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

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Module No.6
Lecture No.26
Regular solution: Using Octave

Welcome we are looking at solution models and trying to understand them by using gnu octave we looked at ideal solution let us took a regular solution model what is the regular solution expression say.

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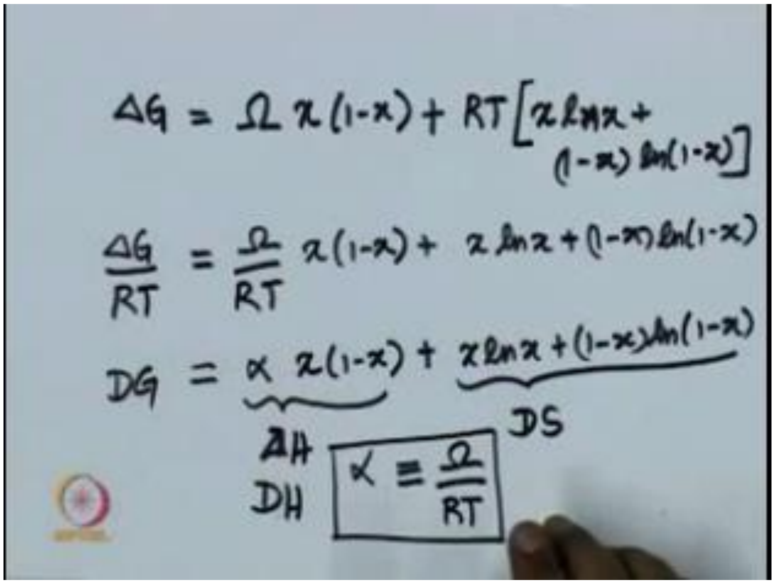

$$\Delta G = \Omega x(1-x) + RT\left[x \ln x + (1-x)\ln(1-x)\right]$$

$$\frac{\Delta G}{RT} = \frac{\Omega}{RT} x(1-x) + x \ln x + (1-x)\ln(1-x)$$

$$DG = \underbrace{\alpha\, x(1-x)}_{\substack{\Delta H \\ DH}} + \underbrace{x \ln x + (1-x)\ln(1-x)}_{DS}$$

$$\boxed{\alpha \equiv \frac{\Omega}{RT}}$$

Regular solution expression says that ΔG of mixing is nothing but Ω X (1-x) that is the enthalpy part and this is the regular solution parameter +RT the entropy expression is as in the ideal solution model so that is what the approximation was that the mixing is random as far as entropy calculation is concerned so RT [x ln x+(1-x) ln (1-x)] as usual let us do the non-dimensionalization so I am looking at ΔG / RT = Ω/RT x(1-x) + x ln x +(1-x)ln (1-x), okay.

So let us call this ΔG / RT as some α, so that is non-dimensional regular solution parameter times x (1 – x) plus okay , so let me call this entire expression as Δ H so in octave script for example I will refer to this as DH similarly this is x lon x + (1 – x) lon (1- X) and this expression as I did earlier I am going to call as DS this time to distinguish it between this is DG ΔG / RT is what I will call as DG so this is D H so this is DS.

So I am going to do these two calculations and we are going to assume different α parameters and remember α because it is defined as Ω / RT is inversely proportional to temperature which means what smaller values α refer to higher temperature higher values α means lower temperature this is very important because as you remember at higher temperatures it is always this quantity which is nominated which means α will become smaller and smaller so relatively that contribution is going to become smaller and smaller.

And then this quantity will dominate as α becomes larger and larger that means the enthalpy contribution becomes important that means we are at lower temperatures okay so we are going to use different α values but remember α is a non-dimensional scaled sort of regular solution parameter okay so that is what we are going to deal with it so let us take the case so let us again go back to octave and try to calculate these quantities and try to plot it and see how it works okay.

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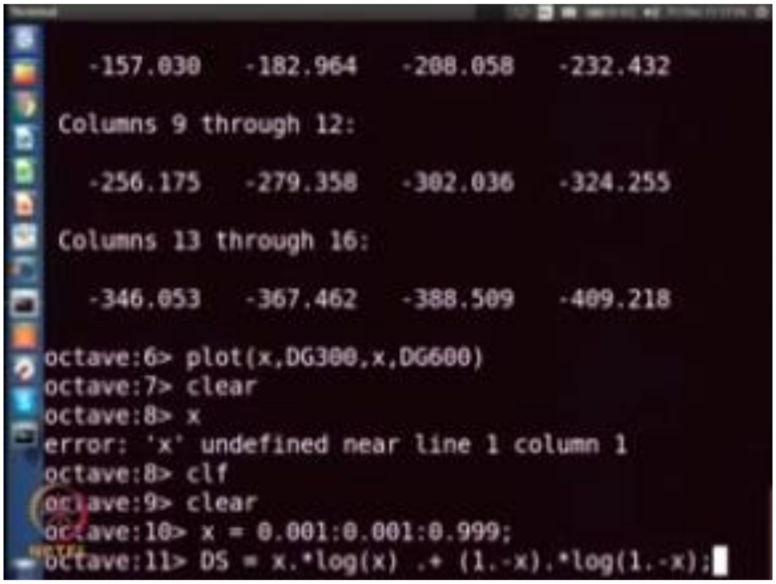

```
   -157.030   -182.964   -208.058   -232.432

 Columns 9 through 12:

   -256.175   -279.358   -302.036   -324.255

 Columns 13 through 16:

   -346.053   -367.462   -388.509   -409.218

octave:6> plot(x,DG300,x,DG600)
octave:7> clear
octave:8> x
error: 'x' undefined near line 1 column 1
octave:8> clf
octave:9> clear
octave:10> x = 0.001:0.001:0.999;
octave:11> DS = x.*log(x) .+ (1.-x).*log(1.-x);
```

So our first I am going to clear everything that I have okay and clear is for clearing all the variables that I have so if I now ask X it will say that it is undefined clf is to clear the figure okay so it shows you an empty page for the feeder okay so we are going to use this let me define X again I am going to define it between 0.001 and it is going to increase insteps of 0.001 let us go up to 0.999 okay so that is the x value.

The d/s value which is the non dimensional zed entropy of mixing part we are going to calculate as we did last time x dot star logarithm of X + 1.-x.*log (1.-x), okay so this is the entropy of mixing non dimensional zed that is why there is no Artie term okay.

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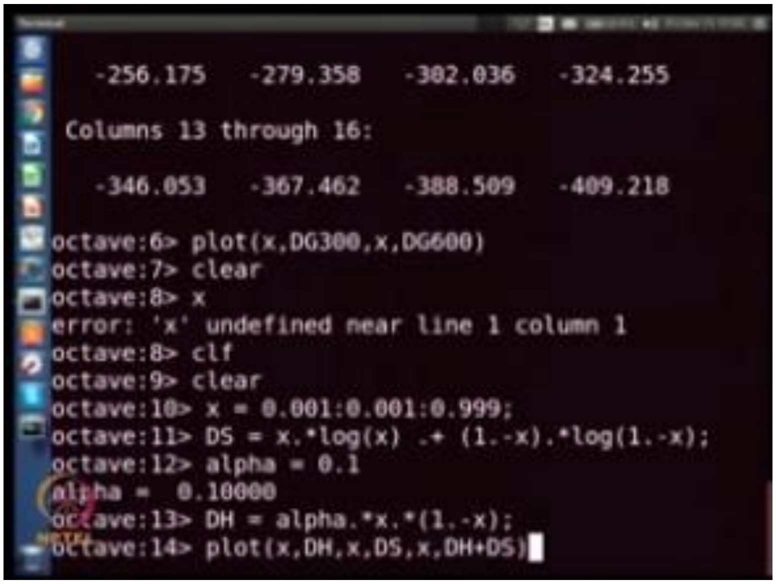

```
   -256.175   -279.358   -302.036   -324.255

  Columns 13 through 16:

   -346.053   -367.462   -388.509   -409.218

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octave:11> DS = x.*log(x) .+ (1.-x).*log(1.-x);
octave:12> alpha = 0.1
alpha =  0.10000
octave:13> DH = alpha.*x.*(1.-x);
octave:14> plot(x,DH,x,DS,x,DH+DS)
```

We are going to calculate the H term that is nothing but α okay so let me define α first let us define α to be equal to say point one okay now DH = α.* x x(1-x), right so that is the H now I am going to plot what are the things I am going to plot I am going to pause X DH X DS then I am going to plot x DH + DS right so α is positive which means this is a system that will undergo phase separation but α is point one which is a very small number which means compared to Ω the RP is very high. So the ratio is point one and so it is going to be dominated by temperature so let us see what the figure looks like.

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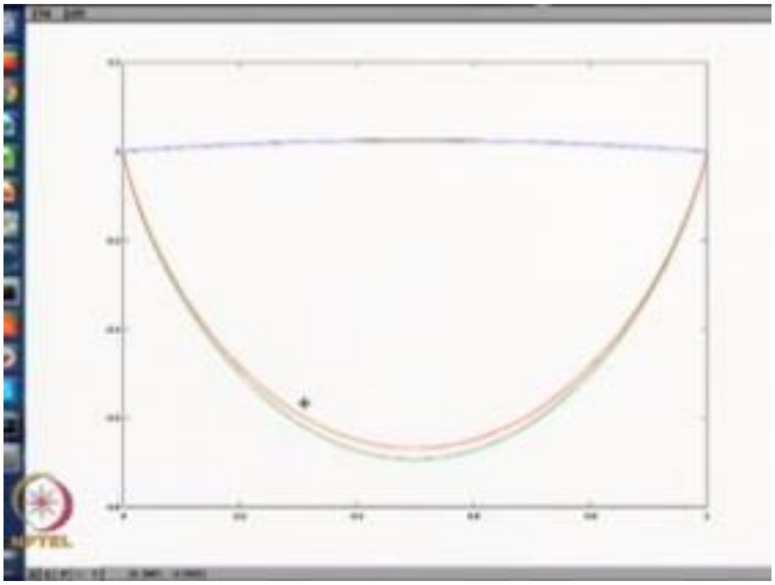

So as you can see so you have this quantity positive that what you see above therein blue line is the DH because DH is positive remember so it will be above zero the other line that you see is the entropy line that is the green line that is the one which is the lowest but to this negative quantity you are adding this positive quantity so the red line that you finally see is the non-dimensional zed free energy for this regular solution okay so now what we are going to do is that let us go change the α value let us change the α value to be equal to some 1.5 right and let us redefine the DH now let us plot so what do we get.

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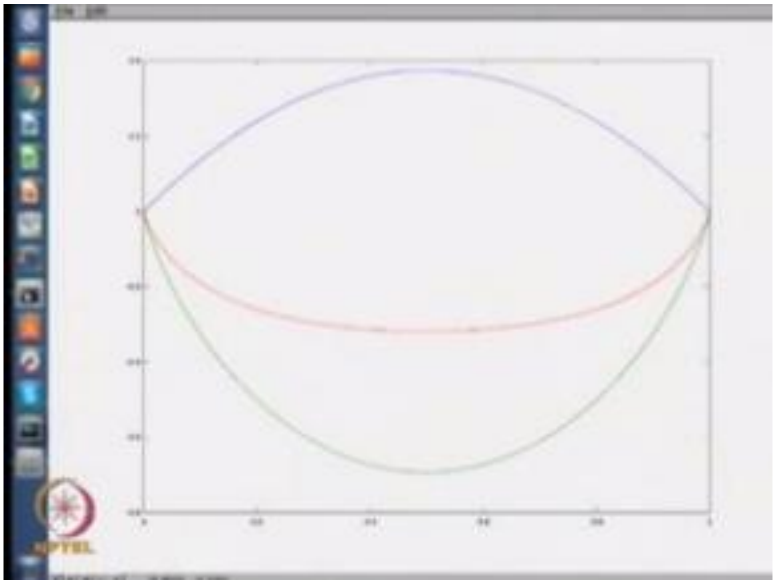
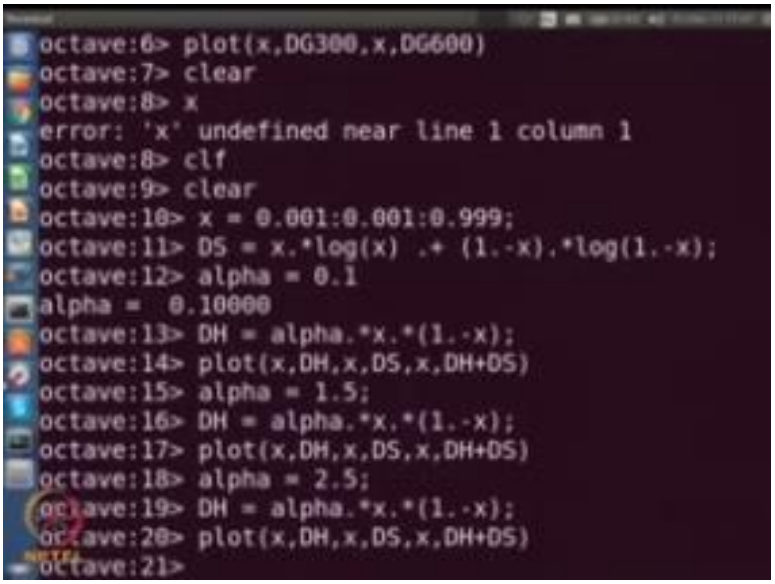


Well obviously we have made larger contribution to enthalpy remember we said that this is higher temperature the lower temperature because higher α value and so the entropy had this negative value but compared to that this quantity is comparable right so this is going from somewhere 0.6.7 and you can see already we are having 0.2, so if you add it then you get the red line that is the total free range let us go to still lower temperatures.

(Refer Slide Time: 07:26)



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octave:8> x
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octave:9> clear
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alpha =  0.10000
octave:13> DH = alpha.*x.*(1.-x);
octave:14> plot(x,DH,x,DS,x,DH+DS)
octave:15> alpha = 1.5;
octave:16> DH = alpha.*x.*(1.-x);
octave:17> plot(x,DH,x,DS,x,DH+DS)
octave:18> alpha = 2.5;
octave:19> DH = alpha.*x.*(1.-x);
octave:20> plot(x,DH,x,DS,x,DH+DS)
octave:21>
```

How do I go to lower temperatures I increase α value so let me make the α value to be equal to say 2.5 I calculate DH I plot this quantities how does the curve look.

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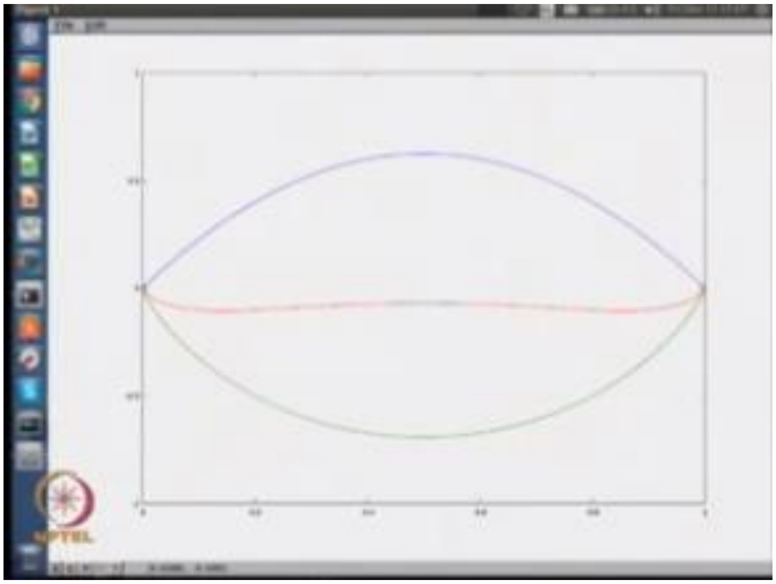

Interesting things start happening right so this δ H is comparable to the Δ S that we have so when you add them up at these two extreme points you can still see that the entropy has the say so it still goes like that in the same way as entropy but somewhere in between you can see that this quantity is having the curvature which is like this not like this right so this becomes much more prominent of course there are two ways of seeing it one is just plotting X and the overall free energy okay.

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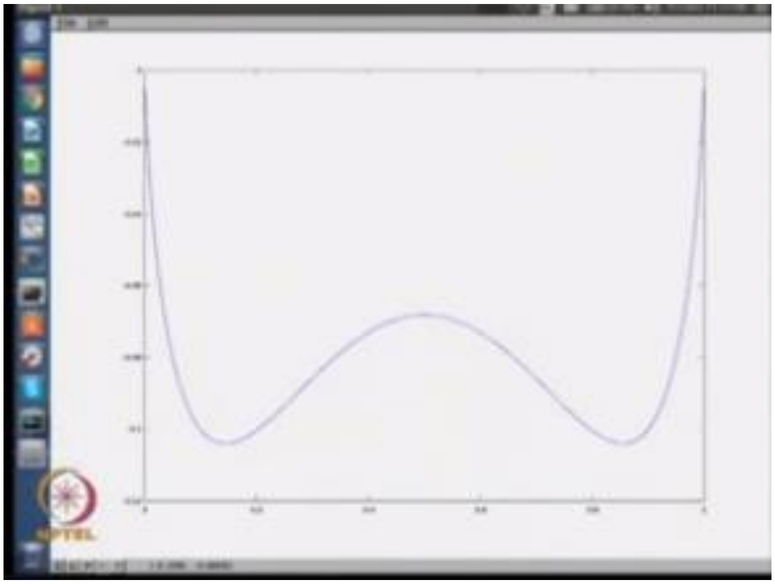

So you can see that right so it has developed this kind of so the curvature on this side and on this side is like the DS curve which went something like this and the curvature in the middle is like Δ H which had a curvature like that so in between obviously it is going to develop these two well states remember and these two wells are the ones I mean if you draw a common tangent then those points where the common tangent such are the points which are going to determine what the phase diagram is going to look like.

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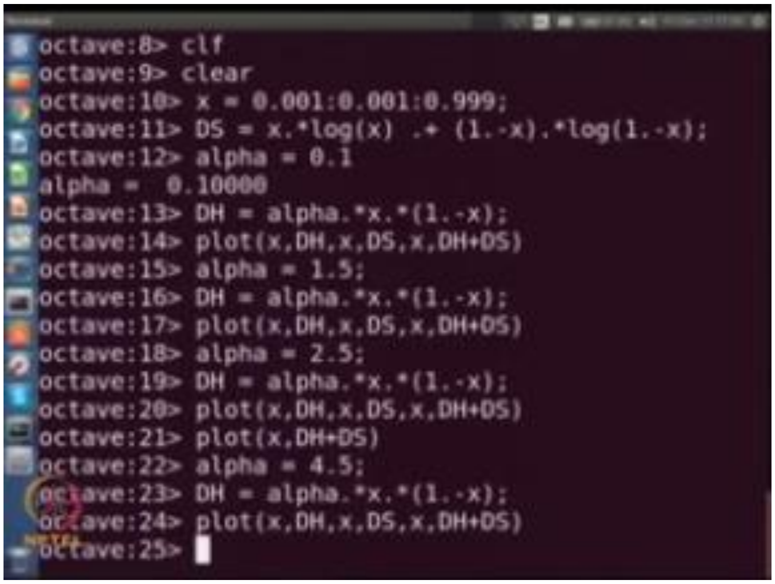
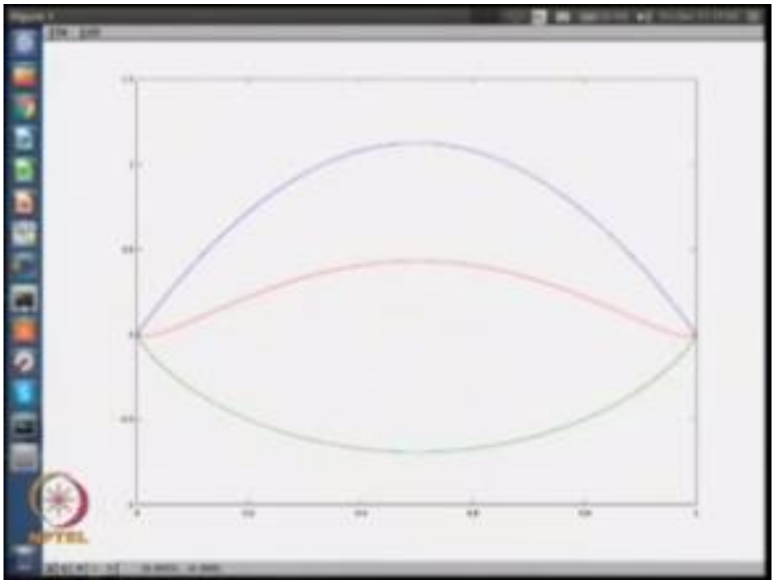


```
octave:8> clf
octave:9> clear
octave:10> x = 0.001:0.001:0.999;
octave:11> DS = x.*log(x) .+ (1.-x).*log(1.-x);
octave:12> alpha = 0.1
alpha =  0.10000
octave:13> DH = alpha.*x.*(1.-x);
octave:14> plot(x,DH,x,DS,x,DH+DS)
octave:15> alpha = 1.5;
octave:16> DH = alpha.*x.*(1.-x);
octave:17> plot(x,DH,x,DS,x,DH+DS)
octave:18> alpha = 2.5;
octave:19> DH = alpha.*x.*(1.-x);
octave:20> plot(x,DH,x,DS,x,DH+DS)
octave:21> plot(x,DH+DS)
octave:22> alpha = 4.5;
octave:23> DH = alpha.*x.*(1.-x);
octave:24> plot(x,DH,x,DS,x,DH+DS)
octave:25> 
```

Okay so this is one way of saying that there is also another way of course we can do that by going to really, really low temperature ok so let us go to some temperature non dimensional universe temperature right this is an inverse of temperature α of some 4.5 then what happens so I calculate the DH then I plot the quantity you will see.

(Refer Slide Time: 09:22)



The unmistakable the majority of the portion of this overall free energy curve has a curvature which is similar to Δ H very small regions at the extreme has curvature like the entropy so again to see it clearly.

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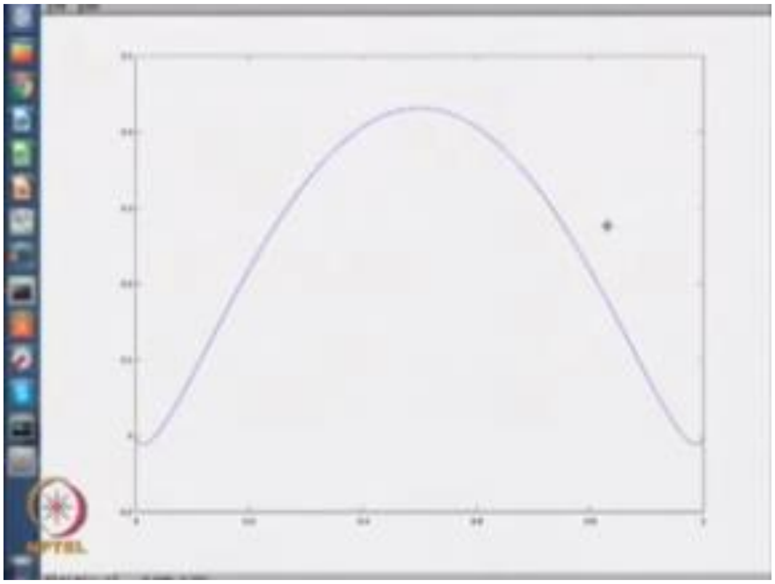

Let us just plot the overall free energy of mixing you can see that at these extreme points is where you see a curvature which is looking like that of the entropy so it is like this and it is like this so this part if you extend you will see a curvature that is looking like that but majority of it is because α is very high which means that I mean for example **Ω** as compared to RT the temperature at which you are looking at as compared to **Ω** that that ratio is like 4.5 RT4.5 times if you multiply you get **Ω** so that is the kind of **Ω** we are looking at.

So obviously **Ω** is a dominating so this is very, very low temperature but this kind of behavior where entropy is going to dominate is never going to disappear except at Absolute Zero then when the entropic contribution is not there at all that is because the entropy is calculated using the configurationally argument the configurationally argument says that I replace some B atoms or a atoms by the other type if I have say puree or pure B which is what these two extreme correspond to and if I take very small number of atoms of other type.

Suppose I take puree and then I have pure A there is only one configuration but the moment I introduced one be atom into this pure A then if there are some n number of sites then there are n different configurations so that much will be the increase in entropy in other words as you go to the purer and purer Systems the entropy configurationally entropy contribution is going to increase exponentially right so it is a very large number and towards the pure component it is going to increase very steeply.

And that is the reason why there is there will always be this dominance at the end points of the effect of entropy but other places once you are beyond that point the rate of change of entropy is not going to be very large with composition so exponential is not the right way of describing it the right way to describe is that a rate of change of entropy with composition when you are moving towards the pure components is very high as you move away from near pure compositions the rate of change of entropy is not that high so that the contribution from that part of entropy starts coming down so it end points will always be like this.

But otherwise you will see the free energy coming like this so the very energy curve it actually joins the y axis parallel to y axis okay so if you try to take the slope at these two extreme points that is like infinity and that is why we skip them while plotting because that will give you an auto number so that is that is going to join like with infinite slope okay, so this is with respect to different α values how the regular solution free energy of mixing looks like.

Let us try to do it a little bit more nicely okay and for that what I want to do is the following so I want to take few α values and I want to plot the regular solution free energy for few different α and see how the curve looks like this is the kind of curve that you might have seen in any thermodynamic textbook like Gaskell for example but we are going to produce it in octave and see how the curves the curve looks very, very nice so let us try to do that in so how are we going to do that so let me take I am going to define a function okay.

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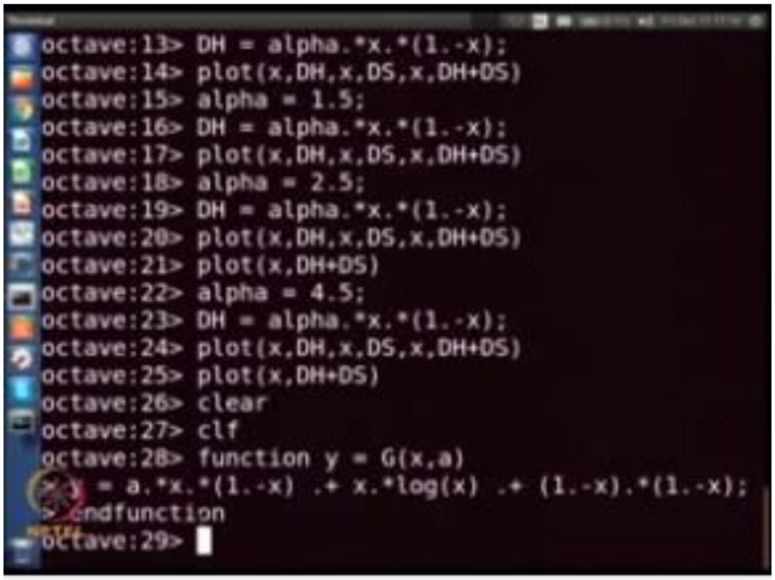

```
octave:13> DH = alpha.*x.*(1.-x);
octave:14> plot(x,DH,x,DS,x,DH+DS)
octave:15> alpha = 1.5;
octave:16> DH = alpha.*x.*(1.-x);
octave:17> plot(x,DH,x,DS,x,DH+DS)
octave:18> alpha = 2.5;
octave:19> DH = alpha.*x.*(1.-x);
octave:20> plot(x,DH,x,DS,x,DH+DS)
octave:21> plot(x,DH+DS)
octave:22> alpha = 4.5;
octave:23> DH = alpha.*x.*(1.-x);
octave:24> plot(x,DH,x,DS,x,DH+DS)
octave:25> plot(x,DH+DS)
octave:26> clear
octave:27> clf
octave:28> function y = G(x,a)
> y = a.*x.*(1.-x) .+ x.*log(x) .+ (1.-x).*(1.-x);
> endfunction
octave:29> 
```

Function definitions we have not done till now so I am going to now define a function the wave function definition is done is as follows so I am going to define this function called the Y which is a function of composition and α, right because the free energy depends on composition and α so let me define function the function return value is Y, Y is nothing but a function of X and A okay so before that let me first do the clear operation let me clear everything okay so then I say a function so let me define this function y = G(x, a) okay.

Now it wants to know what the function is y =a.*x.*(1.-x) so A is nothing but the α that we defined and this is the BH part that we are writing of the free energy function then .+ x.*log(x) .+ (1.-x) .*(1.-x), right so this is the expression I am going to put the column here because when this function is evaluated I do not want anything to be printed onto the screen like I said if you want to suppress any printing to the screen you should put the column at the edge semicolon at the end so that is what I have done.

So I am going to say ok now I have defined my function so end function okay so this is an important syntax that you should know how to define functions you can define so I have defined the function and it has a return value Y and I called it as G because that is the free energy function and it depends on composition X and the A parameter which I decided to call it because I do be writing α every time and I have defined the functional expression so I have given the expression and you say end function so this is how functions are defined.

So defining functions becomes very important if you want to do lots of computations and so this is a way of defining functions there is also a way of in liming functions which we have done probably I did not say that I am in lining a function or something but we will see more examples of that type later also.

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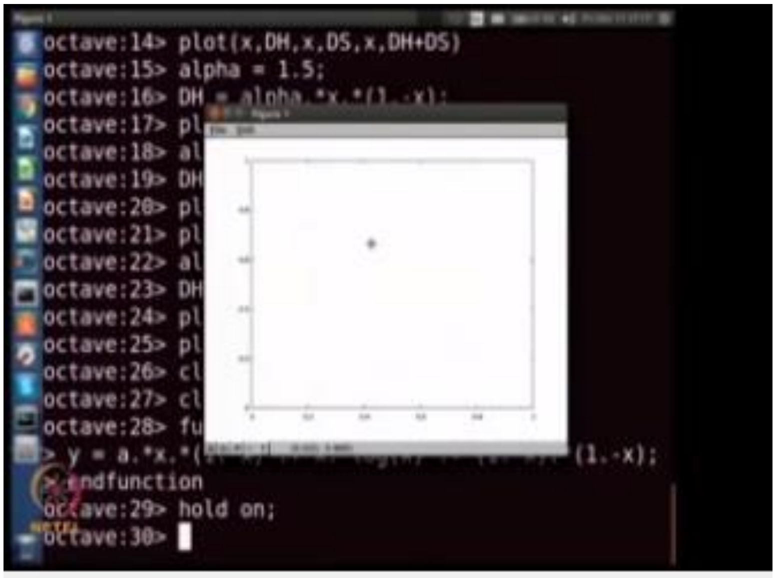

```
octave:14> plot(x,DH,x,DS,x,DH+DS)
octave:15> alpha = 1.5;
octave:16> DH = alpha.*x.*(1.-x);
octave:17> pl
octave:18> al
octave:19> DH
octave:20> pl
octave:21> pl
octave:22> al
octave:23> DH
octave:24> pl
octave:25> pl
octave:26> cl
octave:27> cl
octave:28> fu
> y = a.*x.*(                              (1.-x);
> endfunction
octave:29> hold on;
octave:30>
```

So this is the function now I am going to introduce a command called hold on when you say hold on what happens is that the plot that you have made is going to be kept and in the same plot the next move one will also be plotted right so it is going to keep this same figure and it is going to keep plotting everything that I asked it to plot in the same one so this is a way of getting more than one figure we have seen the other examples right you can say plot X, Y, X, Z, X, A, whatever so for each pair it will plot one curve and they will all appear in the same figure.

Now here is another way of getting all the plots in the same figure that is by using what is known as hold on which means keep this whatever figure and keep plotting everything that I asked you to plot on the same figure that is what hold on thus and so I have introduced hold on here of course we define X okay.

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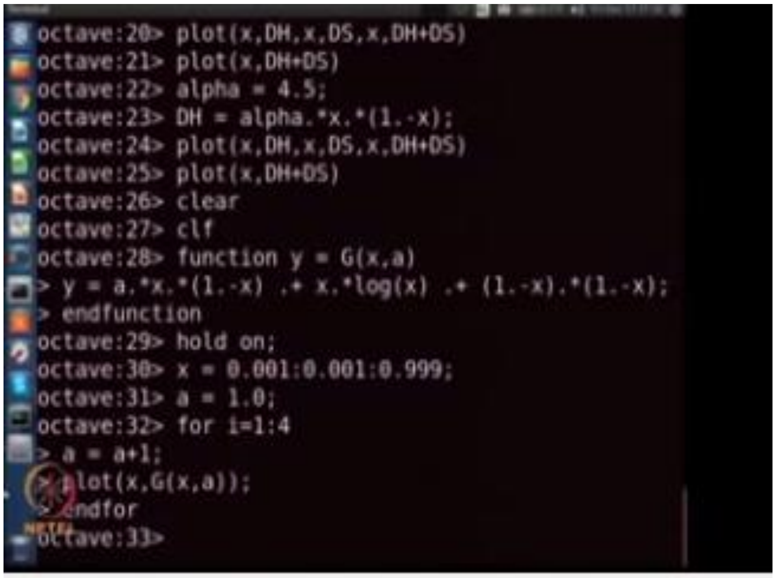

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octave:20> plot(x,DH,x,DS,x,DH+DS)
octave:21> plot(x,DH+DS)
octave:22> alpha = 4.5;
octave:23> DH = alpha.*x.*(1.-x);
octave:24> plot(x,DH,x,DS,x,DH+DS)
octave:25> plot(x,DH+DS)
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octave:27> clf
octave:28> function y = G(x,a)
> y = a.*x.*(1.-x) .+ x.*log(x) .+ (1.-x).*(1.-x);
> endfunction
octave:29> hold on;
octave:30> x = 0.001:0.001:0.999;
octave:31> a = 1.0;
octave:32> for i=1:4
> a = a+1;
> plot(x,G(x,a));
> endfor
octave:33>
```

So let us go define X =0.001: 001 0.999 right so this is what X goes okay so now I am going to say a =1.0 so let us start with the a =1 the α =1and then I am going to introduce the other command which is the formal so I want to calculate the x and the g for different α right remember is each x and each G corresponding to that x is basically a vector right so what I am going to do I am going to use four different α values the first one is α =1 now with α =1so I am going to say for i = 1 to 4 okay.

A = A+ 1 okay plot x, G(X, A) remember it is going to change α and for each α value it is going to plot this curve once okay plot G(X, A) and then we are still inside the for loop so what is the last command I say end for okay so let us go look at the figure.

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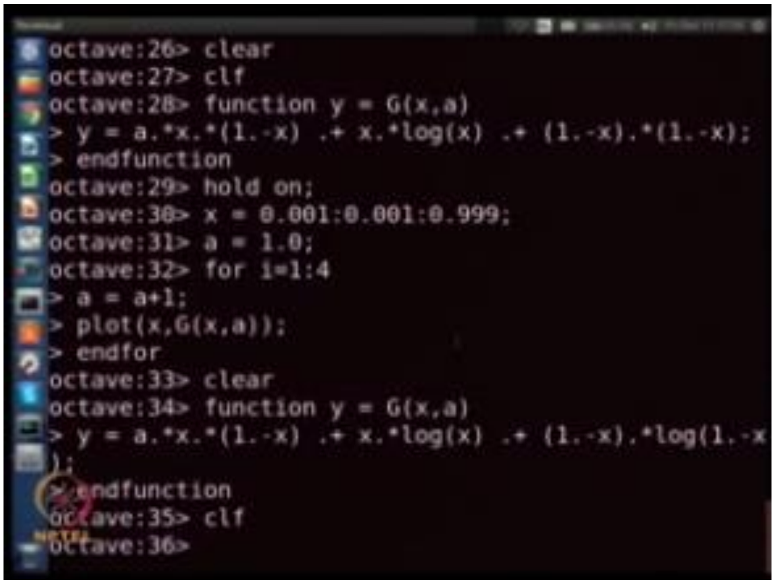

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octave:26> clear
octave:27> clf
octave:28> function y = G(x,a)
> y = a.*x.*(1.-x) .+ x.*log(x) .+ (1.-x).*(1.-x);
> endfunction
octave:29> hold on;
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octave:34> function y = G(x,a)
> y = a.*x.*(1.-x) .+ x.*log(x) .+ (1.-x).*log(1.-x
);
> endfunction
octave:35> clf
octave:36>
```

Okay so there is something wrong yeah so I know what the error is the function I defined it is 1 minus x times logarithm of 1 minus X so I miss the logarithm so let us go back and redo okay and let us define so before that let me do a clear so let us see clear only clears it from the memory of the octave from its working memory the commands that you gave are still remember so you can still access those commands using the up key okay so function y and what does the function is like this time I should not make this mistake so it is logarithm of this and then I end function ok so then I do the other thing what did I do.

So I need to define I need to say hold on but before doing that I have to clear function otherwise whatever plot it had earlier it is going to keep plotting on the same one okay. So I just want to start with the empty page so clf and then hold on so it is always a good idea if you are going to introduce commands like hold down when you start any new script the first line to be CLS and the second line to be clear and then start because if you are running this script and if octave has already run something so it will remember all those values and sometimes they can interfere with your calculation so it is always a good idea to start your scripts with clear at CLM okay. So CLF then hold on.

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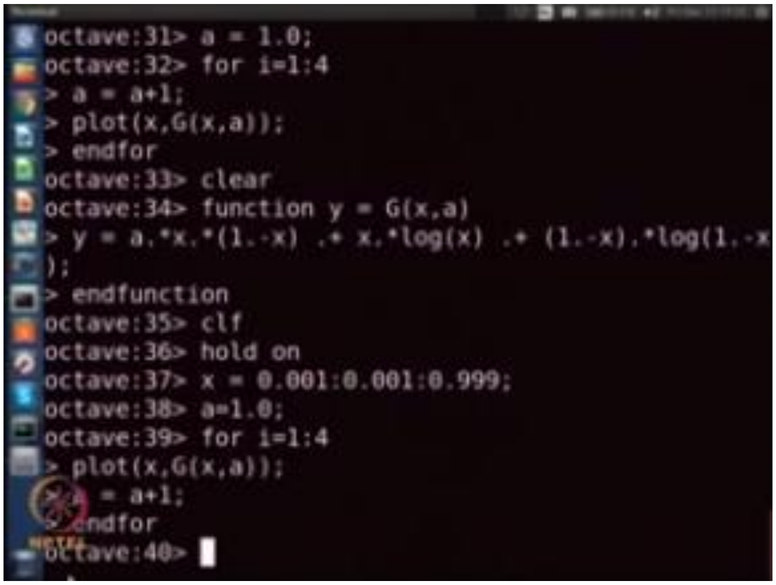

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octave:31> a = 1.0;
octave:32> for i=1:4
> a = a+1;
> plot(x,G(x,a));
> endfor
octave:33> clear
octave:34> function y = G(x,a)
> y = a.*x.*(1.-x) .+ x.*log(x) .+ (1.-x).*log(1.-x
);
> endfunction
octave:35> clf
octave:36> hold on
octave:37> x = 0.001:0.001:0.999;
octave:38> a=1.0;
octave:39> for i=1:4
> plot(x,G(x,a));
> a = a+1;
> endfor
octave:40> 
```

Okay so it starts with a new one so I am good 0.001, 0.001 as sorry when 0.999 right so this is the X so I am going to say a =1right for I = 1to 4, okay I want to say is a = a+1 in fact we can put a =a+1 after plotting okay so we will plot for a=1 also so plot X, G(X), A okay a =a+1 so next plot that it comes a will be to A will be 2 A will be 3 A will be 4 and so on and then say end for okay, so this is the interactive mode so I gave the commands and it executed everything and it must be having the figure.

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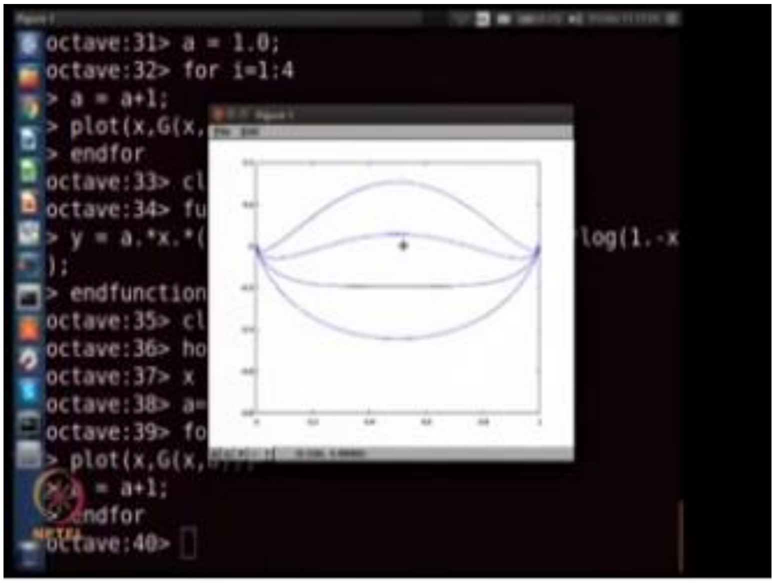

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> endfor
octave:33> cl
octave:34> fu
> y = a.*x.*(                                    log(1.-x
);
> endfunction
octave:35> cl
octave:36> ho
octave:37> x
octave:38> a=
octave:39> fo
> plot(x,G(x,
> a = a+1;
> endfor
octave:40> 
```

And you can see the figure this is the kind of figure that you will get to see of course everything now is in blue because every curve is plotted one so it takes a value of one it will plot take a value of two it will plot it will take a value of three it will plot it will take a value of four it will plot when you plot like X,G(X), A1 and X,X, G(X), 2 then there is a first plot which will be blue second plot which will be green third clock which will be red and so on and so forth so.

So there are advantages to doing it that way but here also there are ways of making sure that you have a legend which says what is what and then getting off course in this case we know that the A=1 is the high temperature one because that low α so that is like this and as you reduce the temperature you start developing these minimum and as you are going to lower and lower temperature the minima is going towards purer and purer compositions.

Because that is how the fear the phase diagram look you remember if you go to very low temperature the phase diagram boundaries are closer to the end compositions as you come to higher and higher temperatures so the phase diagram so it is like a parabola it is somewhere about point five is where its top point is so as you go to higher and higher temperature these points come closer and closer together and at some point they merge and the point five becomes a point at which they have the same value.

Above that the curve becomes like this the curve becomes the same as the entropy curve which means there is no longer heavy two-phase region so this is the kind of curve that you would have seen in materials thermodynamics courses for example you can go and take a look at Gaskell's textbook of the regular solution chapter in which you will see something like this and they will show you that there is this critical point about 2 for Ω by our p-value and below that you will have these two phase region above that you will have a single phase region.

So that is basically the same information that we are showing but here we are showing it in terms of the normalized free energy versus composition okay of course the next step is to construct the phase diagram itself using the regular solution free energy so which is what we will do in the next part of this lecture. Thank you.

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