Thermodynamics of Fluid Phase Equilibria
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Lecture – 36

Welcome back in this lecture I will start with kind of topic which is slightly different from the topics which we are which we were trying to cover. So, in this lecture I will go through intermolecular forces and molecular basis for corresponding states.

Let me start with a very popular equation of state, which we have been taught earlier that is a virial equation of state; it has an origin from statistical mechanics.

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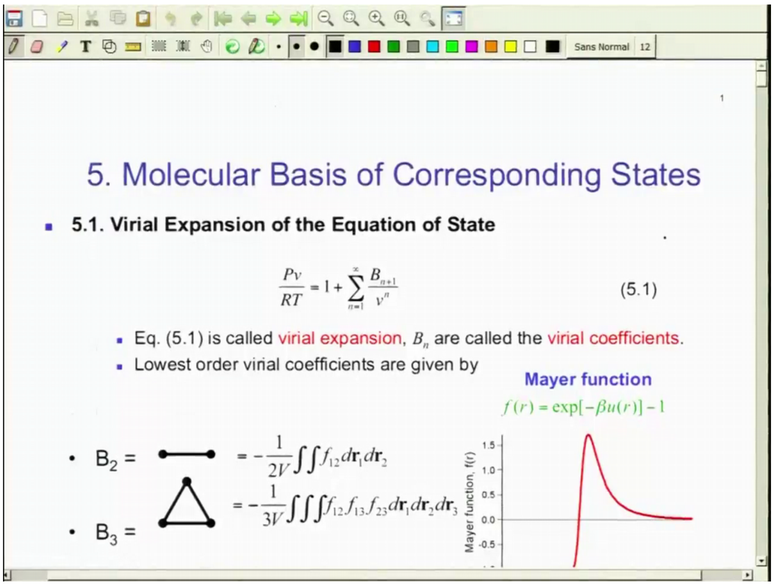


5. Molecular Basis of Corresponding States

- 5.1. Virial Expansion of the Equation of State

$$\frac{Pv}{RT} = 1 + \sum_{n=1}^{\infty} \frac{B_{n+1}}{v^n} \qquad (5.1)$$

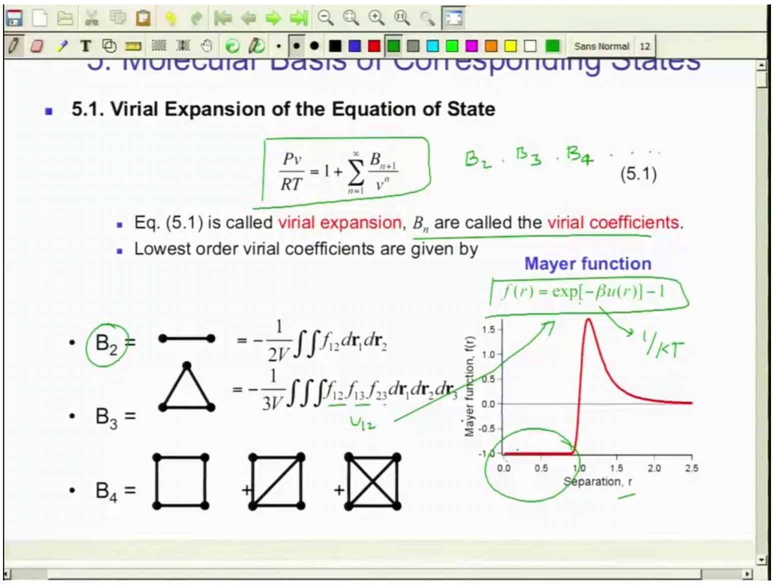
  - Eq. (5.1) is called virial expansion, B_n are called the virial coefficients.
  - Lowest order virial coefficients are given by

Mayer function

$f(r) = \exp[-\beta u(r)] - 1$

- $B_2 =$ $= -\frac{1}{2V}\int\int f_{12} d\mathbf{r}_1 d\mathbf{r}_2$
- $B_3 =$ $= -\frac{1}{3V}\int\int\int f_{12} f_{13} f_{23} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$

So, a typical virial expansion of the equational state is given by this expression ok; where P molecular molar volume P molar volume divided by RT is 1 plus summation of B divided by molar volume to the power n, where n from 1 to infinity where B is nothing but the virial coefficients.



5. Molecular Basis of Corresponding States

- **5.1. Virial Expansion of the Equation of State**

$$\boxed{\frac{Pv}{RT} = 1 + \sum_{n=1}^{\infty} \frac{B_{n+1}}{v^n}} \qquad B_2 . B_3 . B_4 \dots \qquad (5.1)$$

  - Eq. (5.1) is called virial expansion, B_n are called the virial coefficients.
  - Lowest order virial coefficients are given by

Mayer function

$$\boxed{f(r) = \exp[-\beta u(r)] - 1}$$

- $B_2 = \; = -\frac{1}{2V}\int\int f_{12} d\mathbf{r}_1 d\mathbf{r}_2$
- $B_3 = \; = -\frac{1}{3V}\int\int\int f_{12} f_{13} f_{23} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$

u_{12}

- $B_4 = \; + \; +$

So, essentially this is B 2, B 3, B 4, and so forth ok. Now virial coefficients has origin of statistical mechanics, it is not arbitrary and this is directly related to the molecular number of molecules so; that means, B 2 for example, relates to the contribution of two molecules that means a pair of molecules B 3 will be three molecules and B 4 is four molecules.

So, these are the contribution of individual clusters of different sizes to the different sizes to the properties. So, the way it is represented in statistical mechanics is that, B 2 is basically nothing but two particles connected by a Mayer bond, which is given by function f; f is nothing but Mayer function, which is exponential of minus beta is nothing 1 by KT and u is nothing but, the potential of potential energy between these two molecules or two atoms in this case. And this is given as the B 2 is given as double integral of f 1 to d r 1, where r is the vector d r 2.

So, basically you are integrating this Mayer function as a function of distance r between this two from very small values to infinity around the space ok. And that is why in also normalizing by this volume v. You can extend this without going into the details the B 3 has 3 Mayer bonds ok, where now 1, 2 it means that we are considering u 1 2 in this expression and B. Similarly B 4 we will have contribution from three different type of cluster containing four particles having Mayer bonds as depicted in this solid line here ok.

Now, Mayer function is not exactly the potential function, it depends on this function though it depends on this potential energy and as it is different from the typical potential energy, so it is if you plot it this function as a function of r it looks like this function ok. So that means, there is certain contribution where it is 0. So, if you multiply this one Mayer bond by another one, if one of them is 0 of course, the rest the contribution is going to be 0 ok.

So, this is how we express the coefficients in terms of the Mayer functions and, if you can express the Mayer functions in terms of the potential models, then you can evaluate numerically analytically these virial coefficients. However, the difficult part is expressing the potential models. So, that is why; the model potential comes into the picture, which we are going to talk little later or let me also explain how this B 2 gets evaluated experimentally.

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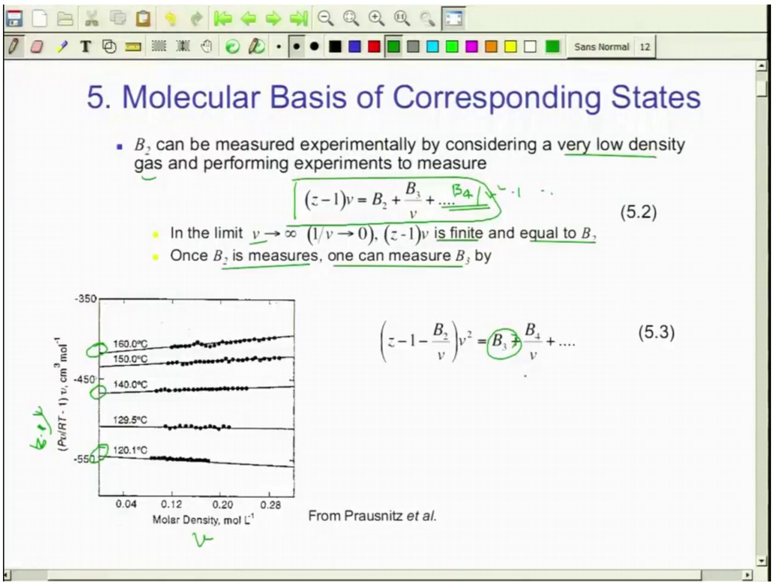

5. Molecular Basis of Corresponding States

- B_2 can be measured experimentally by considering a very low density gas and performing experiments to measure

$$(z-1)v = B_2 + \frac{B_3}{v} + \dots \frac{B_4}{v} \qquad (5.2)$$

- In the limit $v \to \infty$ $(1/v \to 0)$, $(z-1)v$ is finite and equal to B_2
- Once B_2 is measures, one can measure B_3 by

$$\left(z - 1 - \frac{B_2}{v}\right)v^2 = B_3 + \frac{B_4}{v} + \dots \qquad (5.3)$$

From Prausnitz *et al.*

Now, if you can look at this equation again back here this is the virial expansion or this is a virial question. And you expand it in terms of B's and this is nothing but if you look at it here this is nothing but z; so if you multiply if you take z minus 1 multiplied by v you are going to get this expression ok, whether this other terms are high order terms. Now, so that means, you the first equation can be rearranged to get this equation easily, because P v by RT is nothing but z.

So, z minus 1 multiplied by v is nothing but B 2 plus B 3 plus B 4 by v square and so forth. So, if you ignore higher order terms, then you can try to exploit this expression to evaluate B 2, and how do you do that; by considering v molar volume infinity of 1 by v to be 0; that means, we are talking about extremely dilute or very low density systems. So, this can be easily evaluated the B 2 can be easily evaluated for very low density gas. By plotting this z minus 1, v as a function of v in molar volume and you can extrapolate the values in order to get, in order to get B 2 for very low value of v's ok.

And this; so and the limit of v infinity or 1 by v, which goes to 0 z minus 1 v is finite and this is equal to B 2, that is what we are talking about; once B 2 is measured we can measure B 3 by re again rearranging. So, you can take out the B 2 here, now again you look at to this and you can get it of course, this is only at a low density gas and you know that as you increase the number of cluster that me you are interested in more number of particles and; that means, they would be error associated with this approach for the higher order virial coefficient ok. But for the B 2 it turns out to be very nice approach to obtain from this experiment.

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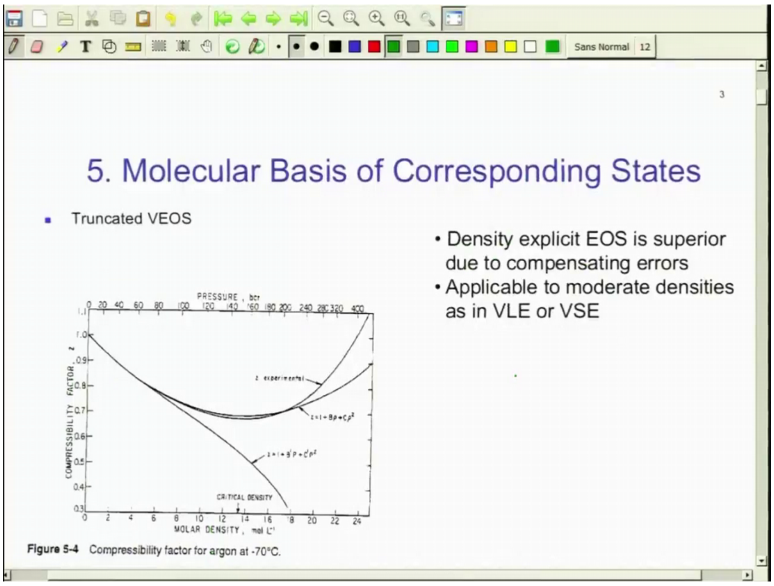

5. Molecular Basis of Corresponding States

- Truncated VEOS

- Density explicit EOS is superior due to compensating errors
- Applicable to moderate densities as in VLE or VSE

Figure 5-4 Compressibility factor for argon at -70°C.

Now, the question is; how good is this virial equation of state ok. Now the virial equation of state also depends on the number of terms, which you go to add, but typically if you connect us consider only up till third coefficient it is a very reasonable approximation for low density gas.

Now, you can express a virial equation at a state in terms of a density or in terms of density or in terms of the pressure in that case the B dash the B's which are typically which we expressed in terms of the Mayer function, this is B's and C's and dash are basically when you rearrange in terms of the pressure ok, where rho is nothing but 1 by v. Now, we can see clearly is that, when you when we plot z as a function of molar density. So, this is nothing but 1 by v that was also the last one this was also 1 by v here ok.

So, if you look at it this is the experimental one ok, z decreases and these increases as you increase the molar density ok. Now, the one which is based on density is very close to the experimental values whereas, the one which is based on pressure deviates from the expansion value. So, the density explicit equation of state virial equational that a state is superior due to the compensating errors, that is something which we asserting here rather than explaining it to in the details, but this is far better superior equational of state, which is better than the pressure one, but is also applicable to a moderate density as in the case of this vapour liquid equilibria or vapor solid equilibria ok.

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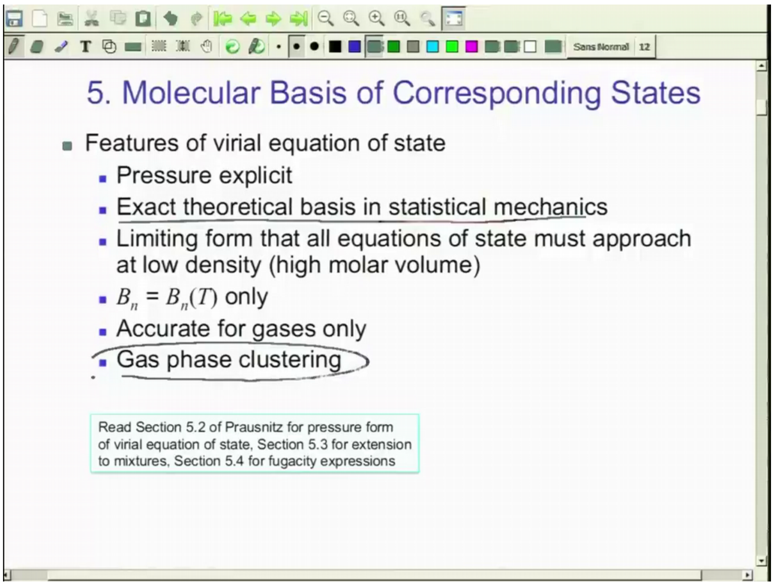

5. Molecular Basis of Corresponding States

- Features of virial equation of state
  - Pressure explicit
  - Exact theoretical basis in statistical mechanics
  - Limiting form that all equations of state must approach at low density (high molar volume)
  - $B_n = B_n(T)$ only
  - Accurate for gases only
  - Gas phase clustering

Read Section 5.2 of Prausnitz for pressure form of virial equation of state, Section 5.3 for extension to mixtures, Section 5.4 for fugacity expressions

Now, what are the features of virial equation of state ok, you can have this pressure explicit you can have density explicit? These are the exact theoretical basis in statistical mechanics ok. The limiting form that all equation of state much approach at the low density, so this is it tells you that that, the first term, when the 1 by v goes to 0 here this is exact as and this is something which all theoretical all equations are much approach to that. The other thing which is very interesting is important is that, the virial coefficient only depends on temperature. This is very accurate for gas only; oh and it can address the gas phase clustering by using virial equation of state you can try to explain that as well ok.

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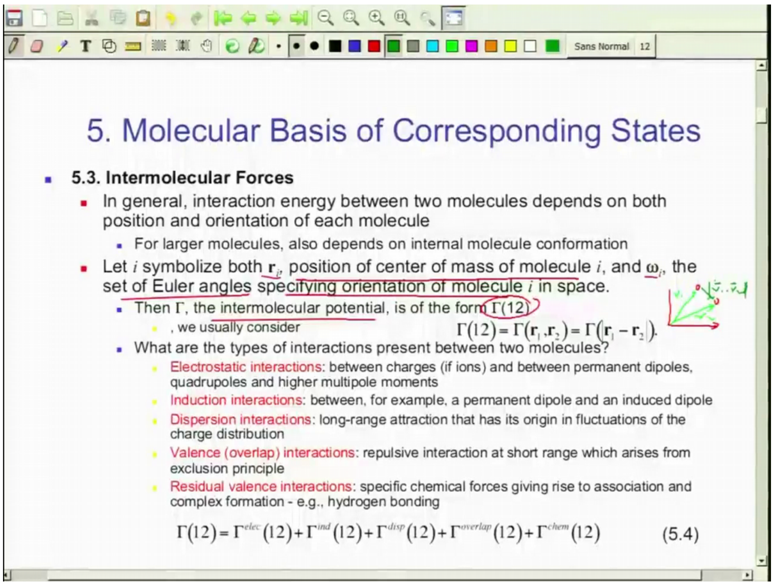

5. Molecular Basis of Corresponding States

- **5.3. Intermolecular Forces**
  - In general, interaction energy between two molecules depends on both position and orientation of each molecule
    - For larger molecules, also depends on internal molecule conformation
  - Let *i* symbolize both $\mathbf{r}_i$, position of center of mass of molecule *i*, and $\boldsymbol{\omega}_i$, the set of Euler angles specifying orientation of molecule *i* in space.
    - Then Γ, the intermolecular potential, is of the form $\Gamma(12)$
      - , we usually consider $\Gamma(12)=\Gamma(\mathbf{r}_1,\mathbf{r}_2)=\Gamma(|\mathbf{r}_1-\mathbf{r}_2|)$.
    - What are the types of interactions present between two molecules?
      - Electrostatic interactions: between charges (if ions) and between permanent dipoles, quadrupoles and higher multipole moments
      - Induction interactions: between, for example, a permanent dipole and an induced dipole
      - Dispersion interactions: long-range attraction that has its origin in fluctuations of the charge distribution
      - Valence (overlap) interactions: repulsive interaction at short range which arises from exclusion principle
      - Residual valence interactions: specific chemical forces giving rise to association and complex formation - e.g., hydrogen bonding

$$\Gamma(12)=\Gamma^{elec}(12)+\Gamma^{ind}(12)+\Gamma^{disp}(12)+\Gamma^{overlap}(12)+\Gamma^{chem}(12) \qquad (5.4)$$

So, let me now touch upon the most important part of this lecture is the intermolecular forces. Now, invariably the interval molecular forces is governs the way the particles behave and the collectively, when the behavior are in some way you get a certain property and the way we are and other way you get a different kind of properties. And this is important to understand, how to come up with a model potential model; which can represent the systems in a way which you can characterize the experiment very well. And those in a reverse way you can understand how the particles interact and quantifying various different properties in terms of intermolecular forces.

Now, let me define first this ok; and now we are going to change the little bit of terminology here ok. So, the first important thing is one must understand that the interaction energy between two molecules not only depends on the distance between them, but as well as how they orient amongst themselves ok; that means, they depends on r as well as omega; so let me first define let i symbol i both ri, which is the position of the center of mass of the molecule, and wi the set of the Euler angles space finally, intention of molecule i in space.

So, in that case we are defining the intermolecular potential, between particle 1 and 2; 1 2 as gamma 1 2 which is nothing but gamma r 1 comma r 2 and that will be the difference between these two particle; between the difference between these two positions in space. Now, this is what typically we use that ok. So, since it is a space this is our interest, then this may be r 1 this may be r 2 ok, but our interest basically is nothing but this which is nothing but r 1 minus r 2 and the modulus of that.

Now, what are the different types of interaction between two molecules let me first summarize that.

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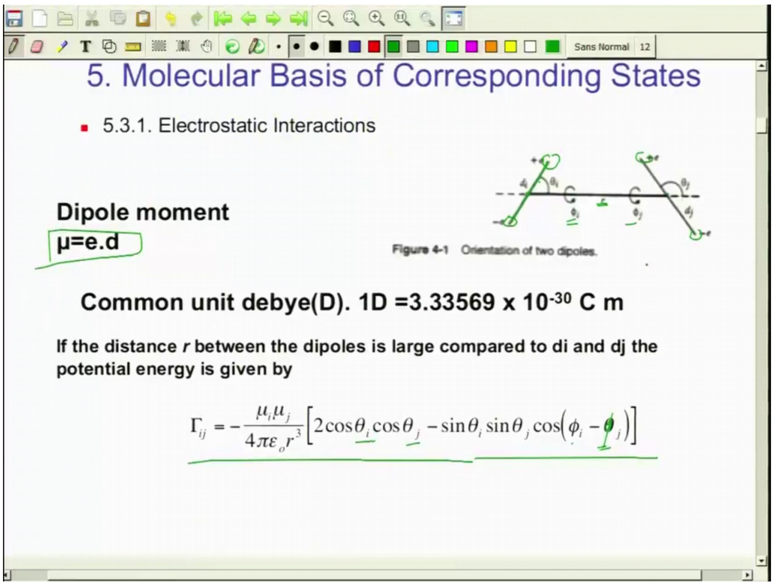

5. Molecular Basis of Corresponding States

- 5.3.1. Electrostatic Interactions

Dipole moment

$\boxed{\mu = e.d}$

Figure 4-1 Orientation of two dipoles.

Common unit debye(D). 1D =3.33569 x 10^{-30} C m

If the distance *r* between the dipoles is large compared to di and dj the potential energy is given by

$$\Gamma_{ij} = -\frac{\mu_i \mu_j}{4\pi\varepsilon_o r^3}\left[2\cos\theta_i\cos\theta_j - \sin\theta_i\sin\theta_j\cos(\phi_i - \phi_j)\right]$$

The one is electrostatic interactions ok, which is mainly because the particles the molecules will have charges ok. Now, so if you have charges or ions and between and if there is a permanent dipole, quadrupole and the higher multiple, then it will lead to electrostatic interactions ok. Now, in addition to electrostatic interaction you will have induction interactions, this is between; for example, a permanent dipole and an induced dipole.

So, we will come back to this individual contributions or interactions in detail you know shortly. In addition to induction interaction, you will have dispersion interaction very commonly available among the particles or molecules and is very important interaction. This is a long range attraction, that has it is origin in fluctuations of the charge distribution. Essentially, it means that the molecules may be neutral, but even if it is neutral due to the fluctuations of the electronic cloud, it can have dispersion interaction, that is what we are going to understand; slow you know shortly.

In addition to a dispersion we may have balance or interaction, which is nothing but repulsive interaction at short range ok, which arises bit from the policy exclusion principle. Now, at the end we may have this residual valence interaction, which is a specific chemical forces giving a rise to association in the complex formation such as hydrogen bonding. So, two molecules may have not just one kind of interaction, but many kind of interactions. So, we can summarize it; the total interaction will be due to the electrostatic, interaction, dispersion, overlap and chemical ok.

So, let me start and explain each of them. Now, electrostatic interaction is something which is very well known; given a charge or the permanent dipole this is the case for the molecule having charges here, such that is the permanent dipole ok. And this is the distance between them, this is the again the other one, it has a specific orientation, so the way we are written is basically theta, which is the distance between these two center of mass of the molecule ok, which is r i is the distance between the center of mass of the molecule within the molecule the charges are connected by this length and given by this dipole ok.

And of course, dipole movement is this mu is equal to e multiplied by the d ok, which is here from here to here ok. Now, what we can write is, if you do this calculation of using the columbic interaction and sum it up all possible interaction between; because you have charges here here here. So, thick there are many possibilities. So, you would have to add up all these columbic interactions and then the expression will turn out to be this ok. So, this is the final expression, which not only depends on the dipole moment of molecule 1 and 2, but as well as the theta i and theta j, which is making with respect to the distance between the axis of the vector connecting the center of mass of this two molecule.

In addition you have this phi i and phi j this must be phi j ok, which is nothing but between this.

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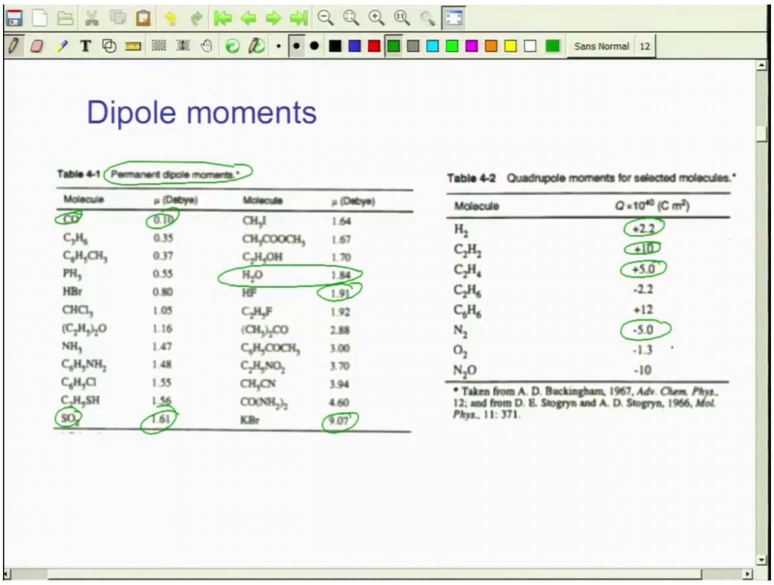

Dipole moments

Table 4-1 Permanent dipole moments.*

Molecule	μ (Debye)	Molecule	μ (Debye)
CO	0.10	CH_3I	1.64
C_3H_6	0.35	CH_3COOCH_3	1.67
$C_6H_5CH_3$	0.37	C_2H_5OH	1.70
PH_3	0.55	H_2O	1.84
HBr	0.80	HF	1.91
$CHCl_3$	1.05	C_2H_5F	1.92
$(C_2H_5)_2O$	1.16	$(CH_3)_2CO$	2.88
NH_3	1.47	$C_6H_5COCH_3$	3.00
$C_6H_5NH_2$	1.48	$C_2H_5NO_2$	3.70
C_6H_5Cl	1.55	CH_3CN	3.94
C_2H_5SH	1.56	$CO(NH_2)_2$	4.60
SO_2	1.61	KBr	9.07

Table 4-2 Quadrupole moments for selected molecules.*

Molecule	$Q \times 10^{40}$ (C m^2)
H_2	+2.2
C_2H_2	+10
C_2H_4	+5.0
C_2H_6	-2.2
C_6H_6	+12
N_2	-5.0
O_2	-1.3
N_2O	-10

* Taken from A. D. Buckingham, 1967, *Adv. Chem. Phys.*, 12; and from D. E. Stogryn and A. D. Stogryn, 1966, *Mol. Phys.*, 11: 371.

So, I do not expect people to remember this ok, but something the idea is behind is that to understand that these are the complex equations, which turns out to be and there is a rigorous means to obtain the expression. Now, let me summarize some of the values, which we have for the different molecules. Now you and we are talking about the permanent dipole moment, which will lead to the electrostatic interactions.

So, you can see that we have summarized carbon monoxide 0.1 by debye and so on those as a tool is very strongly polarized molecule 1.61, if you look at the water again very polarized 1.84, HF is highly polarized, KBr 9.09 and of molecule. Now, similarly to the permanent dipole we may have this quadruple moment, which may be very very small compared to the dipole, but it is also relevant and this is something which we will learn a bit later and these are the values we can see this as 2 is 0.22 plus 10 plus 5 these are minus.

Now, the way we make use of quadrupole moment, it can also lead to negative values of it ok.

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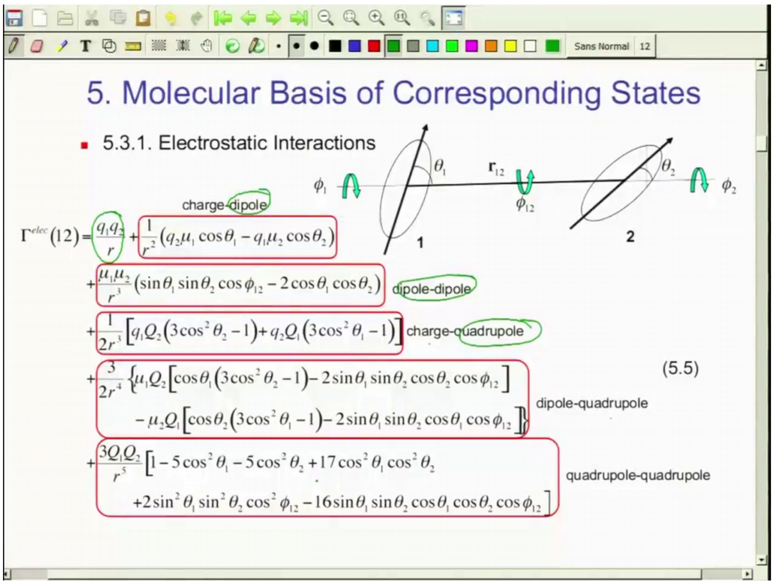

5. Molecular Basis of Corresponding States

- 5.3.1. Electrostatic Interactions

$$\Gamma^{elec}(12) = \frac{q_1 q_2}{r} + \underbrace{\frac{1}{r^2}\left(q_2\mu_1\cos\theta_1 - q_1\mu_2\cos\theta_2\right)}_{\text{charge-dipole}}$$

$$+\underbrace{\frac{\mu_1\mu_2}{r^3}\left(\sin\theta_1\sin\theta_2\cos\phi_{12} - 2\cos\theta_1\cos\theta_2\right)}_{\text{dipole-dipole}}$$

$$+\underbrace{\frac{1}{2r^3}\left[q_1Q_2\left(3\cos^2\theta_2-1\right)+q_2Q_1\left(3\cos^2\theta_1-1\right)\right]}_{\text{charge-quadrupole}}$$

$$+\underbrace{\frac{3}{2r^4}\left\{\mu_1Q_2\left[\cos\theta_1\left(3\cos^2\theta_2-1\right)-2\sin\theta_1\sin\theta_2\cos\theta_2\cos\phi_{12}\right] - \mu_2Q_1\left[\cos\theta_2\left(3\cos^2\theta_1-1\right)-2\sin\theta_1\sin\theta_2\cos\theta_1\cos\phi_{12}\right]\right\}}_{\text{dipole-quadrupole}} \qquad (5.5)$$

$$+\underbrace{\frac{3Q_1Q_2}{r^5}\left[1-5\cos^2\theta_1-5\cos^2\theta_2+17\cos^2\theta_1\cos^2\theta_2 +2\sin^2\theta_1\sin^2\theta_2\cos^2\phi_{12}-16\sin\theta_1\sin\theta_2\cos\theta_1\cos\theta_2\cos\phi_{12}\right]}_{\text{quadrupole-quadrupole}}$$

So, let me in general summarize, so you may have various different contribution of electrostatic you can have charge the simple columbic interaction ok, because of this, you can have charge-dipole if you have a permanent dipole it can have this you can have dipole-dipole if you can charge permanent dipole, dipole-quadrupole quadrupole-quadrupole. So, that means, all these possibilities can occur and for a given set of molecules leading to a very complex electrostatic interaction terms.

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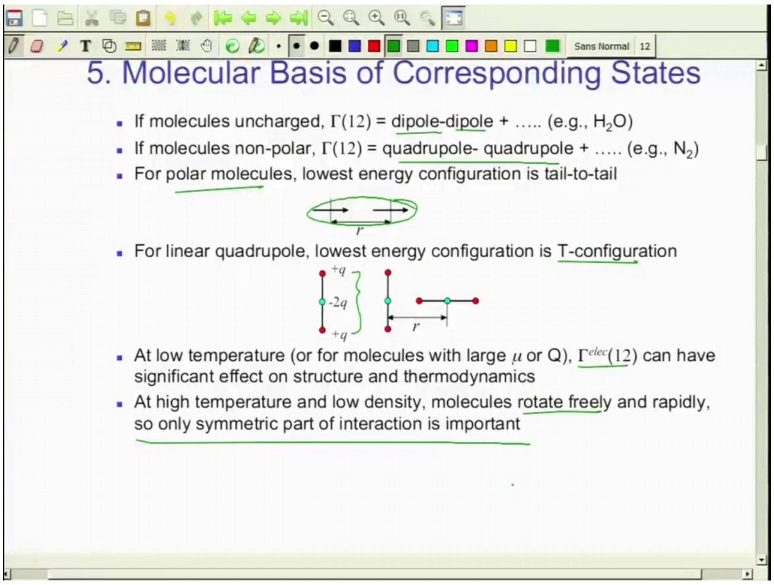

5. Molecular Basis of Corresponding States

- If molecules uncharged, $\Gamma(12)$ = dipole-dipole + ….. (e.g., H_2O)
- If molecules non-polar, $\Gamma(12)$ = quadrupole- quadrupole + ….. (e.g., N_2)
- For polar molecules, lowest energy configuration is tail-to-tail
- For linear quadrupole, lowest energy configuration is T-configuration
- At low temperature (or for molecules with large μ or Q), $\Gamma^{elec}(12)$ can have significant effect on structure and thermodynamics
- At high temperature and low density, molecules rotate freely and rapidly, so only symmetric part of interaction is important

Let me just try to explain a bit related to his arrangement. So, if molecules are uncharged, then of course you can have the charges interaction would be negligible or will be 0, only the dipole-dipole or other contribution will come. If the molecule is nonpolar ok, in that case it does not have a dipole, but it can have quadruple-quadropple interaction that is what it can have like this. For polar molecules lowest energy configuration is tail to tail, this directly comes from the expression, which we written here and for linear quadrupole such as this the lowest energy conformation is a T-configuration; that means, you have one molecule like this another molecule like this ok.

So, these arrangements comes clearly from the these energy values, which you can plug in this thetas the way it is erased and you can clearly see which one; which particular element will allow the list of the lowest energy conformation. The other thing is important is the temperature. At low temperature or for molecules with a large dipole moment or quadrupole moment, the electrostatic energy can have significant on the structure in thermodynamics, because energy or the arrangement of the dipole and the orientation and gets significantly affected by the temperature.

At high temperature and low density, molecules rotate freely and rapidly, so only symmetric part of interaction is important. And this means that you can consider the mean value of these interactions by integrating across the volume and the orientation of space ok.

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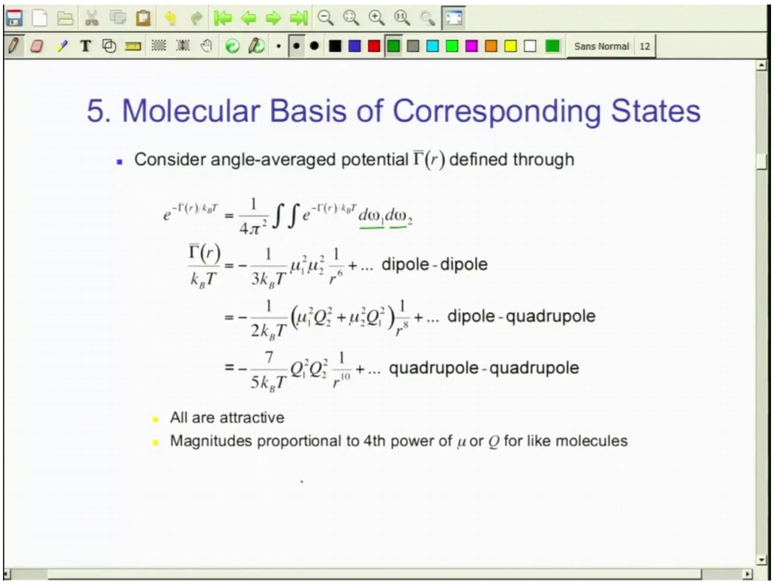

5. Molecular Basis of Corresponding States

- Consider angle-averaged potential $\bar{\Gamma}(r)$ defined through

$$e^{-\bar{\Gamma}(r)/k_BT} = \frac{1}{4\pi^2}\int\int e^{-\Gamma(r)/k_BT}\,\underline{d\omega_1}\,\underline{d\omega_2}$$

$$\frac{\bar{\Gamma}(r)}{k_BT} = -\frac{1}{3k_BT}\mu_1^2\mu_2^2\frac{1}{r^6}+\ldots \text{ dipole - dipole}$$

$$= -\frac{1}{2k_BT}\left(\mu_1^2Q_2^2+\mu_2^2Q_1^2\right)\frac{1}{r^8}+\ldots \text{ dipole - quadrupole}$$

$$= -\frac{7}{5k_BT}Q_1^2Q_2^2\frac{1}{r^{10}}+\ldots \text{ quadrupole - quadrupole}$$

- All are attractive
- Magnitudes proportional to 4th power of μ or Q for like molecules

So, if you are considering typically average value you integrating the orientation space, if it is; let us assume that freely rotate that will be the case for high temperature.

So, if you freely rotate you just to consider for the case of average potential. So, we are looking at only the Boltzmann factor as we know that this is the most important part as for the statistical mechanics is concerned, and this is a term which provides you the probability of the conflict configuration. And those we are more interested in basically this part ok. So, so this is you can consider this average as simply the average of this ok, where we are dividing by this for normalization.

Now, the this part you can show without showing all the details, that is the average energy divided by k T can be written as in this form, where you have minus 1 by 3 k T mu 1 square mu 2 square 1 by r 6 this is the dipole-dipole part or for the case of dipole-quadrupole is this and this is the case of the quadruple-quadropple. Now, so that means, if you plug in this information depending on which part you are interested in you will get these conditions for different combination.

So, it tells you that the dipole-dipole is basically proportional to 1 by r 6 dipole-quadrupole is decays faster, quadruple-quadrupole is decay much faster ok. But nevertheless all are attractive and the important thing is the magnitude pro is proportional to the fourth power of mu or Q for like molecules.

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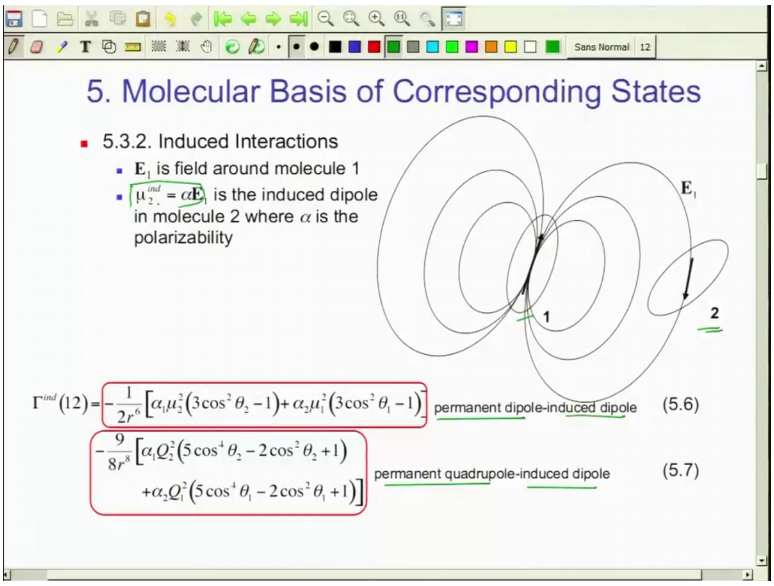

5. Molecular Basis of Corresponding States

- 5.3.2. Induced Interactions
  - $\mathbf{E}_1$ is field around molecule 1
  - $\boxed{\mu_2^{ind} = \alpha \mathbf{E}_1}$ is the induced dipole in molecule 2 where α is the polarizability

$$\Gamma^{ind}(12) = \boxed{-\frac{1}{2r^6}\left[\alpha_1\mu_2^2\left(3\cos^2\theta_2 - 1\right) + \alpha_2\mu_1^2\left(3\cos^2\theta_1 - 1\right)\right]} \quad \text{permanent dipole-induced dipole} \quad (5.6)$$

$$\boxed{-\frac{9}{8r^8}\left[\alpha_1 Q_2^2\left(5\cos^4\theta_2 - 2\cos^2\theta_2 + 1\right) + \alpha_2 Q_1^2\left(5\cos^4\theta_1 - 2\cos^2\theta_1 + 1\right)\right]} \quad \text{permanent quadrupole-induced dipole} \quad (5.7)$$

So, this is what the average part comes out to be. Now, let me continue this and come to the case of the induced interaction. Now, so you consider this molecule 1 and this is molecule 2.

Now, due to the fluctuations of the charges, there is a transient electric field, which gets around the molecule one and due to that field, there is an induced dipole in molecule two ok. Now, the induced dipole is given by the alpha multiplied by the electric field; can let me restate this statement here. Now, due to the permanent dipole here there is a electric field in around a molecular 1 and due to that it induces transient or it induces a dipole moment in molecule 2, which is given by this expression ok.

So, now, you have a case of a permanent dipole permanent quadrupole and induced dipole here. And this is where you can get again expressions of this, which you can come up with. So, I am not going into details of how this has been evaluated, but what is important that this expression exists, if you have a such a case where your permanent dipole, then there will be induced dipole or if we have a case of permanent quadrupole and another molecule will have induced dipole and this is the contribution due to that.

So, let us consider and of course, most important thing is that the induced dipole depends on the polarizability, if you have a highly polarizable molecule it will you have you will have large value of induced dipole.

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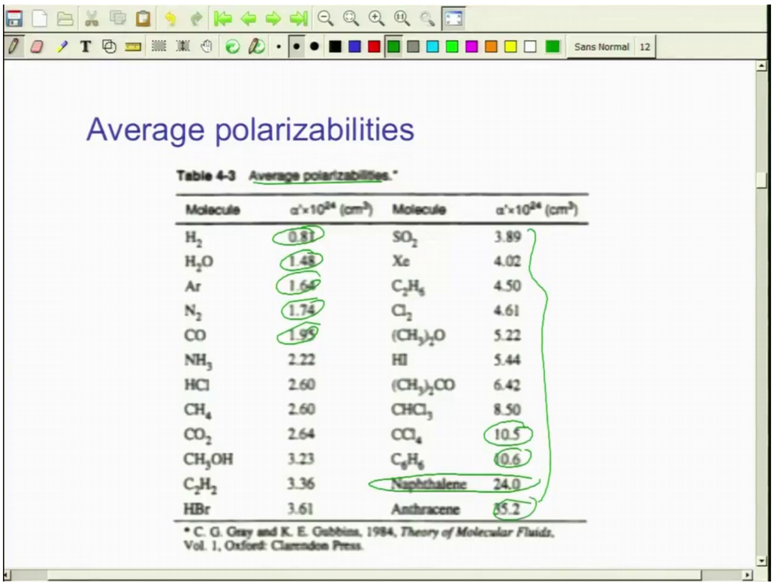

Average polarizabilities

Table 4-3 Average polarizabilities.*

Molecule	$\alpha' \times 10^{24}$ (cm^3)	Molecule	$\alpha' \times 10^{24}$ (cm^3)
H_2	0.81	SO_2	3.89
H_2O	1.48	Xe	4.02
Ar	1.64	C_2H_6	4.50
N_2	1.74	Cl_2	4.61
CO	1.95	$(CH_3)_2O$	5.22
NH_3	2.22	HI	5.44
HCl	2.60	$(CH_3)_2CO$	6.42
CH_4	2.60	$CHCl_3$	8.50
CO_2	2.64	CCl_4	10.5
CH_3OH	3.23	C_6H_6	10.6
C_2H_2	3.36	Naphthalene	24.0
HBr	3.61	Anthracene	35.2

* C. G. Gray and K. E. Gubbins, 1984, *Theory of Molecular Fluids*, Vol. 1, Oxford: Clarendon Press.

And this is the case here this is the average polarizability and you can see this as a valid information here. So, for example, in the case of naphthalene is a very high polarizable; that means, it will get very high induced dipole here ok.

On the other your water is here, argon is here, these are very small values compared to CCL 4; CC has 6 anthracene and so forth ok.

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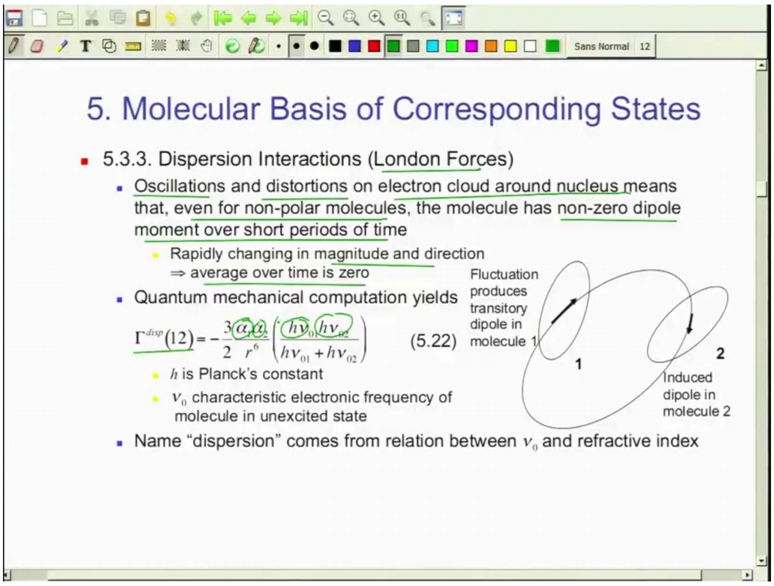

5. Molecular Basis of Corresponding States

- 5.3.3. Dispersion Interactions (London Forces)
  - Oscillations and distortions on electron cloud around nucleus means that, even for non-polar molecules, the molecule has non-zero dipole moment over short periods of time
    - Rapidly changing in magnitude and direction $\Rightarrow$ average over time is zero
  - Quantum mechanical computation yields

$$\Gamma^{disp}(12) = -\frac{3}{2}\frac{\alpha_1\alpha_2}{r^6}\left(\frac{h\nu_{01}h\nu_{02}}{h\nu_{01}+h\nu_{02}}\right) \qquad (5.22)$$

    - h is Planck's constant
    - ν_0 characteristic electronic frequency of molecule in unexcited state
  - Name "dispersion" comes from relation between ν_0 and refractive index

Fluctuation produces transitory dipole in molecule 1

1

2

Induced dipole in molecule 2

So, that was induced interaction. Now let me come to the dispersion interaction ok. Now our dispersion the interaction is relevant for the case where you; you do not have any polarity or; that means, it is for relevant for nonpolar molecules. So, oscillation and dissolution on electron cloud around nucleus means that; even for non polar molecules the molecules can have non-zero dipole moment over a short period of time ok.

The way you can understand is that you have a molecule 1, which is basically nonpolar. The electronic cloud will fluctuate and because of the fluctuations, you have you will have a transient in electric field or transient a dipole, which we cause the electric field and this will induce dipole in the molecule tube ok, but remember that you know, if you take the average or an average there would be the mean values of this was going to be 0, but as far as the dipole is concerned.

So, rapidly changing the dipoles can have rapidly changing in magnitude and direction and there is an average value of the dipoles would be 0, but nevertheless due to this there is induced dipole and then you have this interaction between them ok, which we call it as a dispersion interaction also called it as also known as London Forces ok. So what are the values here? What is the expression which is for this London dispersion term or dispersion term or dispersion interaction is? It depends on the polarizability of one molecule 1 and molecule 2 ok.

So, which is obvious because you are creating a non creating a dipole moment for a non polar molecule. And this also depends on this plank constants and characteristic it electronic frequency molecule in an excited state. So, this is the amount which to take out, this is the energy to take out from the ground state basically for individual molecules here ok.

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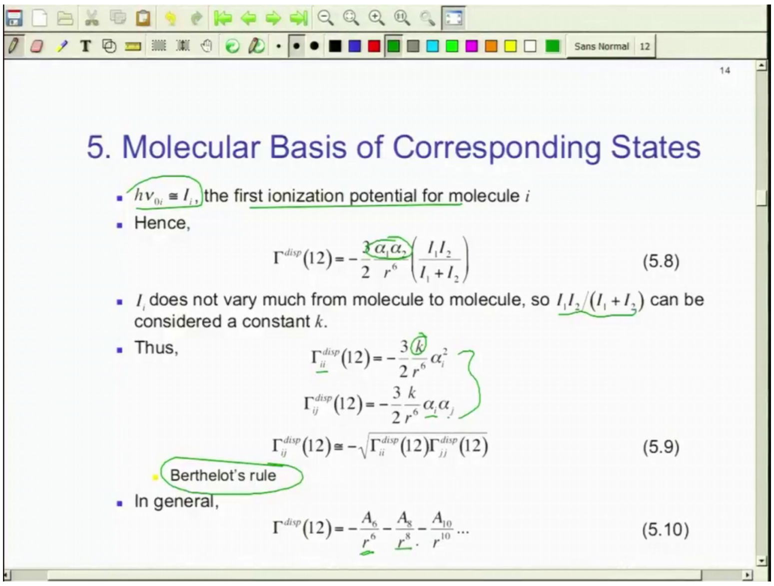

5. Molecular Basis of Corresponding States

- $h\nu_{0i} \cong I_i$, the first ionization potential for molecule i
- Hence,

$$\Gamma^{disp}(12) = -\frac{3}{2}\frac{\alpha_1\alpha_2}{r^6}\left(\frac{I_1 I_2}{I_1 + I_2}\right) \quad (5.8)$$

- I_i does not vary much from molecule to molecule, so $I_1 I_2/(I_1 + I_2)$ can be considered a constant k.
- Thus,

$$\Gamma_{ii}^{disp}(12) = -\frac{3}{2}\frac{k}{r^6}\alpha_i^2$$

$$\Gamma_{ij}^{disp}(12) = -\frac{3}{2}\frac{k}{r^6}\alpha_i\alpha_j$$

$$\Gamma_{ij}^{disp}(12) \cong -\sqrt{\Gamma_{ii}^{disp}(12)\Gamma_{jj}^{disp}(12)} \quad (5.9)$$

  - Berthelot's rule
- In general,

$$\Gamma^{disp}(12) = -\frac{A_6}{r^6} - \frac{A_8}{r^8} - \frac{A_{10}}{r^{10}} \ldots \quad (5.10)$$

So, how do we come up? So, the we approximate how do you simplify this expression; we approximate this h nu by this i, which is the first ionization potential for the molecule does this expression turns out to be i 1, i 2 divided by i 1 plus i 2 and this is the polarizability. Typically i is the ionization potential does not vary much from molecule to molecule. So, we can consider this to be a constant k and that is where it turns out to be this.

So, for the case of a same molecule it would be 3 kb divided by 2 r 6 alpha i square for the mixed case between 1 and 2 it would be alpha i alpha j and does we can use this information to come up with a mixing model, which means that if you are interested in obtaining the potential models of due to dispersion between 1 and 2, you can approximate this as a geometric mean between 1, 1 and 2, 2 and this is nothing but the Berthelot rule.

In general, we because this is an approximation ok, in general the dispersion term will have not only this a by r 6, which is this case, but as well as the other terms also, which usually is very small, but is relevant ok.

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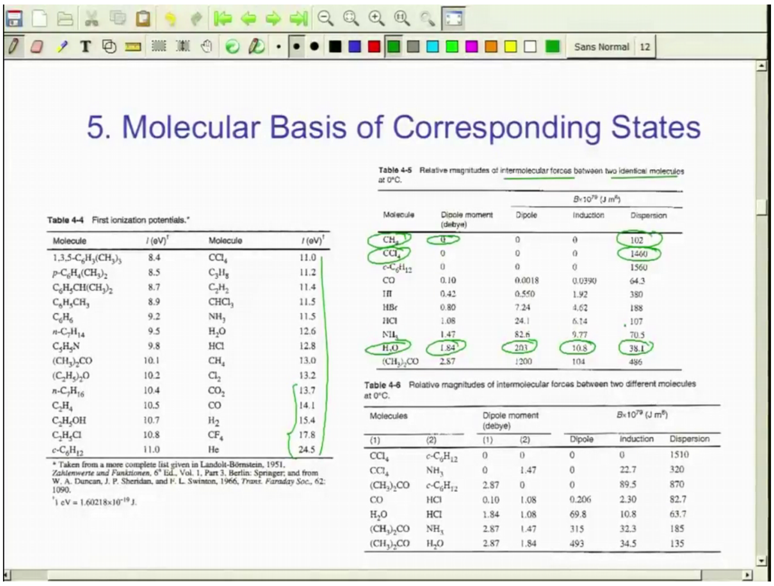

5. Molecular Basis of Corresponding States

Table 4-4 First ionization potentials.*

Molecule	I (eV)†	Molecule	I (eV)†
1,3,5-$C_6H_3(CH_3)_3$	8.4	CCl_4	11.0
p-$C_6H_4(CH_3)_2$	8.5	C_3H_8	11.2
$C_6H_5CH(CH_3)_2$	8.7	C_2H_2	11.4
$C_6H_5CH_3$	8.9	$CHCl_3$	11.5
C_6H_6	9.2	NH_3	11.5
n-C_7H_{14}	9.5	H_2O	12.6
C_5H_5N	9.8	HCl	12.8
$(CH_3)_2CO$	10.1	CH_4	13.0
$(C_2H_5)_2O$	10.2	Cl_2	13.2
n-C_7H_{16}	10.4	CO_2	13.7
C_2H_4	10.5	CO	14.1
C_2H_5OH	10.7	H_2	15.4
C_2H_5Cl	10.8	CF_4	17.8
c-C_6H_{12}	11.0	He	24.5

* Taken from a more complete list given in Landolt-Börnstein, 1951, *Zahlenwerte und Funktionen*, 6th Ed., Vol. 1, Part 3, Berlin: Springer; and from W. A. Duncan, J. P. Sheridan, and F. L. Swinton, 1966, *Trans. Faraday Soc.*, 62: 1090.

† 1 eV = 1.60218×10^{-19} J.

Table 4-5 Relative magnitudes of intermolecular forces between two identical molecules at 0°C.

		$B \times 10^{79}$ (J m^6)		
Molecule	Dipole moment (debye)	Dipole	Induction	Dispersion
CH_4	0	0	0	102
CCl_4	0	0	0	1460
c-C_6H_{12}	0	0	0	1560
CO	0.10	0.0018	0.0390	64.3
HI	0.42	0.550	1.92	380
HBr	0.80	7.24	4.62	188
HCl	1.08	24.1	6.14	107
NH_3	1.47	82.6	9.77	70.5
H_2O	1.84	203	10.8	38.1
$(CH_3)_2CO$	2.87	1200	104	486

Table 4-6 Relative magnitudes of intermolecular forces between two different molecules at 0°C.

Molecules		Dipole moment (debye)		$B \times 10^{79}$ (J m^6)		
(1)	(2)	(1)	(2)	Dipole	Induction	Dispersion
CCl_4	c-C_6H_{12}	0	0	0	0	1510
CCl_4	NH_3	0	1.47	0	22.7	320
$(CH_3)_2CO$	c-C_6H_{12}	2.87	0	0	89.5	870
CO	HCl	0.10	1.08	0.206	2.30	82.7
H_2O	HCl	1.84	1.08	69.8	10.8	63.7
$(CH_3)_2CO$	NH_3	2.87	1.47	315	32.3	185
$(CH_3)_2CO$	H_2O	2.87	1.84	493	34.5	135

So, let me just try to give you an idea, that what is the order of this dispersion with respect to the induced and dipole interactions ok. Now of course, dispersion term depends on as ionization potential, which is you can see that it is not much wearing, but in some case it does have significantly different from the other one.

Now, if you consider the intermolecular forces between two identical molecules, which is this CH 4, CCL 4. Now, they do not have let us say any dipole, but they will have strong dispersion interaction all in the same units CCL 4, again does not have any dipole, but it has strong dispersion you know almost 10 times higher than CH 4. Let us consider H 2 O it has a dipole moment and that is why it called dipole contribution, and then it will have also induced induction comes from position, because it has polarizability and it has a dispersion interactions.

Definitely, the dipole interaction is much more than the dispersion, but it is also relevant ok.

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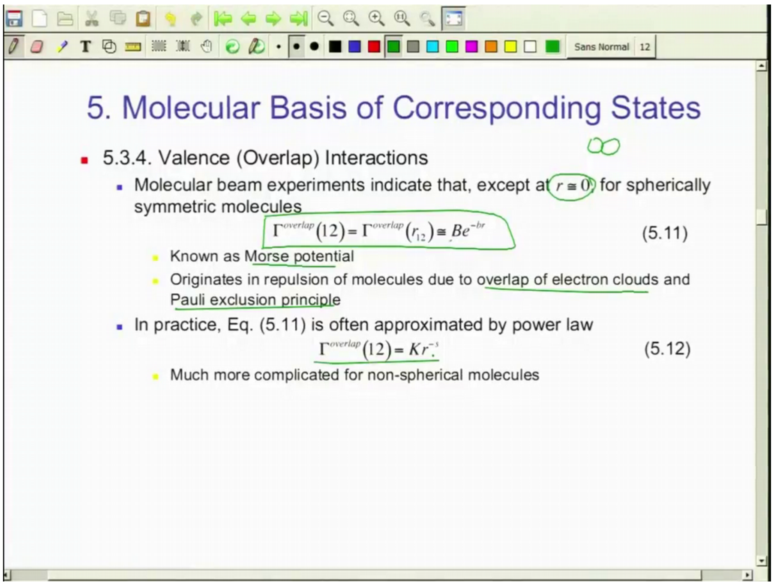

5. Molecular Basis of Corresponding States

- 5.3.4. Valence (Overlap) Interactions
  - Molecular beam experiments indicate that, except at $\boxed{r \cong 0}$ for spherically symmetric molecules

$$\boxed{\Gamma^{overlap}(12) = \Gamma^{overlap}(r_{12}) \cong Be^{-br}} \qquad (5.11)$$

    - Known as Morse potential
    - Originates in repulsion of molecules due to overlap of electron clouds and Pauli exclusion principle
  - In practice, Eq. (5.11) is often approximated by power law

$$\underline{\Gamma^{overlap}(12) = Kr^{-s}} \qquad (5.12)$$

    - Much more complicated for non-spherical molecules

Now, let us consider case of relative magnitude of intermolecular force between two different molecules. Let us consider this here both of them have does not have a dipole. So, you have very high order of dispersion, because of the fact that this has a high I am because of the fact that this has a strong polarizability.

Now, you consider H 2 O, H C L both of the dipole moment. Dipole is this induction is this, but it has also very strong comparable dispersion attraction. So, it tells you that the dispersion cannot be ignored ok, compare to this dipole for many set of molecules and combinations. In addition to this dispersion we also have to consider the valence overlap or repulsive interaction. So, molecular beam experiments indicate that except at r equal to 0; that means, when the particles are close by for spherical symmetric molecules we can approximate this potential for overlap as simply a constant B multiplied by exponential minus another constant small br and this is sometimes also called mass potential ok. So, it has the origin due to the overlap electron clouds and Pauli's exclusion principle. In practice we often approximate by a power law like this ok.

So, at this point I will stop here. And now, what we are going to focus in the next lecture is the different kind of models to appreciate what we have just learned and hopefully you will get more clarity on this model and as far as the kind of interaction ok, when we are going to cover the different types of models in the next lecture, ok.

So, I will see you in the next lecture.