Thermodynamics of Fluid Phase Equilibria
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Lecture – 37
Models for Molecular Pair Potentials

Welcome back. In this lecture we will start a discussion and on Molecular Models. Particularly I will be describing commonly or popular models used to express thermodynamic properties ok.

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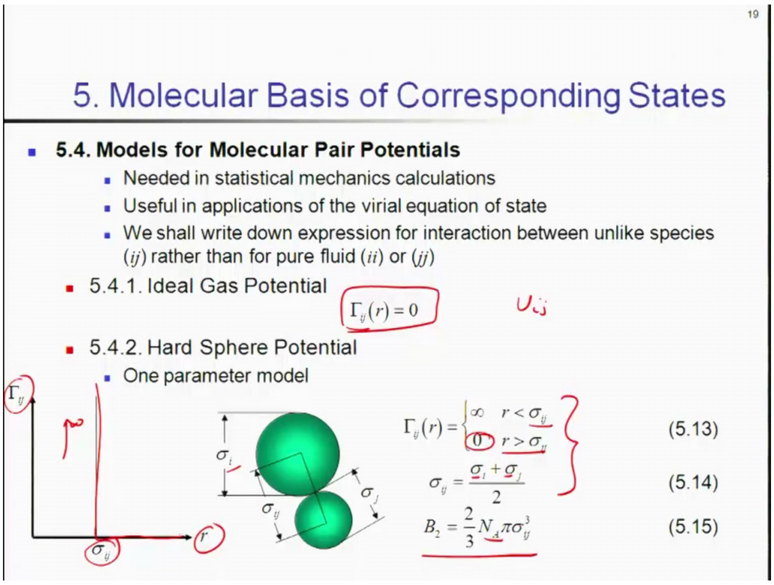

5. Molecular Basis of Corresponding States

- **5.4. Models for Molecular Pair Potentials**
  - Needed in statistical mechanics calculations
  - Useful in applications of the virial equation of state
  - We shall write down expression for interaction between unlike species (*ij*) rather than for pure fluid (*ii*) or (*jj*)
- 5.4.1. Ideal Gas Potential

$$\boxed{\Gamma_{ij}(r)=0} \qquad U_{ij}$$

- 5.4.2. Hard Sphere Potential
  - One parameter model

$$\Gamma_{ij}(r)=\begin{cases}\infty & r<\sigma_{ij}\\ 0 & r>\sigma_{ij}\end{cases} \tag{5.13}$$

$$\sigma_{ij}=\frac{\sigma_i+\sigma_j}{2} \tag{5.14}$$

$$B_2=\frac{2}{3}N_A\pi\sigma_{ij}^3 \tag{5.15}$$

So, these are Molecular Pair Potential Models ok. And it is usually used in statistical mechanics calculation. This is useful also in the application of virial equation of state and, something which we are going to do this exercise in a later part of this lecture. Let me write down the expression for a simple model which we which is basically idle gas potential model. So, as we already say that we are going to define the potential in general by gamma i j, we could have also used something like a U i j ok, but this is used in the text of this particular course and as we would stick to this.

Now, for the case of a like particle, such as pure fluid it will be considering i i for the case of unlike species. Let us say solute in solution will be considering i j. So, for the case of ideal gas potential, we know the ideal gas do not interact and this gamma i j that should be 0 ok. The other most common potential model which is used in statistical mechanics is basically hard sphere potential model ok.

So, in this case what we have is that it is like a billiard ball elastic collisions will occur and, there is there 2 part of the potential depending on the contact of the particle ok. So, if the particle that say of type i and this is of type j, they separated more than this center to center distance sigma i j, in that case if they are separated more than that the potential is 0, if they are less than or at that location the potential is infinity ok.

So, in other word the potential as a function of r will look like a spike at sigma i j ok. So, basically it means this is 0 and, then it shoots to infinity ok. So, in this case sigma i j is basically nothing but the mean value of the diameter ok, we sigma is the diameter in this case. So, it is basically average diameter. Now using this potential model we can obtain the virial coefficient ok, which turns out to be 2 by 3 N A considering the Avogadro number and number of molecules here in a mole and, this pi sigma i j q for a specific 2 particle we can evaluate the virial coefficient, where is easily by considering this potential model.

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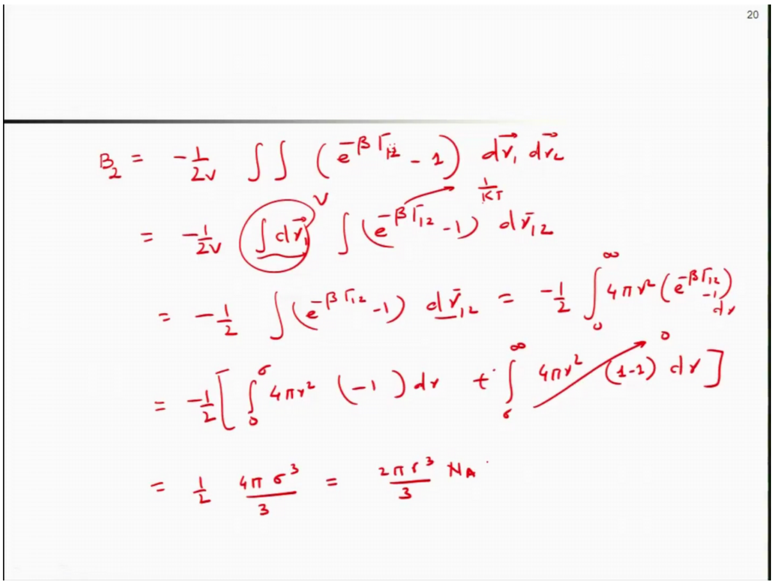

$$B_2 = -\frac{1}{2V}\iint \left(e^{-\beta\Gamma_{12}} - 1\right) d\vec{r}_1\, d\vec{r}_2$$

$$= -\frac{1}{2V}\overset{V}{\boxed{\int d\vec{r}_1}} \int \left(e^{-\overset{\frac{1}{KT}}{\beta}\Gamma_{12}} - 1\right) d\bar{r}_{12}$$

$$= -\frac{1}{2}\int \left(e^{-\beta\Gamma_{12}} - 1\right) d\bar{r}_{12} = -\frac{1}{2}\int_0^\infty 4\pi r^2 \left(e^{-\beta\Gamma_{12}} - 1\right) dr$$

$$= -\frac{1}{2}\left[\int_0^\sigma 4\pi r^2 (-1)\, dr + \int_\sigma^\infty \overset{0}{\cancel{4\pi r^2 (1-1)}}\, dr\right]$$

$$= \frac{1}{2}\,\frac{4\pi\sigma^3}{3} = \frac{2\pi\sigma^3}{3} N_A$$

So, let me just describe that. So, what is a virial coefficient? So, virial coefficient in for the second one is defined as minus 1 by 2 v integral double integral Mayer function which is e to the minus beta potential energy of i and j minus 1 d r 1 d r 2. So, this we can replace this as 1 2 ok. Now I can rewrite this expression as d r 1 e to the minus beta gamma 1 2 minus 1 d r 1 2 well remember that beta is nothing but 1 by K T, where K is Boltzmann constant.

Now, this is basically a vector. So, if you integrate a vector you will get a volume V. So, what we have is 1 by 2 integral minus beta gamma 1 to minus 1 d r 1 2, or I can write this as a simple simply 1 bias 2, this is a volume element in differential form ok, remember this is a vector. So, this is going to be 4 pi r square d r beta gamma 1 2 minus 1 d r now this is in scalar.

Now, if we are going to integrate from 0 to infinity using the potential model. So, since the potential model has 2 parts and it depends on the condition whether it is less than or greater than sigma i j. So, considering is the same particle that means, of size sigma we can rewrite this expression as 1 by 2 0 to sigma ok, 4 pi r square d r plus sigma to infinity 4 pi r square this d r. Now, when r is less than sigma we know is infinity. So, in that case exponential term will be 0 when gamma is infinity this is 0; that means, this would be only minus 1 in this case when r is greater than sigma gamma is 0 in that case exponential term is 1 1 minus 1 is basically 0 and this would be 0 ok.

So, what we have is 1 by 2 4 pi sigma q by 3 and, this is 2 pi sigma q by 3 ok. So, that is what we have written here, but this is only for pair of molecule. So, if you consider Avogadro number of molecules it will be for the molecular systems, it will be simple if multiplied by N A ok; that means, you are considering the mole of the system. So, this is how we can evaluate virial coefficient for a simple model such as hard sphere model.

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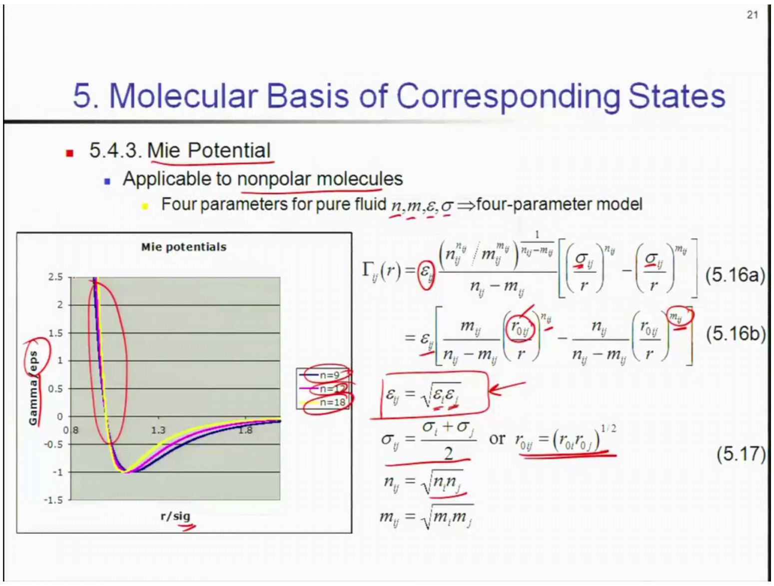

5. Molecular Basis of Corresponding States

- 5.4.3. Mie Potential
  - Applicable to nonpolar molecules
    - Four parameters for pure fluid $n, m, \varepsilon, \sigma \Rightarrow$ four-parameter model

$$\Gamma_{ij}(r) = \varepsilon_{ij}\frac{\left(n_{ij}^{n_{ij}} / m_{ij}^{m_{ij}}\right)^{\frac{1}{n_{ij}-m_{ij}}}}{n_{ij}-m_{ij}}\left[\left(\frac{\sigma_{ij}}{r}\right)^{n_{ij}} - \left(\frac{\sigma_{ij}}{r}\right)^{m_{ij}}\right] \quad (5.16a)$$

$$= \varepsilon_{ij}\left[\frac{m_{ij}}{n_{ij}-m_{ij}}\left(\frac{r_{0ij}}{r}\right)^{n_{ij}} - \frac{n_{ij}}{n_{ij}-m_{ij}}\left(\frac{r_{0ij}}{r}\right)^{m_{ij}}\right] \quad (5.16b)$$

$$\boxed{\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}}$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad \text{or} \quad r_{0ij} = \left(r_{0i} r_{0j}\right)^{1/2} \quad (5.17)$$

$$n_{ij} = \sqrt{n_i n_j}$$

$$m_{ij} = \sqrt{m_i m_j}$$

Now, let me describe a bit more on other models which are also available the reason is that we have to take consider other models because, the hard sphere model do not capture the attractive part ok. So, it is only the repulsive part here.

On the other hand we know the molecular system does have attraction, as we have already looked into or went through the intermolecular forces which are available in molecular systems, such as dispersion you know dipole interactions and so forth inductions let us start again. So, all right so we must have the attractive part in the potential model and, as there are various different potential models which have been developed which depends on different parameters.

So, let us consider the 1 which is a very generic potential model that is a Mie potential ok. It is applicable to nonpolar molecules, it is a 4 parameters for pure fluid and m epsilon sigma and this is written in this form epsilon is of course, we know is a well depth of the potential model ok, epsilon is well depth and then the other parameter sigma is of course, the size of the particles. So, this can be written in this form epsilon i j m i j and i j minus m and this r 0 ok, is used r 0 i j divided by r and i j and m i j and i j minus m i j and this is again in term in terms of m i j.

So, it appears to be very very complex, but the reason for designing it because this allows some flexibility in the potential by parameterising, to a specific molecules of fluids properties and obtaining the right values of n n m. Usually n and m are considered not same. Now I usually you know this can vary depending on the molecular complexity, but let me just first explain what is epsilon i j. So, epsilon i j is basically nothing but we considered to be geometric mean of epsilon i and j, which are corresponding well depth of particle i, or molecule i and epsilon j is basically well depth of molecule j sigma i j is nothing but the average of the diameter ok.

Similarly, sigma we can consider this also, or we can also considered in this form ok. So, because one of the important thing is that this is this has a very sound statistical mechanical origin whereas, this is a bit of weak approximation. So, we can consider these or that m i j is considered as a geometric mean of n i and n j and m i j is m i m j, if it is a pure fluid of course, this becomes much simpler, but this is applicable to a mixed system.

Now, if you consider this by potential as a function of r, particular in reduced form where r is reduced by the sigma and as gamma is reduced by epsilon, what we can notice is that is the shapes is more or less same the well depth since it is divided by epsilon is here minus 1, but the tail here varies depending on what is the value of n here ok; however, you look at the this repulsive part is more, or less not getting affected by this number m here.

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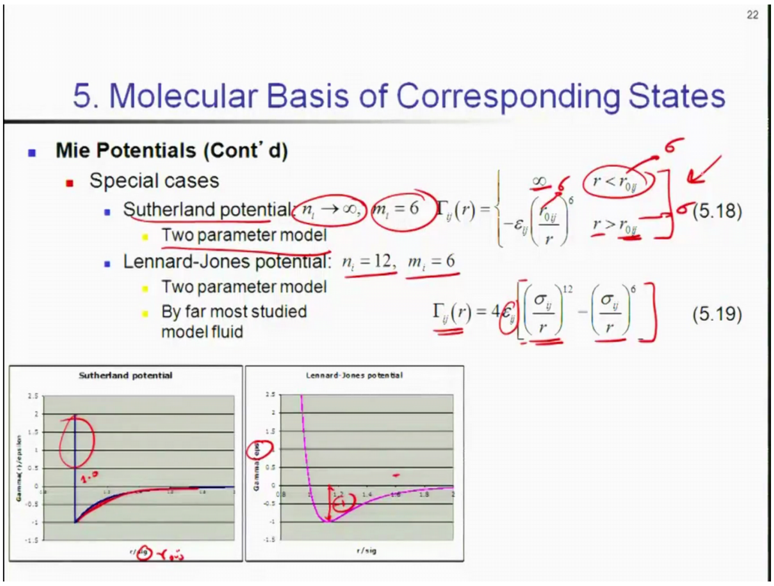

5. Molecular Basis of Corresponding States

- **Mie Potentials (Cont' d)**
  - Special cases
    - Sutherland potential: $n_i \to \infty$, $m_i = 6$
      - Two parameter model
    - Lennard-Jones potential: $n_i = 12$, $m_i = 6$
      - Two parameter model
      - By far most studied model fluid

$$\Gamma_{ij}(r) = \begin{cases} \infty & r < r_{0ij} \\ -\varepsilon_{ij}\left(\dfrac{r_{0ij}}{r}\right)^6 & r > r_{0ij} \end{cases} \qquad (5.18)$$

$$\Gamma_{ij}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^6\right] \qquad (5.19)$$

Now, there are special cases which are more popular based on the Mie potential. So, you have Sutherland potential, where n i is are considered to be infinity and a m i is 6. So, when you plug in this x is this values here, this values to this equation, what you get is basically this expression that for r less than r 0 i j which is basically the average kind of diameter, which is basically the mean or the specific diameter or the distance between i and j, this is infinity on the other hand when r is greater than this value you have this epsilon i j and r 0 i j divided by r to the power 6 ok.

Now, this is a 2 parameter model because, you still have epsilon r you can replace r by sigma also it will work in this way sigma 0 i j or something like that. So, there are 2 variables which we have to worry about it ok, or more commonly potential models which are by far most studied is with Lennard Jones model and, here the n i and m m is are absolutely fixed. So, what we have is n i is 12 m i is 6 and this is sometimes also called 12 6 potential ok.

So, you have 4 multiplied epsilon i j again well depth and, sigma by r sigma by r here to note that this is a non dimensional parameter, or non dimensional term and the potential model is basically the unit of epsilon. Now you can compare these expressions here. So, gamma by epsilon divided by r is absolutely infinitely infinite here, up till this if you if you divide by sigma that is here in this case i j, then you can see this is 1 and from here this is the tail which we get ok.

On the other hand if you the Lennard Jones molecule, you can this is a soft repulsion here this is a hard repulsion remember, this is a hard sphere potential model repulsive part, it is a hard repulsion, this is soft repulsion and this is the well depth here, you can see again it is a minus 1 because, it is divided by epsilon otherwise it was going to be minus epsilon. Now what we can do is we can actually try, now using this motor potential model. And try to connect particularly this 1 and, try to connect this potential model to Van der Waals equation of state virial coefficient ok. And let us first try to evaluate virial coefficient for Sutherland kind of potential.

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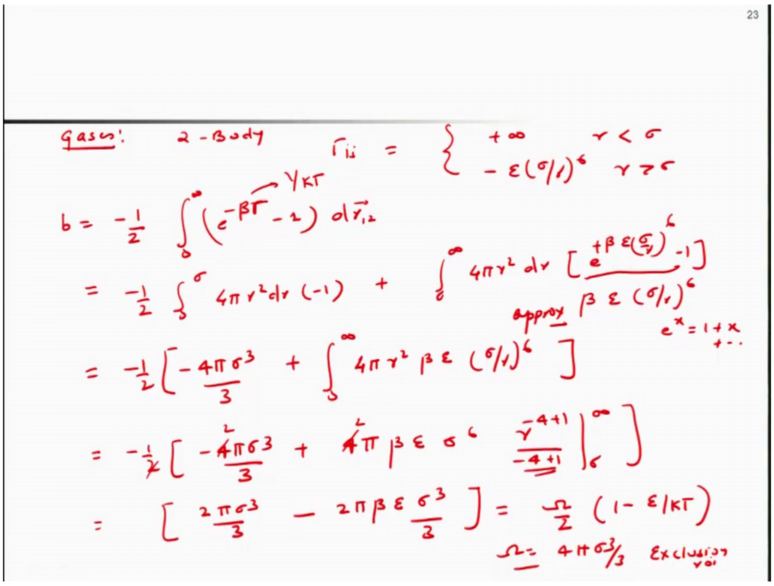

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Gases: 2-Body $\Gamma_{ij} = \begin{cases} +\infty & r < \sigma \\ -\varepsilon(\sigma/r)^6 & r > \sigma \end{cases}$

$$b = -\frac{1}{2}\int_0^\infty \left(e^{-\overset{\nearrow 1/kT}{\beta}\Gamma} - 1\right) d\vec{r}_{12}$$

$$= -\frac{1}{2}\int_0^\sigma 4\pi r^2 dr\,(-1) + \int_\sigma^\infty 4\pi r^2 dr\left[\underbrace{e^{+\beta\varepsilon(\sigma/r)^6} - 1}_{\text{approx } \beta\varepsilon(\sigma/r)^6}\right]$$

$e^x = 1 + x + \dots$

$$= -\frac{1}{2}\left[-\frac{4\pi\sigma^3}{3} + \int_\sigma^\infty 4\pi r^2 \beta\varepsilon(\sigma/r)^6\right]$$

$$= -\frac{1}{\cancel{2}}\left[-\frac{\overset{2}{\cancel{4}}\pi\sigma^3}{3} + \overset{2}{\cancel{4}}\pi\beta\varepsilon\sigma^6 \frac{r^{-4+1}}{-4+1}\Big|_\sigma^\infty\right]$$

$$= \left[\frac{2\pi\sigma^3}{3} - 2\pi\beta\varepsilon\frac{\sigma^3}{3}\right] = \frac{\Omega}{2}(1 - \varepsilon/kT)$$

$\underline{\Omega} = 4\pi\sigma^3/3$ Exclusion vol

So, this is commonly used for gases again we are gases. So, we are going to consider 2 body interaction model and here, this is plus infinity when r is less than sigma minus epsilon sigma by r for r is greater than sigma. So, we are going to consider pure fluid at this point ok. So, our interest is b 2 b 2 into particle. So, let me first wind out b here so, I am I am using the small b here because it is per particle. So, I do not have to write n a here so, per molecule in that sense.

So, we are going to write directly this 0 to infinity. So, I am taking out the double integration and e to the minus beta gamma minus 1 d r 1 2 vector ok. And this I can simplify by considering sigma 0 to sigma in this case we have already known this is nothing but minus 1 and this is sigma by infinity 4 pi r square d r, this term which is going to be exponential plus beta epsilon sigma by r 6 minus 1 ok, remember that beta is nothing beta is 1 by K T all right.

So, now this is fine, but what about this how do we solve it. So, we are going to consider an approximation that at high temperature, I can write I can use this exponential term expansion and consider that e to power x minus 1 is nothing but x this would be the case for high temperature, when 1 by beta or beta is very close to 0 ok.

So, in this case I can replace this by beta x is nothing but here beta epsilon sigma by r by 6. So, this is an approximation, in that case what we have is minus 1 by 2 minus of 4 pi sigma cube by 3 plus 0 to infinity 4 pi r square beta epsilon sigma by r to the 6 ok. Now I can further simplify sigma 6 r 2 minus 4 plus 1 minus 4 plus 1 from sigma to infinity and, I can divide this 2 to get 2 here 2 here. So, what we have is 2 pi sigma cube by 3 and this will become minus 2 pi beta epsilon sigma cube by 3 ok.

So, 3 comes from here and, sigma this will this will cancel out the 6 with 3 and 3 from here ok. So, now I can simplify this expression as simply omega by 2 1 minus epsilon by K T or beta this ok, where omega is nothing but where omega is nothing but 4 pi cube by 3 which is an exclusion volume ok. So, you got an expression of b ok.

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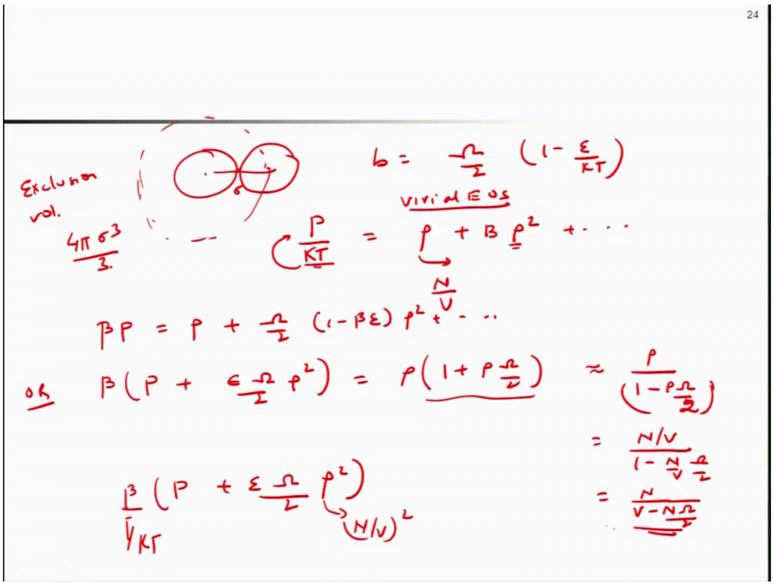

$\frac{4\pi\sigma^3}{3}$

$b = \frac{\Omega}{2}\left(1 - \frac{\varepsilon}{KT}\right)$

virial EOS

$\frac{P}{KT} = \underset{\hookrightarrow \frac{N}{V}}{\rho} + B\rho^2 + \dots$

$\beta P = \rho + \frac{\Omega}{2}(1 - \beta\varepsilon)\rho^2 + \dots$

ok $\beta\left(P + \frac{\varepsilon\Omega}{2}\rho^2\right) = \rho\left(1 + \rho\frac{\Omega}{2}\right) \approx \frac{\rho}{\left(1 - \rho\frac{\Omega}{2}\right)}$

$= \frac{N/V}{1 - \frac{N}{V}\frac{\Omega}{2}}$

$= \frac{N}{V - \frac{N\Omega}{2}}$

$\underset{1/KT}{\beta}\left(P + \frac{\varepsilon\Omega}{2}\underset{\hookrightarrow (N/V)^2}{\rho^2}\right)$

So, remember that exclusion volume is nothing but, if you take this and this. So, that this is your sigma ok. So, this is the amount or this is the volume in spherical volume you are excluding, or this is a volume which we call it exclusion volume. So, considering sigma, it is going to be 4 pi sigma cube by 3, ok.

So, that is what we have done that. So, b is now omega by 2 1 minus epsilon by K T ok. Now the next question is how do we use this expression in equation of state. So, let me apply this to T by K T is so, instead of volume I am going to use density. So, this is the virial equation of state in terms of density b rho square plus this ok. Now the density is a scale about to the molar. So, this would be this is the molar density we will be writing like this N by V, ok.

So, you can get back to the same expression earlier or whatever the earlier in terms of V. So, if you take this in this as 1 by V, you can you can divide this N here and you can get that expression in terms of r T also. So, I am going to use this virial equation of state in this form ok. And now I plug this expression. So, I can write this as beta P this is rho plus omega by 2 1 minus beta epsilon rho square ok, rearrange this expression as beta P plus epsilon by 2 rho square is equal to rho 1 plus rho by 2.

So, I am ignoring the high order term. So, this is rearranging this term here, now this I can approximate this term I can approximate it as rho by 1 minus rho omega by 2 ok. So, this (Refer Time: 19:47) approximate this, then only I am going to get this expression and this is nothing but N by V divided by one minus N by V omega by 2 or in other word N V minus N omega by 2.

Now, this is if you look at this expression this here, beta P plus epsilon this by 2 rho square, then this expression has some commonality to the Van der Waals equation of state. In fact, this is exactly the Van der Waals equation of state. So, let me show this to you so, if I rewrite this expression the last one expression here, instead of rho I can write N by V square and beta is 1 by K T K T I can take it to the other side and, this I can bring it to this side.

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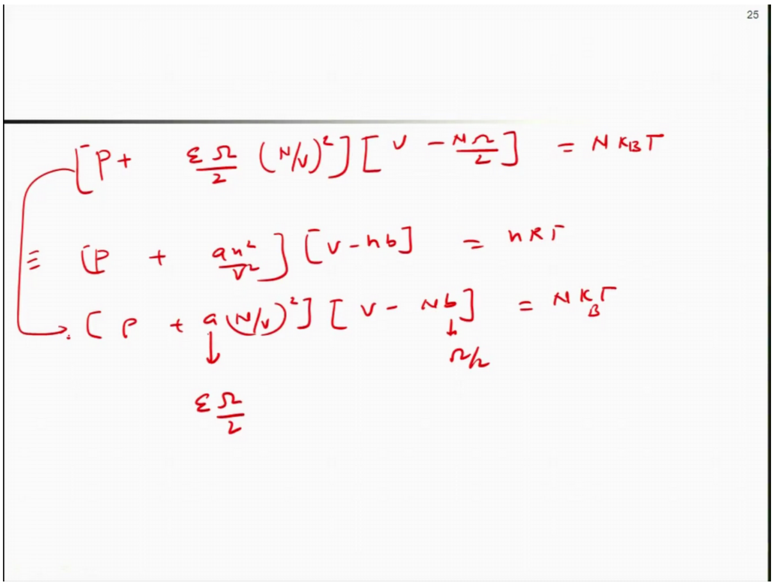

$$\left[P + \frac{\varepsilon\Omega}{2}(N/V)^2\right]\left[V - \frac{N\Omega}{2}\right] = N k_B T$$

$$\equiv \left[P + \frac{an^2}{V^2}\right]\left[V - nb\right] = nRT$$

$$\left[P + \underset{\underset{\frac{\varepsilon\Omega}{2}}{\downarrow}}{a}(N/V)^2\right]\left[V - N\underset{\underset{\Omega/2}{\downarrow}}{b}\right] = N k_B T$$

What I get pressure epsilon omega by 2 N by V square V minus N by 2 is equal to N K B T.

Now, this is synonymous to writing here as a n square by V square, V minus n b is equal to n r T in molar terms, or P plus a N by V square V minus N b is equal to N K T. So, naturally in this case if you look at it b is nothing but omega by 2, for each particle we can consider the exclusion volume contribution from each particle and a is nothing but epsilon omega by 2.

So, this is how it you can compare from here alright. So, this is what we have done using a simple Sutherland potential, we could get a Van der Waals equation of state here.

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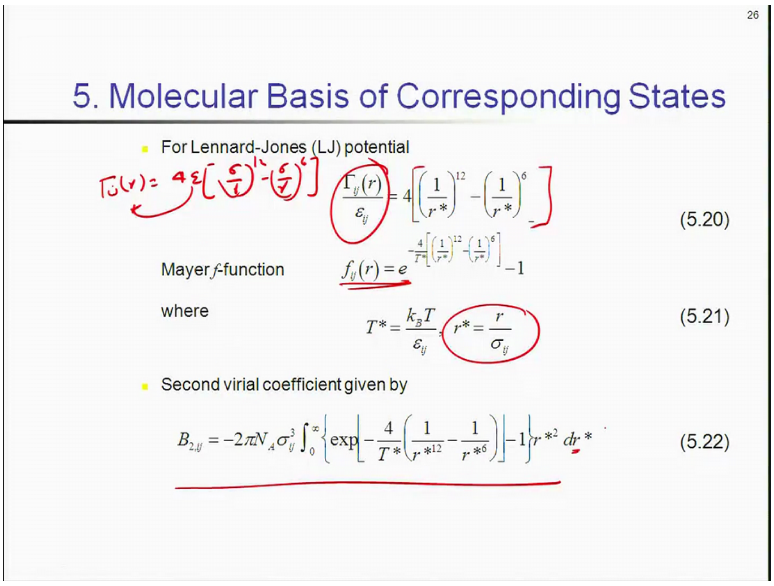

5. Molecular Basis of Corresponding States

- For Lennard-Jones (LJ) potential

$$\Gamma_{ij}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\frac{\Gamma_{ij}(r)}{\varepsilon_{ij}} = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right] \quad (5.20)$$

Mayer *f*-function $$f_{ij}(r) = e^{-\frac{4}{T^*}\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right]} - 1$$

where $$T^* = \frac{k_B T}{\varepsilon_{ij}}, \; r^* = \frac{r}{\sigma_{ij}} \quad (5.21)$$

- Second virial coefficient given by

$$B_{2,ij} = -2\pi N_A \sigma_{ij}^3 \int_0^\infty \left\{ \exp\left[-\frac{4}{T^*}\left(\frac{1}{r^{*12}} - \frac{1}{r^{*6}}\right)\right] - 1 \right\} r^{*2}\, dr^* \quad (5.22)$$

Let me further continue this exercise. Now for the case of Lennard Jones as you can see that we have a term on the right hand side which is which was which is non dimensionalized ok. Now I can rewrite this expression, where instead of writing gamma i j r is equal to 4 epsilon sigma by r 12 minus sigma by r 6, I can write this as if I take out here, this is a non dimensional term. And this 4 multiplied by this non dimensional term which now I can put r star as r by sigma i j I get this expression. And similarly this would be also due to the fact that r star this. So, I can write this form.

So, this has become completely non dimensionalized. Now similarly I can use this expression the Mayer function. And if you use this expression the b 2 will be calculated in this form, where r is basically non dimensional form. So, r is in the units of r star is in the units of sigma ok. So, let us look at what is typically the kind of virial coefficient for Lennard Jones ok.

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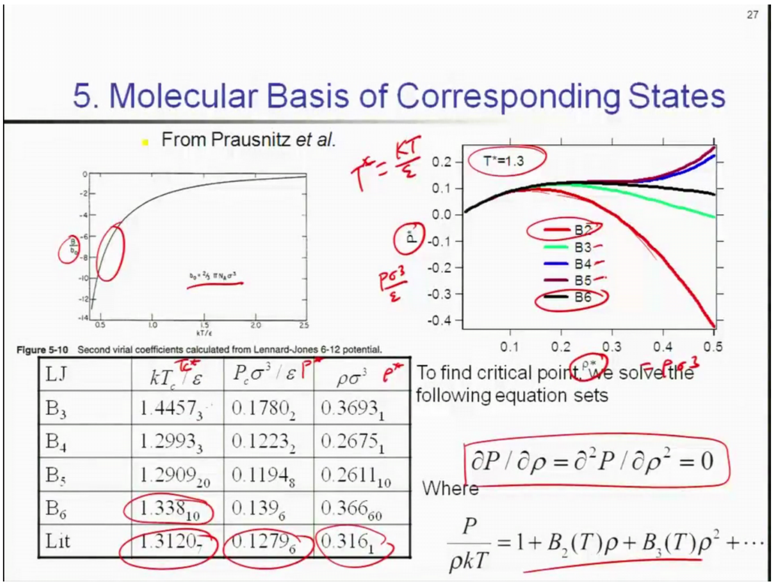

5. Molecular Basis of Corresponding States

- From Prausnitz *et al.*

Figure 5-10 Second virial coefficients calculated from Lennard-Jones 6-12 potential.

LJ	kT_c/ε T_c^*	$P_c\sigma^3/\varepsilon$ P^*	$\rho\sigma^3$ ρ^*
B_3	1.4457_3	0.1780_2	0.3693_1
B_4	1.2993_3	0.1223_2	0.2675_1
B_5	1.2909_{20}	0.1194_8	0.2611_{10}
B_6	1.338_{10}	0.139_6	0.366_{60}
Lit	1.3120_7	0.1279_6	0.316_1

To find critical point, we solve the following equation sets

$$\partial P/\partial\rho = \partial^2 P/\partial\rho^2 = 0$$

Where

$$\frac{P}{\rho kT} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots$$

As so, what we have done here is that second virial coefficient is being plotted. Now this is divided by B 0 which is basically the virial coefficient of hard sphere that is what it is ok.

So, this is why this is non dimensionalize and this is how it increases ok. It tells you that at a lower interaction this is more negative and high interaction it approaches to was 1. So, it is far from that lower interaction it is very close. So, negative virial coefficient indicates there is a cluster of molecules which is close by, if it approaches to our large values closer to 0 and beyond, then it indicates that they are far apart.

So, dispersion or the particles accessibility to the space without being clustered would be indicated by the second virial coefficient having more positive value. Now the virial coefficient has traditionally be also used to see whether we can predict the critical temperature of a given fluid ok, using virial coefficient and what is the number of the virial coefficients which can include in the equation of state.

So, if you can see or this particular expect is being plotted here, for Leannard Jones. So, this is a reduced pressure ok, this is a reduced density here. So, this is nothing but rho sigma cube and this is nothing but so if you include only the in equation state video coefficient 2, then you can see this is something which is it increases the pressure and then decreases ok. And this is at a reduced temperature K T by epsilon, which is T star is 1.3 it is very close to his critical point ok.

As you increase the virial coefficient we observe that certain point there is infection point here ok, which only occurs when you conclude B 4 and B 5 and, somewhere when you include B 6 you do not see that change in the curvature, as seen in B 4 B 5. So, which means basically the virial coefficients are makes the equation of state very sensitive particularly near the critical point.

Now, to find the critical point we can solve this equation ok, this first derivative and second derivative should be 0 due to this inflection point where of course, we know this equation here ok. Now this has been done by some people and, if you include B 3 you can see only B 3 till B 3 the Lennard Jones values the critical point that is your T star, this is your P star and this is your rho star is given in this way ok. So, there is a fluctuation in the value the literature value which is very precise tells you that T star good T C star that is critical point is 1.31 and, the pressure critical pressure is 0.1279 and this is density is 0.3 ok. And we can see that T C is this gets operated when you include only B 5 is under productive, but very close to things.

So, up till b 5 is fine, but when you include B 3 is absolutely over predicts that ok. So, there is a lot of sensitivity and of course, for B 2 there is no there is no way you can obtain the critical point ok.

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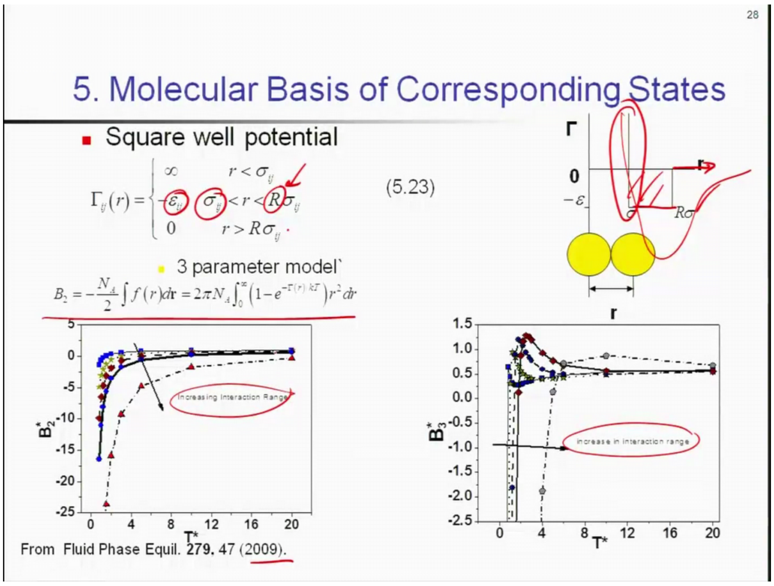

5. Molecular Basis of Corresponding States

- Square well potential

$$\Gamma_{ij}(r)=\begin{cases}\infty & r<\sigma_{ij}\\ -\varepsilon_{ij} & \sigma_{ij}<r<R\sigma_{ij}\\ 0 & r>R\sigma_{ij}\end{cases} \quad (5.23)$$

- 3 parameter model`

$$B_2=-\frac{N_A}{2}\int f(r)d\mathbf{r}=2\pi N_A\int_0^\infty\left(1-e^{-\Gamma(r)/kT}\right)r^2dr$$

From Fluid Phase Equil. 279, 47 (2009).

Now, we can extend this idea this understanding to other potential model, but I would not go into details of that, let me just also summarize what other potential model before we conclude this lecture.

So, is one of the popular early days model has been square well potential, for simplicity it had this heart spherical system, but then there is a constant attractive term. So, there is no gradual changing in the interaction energy as a function of r as in the case of linear Jones potential ok. So, this is very straightforward when they are close by it is infinite potential infinite energy through, which positive energy. Otherwise it is a constant energy up till a well depth lambda, or in this case r and after beyond that it goes to 0 that is what this is a 3 parameter model because, you have to worry about epsilon, you have to worry about the sigma and as well as a this has to be parameterized based on the potential model, or based on the fluids.

Now, you can also evaluate B 2 for that, but we would not do that we can straight away to use the work done earlier by one of my student.

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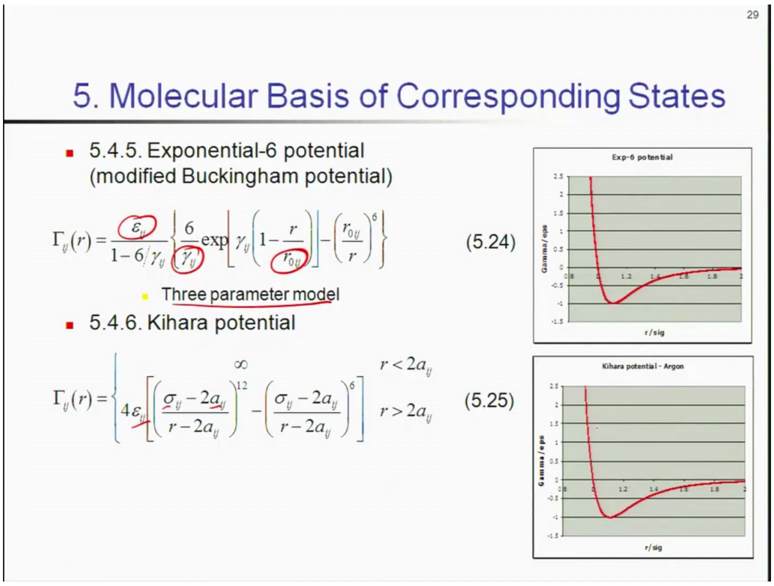

5. Molecular Basis of Corresponding States

- 5.4.5. Exponential-6 potential (modified Buckingham potential)

$$\Gamma_{ij}(r) = \frac{\varepsilon_{ij}}{1-6/\gamma_{ij}}\left\{\frac{6}{\gamma_{ij}}\exp\left[\gamma_{ij}\left(1-\frac{r}{r_{0ij}}\right)\right]-\left(\frac{r_{0ij}}{r}\right)^{6}\right\} \qquad (5.24)$$

  - Three parameter model

- 5.4.6. Kihara potential

$$\Gamma_{ij}(r) = \begin{cases} \infty & r < 2a_{ij} \\ 4\varepsilon_{ij}\left[\left(\dfrac{\sigma_{ij}-2a_{ij}}{r-2a_{ij}}\right)^{12}-\left(\dfrac{\sigma_{ij}-2a_{ij}}{r-2a_{ij}}\right)^{6}\right] & r > 2a_{ij} \end{cases} \qquad (5.25)$$

So, here is B 2 as a function of T star and, you can clearly see that when you increase the interaction energy range that is you are these are changes in the B 2 values. Similarly you also calculated B 3 using something a very sophisticated technique and here, also it depends on the interaction range ok. As we already discussed earlier the B to the negative for such kind of potential, as well as Lennard Jones at low temperature and, it increases to 0 or it increases to positive value at higher temperature ok.

Now, you can extend the potential models for a bit of more complicated molecular structures. So, one of those is exponential 6 potential, which is a 3 parameter model epsilon gamma and r 0 or sigma ok, this is how it looks like it appears to be very close to the Lennard Jones potential, but Lennard Jones is a 2 parameter model. And this it may not be easy for many molecules to get fitted in just 2 parameters the others are high, where as expansion since model as a 3 parameter and hence many molecules such as alkenes are very well fitted with exponential 6 models.

On the other hand if the molecule is non spherical, then it becomes a problem we using this kind of potential model. And have a potential turns out to be one of the good models for that. So, it has epsilon sigma a, these are the parameters and, this it has again 3 parameters here. So, this is the potential model for argon again it may look like similar to the exponential 6 over the Lennard Jones model.

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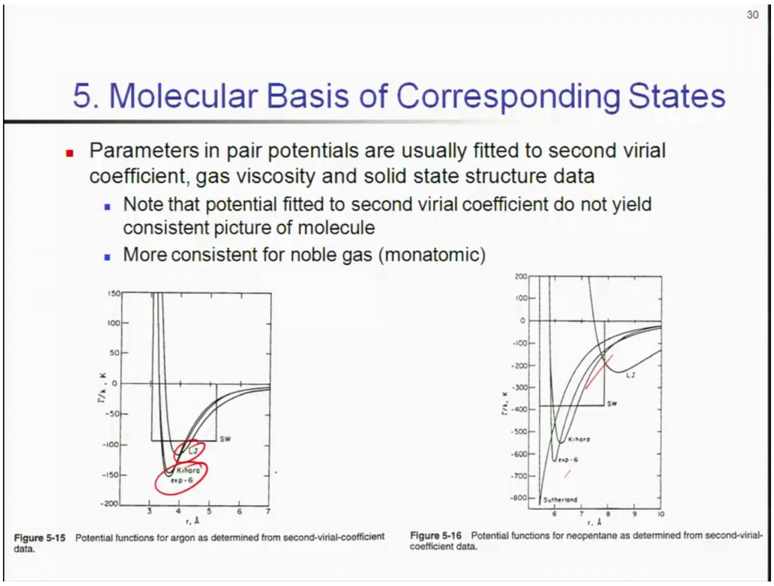

5. Molecular Basis of Corresponding States

- Parameters in pair potentials are usually fitted to second virial coefficient, gas viscosity and solid state structure data
  - Note that potential fitted to second virial coefficient do not yield consistent picture of molecule
  - More consistent for noble gas (monatomic)

Figure 5-15 Potential functions for argon as determined from second-virial-coefficient data.

Figure 5-16 Potential functions for neopentane as determined from second-virial-coefficient data.

Now, these parameters in the pair potentials how do we evaluate ok, typically we use we try to fit to the second video coefficient and, gas viscosity and solid state structures obtained from the experiment. We have already we already discussed that how to evaluate second virial coefficient, considering very dilute you know density. Now the problem is that when you try to fit the potential model using second virial coefficient it does not provide a consistent picture of molecule, which you can see from simple argon and for another case is new penton.

For argon it may look pretty much because, you have what you have done is you can see that for argon different potential model has been fitted and the way it looks like that there is a much lot of large variations in the way the potential models are, but kihere an exponential 6 and L J seems to be the good ones ok, which are close by, on the other hand if you look at new painting there is large variations in that and this all this yield similar potential a similar second video coefficient.

So, it may not yield that if you have a good, if you have a parameters based on circuit video coefficient it will yield all of the properties correctly ok. So, in other ways you consider many different parameters to refine this potential model, but this is an art which we are not going to cover in this course.

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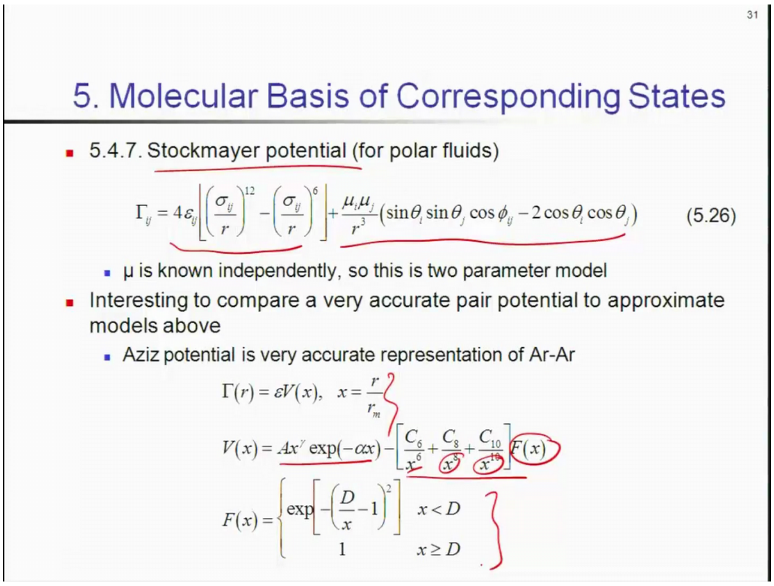

5. Molecular Basis of Corresponding States

- 5.4.7. Stockmayer potential (for polar fluids)

$$\Gamma_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{\mu_i\mu_j}{r^3}\left(\sin\theta_i \sin\theta_j \cos\phi_{ij} - 2\cos\theta_i\cos\theta_j\right) \qquad (5.26)$$

  - μ is known independently, so this is two parameter model
- Interesting to compare a very accurate pair potential to approximate models above
  - Aziz potential is very accurate representation of Ar-Ar

$$\Gamma(r) = \varepsilon V(x), \quad x = \frac{r}{r_m}$$

$$V(x) = Ax^{\gamma}\exp(-\alpha x) - \left[\frac{C_6}{x^6} + \frac{C_8}{x^8} + \frac{C_{10}}{x^{10}}\right]F(x)$$

$$F(x) = \begin{cases} \exp\left[-\left(\frac{D}{x} - 1\right)^2\right] & x < D \\ 1 & x \geq D \end{cases}$$

Now, if the potential models are if the fluids are polar then we have to consider not just the dispersion term which is typically given by the Lennard Jones, but other terms which will have the dipole dipole interaction. So, when you include this L J plus this term where mu is basically the dipole moment. And then we consider such a potential model less Stock Mayer potential.

Now, I will try to explain a argon argon potential, as we have already seen that you know you can have many different potential model. So, exponential says k i L J and square well, that if you indeed for the case of argon how much we lose if we have potential model which is very simple such as Lennard Jones compared to the very complicated potential model as described by Aziz and we call it a as Aziz potential. So, this is the potential which has term, the exponential term here plus this is expansion this is a term which includes r to the power 6, in the reduced term here and this other higher order terms with a with a factor F which is given here ok. Now, I would not go into details of how it was evaluated.

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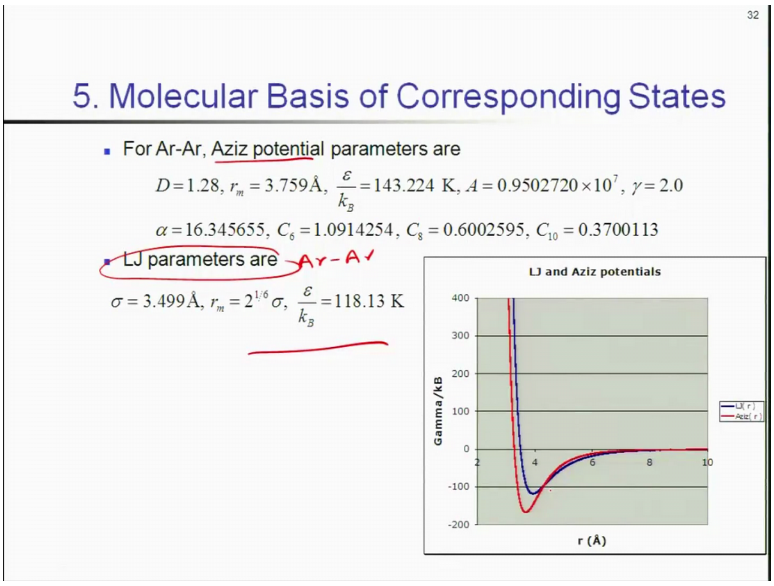

5. Molecular Basis of Corresponding States

- For Ar-Ar, Aziz potential parameters are

$D=1.28,\ r_m=3.759Å,\ \frac{\varepsilon}{k_B}=143.224\ K,\ A=0.9502720\times10^7,\ \gamma=2.0$

$\alpha=16.345655,\ C_6=1.0914254,\ C_8=0.6002595,\ C_{10}=0.3700113$

- LJ parameters are Ar-A✓

$\sigma=3.499Å,\ r_m=2^{1/6}\sigma,\ \frac{\varepsilon}{k_B}=118.13\ K$

So, if you use all these parameters which 1 can get it for Aziz potential and, then compare that to the Lennard Jones parameter are argon argon ok, then it turns out to be that that L J potential is here, the blue 1 and Aziz potential is the red 1, very close by and thus we lose some information and Aziz is a very accurate potential.

So, we lose some information if you use simple models such as algae, but then it is necessary that we can use such models analytically, or numerically and thus we do not prefer to take very complicated though correct models and, we would rather prefer to a simple analytical model which can be solved easily.

So, I hope that in this lecture you got an idea of this intermolecular potential, how to evaluate virial coefficient for such a model and the issues with the parameters as well. So, that will be the end of the lecture I will see you in the next lecture.