Thermodynamics of Fluid Phase Equilibria
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Lecture – 38
Molecular Theory of Corresponding States

Welcome back in this lecture I am going to cover Molecular Theory of Corresponding States. The theory of the corresponding states goes back to Van der Waals.

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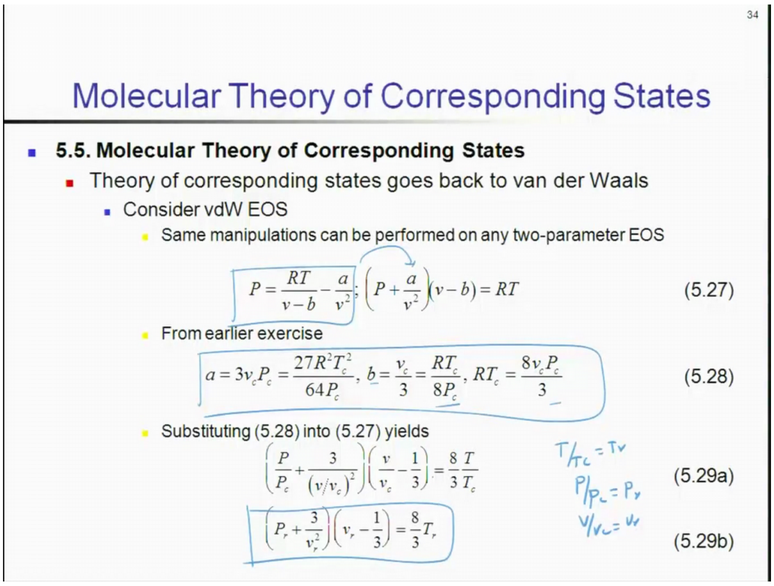

So, let us first consider our Van der Waal equation of state now a typical a two parameter Van der Waal equation of state is given by this expression right or you can write this in this expression.

Now, the a’s and b’s are all calculated based on the fact that at critical point the first and second derivative of pressure with respect to the volume is basically 0 ok. And thus you can obtain as and b’s and in this term which I have written here that a is equal to 3 v c P c ok, this is the term where P is v c by 3 which is this and r T c is nothing, but this.

Now, if you substitute this in this equation you get the following P by P c plus 3 divided by v by v c to the power square v by v c minus 1 by 3 is equal to 8 by 3 T by T c. Now what we are going to define that T by T c is T r, P by P c is P r and V by vc has v r. So, what we got an expression is basically Van der Waals equation of state in reduced temperature pressure and molar volume so, that is an expression of that.

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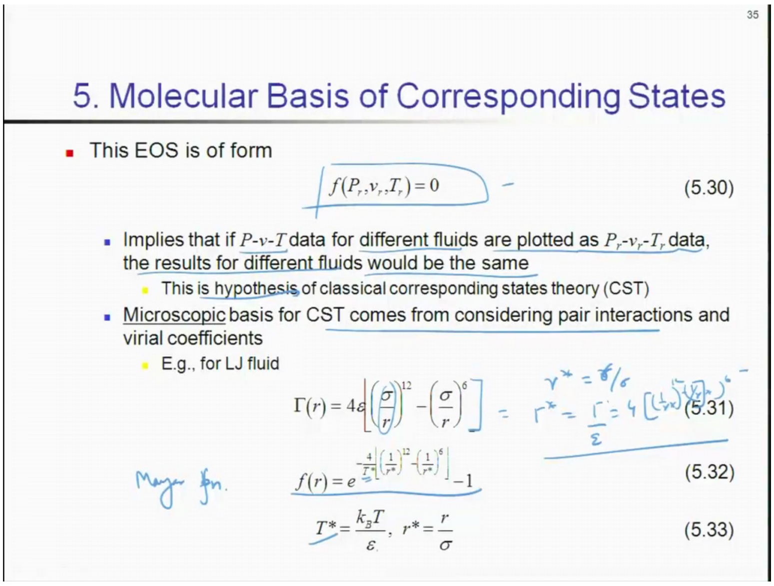

Now this equation basically is in this form ok, and that is what we are talking about in terms of corresponding state theory. So, it this implies that this equation implies that that if P v T data for different fluids are plotted as P r, v r, T r data. The results for different fluid would be same and that is basically the hypothesis of classical corresponding state theory ok.

Now, this is quite useful for if you are using molecular models such as Lennard Jones where sigma's and epsilon are parametized; that means they have different for different fluids. But you can get rid of this epsilon and sigma such that everything is a reduced form then from the same plot you can extract many different properties for different fluids, so that is basically the idea which we try to make use of it.

Let me elaborate on it the microscopic basis for CST is come from the pair interaction and virial coefficient. Let me just go into detail a bit so this is the potential model of Lennard Jones as we have already discussed that this is a non dimensional term. So, if you reduce r as r by sigma ok, then we can get this in terms of reduced potential where gamma star is going to be gamma by epsilon this is 4, and you have this 1 by r star 12 minus 1 by r star 6 ok.

So, this is something which we have already looked at into earlier remember that rs you know in terms of your T star for the Lennard Jones is k T by epsilon r we know already. And this is something which you can write as a Mayer bond or function so where T star here is now simply k T by epsilon.

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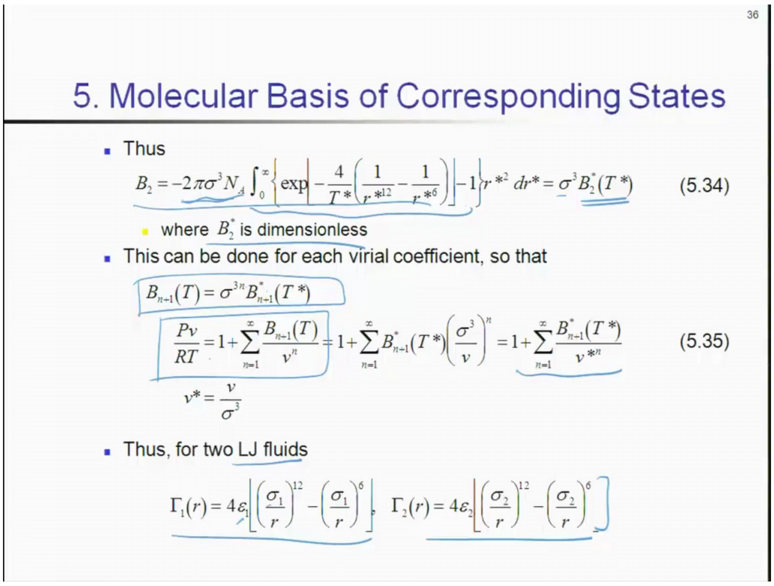

So, you can write this expression B 2 in this term which tells you that that now B 2 if you consider this part then this is basically dimensionalized. So, if this is B 2 is in the terms of the volume, so B 2 if you divide by sigma cube you are going to get or the B 2 star that is what because this is non dimension ok. This part is going to be non dimensional. So, whatever it there can be written in this form where B 2 star is non dimension. Now if you extend this exercise for B 3 B 4 and so forth.

Then one can show that B n plus 1 is equal to sigma to the power 3 n multiplied by the reduced virial coefficient if I order or n plus 1 order and now this understanding I can plug in this virial equation of state which is written here I can write this B n plus 1 in terms of B n star T star sigma cube by v to the power n and thus I got a right hand side which is absolutely independent of the type of molecule so because it is always basically dimensionless.

So, which means basically if I use different sigma and epsilon for 2 Lennard Jones potential the right hand side is going to be same. Now let me just elaborate also on that. So, let us consider 2 l j fluids which is given here, which has different epsilon and sigma's ok. Now for both of them your for both of them for given T star which is a reduced property and v star for both of them they are same then P v by r T must be same ok.

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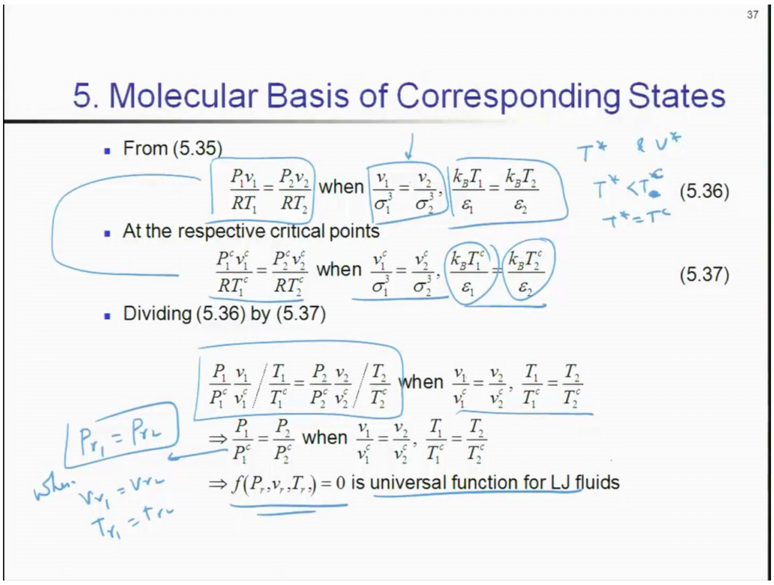

So, ah; that means, when T star and v star are same ok, then that is v star this is T star if they are same for both the fluids then; that means, the right hand side is going to be same in that case the left hand side which is P v by r T must be same. Now I take respective critical points here which means that since v's are same. So, we can consider at a respective critical point v 1 c your v 1 c star is equal to v 2 star and similarly the reduced temperature would be same for simple reason is basically this is at the respective critical point your this expression should hold as well when you have this condition ok.

So, so, this expression below critical at critical will be same once you once you fix this v star and T star. So, this once you fixed it your this expression will be same now. So, you have 2 equations; one when you have T star less than the T c T c here and when we considering T star is equal to T c ok.

So, using these two expressions I can divide it here when they divide this expression this is the two equations ok. What we what I get that P 1, v 1 T 1 P 2 P 1 c v 1 c T c 1 c and this is this will be the for the right hand side P 2 v 2 T 2 v 2 c v 2 c T 2 c and this would be when we are considering the ratio corresponding to v 1 by v c v 2 by v c and T 1 by T c T 2 by T to 2 ok. This we can you can show that this is the case when this will happen ok.

And this would indicate that P 1 by P 1 c and P 2 by P 2 c should be same which essentially means nothing, but P r 1 is nothing, but P r 2 when v r 1 is equal to v r 2 and T r 1 is equal to T r 2. So, when the reduced temperatures are fixed reduced volumes are fixed or same for two different molecules of fluids then the reduced pressure should be also same. This basically tells you or implies that this function is a universal function for Lennard Jones fluids ok.

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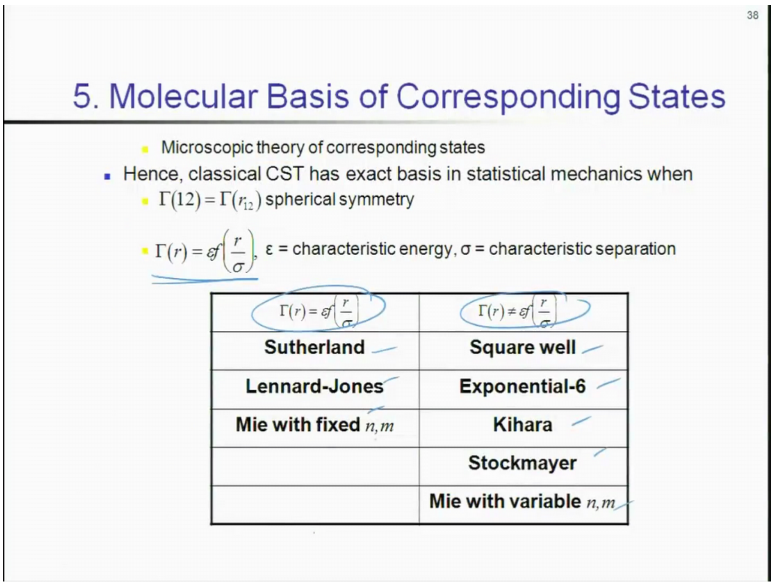

Now, this is beautiful because you can using this expression you can evaluate many things ok. So, this is our microscopic theory of corresponding state, now this particular expression we could evaluate because you are Lennard Jones is basically can be written in this very simple form which is this here.

So, for the case of this we can come up with the classical CST and you have this for Sutherland, Lennard-Jones my with fixed n and m, but if this is not the case such as for the example square well exponential Kihara, Stockmayer Mie with variable, n m then such an expression are not possible to value it ok.

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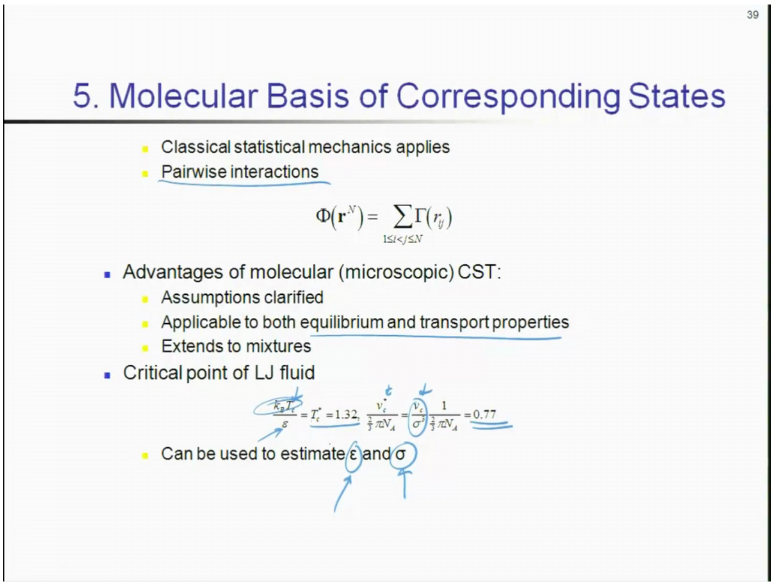

So, the other thing is that for the case of the corresponding state principle the pair wise interactions are important this is something from classical statistical mechanics can be applied for. Advantage of this molecular corresponding state theory is that that this is applicable for both equilibrium and transport properties and it can be extended to mixtures. Now given this information we can evaluate or estimate epsilon and sigma because for Lennard Jones reduced at critical point is known, and reduced volume is known, so the reduce critical point is 1.32 reduced volume is 0.77.

Now given these information you can easily evaluate the epsilon ok, and sigma for Lennard Jones models. Because you would know T c of let us say methane and you know v c also correspondingly v c. So, from v c known knowing that this is 0.77, you can obtain sigma. Similarly oh 1.32 multiplied by k T known from the experiment. You can evaluate epsilon correspond to the Lennard Jones model for that particular fluid ok.

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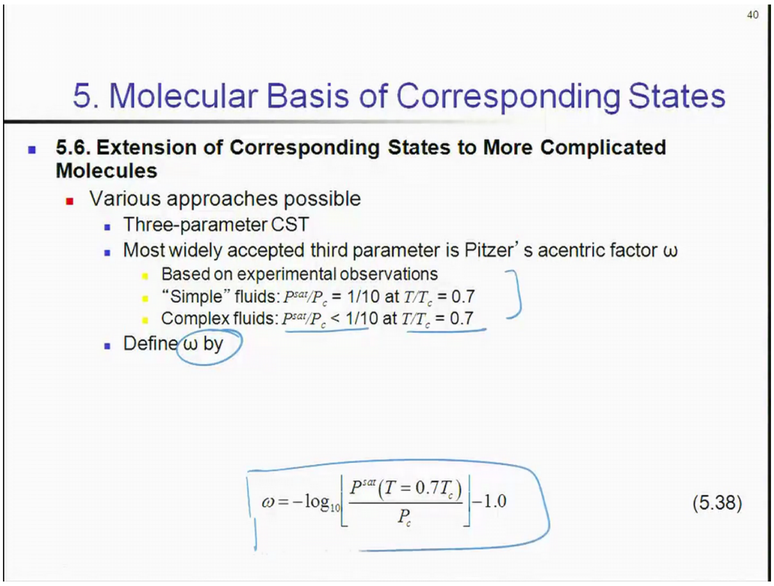

So, let me try to extend this corresponding state to more complicated molecules. A various approaches are possible are usually a 3 parameter CST is considered most widely acceptable third parameter is a Pitzer acentric factor which basically takes care of the shape. Based on the experimental observation a simple fluid is considered when you have P sat by P c; that means, P sat at reduced P sat is equal to one point 1 by 10 at T by T c is 0.7 and we consider a fluid to be complex when reduced P sat is less than 0.1 at reduced temperature of 0.7 ok.

So, using this information we defined a central factor as simply the deviation from 0.1 in a logarithmic scale ok. So, this is P sat at T is equal to 0.7 T c divided by P c log of that minus 1.0 ok. So, this is our acentric factor.

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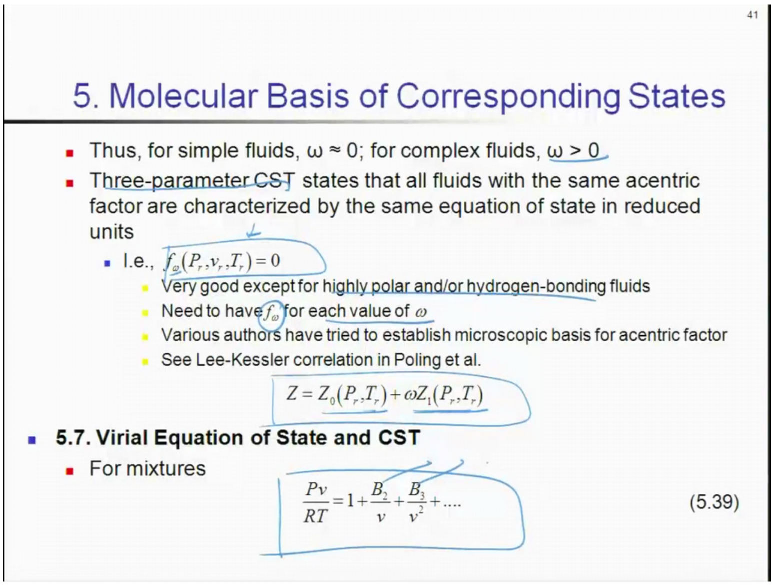

So, for the simple case simple fluid the acentric factor should be 0 because this is going to be 1 by 10 and which will cancel out this and w should be 0 for complex w will be greater than 0.

So the three parameter CST states, that all fluids with the same acentric factor are characterized by the same equation of state in reduced energy. In other word we have the same corresponding state principle, but now you have three parameter using this three parameter CST the property can be characterized by the this equation of state in a reduced form. So, the w here in subscript indicates that this is basically equation incorporates the acentric factor.

So, very good approximation except for highly polar oil hydrogen bonding fluids the problem is that we must find out f of w for each value of w. Now various authors try to establish this macroscopic basis for acentric factor and typically you know people like Lee Kessler and others have extensively work in this area. So, here the usual way to add this contribution is by considering the case of simple fluid here plus add the term which is due to the acentric bond that is why you have Z 0, P r T r and w Z 1 P r T r ok.

So, let us try to understand this how to deal with this ok. So, I will come back to this part and let me just first describe this virial equation of state for the mixtures for the mixtures we will consider the same expression.

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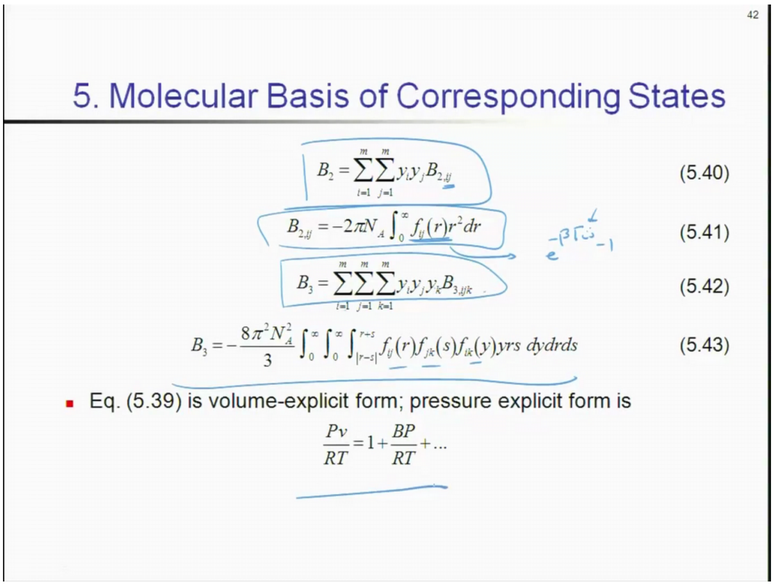

But now the B two's B B 2's B 3's and so forth will be a combined value for the mixtures which typically written here as B 2 is summation double summation of y 1, y j the composition multiplied by B 2 of ij where B 2 y j can be related to the Mayer function as we have already seen the except that B ij contains e to power minus beta ij minus 1. So, this becomes that interaction parameter or potential energy between the unlike species i and j.

Similarly, B 3 is a is a triple and summation where we considered y i, y j, y k, B 3 ij k where y range from 1 to m and so forth others. And B 3 is more complicated expression where we considered 3 major bonds ok. So, I would not go through in the details of that ok. So, we can consider volume explicit term or as well as for mixtures you can also consider pressure explicit terms ok.

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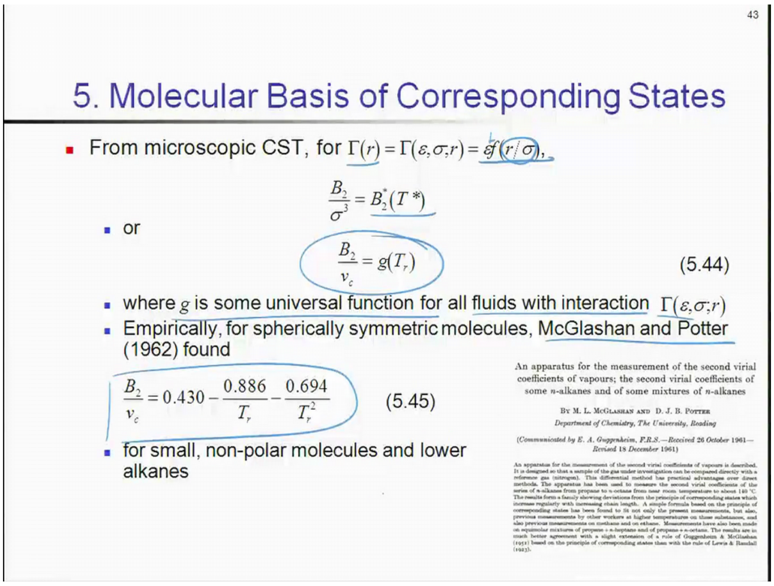

Now, let us go back to the to the corresponding state here for the from macroscopic corresponding state theory we always try to use this potential model having similar, having this kind of expressions where you have epsilon is outside and f is just a function of reduced distance ok.

Now, for B 2 we have already evaluated that B 2 can be reduced by sigma cube getting B 2 star as a function of T star or we can consider B 2 by v c is equal to g T is r where g is some universal function for all fluids with interaction parameter. Now empirically people have tried to use obtained this term in terms of T r. So, one of those is McGlashan, and Potter we have they have tried to come up with this expression, this is for small non-polar molecules, and lower alkanes.

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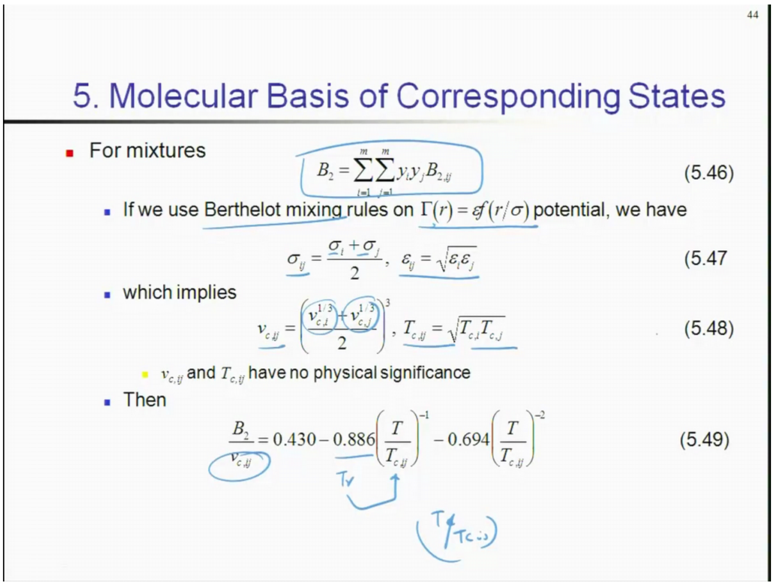

Now, this has been extended for mixtures also. So, for mixtures we have already discussed this now given that potential model is this for which this is applicable this the average distance of sigma ij is considered as arithmetic mean of the individual sigma's, epsilon ij is considered as a geometric mean that is due to the Berthelot mixing rule. Now this implies that I can consider v cij as simple this because sigma can be considered from here, to the power 3 and T c ij is nothing, but T c as a geometric mean of T c 1 and T c 2 or T c i and T c j.

Now, having this information known the virial coefficient here can be only modified for v c ij and T r this is T r, this was T r. Now T r can be given as here T c T by T c ij ok. So, the same expression as was found by Glashan and Potter can be utilized to obtain v 2 from B 2 from the experimental data’s or in general these correlations can be used.

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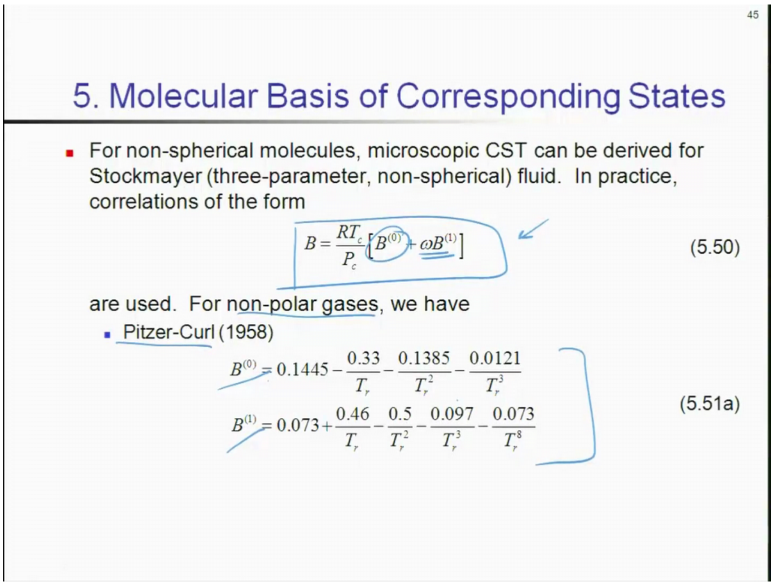

So, for non spherical molecules the microscopic CST can be derived for noise you know Stockmayer three particle, non spherical fluid. Now, typically for non spherical fluid we have come up with an expression which is given here the B second virial coefficient, contains r T c by P c this is a term which is a due to spherical, this is due to the contribution due to non space spherical nature of the particle.

This is a commonly used expression, for non polar gases many different expressions have come the Pitzer Curl expression suggests this term where B 0 is this and B 1 is given by this which depends on T r. Remember that B is only dependent on temperature and that is why only temperature is given here.

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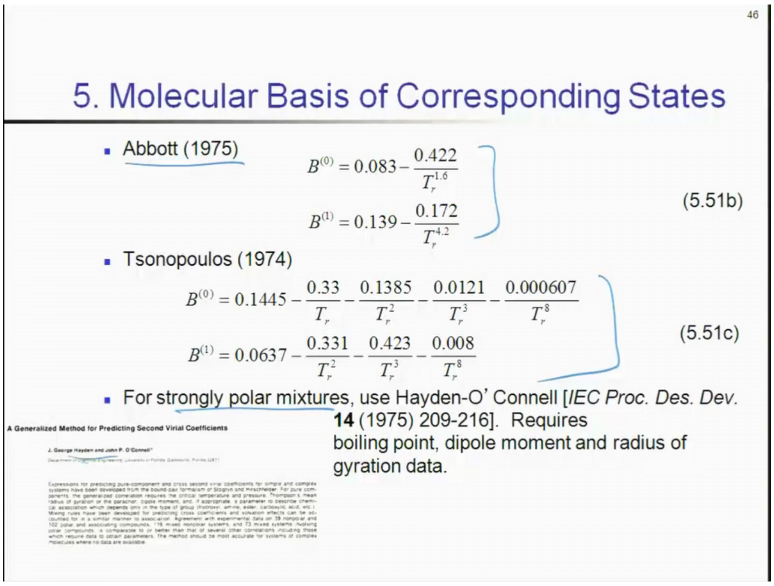

Abbott has also come up with the expression 1975 this is the expression for that. So, the plus gives you expression for these for strongly polar mixtures we one can use the expression given by Hayden, and Connell. Hayden and Connell, but of course, we do not have to remember this remember this is an expression which came up with the extensive exercises.

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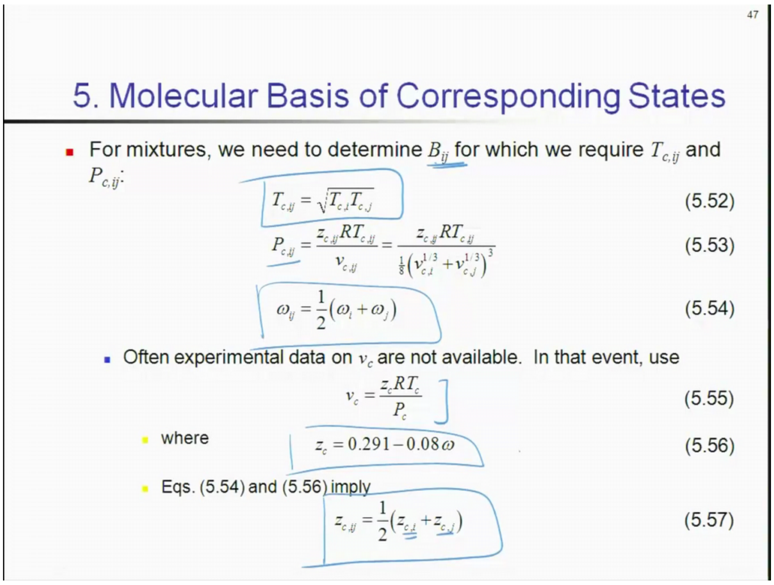

What is important is the methodology what to solve problems using this kind of expressions for ah, so let me just further elaborate on this that this T c s we have to calculate for you know determining B ij we need to find out T r, T r means you need to know T versus T or T v T divided by T c I which was shown here alright.

So, we need to find T c ij in any case T c ij is nothing, but geometric mean of T cs and using the compressibility factor we can get P c ij and omega ij is given as a simple the average of individual acentric factors. Now often experimental data on v c are not available in that case we use simple this expression where Z T r T c divided by P c and this is the expression which is known. So, if you use from this to this we can show that the Z the composite factor is nothing, but the mean value of Z c i and Z c j ok.

Now, this is this may appear to be a little vague and cumbersome, but the idea here is basically there are many correlations which people have come up with to add onto the critical add on to the second wave coefficients based on the non spells spherical nature.

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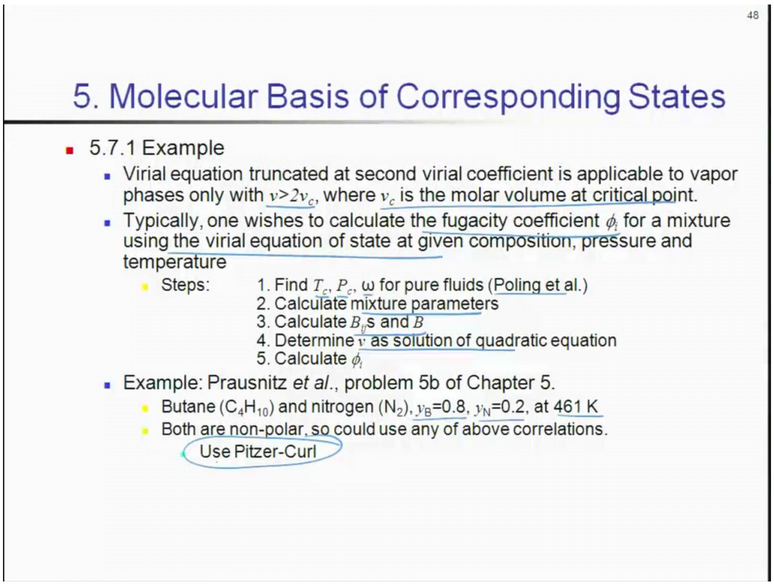

And some of those which we can come up with I will use that to evaluate the fugacity coefficient and that is what the whole idea of being. Why do we use equation of state is because we want to find out fugacity coefficient in order to determine the vapor liquid equilibrium in general the conditions of equilibrium. So, let us try to make use of an example here.

Now, virial equation truncated at second the virial coefficient is applicable to vapor phase only for molar volume greater than 2 v c, where v c is a molar volume at critical point. It tells you simply that a too dense fluid is difficult to represent by virial equation of state, particularly second virial equation of state. Now typically one wishes to calculate the fugacity coefficient for a mixture using the virial equation of state at a given composition pressure and temperature.

So, in that case the typical steps which we like to follow is find T c P c omega for pure fluids this we can get it from pulling at all and many other literature. Calculate mixing or mixture parameters calculate B i S and B, determined molar volume is a solution of quadratic equation and calculate phi's ok. So, let me try to explain using an example from the test book of charter 5.

So, for a given mixture butane and nitrogen the mole compositions are given 0.8 and 0.2 at 461 Kelvin, both are nonpolar and for nonpolar physical expressions are commonly used. So, we have to find out basically phi the fugacity coefficient ok.

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5. Molecular Basis of Corresponding States

	T_c (K)	P_c (atm)	v_c (cc/mole)	ω	z_c
Butane (1)	425.2	37.5	255	0.193	0.274
Nitrogen (2)	126.2	33.5	89.5	0.04	0.290

- From (5.50)

$$B_{mix} = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}$$

$$B = \frac{RT_c}{P_c}\left[B^{(0)}(T_r) + \omega B^{(1)}(T_r)\right]$$

$$T_{r1} = \frac{T}{T_{c1}} = 1.084 \Rightarrow B_{11}(461\text{K}) = -268.8 \text{ cc/mole}$$

$$T_{r2} = \frac{T}{T_{c2}} = 3.652 \Rightarrow B_{22}(461\text{K}) = 15.42 \text{ cc/mole}$$

Now what are the things which we can extract from the literature we can find out the Tc's and Pc's and other emitters. So, let me just summarize it here for butane which is a molecule 1, we have T c given here, P c molar volume figure acentric factor, and comparative factor at critical point at Z c is given to us, similarly nitrogen is given.

So, now what we want to find out is basically the second virial coefficient for the mixtures which from the expression should be this y 1 square B 11 that 2 y 1 y 2 B 1 1 plus y 2 square B 2 2 ok. How do we calculate B's we also know that B is r T c by P c and this is which has a component of acentric factor and this is not 0, which means they are not simple fluids nitrogen is, but not the one which is butane and if you mix it of course, it is not and then thus they this will contribute to something.

Now, let me find out what is the T r now the T is given to us 461, using this we calculate T r 1, T r 2 ok. So, from here we can find B 1 1 and B 2 2 using the expression of B 0 and B 1 using Pitzer Curl expression. So, let me write down here or let me go back and look at this expression again. So, this was a B 0 which would depend it on T r, and this is B 1 which depends on T r.

Now, for individual butane and nitrogen we have calculate, T r so we will be able to calculate B 0, and B 1. Once we calculate B 0 we know T c and P c we care could be B's here; that means, B 1 1 and B 2 2, we can now evaluate. And that is what we did here we evaluated B 1 1 and B 2 2 which came out to be this, but what about B 1 2.

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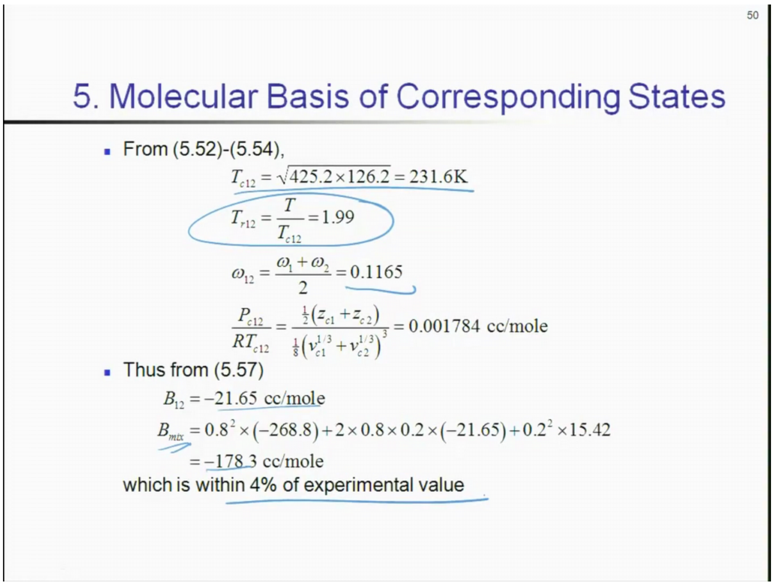

So, in order to calculate B 1 2 we need to find T r and omega. So, to calculate T r we need to find T c 1 2 and can use geometric mean of T c 1 and T c 2 which is what we have calculated here. So, we got an expression of one one, but what about omega. So, omega again we discussed earlier that we will just take out the average value of it, so this is the omega here.

Now given this we should we can directly make use of B 1 2. So, B 1 2 is again we can use it here, we can we can use it here and the T c is there ok. We calculate T c we calculate we can calculate B 0 because we have the information of T r we can calculate B 1, we have the information of T r we know w 1 2 also, but what about P c ok. So, we need to find P c 1 2 also.

So, we know that Z c ij is basically we can take the average value of it. Now Z c if you take the average we know the from here we can and get in it we can we can make use of the average value of this and also the mean value of sigma's and using that information to obtain v c 1 2 also. So, using this we calculate this from there we calculate the Pc's P c once we know we have now B 1 2 P c of 1 2. Once we know we have B 12 which is recovered.

Now, you plug in these expressions of B 1 1, B 1 2, and B 2 2 in a B makes expression which was here ok. So, we obtained the value which is minus 178.3 cc which turns out to be within 4 percent of experimental values, are pretty good you know in that way very nice exercise; that means, B's are good enough for such a system to evaluate.

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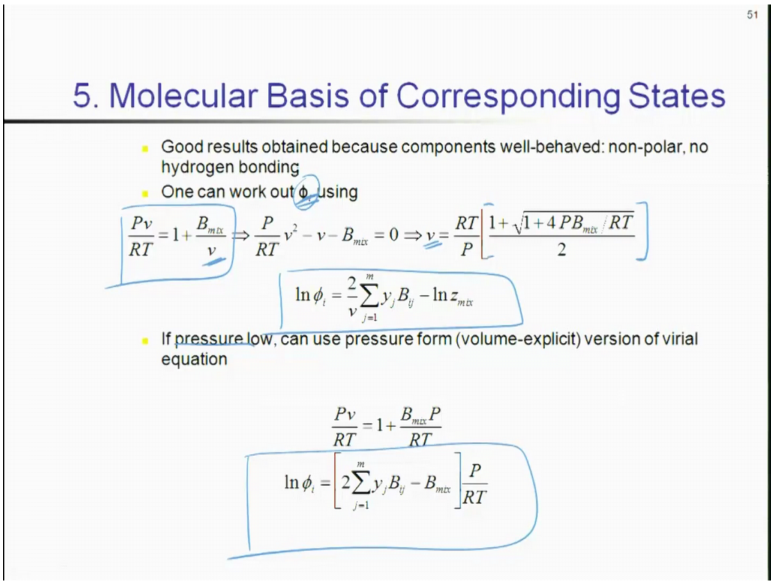

Now, the reason for these good results is because the components were well behaved it was non polar, no hydrogen bond, and that is why it worked well and using this expression now you can obtain phi. So, you have the information of B mix considering the virial equations of state truncated till second virial coefficient. You can write this expression to obtain v the molar volume, and this will be in this way.

So, now once we know the molar volume you can use this expression of fugacity and you can show that this is nothing, but this we will go back to the basics of the identify and show that this is nothing but this one. Now instead of this explicit volume you could have considered the pressure also, and in that case for low pressure we can use such an expression we could get this expression based on the second virial coefficient equation of state for mixtures ok.

So, I would not go to the details how it is it is a straight of it exercise from the basic definition of phi with respect to the integral of terms where the integrand contains the molar volume ok. So, you can extend the exercises by considering the third virial coefficient for the mixtures. So, I will just write down here.

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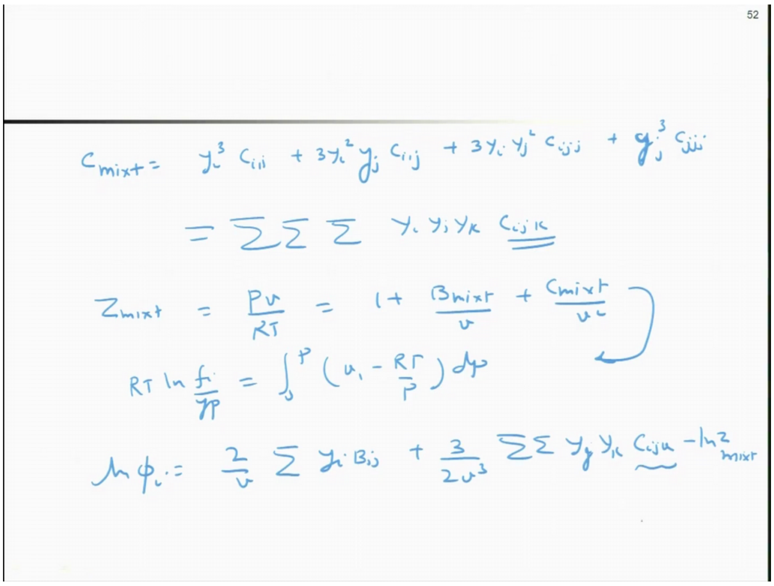

So, this will be the case where if we can evaluate for the third of course, it would become much you know useful, and more accurate the only problem is that it is more cumbersome ok. So, this is the typical c mix we can write in a more compact way as we have shown earlier c ij k ok, where c ij k is nothing, but of course, the second virial of course, but where c ij k is nothing, but the third virial coefficient ok.

Now experimentally you can write this virial equation of state if you recall that the way we calculated virial equation of a second wave coefficient is by considering density very you know approaches towards 0, and that is why we took that the second derivative sorry first derivative of the expressions with respect to the density and obtain the intercept to obtain the second virial coefficient.

Now, in order to obtain this cross coefficient we need to find out significant amount of experimental data. And I would not go into details of this. But let me first write down the Z mix here, which is P v by r T for the case of the mixtures. So, earlier we said that we just would be consider second virial coefficient truncated version, but if you want to add this and somehow you can obtain this then it would be very very useful ok.

So, you can use this expression and obtain your fugacity coefficient ok. And if you can do this exercise for this term you can show that l n phi I is 2 by v summation y i B ij plus 3 two v cube summation double summation y i y j y k c ij k ln Z mixed T ok.

Now this is quite cumbersome in some sense where of course, our difficulty will lie in getting this mixed across third virial coefficients, and for that we need significant experimental data and typically these are very difficult to evaluate, but you can show that using the similar approach as we have done for a second virial coefficient you can also try to do the same thing for third virial coefficient to evaluate these coefficients.

Now, I hope that this discussion helped you to understand the cross putting state principles. Applications of virial coefficient states and particularly second virial coefficient based using different correlations an introduction of acentric factor, to incorporate the non simplicity of the fluids such as a non spherical particle and using that how to obtain fugacity coefficient and this is important because this is something which we use in order to incorporate the fugacity information for the gas phase to evaluate the phase equilibria conditions ok.

Now, with this I think I with this I will stop and we will come back in the next lecture with a new topic. We will start the activity models or particularly the liquid phase mixtures, so I will see you in the next lecture.