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Phase field modeling; the materials science, mathematics and computational aspects

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Module No.6
Lecture No.28
Plotting spinodal

Welcome so we have figured out how to plot the phase diagram for the regular solution model when the regular solution or the regular solution parameter is positive we now want to plot the spinodal line on the curve so to do that we are going to use the same kind of strategy we are going to define the function which is the function which is the second derivative of free energy with respect to composition now what is that function so let us derive that first again this is done for the normalized case so I am going to derive that expression.

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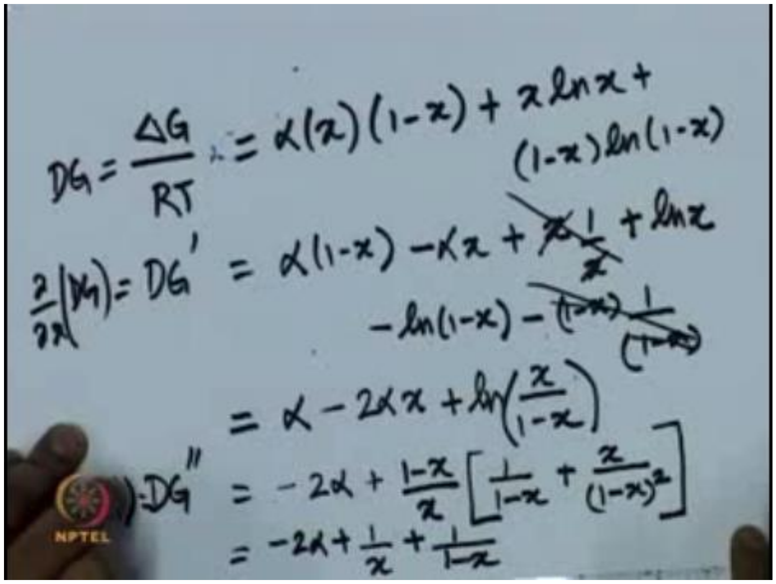

So let us take the Δ G / RT which is nothing but α x (1 –x) + x ln x + (1 -x)ln (1 –x) okay so let me call this as DG so the G´ which is nothing but $\partial/\partial x$(DG) is going to be now α(1 –X) - because when you differentiate this you are going to get a -sign α x + x when you do ln x you are going to get 1 / x + when you do x you are going to get ln x and when you do 1-6 you are going to get-ln(1 –x) and when you do 1- I mean ln(1 –x) you are going to get a -sign 1 –x and by (1 –x) right because it is 1/(1 –x) and then -x so will you a-sign.

So x / x is 1 and 1 –x / 1 -x is also 1 and this is positive this is negative so these two terms are going to disappear so what do we have we have αx and then another -αx 0 -2αx +ln(x /(1 –x))so this is the DG but what we want to get is a DG´´ which is $\partial/\partial x$ of DG´ right this is equal to an α is a constant so -2α and when you do for this quantity first you are going to have less 1 -x by x because logarithm of this so we are going to have 1 /that times then we are going to do by parts okay so it will be 1/(1 -x)-x /(1 –x)^2 and so this 1 -x when you differentiate as -x is going to give another + okay.

So what does this become so this is = -2 α+ so let us take it so 1 -x 1- will go so you will get 1 /x + 1 -x 1 -x will go xx will go it will give 1 / 1 -x so this is the expression so let us write this expression out once more so we five differentiate twice.

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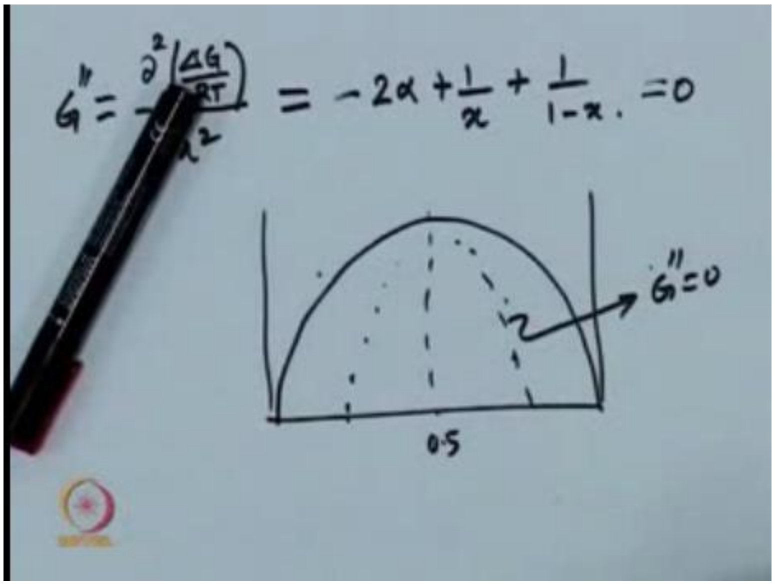

I get this $\delta^2\Delta G/RT/\delta x^2$as nothing but so this is our normalized G ´´okay as what -2α+ 1 / x + 1/ 1 -x so we want to find the 0's of this function where this is equal to 0 that point is what is going to be the spinodal so we have the miscibility gap which is like this and in that miscibility gap then we are going to have identify the points at which this these points are basically G´´ = 0 points so this is what we want to find so which means we want to find the 0's of this function G´´ so our strategy is going to be as earlier we are going to define this function G ´´first in terms of α and x.

And then we are going to identify the 0's of this function again I am going to do it by splitting the domain into two parts about 0.5 so I am going to find the points to the left hand to the points to the right and then I am going to plot okay so that is what we want to do so let us define the function first so let us do the function definition.

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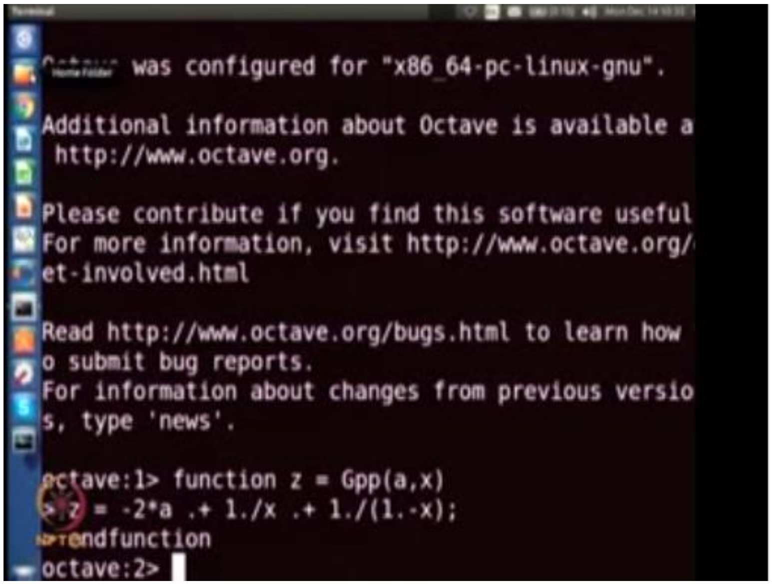

So how this function defined let me call this as Z is equal to let me call this as Gpp to denote that it is G ´´ it again depends on a and it depends on x okay now what is this function so we have identified it as -2a okay because it is -2 α .+1 ./ x . + 1./ 1 .-x so this is the function end function so we have defined the second derivative of the free energy with respect to composition and it takes two input parameters the α parameter and the x which is a composition now we want to find the 0's for finding the 0's there is a command called f0 which is what we are going to use when we are using f0 one of the conditions with f0 is that you have to give the range within which you will find the 0 for this function.

But for the algorithm to work the bounds that you give should enclose a 0 that means on one side it should be negative another side it should be positive see the finding of the 0 works something like this.

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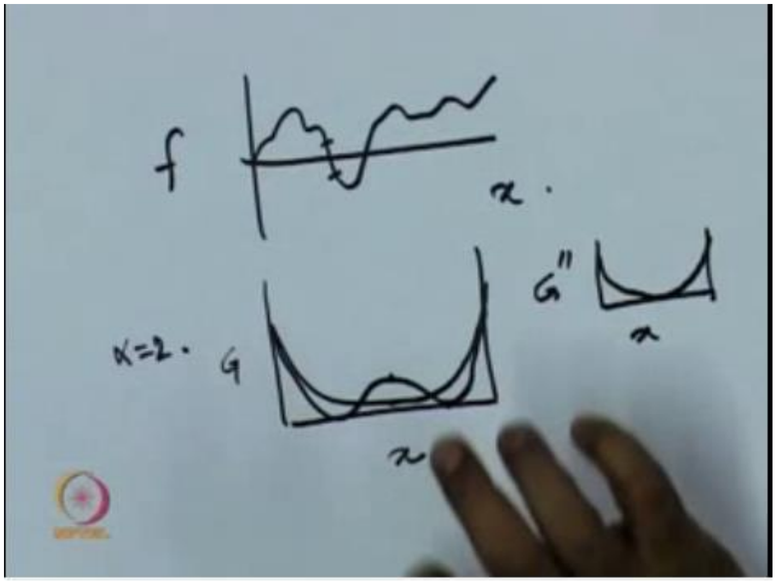

Suppose I have a function f as a function of x and then I have something that looks like this then if I find this range in which a 0 is enclosed then the a f0 will actually identify where it becomes 0 so the algorithm depends on the function being positive on one side negative on another side in this range so it actually tries to then identify which is the exact point where it crosses over from positive to negative and that is the point at which we find d0 so but in our case there is a problem that is a small problem remember at α = 2 the free energy versus composition curve if you look that is a curve that looks something like this okay.

So it actually just touches the point after this it actually will go and it will have points like that okay so this point will become the maxima and then it will develop two minima two of these wells on either side now when you have points like this where it goes below 0 and comes above 0 so then you can identify the points where it is becoming 0 but the second derivative will just touch 0 so this is G versus x if you look at the second derivative the second derivative G´´ as a function of x for this value α = 2 is just is going to touch this set point and go.

So it is not going to go below 0 so it is very difficult to identify that point using this command called f0 so we are going to avoid that point okay so that is all we are going to do so we are going to start with a(1).

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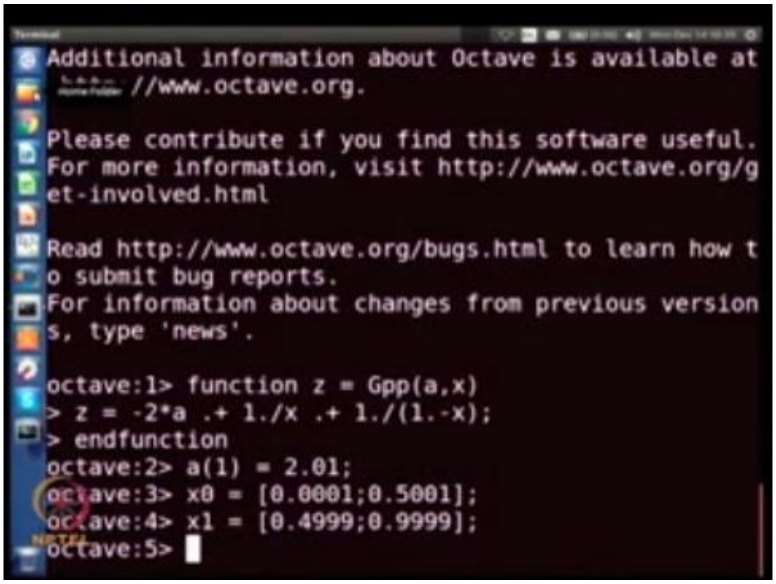

To be 2.01 okay and like to which is what we started in the earlier case which means the exact point to where the spinodal and the phase separation everything just at the 0.5 that we will not get as a solution from this exercise okay but we are okay with that so let us take α starting from 2.01that is we are going into the miscibility gap the just the point at which the miscibility gap is going to develop that we will not be able to capture using this command okay so that is the first thing now second thing we are going to do so we have to give this range in which we are going to find the 0.

So I am going to define the range 1 I am going to define as x0 so x0 is between 0.0001 to 0.5001 okay please note when we did the minimization problem we try to avoid 0.5 but here we are actually in including the 0.5 so similarly here we say x1 = 0.4 999 to 0.99 okay so the x0 and x1 are the range in which it is going to find the 0 for the given function Gpp so that includes 0.5 also so it goes slightly above 0.5 and it starts from slightly below 0.5 for the 0. that you identify to the left and to the right of 0.5 respectively this is because you know 0.5 like I said is the extrema point.

So when you want this function to cross over from positive to negative you need to include the points where it is becoming negative also or where it becomes positive also for that it is important to also include 0.5 okay if you do not do when you try to run the program it will say that your 0 is not enclosed in the limit that you are giving okay so that is the reason why I have to do it like this.

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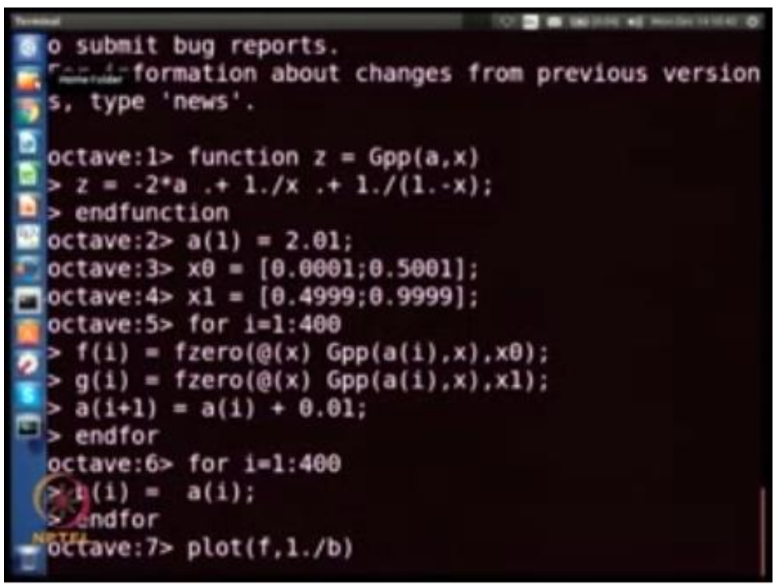

Now again we go we say for i 1: 400 we are going to identify the points where GD´´ becomes 0 the first point that I go I am going to identify where it becomes 0 to the left of 0.5 I am going to take us f(i) is nothing but f0 this is the command which finds the 0 as a function of x for the function right and it takes the range as the bound for finding the minimum and also going to find g(i) which is fzero@x for the function for the same way of i and x but now it is going to look for a minima in the range which is defined by the vector x1 okay remember one vector is defined between point 0001 to 0.5001 and the other vector is defined other range is defined from 0.499 to 0.9999 okay.

So we are going to define this and then we are going to do as usual a (i+1) is nothing but a (i+0.01) okay so octave is now computing the points at which the G ´´ becomes 0 it has computed all that we need to do now is to plot again while plotting we want to use inverse of temperature so I am going to do this for i = 1 : 400 let me define a b(i) which is nothing but a(i) okay end far okay so now I am going to say plot okay what are we going to plot we are going to plot f as a function of inverse of mα which is the temperature.

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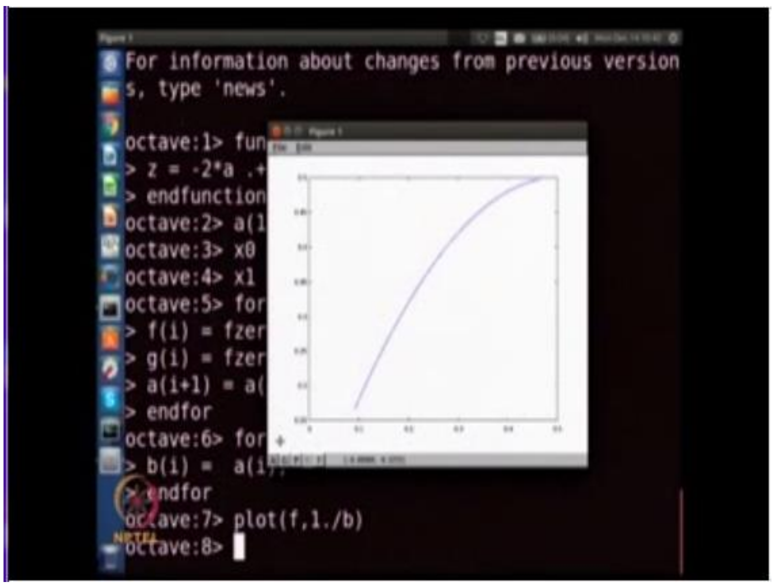

So I plot it so I have got this point then I say hold on.

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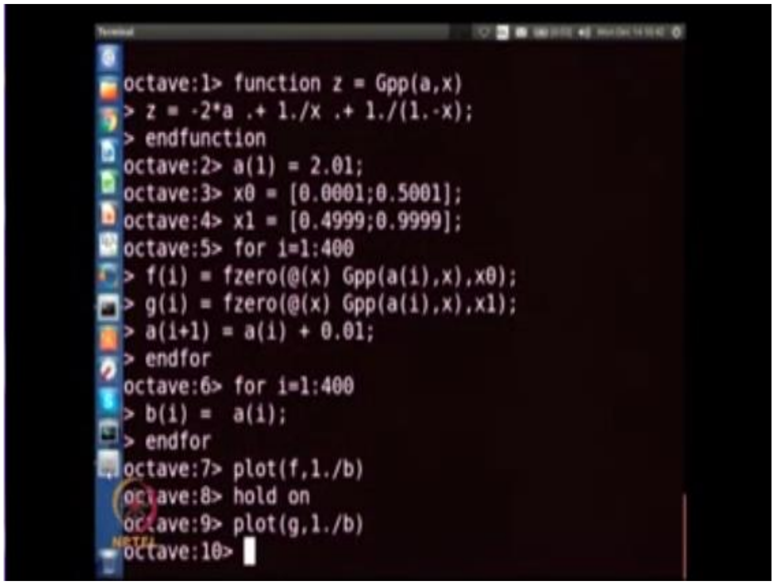

And then I plot the other thing which is to the points to the right okay.

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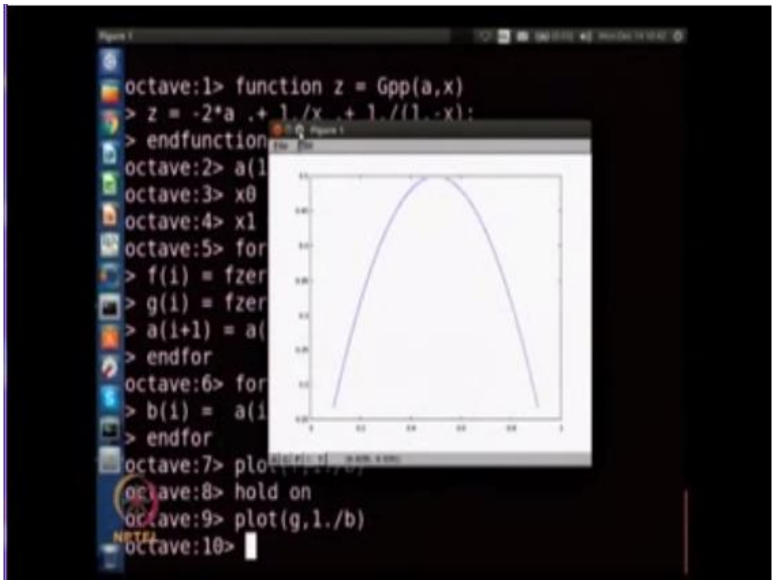

So now we get this so this is the spinodal region okay please remember how the phase diagram looked phase diagram looked like a parabola which went like that and the point quite close to 0.5 also we identified but here we have left it out so this is the spinodal points okay.

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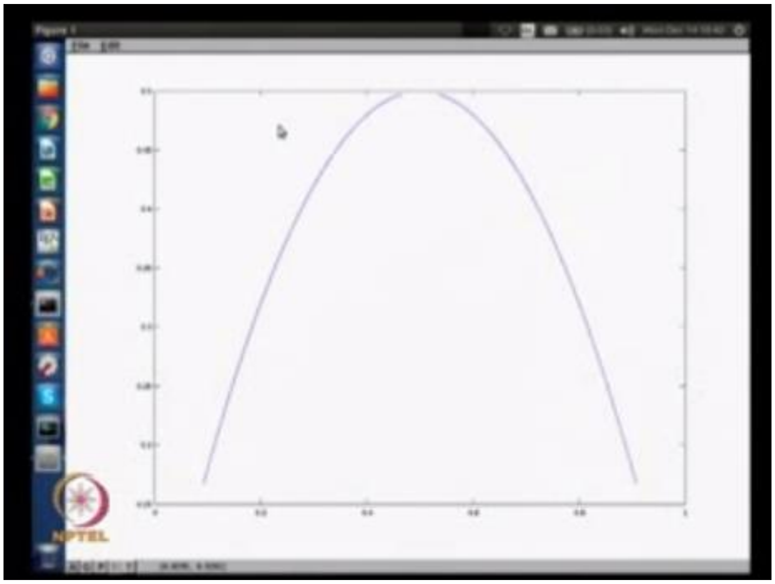

So you can see one advantage in writing the script is because if we had written a script for the phase diagram and in the same thing if you had appended this script which will do this spinodal then you could get both the plots together so you can see the phase separation and you can see the spinodal in fact that is what I have done I have written a script which will be shared with you but for now I am just going to run the script.

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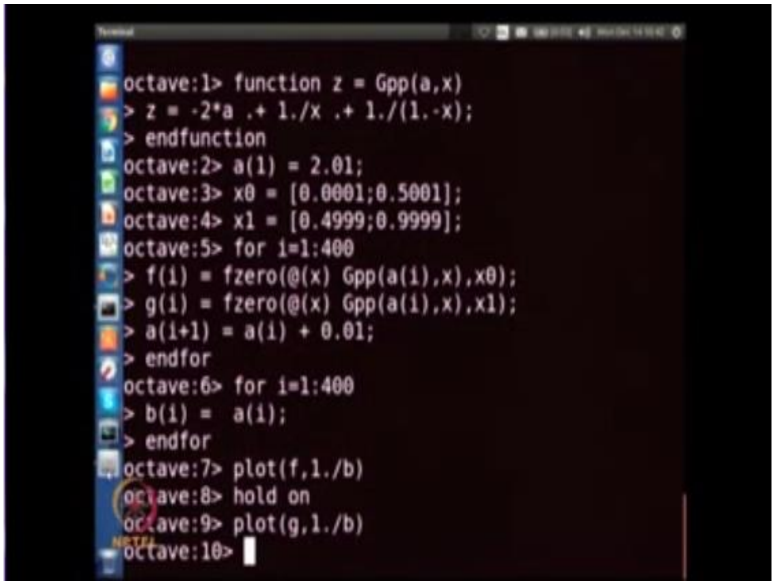

And what the script does is to do the computation that we did in the last part and the computation that I did now together and to distinguish between the spinodal line and the phase diagram it is going to plot this P spinodal line with red square marks okay so let us run that.

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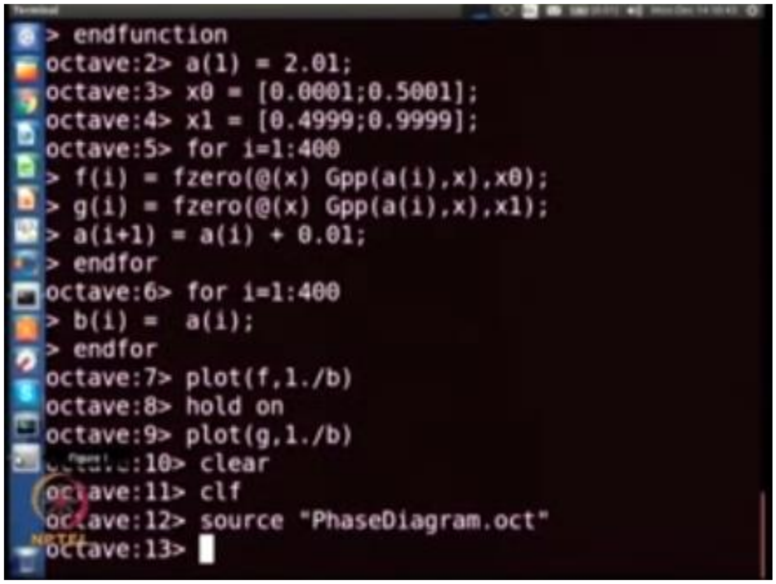

So first let me clear all the variables let me clear the figure and let me start by okay so it does two things first it calculates the phase diagram by doing the minimization then it calculates the spinodal points by finding the 0's of the Gpp.

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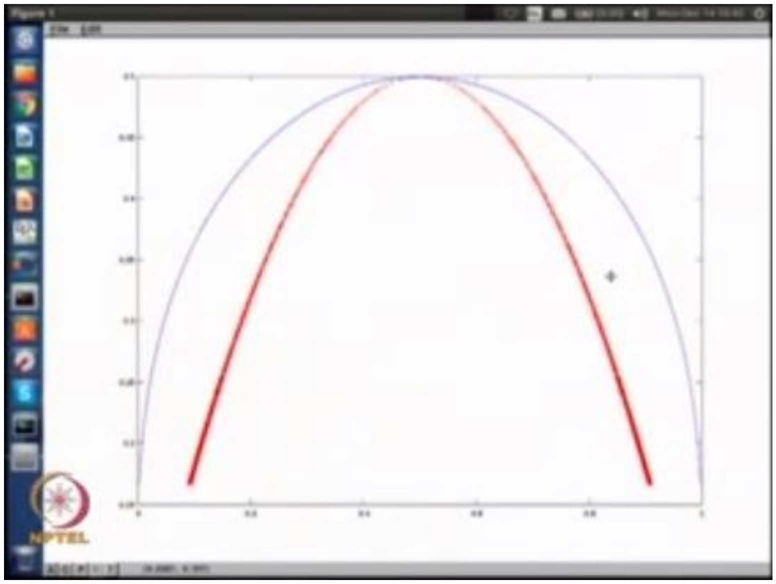

So this is what is the curve so you can see that you have this phase diagram which is giving you the region where the phase separation is going to take place and then it is distinguishing between regions here which is indicating metastable regions and they are separated from the unstable region which is hereby the spinodal line so at every temperature right so this is some normalized temperature t / ω/ r at 0.3 for example this is the range where the phase separation will take place but spinodal will take place only within this range.

And so on so forth and at 0.5 all these points are going to merge and become a one single point so this again is something that you might have seen in a textbook like Poulter d sterling for example the phase diagram and this spinodal lines are shown and this is known as chemical spinodal we will come to some of these things later and it is always inside the miscibility gap and at the critical point they all merge together okay so it always looks like this is so shown in textbooks and what we have done is by using octave we have tried to do it ourselves and plot it and see.

So this is the advantage of using octave that you can do the computations yourself and you can also plot for yourself and you can generate some of these figures that are there in the textbooks which gives you a better understanding of how these things are computed okay so in the next part of course now we have redone some parts of the thermodynamics that we did in the earlier lectures using octave okay so we have looked at all this what is the regular solution kind of thermodynamic model and how the phase diagram is constructed and how the spinodal is defined and so on so all that we have now seen using octave by computing for ourselves the next step is of course to go to the diffusion equation try to solve it there are many different ways in which you can solve there are analytical methods there are the numerical.

So our emphasis is going to be on numerical methods but I will also show you some of the analytical solutions for doing that again because we are going to do lots of computations we have to non-dimensionalize the diffusion equation okay so in the next part of this lecture this is what I am going to do we will take the diffusion equation we will non-dimensionalize it and for the rest of the course we will only solve the non-dimensionalized diffusion equation numerically okay it is always very useful and worthwhile to non-dimensionalized the equation before you solve it numerically so let us do it in the next part of this lecture thank you.

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