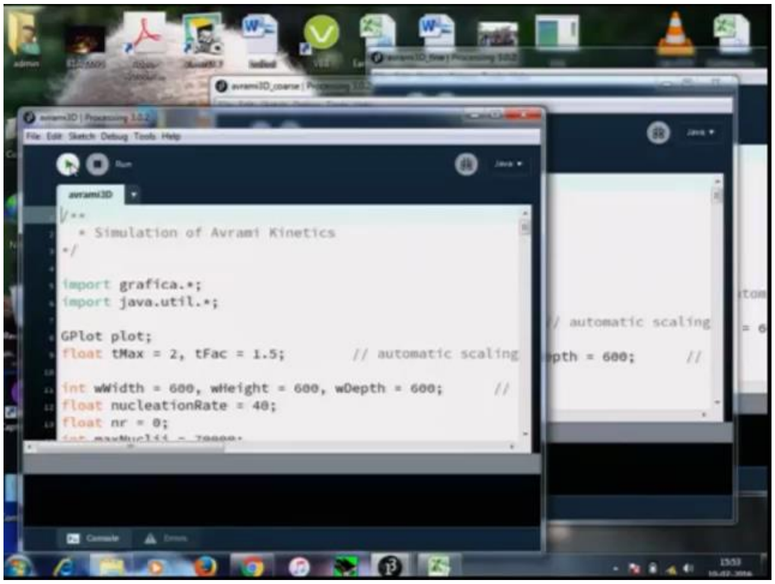
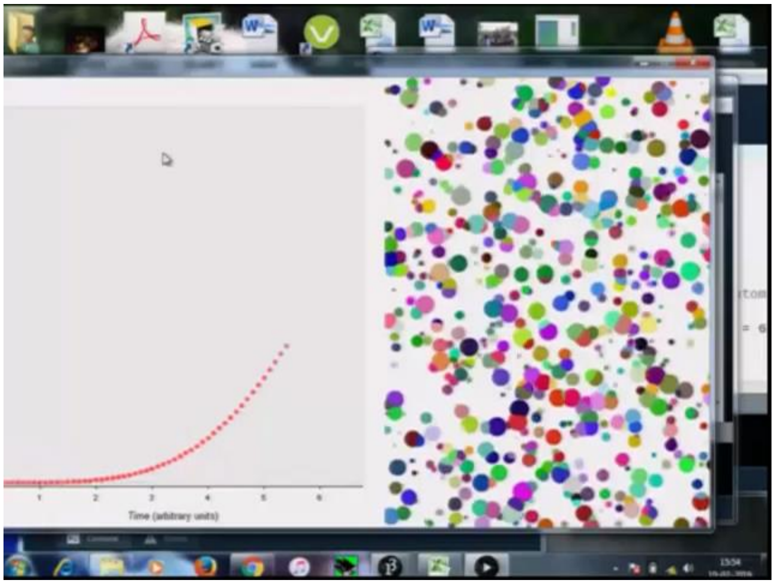


```
/**
 * Simulation of Avrami Kinetics
*/

import grafica.*;
import java.util.*;

GPlot plot;
float tMax = 2, tFac = 1.5;        // automatic scaling

int wWidth = 600, wHeight = 600, wDepth = 600;      //
float nucleationRate = 40;
float nr = 0;
```


1
2
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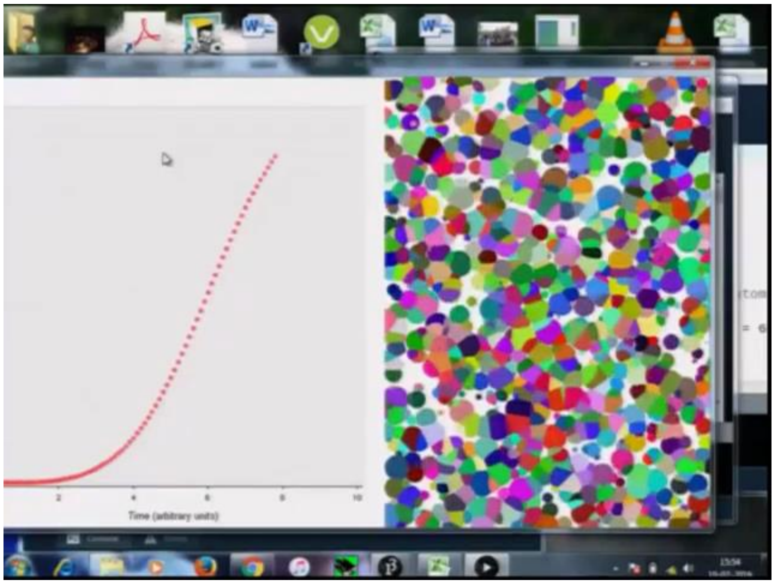
Time (arbitrary units)


2
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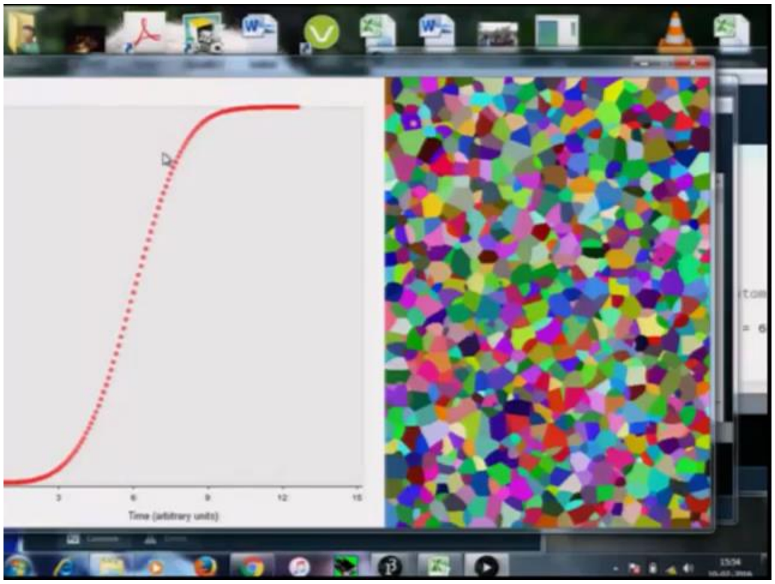
Time (arbitrary units)



If you will look at the structure on the right hand side you have a nuclei forming and then they were growing, and on the left hand side we see a curve where the y axis, shows the scale is not visible here but even then the y axis shows the fraction transform and the scale goes from 0 to 1.

And on the x axis it is time is arbitrary units, let me just show you this simulation once more on the right hand side if you look at you will see nuclei forming and growing and this actually is being done in three dimensions but you are looking at a two dimension section through the structure. So what happened in the simulation was, you had you had nuclei getting created at a certain rate and then they would grow at a constant rate in all directions.

So you had isotropic growth and of course wherever the two nuclei would empench then the growth would stop over there and finally you get this polycrystalline grain structure that you can see.

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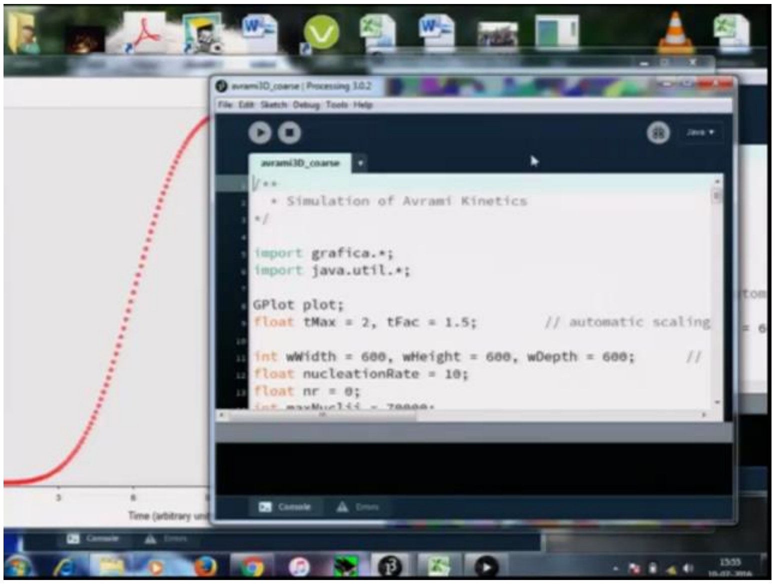

```
/**
  * Simulation of Avrami Kinetics
*/

import grafica.*;
import java.util.*;

GPlot plot;
float tMax = 2, tFac = 1.5;        // automatic scaling

int wWidth = 600, wHeight = 600, wDepth = 600;      //
float nucleationRate = 10;
float nr = 0;
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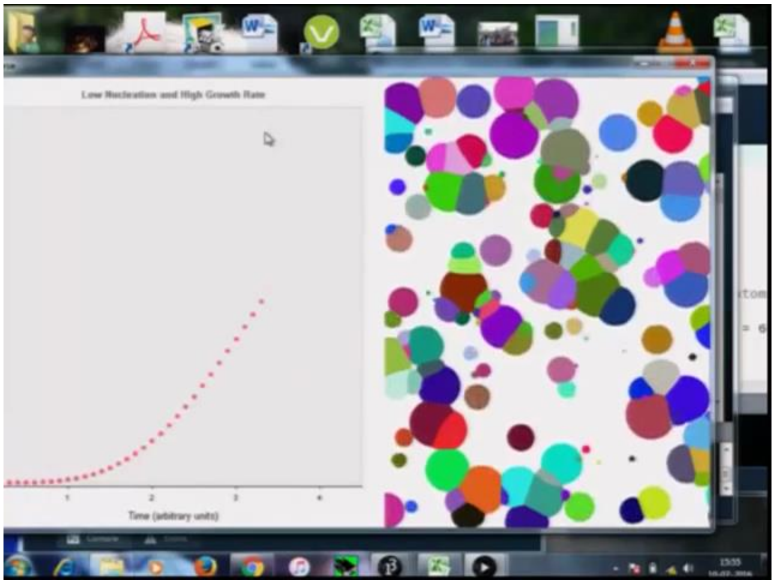

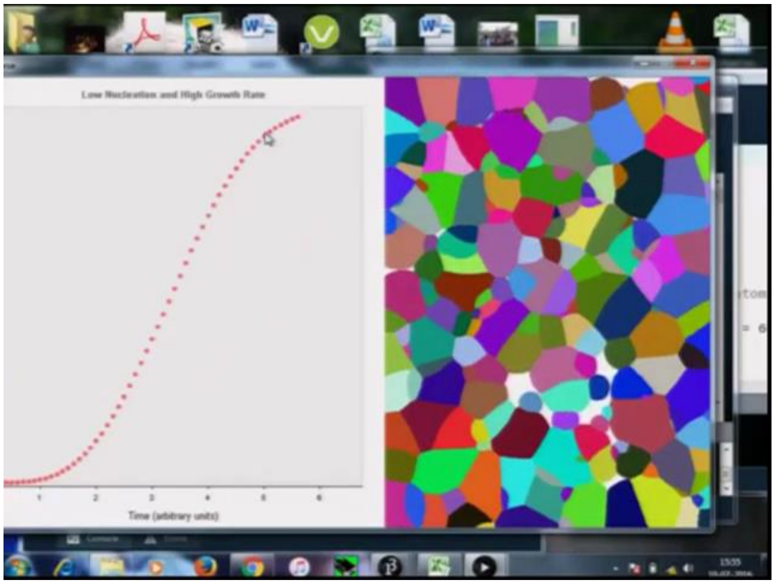

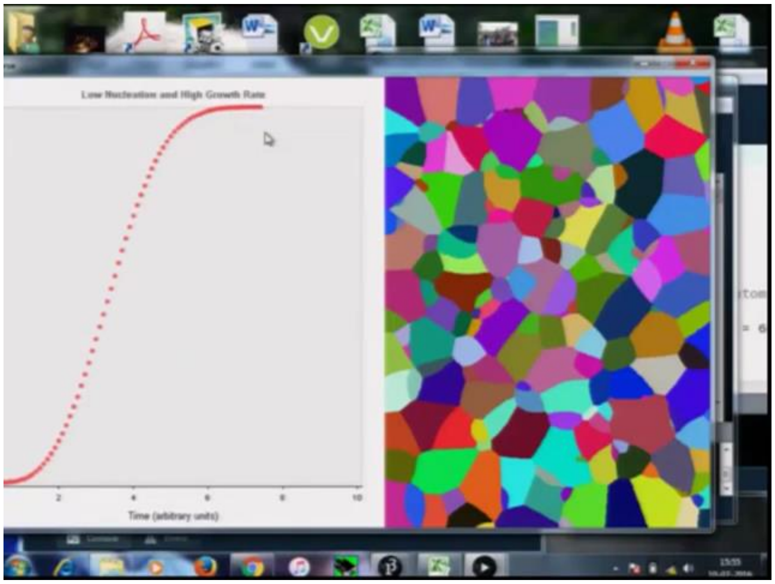

Now let me just look at another example where I am going to now do is a small the nucleation rate would be reduced significantly and the growth rate would be increased. In that scenario if one looks at the structure, one will find that one is formed a bigger grains are produced in this case as opposed to the previous simulation and on the left hand side again we see this fraction transform versus time.

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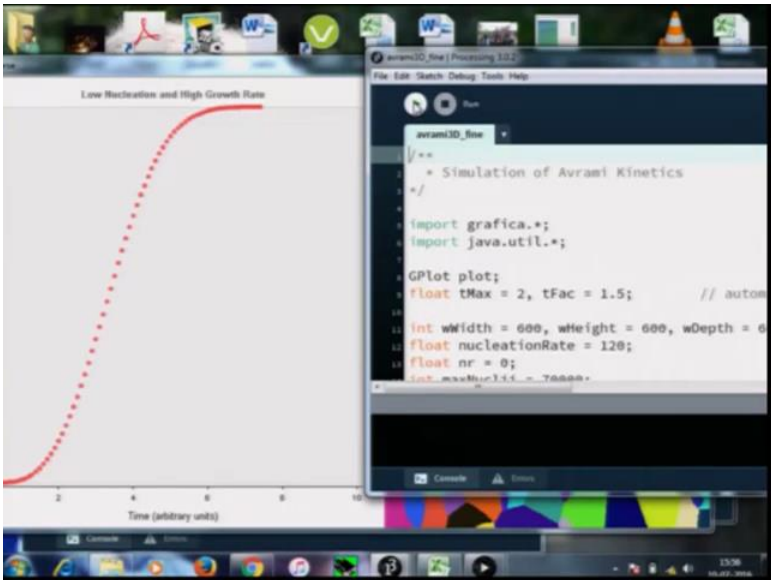

```
/**
 * Simulation of Avrami Kinetics
*/

import grafica.*;
import java.util.*;

GPlot plot;
float tMax = 2, tFac = 1.5;        // autom

int wWidth = 600, wHeight = 600, wDepth = 6
float nucleationRate = 120;
float nr = 0;
int maxNuclii = 70000;
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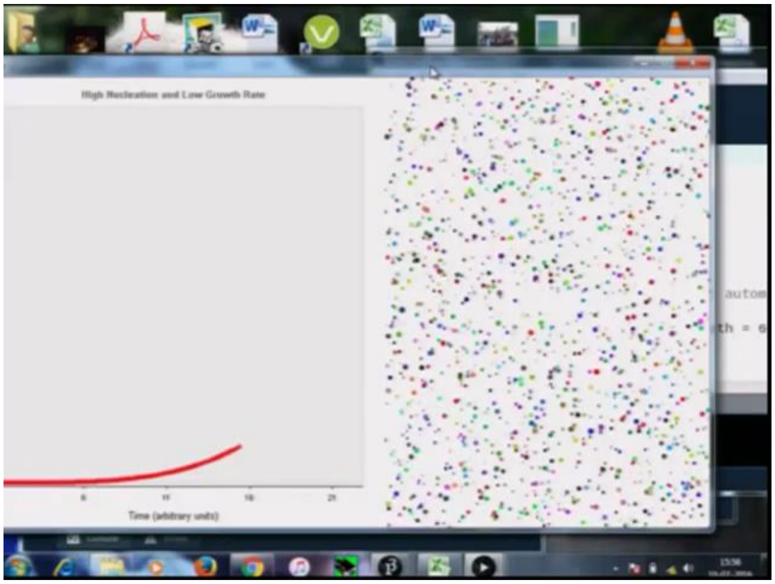

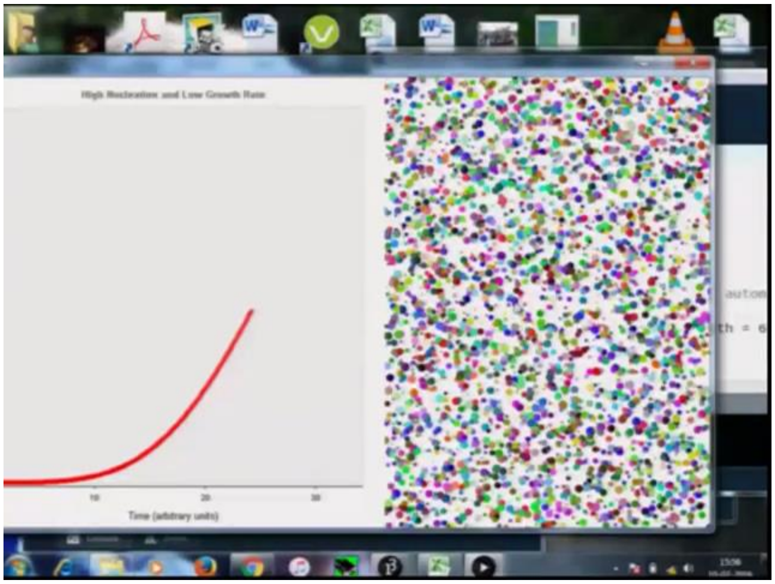

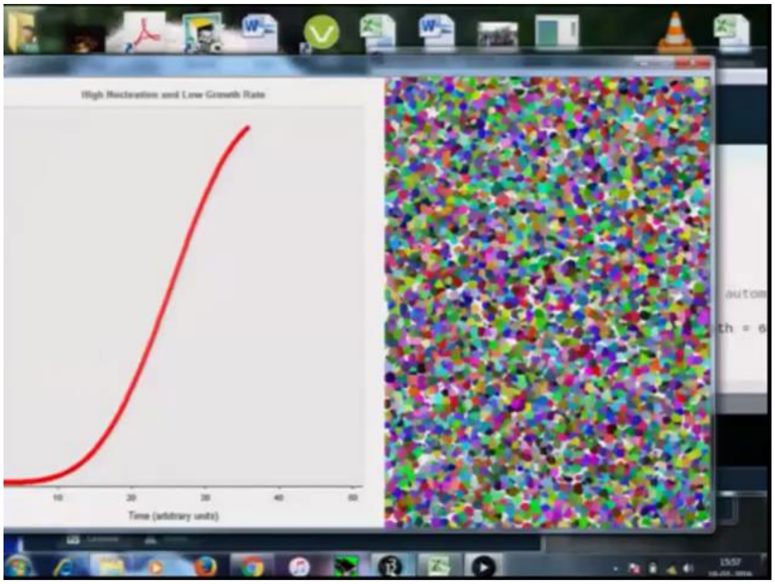

Let me also now look at a third one in which the nucleation rate has been made very high while the growth rate (is has) has been reduced significantly and if we do this, let us see you will find now of course a kinetics of at this stage you can see has become smaller. The rate at which the overall transformation that is taking place is now much smaller. However, large number of nuclei are being produced as you can see as a simulation is proceeding, however they are growing very slowly. And you can see from the evolving structure that in this case the microstructure that is produced has a much smaller scale as compare to the previous one.

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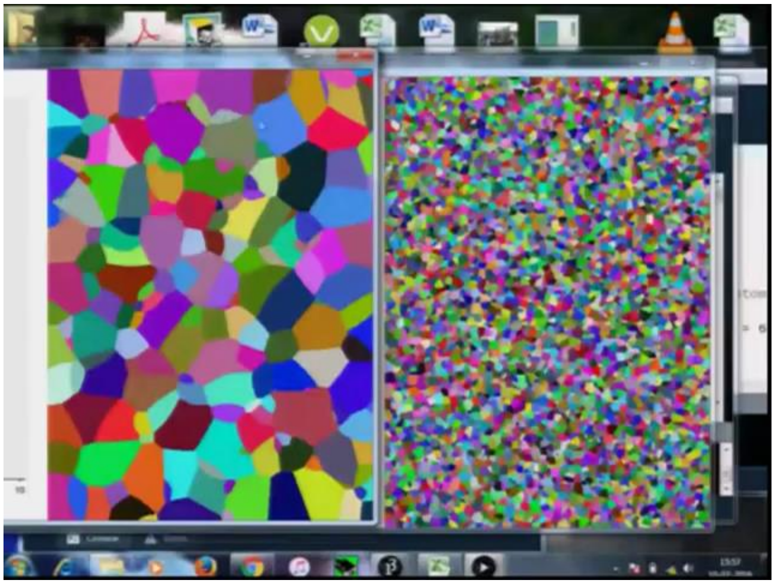

So let me just also put on the side the previous structure (just a sec) in fact that transformation is still not complete as y can see the curve is still going up. But you can see that on left hand side on this side here there is a the grains are much larger where the nucleation rate was small and the growth rate was high. However on the right hand side or on this side the grains are much smaller where the nucleation rate was very high, however the (greth) growth rate was very small. And the first one I had done is some kind of a intermediate nucleation rate and intermediate growth rate and you can see that the grain size is in between the previous two.

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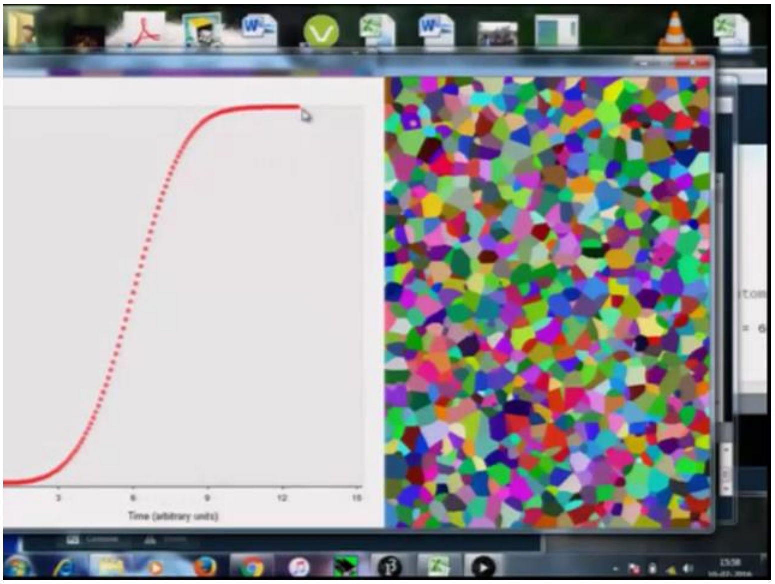

But in all the three cases, if you look at this particular curve now which is fraction transformed versus time, this shape of this curve is called sigmoidal. So the or other it is a curve which has a sigmoidal shape and you can see that in the beginning the transformation rate is small, then it starts to increase at some points it becomes extremely high and then it starts to reduce again towards the end of the transformation. We will be talking about this sigmoidal curve in great detail later and how we can mathematically model this that also we will be looking at later lectures.

First we need to understand very clearly how the nucleation rate and how the growth rate can first be modeled. Once we know that, then when will combine those two, then we would we would be able to obtain this sigmoidal curve for the kinetics of phase transformation.

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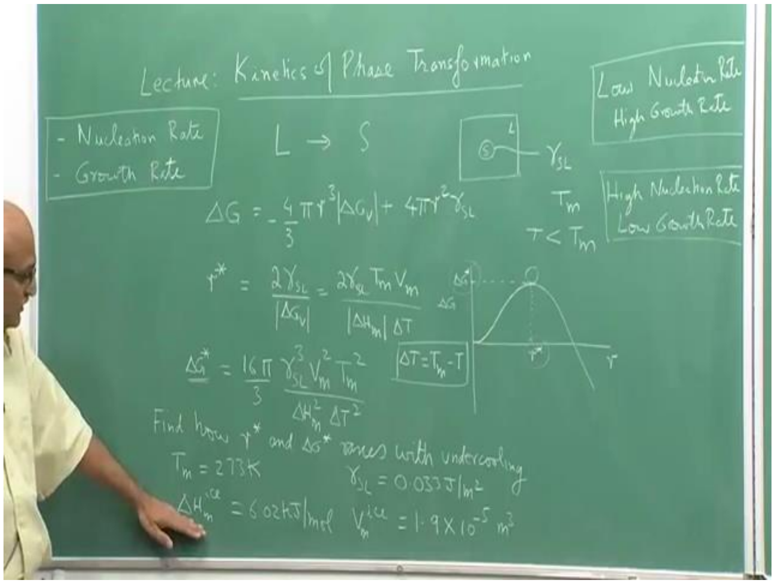

Lecture: Kinetics of Phase Transformation

- Nucleation Rate
- Growth Rate

$L \rightarrow S$

$$\Delta G = -\frac{4}{3}\pi r^3 |\Delta G_v| + 4\pi r^2 \gamma_{SL}$$

γ_{SL}

T_m

$T < T_m$

Low Nucleation Rate
High Growth Rate

High Nucleation Rate
Low Growth Rate

$$r^* = \frac{2\gamma_{SL}}{|\Delta G_v|} = \frac{2\gamma_{SL} T_m V_m}{|\Delta H_m| \Delta T}$$

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma_{SL}^3 V_m^2 T_m^2}{\Delta H_m^2 \Delta T^2}$$

$\boxed{\Delta T = T_m - T}$

Find how r^* and ΔG^* varies with undercooling

$T_m = 273K$ $\gamma_{SL} = 0.033 J/m^2$

$\Delta H_m^{ice} = 6.02 kJ/mol$ $V_m^{ice} = 1.9 \times 10^{-5} m^3$

Now coming back to the board we will proceed further with with this relation and we can then we can find or other in a previous lectures you have already determined that what is r star and what is delta G star. So in fact you have determine r star s two times gamma Sl upon delta Gv and I will put this l epsilon terms to indicate that I will only take the absolute value for this to get me r star.

Similarly, I can get delta G star, so r star which is equal to 2 gamma Sl upon delta Gv can also be written as 2 gamma Sl Tm Vm upon delta Hm times delta T where Tm is a transformation temperature, gamma Sl is the interfacial energy, Vm is the molar volume, delta Hm is a change in enthalpy in molar terms and delta T is the amount of undercooling which is equal to delta T is equal to Tm – T, so T is the temperature at which the transformation is taking place or the nucleation is taking place.

This particular relation has already been (der) derived in the previous lectures, so if you have any doubt at this point of time you may like to review some of the previous lectures to clearly see how this relation came and then finally how this relation came. Similarly the change in free energy or the energy hill delta G star is given by 16 pi by 3 gamma Sl cube Vm square Tm square upon delta Hm square delta T square. Now this should be clear that if delta G star is large, nucleation would be difficult because this hill would be much steeper and if delta G star is small, nucleation would be easier and hence the nucleation rate would be governed by delta G star.

Similarly, if you look at the critical size r star, what is going to be what factor on the right hand side is going to govern what is r star, well for a given system gamma is constant, enthalpy is constant, Vm is constant, Tm is also constant so only thing that is left is the undercooling. So very clearly if delta T is small, r star would be large. Similarly if delta T is small, delta G star would be large. So both r star as well as delta G star would be large for small undercoolings, for large undercoolings that is large delta T r star would be small delta G star would be small.

So one important conclusion that one can draw from here is larger undercoolings should produce higher nucleation rate, but then again we will find if the undercooling becomes very large then also we would find that the nucleation rate would go down, how that happens? That will become clear in subsequent lectures. Now what we are going to do next is the following.

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Find how r star and delta G star varies with undercooling or the transformation temperature. And for this we will take up the following transformation of water transforming to ice, this particular problem has been dealt with professor (ma) Mandal in an earlier lecture where you were shown how to determine for a given undercooling the critical size of the nucleus and the critical free energy.

So let me just write down that data again obviously Tm is 273 degrees kelvin for water, delta Hm ice we can is 6.02 kilo joules per mol, gamma Sl the interfacial energy between the solid liquid interface is 0.033 joules per meter square and the molar volume of ice is 1.9 into 10 to power minus 5 meter cube per mole that what it means that one mole of ice volume would be 1.9 into 10 to power minus 5 meter cube.

And using this data, what we are going to do first we first going to examine in a little bit more detail then what was done earlier, first how the nature of this curve changes with undercooling which means how r star and delta G star shifts as I change the transformation temperature for this, what I am going to do is we are going to solve this problem not on the board but I am going to do it in a spreadsheet program where we can quickly calculate values of delta G for various values of the nucleus size and to be able to plot it and then change the temperature, change the undercooling (an) to obtain to obtain different curves and to see how the nature of the curve changes as the undercooling changes, that will be one.

And second what we will do then is to look at how the critical size and how the delta G star how it varies as I am changing the transformation temperature for that I am going to do a separate calculation and draw curve for that as well to see how this energy hill how rapidly it changes a degree this thing how the size changes and finally I also want to see that for any size critical size of the nucleus how many atoms or in this case how many H2O molecules are there in a nucleus.

Why should that be important? Well, it would important from the point of view that if a critical size nucleus has to form in if it has a certain size for a given temperature, then that size will have a given number of molecules that have to come together and they have to come together in a manner so that they can form the crystal structure of ice.

So that means they have come together with the proper orientation and join with each other to produce the ice crystal structure which is of hexagonal in nature, it is a hexagonal crystal structure. So larger the number of atoms, more difficult it would be for these atoms or molecules to come together to form a structure. Because how this structure is forming? It is forming by the random movement of these molecules and the nucleus forms a (cer) nucleus of a certain size from by chance.

So the probability of formation of a nucleus will be determined by how large the nucleus is or how steep the energy hill is or how many molecules have to come together to form that nucleus. At this point of time I will close this lecture and in the next lecture we will continue with this problem and we will do that in the next lecture we will solve this problem using a spreadsheet program and perhaps before you begin that lecture you may want to revive your concepts on spreadsheets so that you can follow the lecture more easily, okay so we will stop here.