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

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Module No.6
Lecture No.27
Constructing phase diagram

Welcome we have been looking at the plotting the regular solution free energies we plotted the ideal solution free energy then we plotted the regular solution free energy with the regular solution parameter being positive, we plotted it for different temperatures we defined normalized temperature which was are normalized regular solution order parameter which is normalized by RT and so this quantity which we called as α stands for inverse temperature, α is Ω/RT. So you can think of this as a temperature which is normalized by Ω/R and this quantity we then used for different values then the smaller values correspond to higher temperatures and higher values correspond to lower temperatures.

So we saw that there is a critical point at the value of $\alpha=2$, above that which means below the temperature the system phase separates which means it develops two minima with a Maxima in the middle and the minima are symmetric and about 0.5 which is where the maximize this, so in this case then we can go and construct the phase diagram itself. So the phase diagram construction given free energy is something like this.

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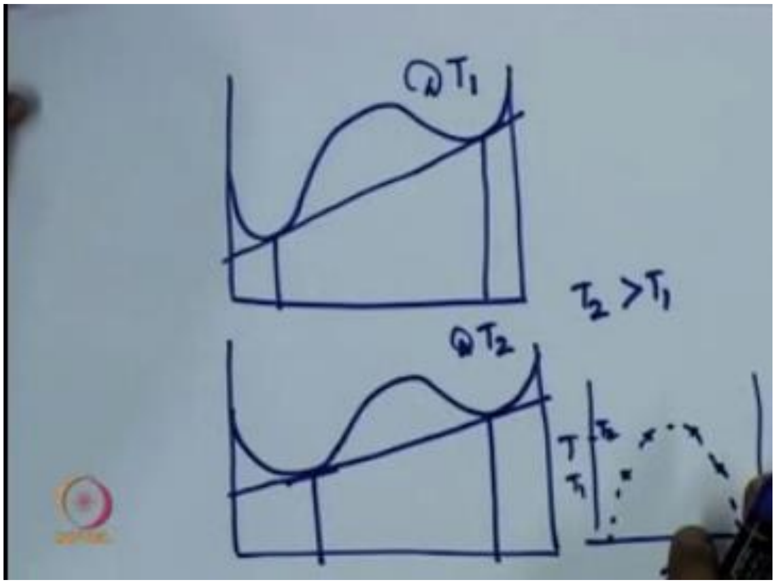

So I have a free energy right, so the free energy is something like that then I need to draw a common tangent and then find out the points so this is at some temperature T_1 and similarly at a temperature which is say higher than $T_1$and T_2 is greater than T_1, if T_2 is higher than these points are going to come closer so the curve looks something like that then you draw a common tangent again and then you get to the points, okay. So this these points then when you plot T versus X and then there are these points which are at T_1 there are these points which are a T_2 this is also T_2.

So if you get all the points then you get something like that, so this is the miscibility gap where you have this two phase region, so this is how we do the construction of the phase diagram given the free energy. Now we have the free energy of mixing which is a very symmetric very nice curve.

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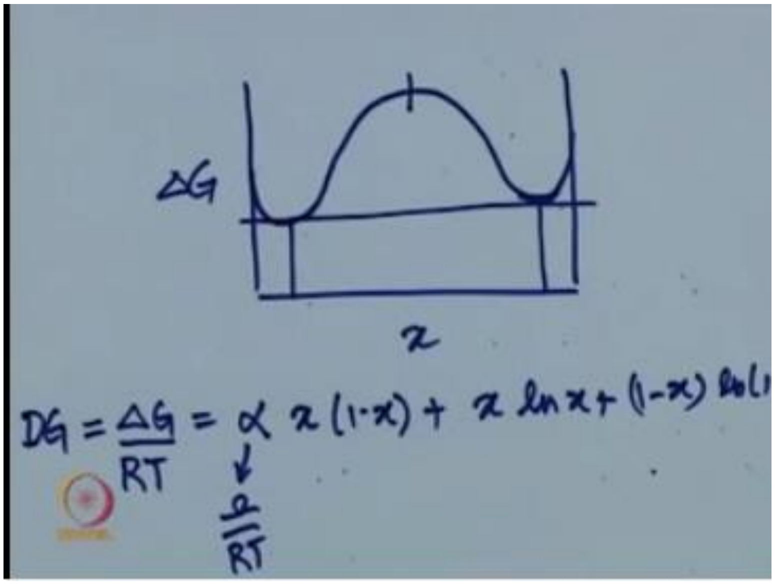

$$DG = \frac{\Delta G}{RT} = \underset{\overset{\downarrow}{\frac{\Omega}{RT}}}{\alpha}\, x(1\cdot x) + x\ln x + (1-x)\ln(1$$

So the free energy versus composition in this case looks like this, right so it is I did something like this so the common tangent is going to be like this, right. So we want to find out, in other words the minima for the curve and the common tangent point happens to be the same so in this case if suppose there is a way to identify to the left of 0.5 and to the right of 0.5 where the minimum point or and it is symmetric about 0.5 we can check that it indeed is so then we can construct the phase diagram by taking this free energy versus composition curve at different temperatures, okay.

So we know that the ΔG is given by RT because we normalized it is given by α which was nothing but Ω/RT right, x(1-x)+x lnx+(1-x)ln(1-x) okay, so we know that when we are doing this kind of calculation for different ax you have to define x itself as a vector and for that vector at different points you can calculate the ΔG so x versus ΔG then is useful in determining the free energy versus composition curve which can then be used along with the minimization routine to obtain the phase diagram, okay.

So the first thing that we are going to do, so we are going to construct the phase diagram for the regular solution free energy the first thing that we are going to do is to define a free energy curve, so let me call this as DG, okay this is a normalized DG this is not the DG that we defined earlier so let me call this as DG and let me define a function. So as usual we go to octave and I generally invoke it from the terminal.

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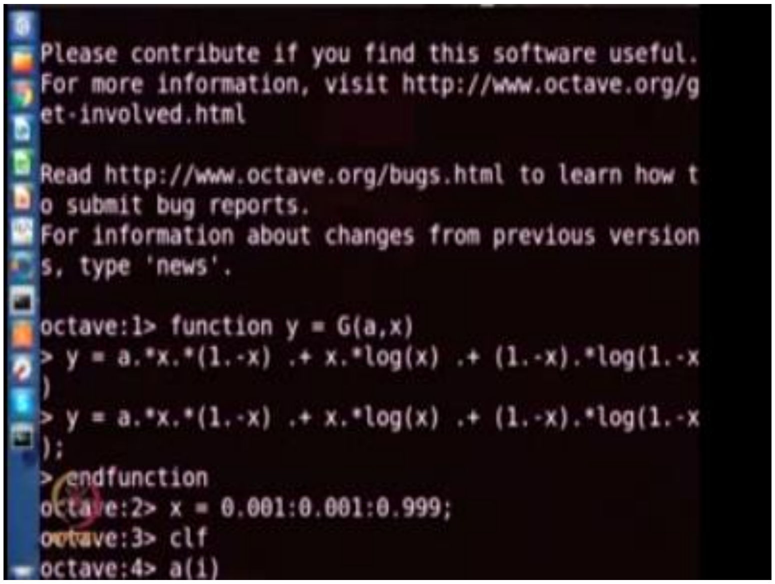

```
Please contribute if you find this software useful.
For more information, visit http://www.octave.org/g
et-involved.html

Read http://www.octave.org/bugs.html to learn how t
o submit bug reports.
For information about changes from previous version
s, type 'news'.

octave:1> function y = G(a,x)
> y = a.*x.*(1.-x) .+ x.*log(x) .+ (1.-x).*log(1.-x
)
> y = a.*x.*(1.-x) .+ x.*log(x) .+ (1.-x).*log(1.-x
);
> endfunction
octave:2> x = 0.001:0.001:0.999;
octave:3> clf
octave:4> a(1)
```

Because it is better so desktop okay, so I am in that directory so i am going to say octave, okay so I have got octave window now. So I am going to define a function and the function definition is done as follows, function let us say y is equal to what are the input values G(a,x) okay, where a stands for α which is Ω/RT okay, and how is the function defined y=a.*x.*(1.-x), right a*x*(1-x) because that is α(x*1-x)+x.*log(x).+(1.-x).*log(1.-x) so it is a good idea to put a : here then say end function, okay.

So we have defined the function and you can define x as 0.0001 and then let it increase, so let us do it 0.001 let it increase by 001: 0.999 I am avoiding the values of 0 and 1 here, I am not going from 0 I am not going to 1 that is because these logarithmic expressions so if i put 0 here then this going to give up, if I am going to put 1 here this is going to give up so when you have expressions like this it is better to not go to 0 and 1 where it will give you a not a number error.

So that is why I am avoiding this so I defined x now, okay and i am going to say that clf which is for clearing the figures so I have an empty figure which is where all plotting will be done, so I am going to start with a=1.0, okay. So first I start with a=1.0 then i am going to let me start with a[i] I am going to define may itself as a vector because there are going to be several a values because the a corresponds to temperature inverse of temperature so taking different a values means that I am looking at different temperatures at those temperatures I am trying to figure out hall the phase diagram looks.

Remember, the phase diagram construction means that the free energy has to be taken at different temperatures and the minimum points are to be identified at those temperatures so the identified minimum points are to be plotted against the temperature which means I need to do this computation at different temperatures, in our case the temperature is in the parameter α so it is inverse of temperature, so I am going to change the α and because it is inverse of temperature lower α means higher temperature and higher α means lower temperature, okay. So α is 0 is actually infinite temperature and α∞ is actually 0 temperature.

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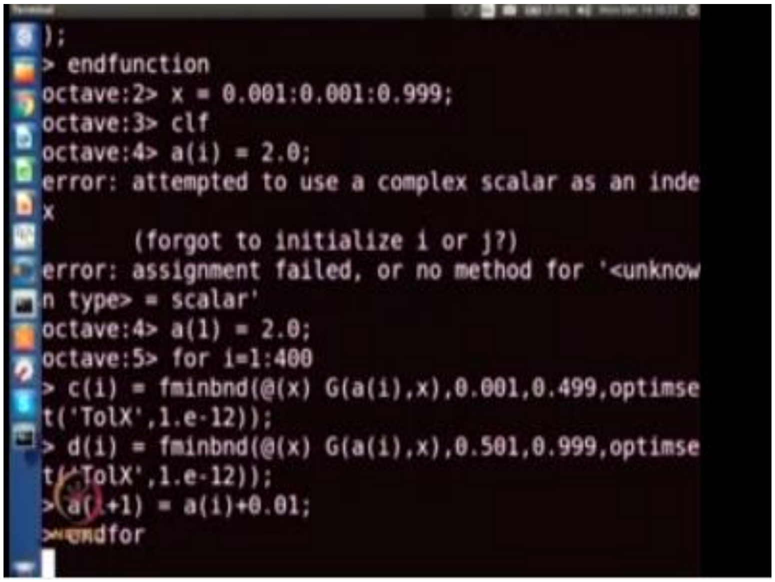

```
);
> endfunction
octave:2> x = 0.001:0.001:0.999;
octave:3> clf
octave:4> a(i) = 2.0;
error: attempted to use a complex scalar as an inde
x
       (forgot to initialize i or j?)
error: assignment failed, or no method for '<unknow
n type> = scalar'
octave:4> a(1) = 2.0;
octave:5> for i=1:400
> c(i) = fminbnd(@(x) G(a(i),x),0.001,0.499,optimse
t('TolX',1.e-12));
> d(i) = fminbnd(@(x) G(a(i),x),0.501,0.999,optimse
t('TolX',1.e-12));
> a(i+1) = a(i)+0.01;
> endfor
```

So we are going to use this so I am going to define a(i) as equal to 2.0 okay so that is be a sorry, a(1) 0, is 2.0 then I am going to say for i=1 to 400 what am I going to do, I am going to identify the minima for that there is a command called fminbnd so this is find the minimum which is bound and where is the minimal, so it has to be found in terms of okay, so you define it in terms of I so the current a so when i=1 it will take a1 and i=2 it we take the corresponding a2which is a different temperature.

So it is going to take a(i,x), then it has to the fmin bind a bound is going to find the minimum for the given function that is for this function, for this function G it is going to find the minima but for that minima you have to say in which interval the minima lies, okay. We know that there is a minima which lies to the left of 0.5 and another minima which lies to the right of 0.5, so i am going to do this minimum calculation twice by giving these two bounds I am going to avoid 0.5 because 0.5 is a point where there is an extreme.

So in order for the computation not to get into difficulty so I am going to do 0012:0.499 so that is the one bound within which it will try to locate a minima and then there is a parameter for the system to do the optimization which is known as tolerance of X, so the tolerance of X I am going to give as 1.e^{-12}, okay. Now this is very important I have a video of mine for about 10, 15minutes trying to figure out what went wrong in one of my earlier recordings, what went wrong is that I also put a ; mark here okay.

So tolerance X is the parameter for which we are giving values, so the value that follows this tolerance X separated by a comma should be just a number okay, so there should be no quote marks on this if you do give then it gives some nonsensical results. So this is very important, so I have defined c, I also define a dfi which is nothing but fminbnd at X so this means that you have to find the minima for this function by varying X for what value of X this function beaches minima, so this is what this art of X means.

So G(a(i),x) and this time we are going to look for a minima in the range 0.501 to 0.999 so opium set I am going to give the same tolerance to which it will determine the minima and that is 1.e^{-12} okay, so we have done this. Now I have to change (i+1)=a(i)+0.01, okay so the temperature or the or the α parameter is going to increase by 0.01 so that is how the temperature is going to be reduced in the calculation.

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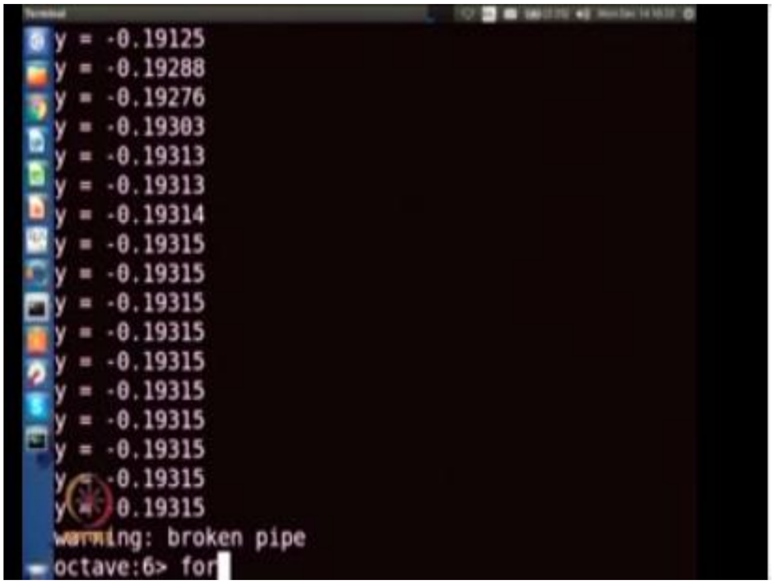

```
y = -0.19125
y = -0.19288
y = -0.19276
y = -0.19303
y = -0.19313
y = -0.19313
y = -0.19314
y = -0.19315
y = -0.19315
y = -0.19315
y = -0.19315
y = -0.19315
y = -0.19315
y = -0.19315
y = -0.19315
y = -0.19315
y = -0.19315
warning: broken pipe
octave:6> for
```

So n for okay, so this is because when I define the function I also did not put the semicolon so it keeps doing this which we can avoid if we do not put the semicolon, so now I am going to I want to plot the phase diagram, right so what is it that we have done so let us take a look at it what I did is in the script.

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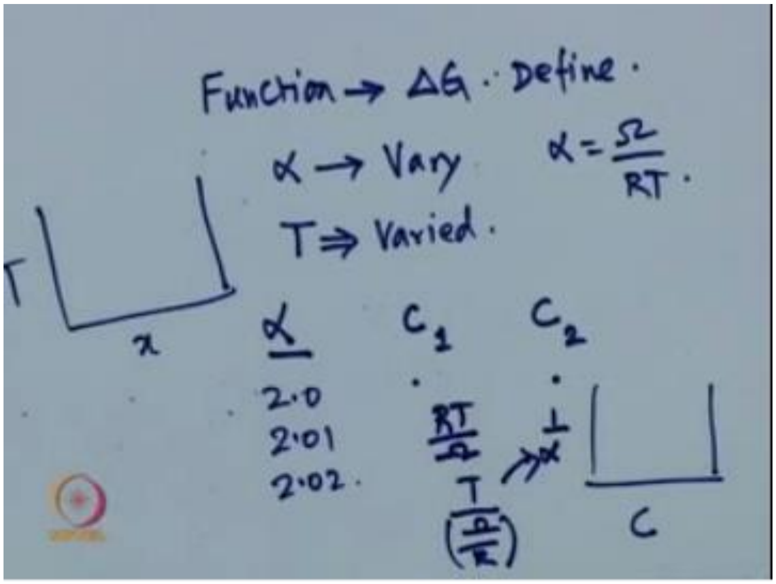

First I define the function, what is the function that I define the Δ G function I defined. Now I took a different α, α vary what does that mean α=Ω/RT so varying α means temperature was varied. So for this varied temperature I found out where the minimum points are, so I have for every α right, a corresponding composition there are two compositions there is one on the A rich side and there is another one on the B rich side okay, so for every α like two or 2.0 or 2.01, 2.02 extra I have identified what this composition is, what this competition is, so we need to plot this so the composition will go here the two compositions corresponding to the particular α value.

But α is actually one by temperature so typical phase diagram is at T versus X. So if I want to plot then I need to plot 1/α, 1/α is nothing but RT/ Ω. In other words the y axis becomes a temperature which is normalized by Ω/R so that is what this is going to be, so I am going to do that exercise.

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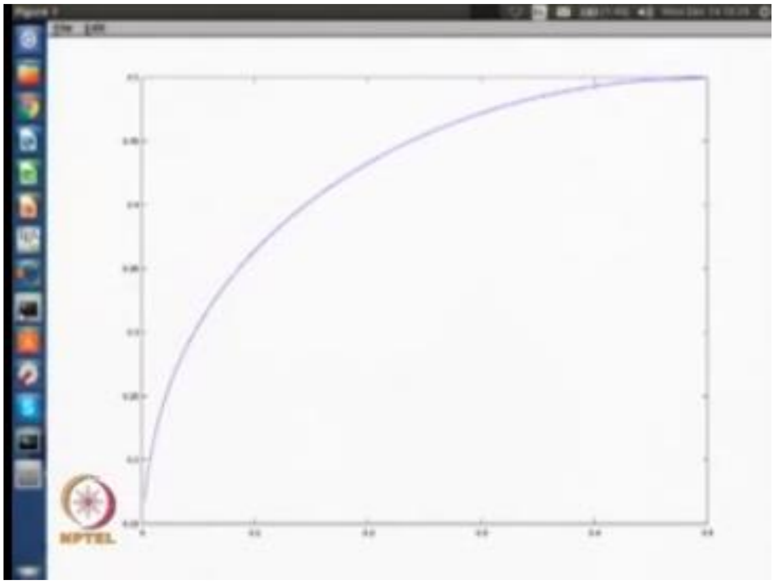

So I am going to say for i=1 to 400 I am going to first take the b(i) as nothing but a(i), okay and far so I have now taken α into a variable called b. What I am now going to do is to plot, first I am going to plot the curve on the left side 2.5 so that minima was identified as (c,1./b) okay, so you have this curve as you can see it is a very nice curve so from 0 to 0.5 it has identified the minimum points.

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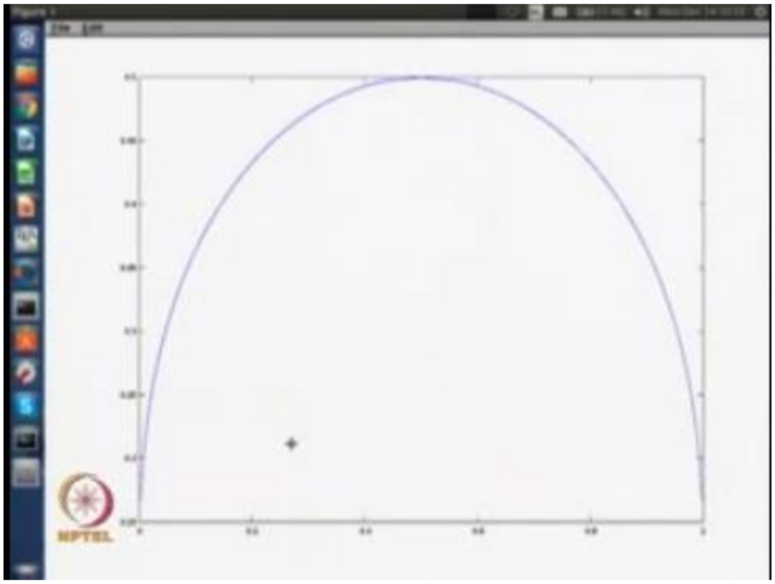

Now I have to plot the other half so I am going to say hold on which means the next plot is going to be plotted on the same curve so i am going to say plot now d which is the minimum points identified to the right of 0.5 I am going to say plot, so now i have a fulfilled diagram, okay. So this again is something that you might have seen in a textbook like gas cal they give both these curves see remember the lost part of this lecture.

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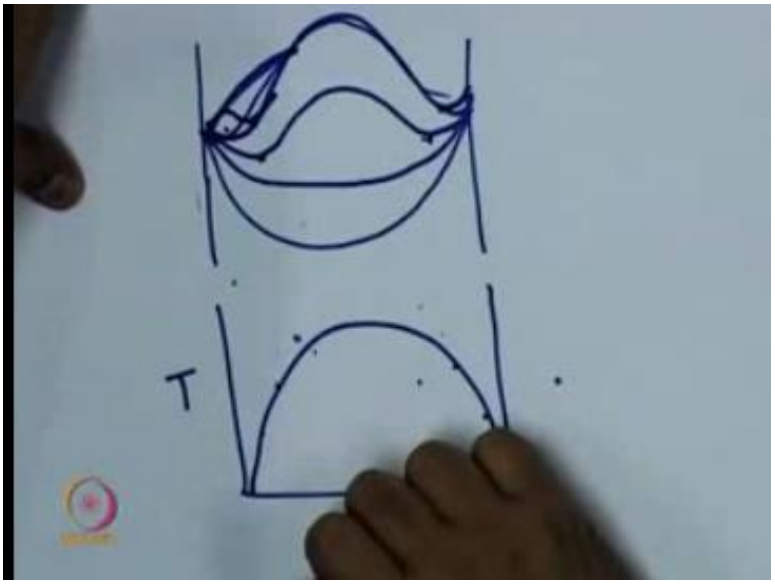

We saw these kind of curves, what were the curves the curves where like you have something like this and then you have something that goes like that and then you have something that goes like that and then that you have something that I think that at temperatures so it will go so subs when the minima point comes so it will still start from here and then it will go something like this like, that okay so this minima points keep shifting to the right and to the left towards the y axis, okay.

So that is what we saw so this should be like this, now what we have done is to identify these points and then plot them, right so you will get T verses in position so that will be like that, so these points actually correspond to these okay, so that is how the phase diagram is identified that is what we have obtained as the phase diagram for the regular solution free energy. Please remember we have used the minimization that is because the ΔG has that structure so the minimum point also happens to be the common tangent point, if it is not then you have to actually do the proper minimization, but in this case because this works we can use this and do this.

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So the next thing to do of course this is the entire phase separation region in which we want to identify this spinodal region. The spinodal region is defined by the points at various temperatures where the second derivative with respect to composition becomes 0, so we will do that and we will try to plot the same thing on this figure so that is the next part of the exercise we will do it next. Thank you.

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