Advanced Chemical Thermodynamics & Kinetics
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Lecture - 10
Molecular Interactions 05

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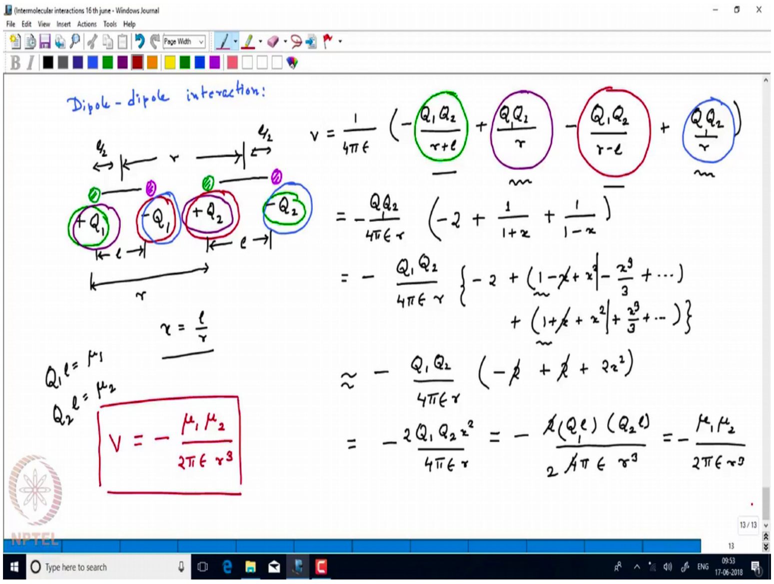

Dipole - dipole interaction:

$$V = \frac{1}{4\pi\epsilon}\left(-\frac{Q_1Q_2}{r+l} + \frac{Q_1Q_2}{r} - \frac{Q_1Q_2}{r-l} + \frac{Q_1Q_2}{r}\right)$$

$$= -\frac{Q_1Q_2}{4\pi\epsilon r}\left(-2 + \frac{1}{1+x} + \frac{1}{1-x}\right)$$

$$= -\frac{Q_1Q_2}{4\pi\epsilon r}\left\{-2 + \left(1 - \cancel{x} + x^2 - \frac{x^3}{3} + \cdots\right) + \left(1 + \cancel{x} + x^2 + \frac{x^3}{3} + \cdots\right)\right\}$$

$$\approx -\frac{Q_1Q_2}{4\pi\epsilon r}\left(-\cancel{x} + \cancel{x} + 2x^2\right)$$

$$= -\frac{2Q_1Q_2x^2}{4\pi\epsilon r} = -\frac{\cancel{2}(Q_1 l)(Q_2 l)}{2\cancel{4}\pi\epsilon r^3} = -\frac{\mu_1\mu_2}{2\pi\epsilon r^3}$$

$x = \frac{l}{r}$

$Q_1 l = \mu_1$

$Q_2 l = \mu_2$

$$\boxed{V = -\frac{\mu_1\mu_2}{2\pi\epsilon r^3}}$$

Now, next section, let us just consider if the dipoles are still parallel, but they have an angle between them.

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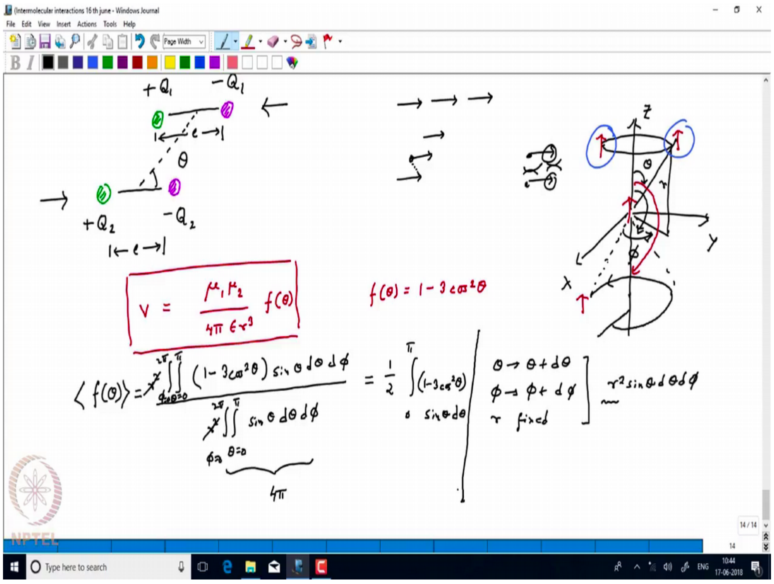

$$\boxed{V = \frac{\mu_1\mu_2}{4\pi\epsilon r^3}f(\theta)}$$

$f(\theta) = 1 - 3\cos^2\theta$

$$\langle f(\theta)\rangle = \frac{\cancel{r^2}\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}(1-3\cos^2\theta)\sin\theta\, d\theta\, d\phi}{\underbrace{\cancel{r^2}\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\sin\theta\, d\theta\, d\phi}_{4\pi}} = \frac{1}{2}\int_0^{\pi}(1-3\cos^2\theta)\sin\theta\, d\theta$$

$\theta \to \theta + d\theta$

$\phi \to \phi + d\phi$

r fixed

$r^2\sin\theta\, d\theta\, d\phi$

So, by that what do you mean is something like this; so, I have a as before we have a positive end of one dipole let say this is Q 1, and then we have a negative wave on the other dipole, which is minus of the same dipole, which is a minus Q 1. And then, we can actually write it in black as before, so this is plus Q 1 and this is minus Q 1.

And then, suppose the other dipole the second dipole has a orientation like this. So, the dipoles are still parallel to each other, but then there is a angle between the dipoles. And this angle let us call as a theta. So, I will have plus Q 2 and I have minus Q 2 here. And as before, the length of the dipoles let us state to be equal, this is l. And also for the length of the other dipole also, we take it to be l. So, we have basically two dipoles, in the earlier, case actually had the dipoles arranged in a head to tail fashion. And in this case, actually the dipoles are still arranged in a favorable condition, but in a parallel condition.

Now, this is very important to understand. So, what we are saying here is that if you draw the dipoles as arrows, so this is one of the orientation that we just talked about. Right now actually we are talking about the dipoles are basically parallel to each other, but if we put up dipoles like this say for example, then actually there will be a repulsion between the positive ends and the negative ends. So, as a matter of fact there will be a slip between the two dipoles, so that these negative end actually interacts comes closer to the positive end something like that. Otherwise, it would not be very much favorable, because you will have the negative ends are closer as well as the positive ends are closer.

So, these kind of arrangements are very interesting. And if you consider molecular aggregates, so these kind of arrangement we often see. Now, by molecular aggregate I mean that it is basically arrangement of molecules, with some permanent electric dipole moment. And then, there is a dipole-dipole interaction, which we just discussed and we are right now discussing also.

And due to this dipole-dipole interaction in the aggregates of molecules, will find a two extreme type of aggregate. So, one aggregate is the head to tail fashion, and the other aggregate is basically parallel fashion, but with a slip between them. And these two aggregates are called J type aggregates or H type aggregates. Now, you actually realize molecular aggregates in nature, which are extremely important. For example, when you talk about light harvesting in natural photosynthesis, you know that photosynthesis is done by chlorophyll molecules, and these chlorophyll molecules do not actually stay in nature in a isolated condition, they always come in aggregates.

Meaning you will always find there is a assembly of pigments or assembly of chlorophyll molecules inside a protein matrix or they may be also outside a protein matrix and then they form some kind of very special structure. In nature actually we get the aggregate structure, somewhat between the J aggregate and the H aggregate. Meaning, they are not perfectly head to tail or the parallel slip stack kind of structure, which we are showing here, but nevertheless this is a very good starting point to understand, what are the interactions between those molecules.

And what are the intermolecular interaction that give rise to such structures. And how after this interaction, the energy levels of the molecules changes, because due to this interaction what will happen is that the energy level will shift accordingly, because you cannot now talk about the energy of the isolated molecules isolated say chlorophyll molecule, it is not like energy of one chlorophyll molecule, and energy of two chlorophyll molecule.

Just like if you bring the two atoms together to form molecules orbitals and in the molecule the molecular, when the molecular orbital forms the electrons or the outermost electrons actually. If you think about their properties, it is basically property of the molecule as such. So, the entire concept of atomic orbital get vanished and we have a new set of orbitals, which are molecular orbitals.

Similarly, when these molecules come together, and if they are close enough that their wave functions overlap, then actually they also interact in such a way that they form new set of orbitals. And these set of orbitals we call as excitonic state, and those which means actually now you cannot talk about excitation of molecule 1 or molecule 2, it is basically excitation of molecule 1 and 2 together, and we have to think it a new energy level. So, we are not going into the details of that, but the point here is that those kind of interactions give rise to excitonic structure in natural pigment protein complexes, which are extremely important to understand light harvesting in nature.

Now, let us look at the interaction potential. If there is a slip angle between them, and the dipoles are actually oriented parallel to each other. Now, we can actually work on it and then, it depends on the like overall interaction will be dependent on function, where actually these function, which is a orientational function we call it. So, let us think that if theta is say 180 degree what will happen, theta 180 or theta 0 degree. Theta 0 means, it is the previous case, where actually the dipoles are arranged in a head to tail fashion.

So, overall we can actually write the interaction potential as something like I have mu 1 mu 2 as before divided by 4 pi epsilon r cube, and then we have a function, which is dependent on the theta. Now, this functional form f of theta is something like 1 minus 3 cos square theta. And then, we can actually discuss what is the origin of this formula, how we actually get the 3 cos square theta.

Now, the point here is that suppose I have actually 0 degree orientation, now 0 degree orientation means the cos 0 will be 1, so I will have 1 minus 3, which is minus 2. So, the interaction will be minus 2 times mu 1 mu 2 by 4 pi epsilon r cube. So, it will be mu 1 mu 2 minus mu 1 mu 2 by 2 pi epsilon r cube, which is our original formula for dipoles which are connected in a head to tail fashion. So, this is a more general formula for two dipoles oriented at an arbitrary angle, now but still we are we are considering this dipoles to be parallel.

You can also think that there is there could be actually another angle, where these dipoles are not just parallel. Right now, we are considering this angle, like how a one dipole dipoles are still parallel, but they are actually as if the center if we just draw an line of the between the center to center, and then I am basically rotating that line keeping one dipole fixed, and I am rotating the other one, but without rotating the orientation of the dipole.

But you can think in the most general case, you could have the second dipole oriented like say this, meaning the first dipole is something like that, but the second dipole is something like this. So, then actually you are talking about another angle, which is basically the tilt angle of the dipole, and that we are not considering right now. So, we are only considering the interaction between the two dipoles, which are parallel to each other [vocalize-noise].

Now, this dipolar interaction if we have between two freely rotating molecules, meaning in reality what will have is that we will have a the function as 1 minus 3 cos square theta that we already know. And we are now asking this question, what will be the average value of this f of theta. If the two dipoles are free to rotate, now you can think that if I have a all possible orientations of this angle theta, then we can actually think that instead of theta actually we could have taken the angle to be phi, because this is basically now the theta can actually go to 0 to 2 pi angle, as you can see.

So usually for that like when a spherical polar coordinate, the angle which actually sweeps from 0 to 2 pi we usually call it as a phi, but this is just a notation that most of the I mean physical chemistry textbook use. But remember that, this theta is not the azimuthal angle which we usually right and that theta variation is 0 to pi by 2 0 to pi 0 to 180 degree.

Now, if I want to calculate, what is the average probability? So, we have to basically integrate the orientation, so this is 1 minus 3 cos square theta that is the function, and then we have to integrate over all possible angle. And you know that again we are not considering any interaction how the interaction potential between these dipoles are varying, but ideally one can actually consider that potential and then introduce a Boltzmann distribution or something like that, but here we are considering only what is the possible orientational averaging between the two dipoles. And then, I will have sin theta d theta d phi, because d phi is the other angle which is basically the spherical polar angle, but in this case, the phi and theta notations have been interchanged.

So, then for our interchanging thing, the theta goes from 0 to 2 pi, and phi goes from 0 to pi. And then, I have to divide, since it is if we want to calculate the average value in terms of say the probability. And then, I have to integrate the spherical polar volume element, which is sin theta d theta d phi, and so because r is fixed. So, there is no component, which is coming from r square d r. And then, I have phi equal to 0 to pi and theta going from 0 to 2 pi and this denominator integration is very straightforward, it will give you 1 over 4 pi over all; and also the d phi integration is also straightforward, it will give you 1 over it will give you 2 pi.

So, overall will get something like the theta integration we are taking to be 0 to 2 pi, and the d phi integration it is giving you 0 to pi not 4 pi. So, what will be getting is something like this, I will have 1 over 4 pi. So, now the question is if this one dipole is fixed suppose this dipole we are keeping fixed, and this second dipole we are basically rotating around the first dipole keeping the orientation parallel, so we are just rotating like this. So, what will be the; I mean overall an or the average orientation for this two dipole or what will be the average of this f of theta.

Now that we can calculate very easily; realizing that this is basically the theta in the spherical polar coordinate. So, if you remember that we have say x, y, z axis and then any position at this moment this is basically the center to center distance of the dipoles, and again the dipoles are parallel to each other, and we are only varying the orientation of the r. In the sense that we have kept say the if the first dipole is kept along z like this, the second dipole also is always kept like this and then only the r is varying. We are not considering the tilt of the dipole with respect to the other meaning if the second dipole gets oriented like this, that we are not considering at this moment.

So, what we can actually get is basically two orientation angle; one is this angle which is theta, which we just described, and of course one is the other angle which is the phi angle, and which we can actually visualize like this. So, this is the phi. Now, phi actually can go from 0 to 180 degree or 2 pi, and theta can go from 0 to 90 degree or 0 pi.

Now, this is basically theta angle, because as you can see if I just have this dipole like this, and if I have the dipole like this, the interaction will be the same. And also you can easily realize that if I actually think the dipole is somewhere here, where r is fixed, it is basically we have inverted basically just the position, but still the interaction will be same. So, the theta actually does not take more than 90 degree. So, maximum value of theta will be basically 90 degree.

So, this is basically an angle, which is a more than 90 degree, but you can actually think this is a combination of some angle, and which is basically say this angle of theta, and then some angle of phi, but since we are measuring phi from this side, so like this. So, this will be the phi angle, so that is how we kind of measure the angles.

So keeping that continuing our discussion, so this will be the phi angle, because it is measured from the positive x-axis so, this will be our phi angles, which is much large angle, as you can see. So, the theta will take always up to 90 degree, which is this. So, now we can actually calculate the average. Now, this average is between two freely rotating dipoles, keeping the dipoles parallel to each other mutually parallel to each other.

Now, freely rotating means this orientation will not actually affect the will not be affected by the interaction potential, because I know that if the dipoles are like this, there will be a preferred orientation, because the head to tail fashion will actually minimize the energy. That we are not considering at this moment, we are going to consider that, because the orientation cannot be just random, because it will be preferred.

Just like we discussed that in a dipole in an electromagnetic field, there is a preferred orientation, there will be always a preferred orientation, because actually there the orientation the energy has an orientation dependence. And the molecule will always try to have their populating those energy levels, which are like according to the Boltzmann distribution.

So, if we calculate the average value of f of theta without considering the biasness, due to the dependence of energy on theta. So, what we will get is basically we are taking f of theta is 1 minus 3 cos square theta we can write it radially and then you have to multiply it by the spherical polar coordinate. If I just vary theta to theta plus d theta and phi to phi plus d phi, so the area swept over a sphere is basically sin theta d theta d phi, because we are keeping the r constant.

So, since we are keeping the r constant, so we can actually ignore that originally this area. So, if I go from theta to theta plus d theta and phi to phi plus d phi for fixed r, so you can easily calculate that this area will be r square sin theta d theta d phi. So, exactly considering that, but since now we are integrating over theta and phi only the r square term does not come.

So, usually textbook do not write this r squared term, but the meaning of that is that this r square is actually omitted in the numerator and the denominator. And the denominator will have basically the integration over sin theta d theta d phi of course, r square is there, and this r square will cancel. And then the theta actually goes from 0 to pi, and phi goes from 0 to 2 pi.

So, the phi integration is the same. As you can see that it depends only on the cos square theta, as we have shown that this orientation. And this orientation the interaction will be the same so, it is independent of that phi. So, as a result what will get basically the (Refer Time: 19:06) equation will give 2 pi angle. So, those 2 pi is will get cancelled from the numerator and denominator, just like r square.

And then, in the numerator the total integral will be 4 pi, because that is the solid angle. So, 4 pi r square is basically the surface of a sphere, so that is why this integration will give always 4 pi. And out of this 4 pi, actually 2 pi will get cancelled out the phi integration in the top. So, will be left with only a factor, which is half. And then, we have to integrate only this part, which is 0 to pi 1 minus 3 cos square theta sin theta d theta. So, this is our integration.

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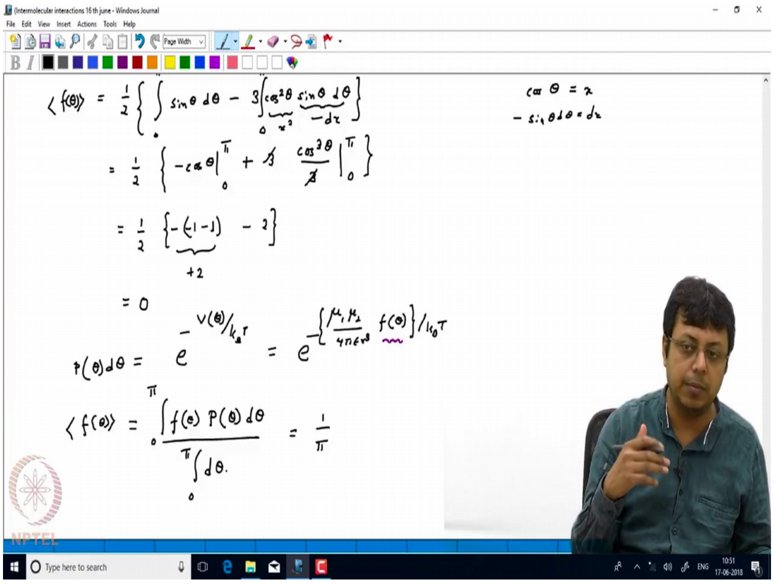

$$\langle f(\theta)\rangle = \frac{1}{2}\left\{\int_0 \sin\theta\, d\theta - 3\int_0 \underbrace{\cos^2\theta}_{x^2}\, \underbrace{\sin\theta\, d\theta}_{-dx}\right\}$$

$\cos\theta = x$

$-\sin\theta\, d\theta = dx$

$$= \frac{1}{2}\left\{-\cos\theta\Big|_0^{\pi} + \cancel{3}\,\frac{\cos^3\theta}{\cancel{3}}\Big|_0^{\pi}\right\}$$

$$= \frac{1}{2}\left\{\underbrace{-(-1-1)}_{+2} - 2\right\}$$

$$= 0$$

$$P(\theta)d\theta = e^{-V(\theta)/k_BT} = e^{-\left\{\frac{\mu_1\mu_2}{4\pi\epsilon r^3} f(\theta)\right\}/k_BT}$$

$$\langle f(\theta)\rangle = \frac{\int_0^{\pi} f(\theta)\, P(\theta)\, d\theta}{\int_0^{\pi} d\theta.} = \frac{1}{\pi}$$

So, let us just try to atom this integration. So, average value of f of theta that will be half. And let us just integrate first term is 0 to pi sin theta d theta and then will have 3 cos square theta sin theta d theta and that is also integration between 0 to pi and we have an overall half factor. Now, you can look at it. So, sin theta d theta it will be nothing but minus cos theta. So, it is half minus cos theta, which is evaluated between 0 and pi minus I will have 3. Now, I have cos square theta, sin theta, d theta.

Now, I can actually make a change in variable cos theta is suppose x, so if I take the derivative of cos theta, it will be basically minus sine theta d theta that will be dx. So, this thing will be basically minus dx, and then this guy will be nothing but x square. So, the integration is very straightforward and then we can actually get back to the integration, it will be basically x cube by 3 with a negative sign, of course.

And then, what will get is I will have x square, and I have minus dx, so the integral will be there will be a plus sign because of that minus sign associated with this, and it will be basically x cube by 3. And since, x is cosine cos theta it will be cos cube by 3 that is the integral and the 3 of course, will cancel with each other, and evaluated between the limits 0 and pi.

Now, if you do this maths, you will find that the first term will be basically plus 2, because cosine pi is a minus 1, but minus of cosine pi is 1. And then, I will have basically minus 1 minus and then the lower limit is basically 0, and then I will have 1 here, so this thing will give me plus 2 value. And similarly, we can figure out the cosine cubed 1; I am just writing the answer, this will give you a minus 2 value. So, overall the orientational average will become 0.

Now, so what we see here is that these two dipoles if they orient randomly of course, our orientation average is 0, but then we have not considered the energy or the dependence of the energy on this orientation, because a particular orientation will maybe favored, because actually there is a interaction potential which is changing. Which means now, there is a probability just like we did for the dipole in a particular in electric field, and which actually depends on the energy. So, this probability will be dependent on something like e to the power minus e by k B T. And then, in this case e is basically nothing but the interaction potential between the two dipoles, which is a dependent on theta divided by k B T.

And what is the interaction potential, we already discussed about it. What is a general form of this interaction potential, and this is the general form of the interaction potential that I had mu 1 mu 2 by 4 pi epsilon r cube into f of theta. So, it will be something like mu 1 mu 2 4 pi epsilon r cube into f of theta. Now, you see that all the theta dependence in e and of course, this will be divided by k B T. So, all the theta dependence is coming here from this term f of theta.

So, now what we have to do, if we want to calculate the average interaction potential, because again this is for the freely rotating or the dipoles are kind of non-interacting and because the dipoles actually do interact with each other. So, the average value will be for to calculate any average value, we have to take that function multiply with the probability distribution, and then integrate over all possible thetas, where theta is going from 0 to pi.

We are not considering the phi right now, we can actually consider the phi and then numerator denominator will again cancel with each other, and divided by I will have basically sin theta d theta. And again instead of P theta, we will have P sin theta d theta, because remember that that is the spherical polar volume and then, we are basically integrating it as like this.

Now, the question is so, if we integrate that, so in this case I am doing a probability integration. So, if the dipoles actually interact with each other, the average value of this orientation now will be have a preferred orientation, the reason is the energy actually depends on the orientation. And then, all we have to do is to calculate how we calculate average value, we have to take the function that average of which we want to calculate. Multiply it by the probability distribution and divide by the all possible angles, so because we are trying to keep this as a normalized function, we could have integrated over phi is also, but phi is integration will just cancel with each other.

So, what will get is something like this, I will have 1 over pi, because this pi actually comes from the dipole-dipole interaction term where coming to that, because as you can see that the theta integration is basically between 0 and pi, so that is just a straightforward integration 1 over pi. Now, do not get confused that we need a sin theta d theta here, because we are just considering the probability distribution, just like we did in the earlier dipole interaction. If you remember that, so if we what will be the interaction potential of average orientation of a dipole inside an electromagnetic field all right.

So, now the theta integration gives you in the denominator as 1 over pi. And then, let us try to attain the integration for in the numerator. So, what I will have is 0 to pi. And then, look at it carefully what I am doing, so I have basically f of theta, and then I am actually writing these potential term as a series expansion assuming that this potential V of theta is much less than k B T. Then actually we can approximate this as an we can actually expand the exponential series. And then, we can write the probability distribution as something like considering only the first term on the second term, it is basically e to the power minus x, so it is 1 minus x plus x square by 2 factorial something like that.

So, I am just considering 1 minus x term, so it is 1 minus V by k B T. And then, we are going to write that, so I have f of theta times I will have the probability distribution, which is 1 minus V by k B T, and then I will have d theta. So, f of theta average of that becomes 1 over pi. So, we have basically two terms and we can actually integrate the two terms separately, I will have 0 to pi f of theta d theta minus then I will have V by k B T. I think this derivation in Atkins is wrong I am just giving Pankaj this thing instruction. So, we can actually write the final expression. So, and then we can actually figure it out later all right.

So, just like we did the averaging for an orientation of a dipole inside an electric field, then we can actually proceed and then will find out that if we want to calculate the f of theta including the probability distribution for we taking into account of the Boltzmann distribution of energy. And then, also using the fact that at very high temperature or room temperature the potential energy, which is a function of theta is much less than the average thermal energy. Then we can actually approximate this series of e to the power minus x as 1 minus x, and then we can actually substitute it.

I am writing the final expression and the final expression will be something like that for if we just calculate it and then that expression will be giving us something like the interaction potential for the two dipoles, which are mutually parallel, but have an very arbitrary orientation. And we will see that there will be some preferred orientation, and due to that the average interaction potential will be including this average value of f of theta, it will be something like mu 1 square mu 2 square into f of theta square an average of that divided by will have 4 pi epsilon 0 squared into k B T into r to the power 6.

Now, there are few things to look at in this expression. So, what else we have, so we have mu 1 square and mu 2 square. So, basically now you think that this is coming, because when you do this exercise how to calculate this average value of f of theta, you will find you will get two averages; one is basically average of f of theta, which is already 0 which we already figured it out and the second one will be basically average of f theta squared, which will be of course, non-zero, which is basically averaging of this quantity 1 minus 3 cos squared theta squared. And that will be non-zero that is why this term is surviving. And then, due to the squaring, I will have mu 1 square and mu 2 square, and also the r cube gets basically r to the power 6.

Now, an also I you can see here that 1 by 4 pi epsilon 0 that also gets squared. And then, so this is basically directly follows from the f of theta squared kind of like average. And then, the interesting thing note that is that the interaction potential, now actually has 1 over r to the power 6 variation. Now, you can now follow go back and see what we did. If the dipoles are kind of fixed, we are having 1 by r to the power 3 term.

And then, one once the dipoles are basically rotating against each other, so then keeping the mutual orientation parallel, then I have 1 over r to the power 6, the reason for this actually there will be 2 1 over r cube kind of potential. One is basically coming from the one dipole that I have a dipole-dipole interaction, and then the second one actually is coming from inherently the averaging of the effect.

Now, we can actually calculate this quantity what will be the average value of that; that actually comes as two-third. So, overall we can say the interaction potential will be two-third of minus mu 1 square mu 2 square divided by 4 pi epsilon 0 squared into k B T times r to the power 6.

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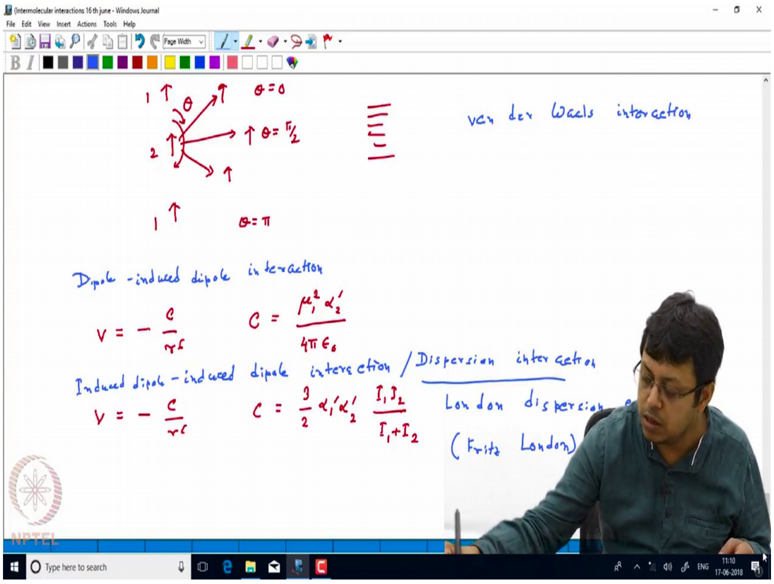

van der Waals interaction

Dipole - induced dipole interaction

$V = -\frac{C}{r^6}$ $C = \frac{\mu_1^2 \alpha_2'}{4\pi\epsilon_0}$

Induced dipole - induced dipole interaction / Dispersion interaction

$V = -\frac{C}{r^6}$ $C = \frac{3}{2}\alpha_1'\alpha_2' \frac{I_1 I_2}{I_1 + I_2}$

London dispersion

(Fritz London)

Second thing to know that actually this interaction depends on the thermal energy of course because as you actually change the theta, we will have some preferred orientation just like we said like I have basically two dipoles; one dipole is like here, and the other dipole can be here, can be here or can be here. So, this is basically the effect of theta, as you can see.

So, this was basically theta and theta can go from 0 to 1 80 degree. So, this is the variation of theta. And we see basically we have two minimum of theta; one is basically at 0, and then the other one is at 90 180 degree. At 90 degree, actually it will be the most repulsive orientation, because as we said that there should be a slip angle always. So, I can have actually head to tail to tail to head kind of interactions, because we fix the dipole 2 here, and dipole 1 we are basically rotating. And with respect to that, will have some preferred orientation of one dipole with respect to the other.

This is the same as basically rotating the dipole in an electromagnetic field. And as we said that will have some preferred orientation, and there we actually talked about the potential energy or a particular scale in the potential energy. So, as you can see here that these two values of theta that theta equal to 0 and theta equal to pi, will be the most preferred orientation; and theta equal to pi by 2 will be the least preferred orientation. And the interaction energies will are different for that. So, at room temperature, the molecules will actually try to populate these energy states, which are basically 0 and pi.

So, there will be a distribution of energy states like this. And then, due to the Boltzmann distribution for a particular temperature, we will have some average value of these interaction dipole, because all kinds of interactions are not all kinds of orientations are not equally probable because of the mutual interaction.

Now, next thing is that what we have, we have talked so far is basically a dipole-dipole interaction and for a particular orientation, which is a parallel orientation between the dipoles. And then, we also took into account of the fact that these dipoles, when they are in parallel, so that one dipole is basically rotating with respect to other and what will be the mutual orientation.

Now, the question is often you will have so, I did not discuss this thing, this equation is known as the Keesam equation, which basically takes into account of all kind of orientational average for the dipoles. But again it is for the parallel orientation, not for the tilt angle orientation.

Now, you can also have a dipole induced dipole kind of interaction for example, suppose I have say water, and I have say benzene, now benzene is a non-polar molecule, it does not have a permanent dipole, but water has a permanent dipole. So, when I bring water and benzene together, what will happen, the permanent dipole of benzene will try to actually polarize the electron cloud permanent dipole of water will try to polarize, the electron cloud in benzene.

And then, will have a dipole induced dipole kind of interaction and that interaction also you can think that one part will be basically the dipolar part, the other part will be basically coming from the polarizability part. But, again so, it is basically after all it is basically interaction between two dipoles, which with all this orientational averaging.

So, basically we will again have the r to the power 6 kind of dependence 1 over r to the power 6 kind of dependence. So, you can actually write it something like all these interactions as minus c over r to the power 6, where c will be something like mu 1 square. So, this mu 1 is basically the permanent dipole. And then, I will have an induced dipole component also, which will be alpha 2 prime. I am using two notation for the second dipole divided by 4 pi epsilon 0 that you can easily figure out how this interaction comes, but the equation that a calculation is little bit more info.

Similarly, you can also think about that what will be the interaction between two benzene molecules, because both of them each of the benzene molecules will have a 0 dipole moment. And as a result, you will not see any like permanent dipole and induced dipole kind of interaction or permanent dipole permanent dipole interaction. So, what happens is that in benzene molecule, the electron cloud actually fluctuating. So, momentarily you are creating an dipole all by itself.

So, it is kind of instantaneous dipole. And that instantaneous dipole actually can interact with another instantaneous dipole or can induce another instantaneous dipole in the other molecule and then they can interact with each other. The reason for this is actually benzene and or say helium gas; where actually we do not have permanent dipole moment for the molecules, they also liquefy, which means actually they should there should be some mechanism for this liquification. And that interaction also will have a form of minus c by r to the power 6, but of course, the c the form of the c will be very different.

In this case, actually there are two polarizability. So, remember that there is no permanent dipole. So, one can actually derive it. And one can show that this is related to the ionization energy of these two molecules. And this equation is known as this London dispersion equation. So, this is after Fritz London, who actually described the dispersion interaction, which is between a induced dipole and another induced dipole London dispersion equation. So, this is between induced dipole, this should be induced dipole induced dipole interaction, which is also known as the London dispersion interaction. And then, you have this dipole-dipole a dipole-induced dipole interaction.

So, we actually talked about many different kinds of interaction. First we started with between two monopoles, which is the coulomb interaction the all are columbic interaction, because it is a columbine interaction by definition is between charges. And dipole is nothing but a distribution of charge. Then we talked about a monopole and a dipole interaction, then we talked about a dipole-dipole interaction and we took into account of the orientation of average. Then we talked about dipole-induced dipole interaction, and we also just mentioned about the London dispersion interaction.

Now, all these interactions are basically you now you can think since the molecules may possess a permanent dipole or may not possess, but this actually can give rise to intermolecular interactions, which is responsible for the liquification of gases or basically the solidification at lower temperature. Now, which means actually if you think in terms of the ideal gas law and the deviation from the ideal gas law, this actually accounts for the existence of the liquid state, which is one of the points that we discussed when we actually have a discussion on real gases. What is why actually one had to modify the ideal gas equation.

And then one of the very successful model if you remember, was the Van der Waals equation of state. And then, which kind of satisfactorily it described or explained many interesting things like inter existence of the critical state or liquification or like it also led to the very interesting case of this critical constants leading to these this general equation, which actually is known as the equation of state independent of the critical constant or the reduce in the reduced form basically, so which actually is obeyed by any gas.

So, all these interactions if you think in terms, these are generally called as Van der Waals interactions. So, these Van der Waals interactions are basically those interactions, which actually account for the deviation from the ideal behavior. And in most of the cases, the dominating interaction for the under the Van der Waals interaction is this dispersion interaction, which is which is described by a Fritz Long.

So, sometimes some textbook actually talk about Van der Waals interaction, and then they mean the dispersion interaction itself, but more generally Van der Waals interaction means, they I inter attractive interactions between the molecules, which can have also dipole-dipole, dipole-induce-dipole or induce dipole-induce-dipole kind of interactions.

Now, when the molecules actually are attracting each other, remember in the Van der Waals equation of state, we said that when you are deriving it that when they actually bring the molecules together we cannot actually bring it to an infinitesimally small distance. Otherwise, if there is only attractive interaction the liquid state or the solid state would have collapsed to a single point, because atomic nuclei.

If we think that they do not they are a kind of dimensionless and molecules are also dimensionless, so there their entire system will basically shrink. And we will have a very small volume, but that never happens, which means actually once we are bringing the molecules together under this attractive potential. If we bring it too close, then actually their electron cloud starts to repel each other. So, there is a repulsive interaction also.

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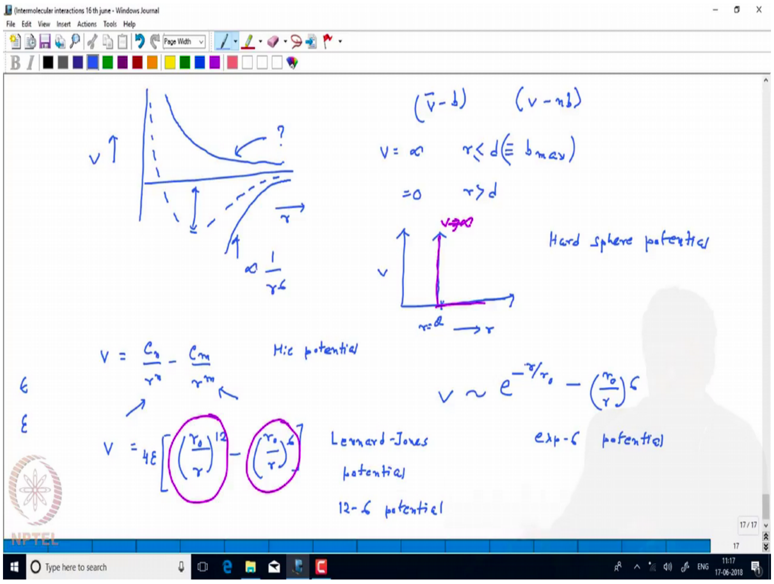

Now, the question is there will be a total interaction, which is basically attractive and repulsive. And basically at some point, these attractive and repulsive potential will balance each other. So, if you ask this question what will be the total potential, how it will look like; if we vary the distance between say two molecules, so or 2 dipole, which you can model as a dipole, which you can model 2 induce dipole or 1 dipole 1 induced dipole something like that, but so far we have talked about only the attractive part of the interaction.

So, you will see that there will be a repulsive attractive interaction, which actually is very it is a stiff function, because actually it goes as 1 over r to the power 6. And then, there is a repulsive interaction, but attractive interaction is a long range interaction, as you can see it is 1 over r to the power 6. So, it falls much earlier, but the repulsion actually takes I mean goes up only when it is too close. So, as a result, what we will see here is that the overall interaction will be something like this. So, this is the overall interaction between the two atoms or 2 molecules, it can be between two atoms also (Refer Time: 42:14) let say two helium atoms.

Now, the question is how do you model this repulsive interaction, now there has been many models. So, for example, we can think at that bare minimum, these are hard spheres. In the sense that this something like we also which is kind of inherent understanding in the Van der Waals equation of state, because we talked about an molecular volume for 1 mole, and that we wrote as simply b. And we excluded that volume, and we wrote it as the real volume is basically connected to the ideal volume as v d l minus b is basically v ideal, so that was in terms of the molar volume.

And for n moles if you remember, that we wrote it as it will be v minus n b, so that was the volume correction. And this volume correction actually comes from this finite size of the molecules, so that is v for volume. And here we are writing v for the potential, and or we could have written the u for the potential. And the idea is that this potential is basically infinite, if the distance is closer or if these hard sphere just touched with each other.

So, basically d is identical to b max, which is nothing but addition of the radii of the two atoms or molecules or the two hard spheres. And it is basically 0 the interaction potential is 0, if the distance between them is more than the r is basically more than the b max or basically they are not touching each other.

So, it this model says that once I am coming like this, and then moment we touch each other, we cannot actually encroach more, we cannot got anything closer. So, if we plot the hard sphere potential, which we already did earlier. So, as a function of r moment r actually is basically equal to d, so the interaction potential goes to infinity, otherwise it is basically 0. So, the plot will be something like this. So, this is going to infinity, otherwise v is tending to infinity. So, this is a v versus r plot for hard sphere.

But, in reality you see that the potential is very different, it basically has a smooth variation. And then, there is there are many other kind of potential for spherical particle, there is something called Mie potential. So, this is for this is known as hard sphere potential, and then there is a something called Mie potential. So, this is after Gustav Mie, who actually did lot of work on scattering by spherical particles of any arbitrary size. And so, then the potential actually looks like of the form like this, where the attractive part actually is 1 over r to the power m and the repulsive part actually goes as 1 over r to the power n.

Now, one special case of Mie potential is a something like, when you consider the repulsive part varying as 1 over r to the power 12. So, instead of c notation, we just write it as r notation. So, we just write it as something like it is r 0 minus r to the power 12. I am coming what is r 0, r 0 is basically the distance at which the two potentials are cancel each other, so that is basically the 0 of the potential. And this is the repulsive part so, the repulsion actually goes as 1 over r to the power 12, and the attractive part is modeled as 1 over r to the power 6. So, attractive model we are keeping it as before.

And then, the overall thing is multiplied by a constant over actually this epsilon we have written it not like this, because this notation of epsilon, we are using for permittivity. So, this epsilon is basically the minima of the interaction energy or minima of this kind of potential. So, this equation again this is a model is known as Lennard-Jones potential. So, this is after Lennard-Jones, who basically modeled the repulsive part as r to the power 12. Sometimes it is known as the 12-6 potential, because of the functional form of this equation.

Now the problem with Lennard-Jones potential that this r to the power 12 thing is very empirical so, there is no reason, why actually it should go like r to the power 12. The r to the power 6 part is kind of logical, because we have already seen that dipole-dipole interaction or Dipole-induced dipole or induced dipole induced dipole, they actually goes as 1 over r to the power 6. But, in this case, what we see that this is the r to the power 12 term is very much empirical.

So, more realistic potential is something like an exponential potential for the repulsion part. Meaning for the repulsion part, we can actually think that this will be something like e to the power minus r by r 0 and minus I will have r 0 by r to the power 6, the attractive part we are keeping the same. If we have the potential of this form, so this is known as exponential-6 potential, because the first part is exponential light or exponential actually. And then, the second part is r to the 1 over r to the power 6 part.

So, these are all different models. And this exponential potential is actually a better model of the repulsion, because you can think that when I have like two electrons coming closer together, so then their orbitals actually interact, and you know that how the orbital energies goes like. So, it is a mostly like that the energy actually shoots up something like as 1 over r by r 0, because the wave function for an 1 s orbital or the electron density actually goes as 1 over r by r 0 or the square of that, so that is how basically it is argued that a more realistic potential will be e to the power minus r by r 0, and which is also experimentally verified. So, at r 0 the potential will be very high, it will go to very high value.

So, overall what we have studied in this lecture is that we talked about what is the origin of intermolecular interactions, why actually gaseous states. If we cool down the temperature, they form liquid. And if we further cool down the temperature, they form solids. And then, there must be some attractive interaction between the molecules. And it now depends how we were modeling the molecule, the molecule can have permanent dipole moments. So, then it is a basically a dipole-dipole interaction, which will dominate. For example, in liquid water, because each molecule of water has a permanent dipole moment, and then I will have a dipole-dipole interaction, but then we also did the orientational averaging. And we found that actually the interaction goes as 1 over r to the power 6.

And then, we argued that there could be water molecule and a benzene molecule, and there could be some interaction between molecule which is a permanent dipole and the molecule which does not have a permanent dipole. So, this kind of interaction is known as dipole induced dipole interaction; and there could be induced dipole induced dipole interaction. And all these interactions actually go as 1 over r to the power 6.

And then, the question was in reality there is also an repulsive interaction. Otherwise, if it is all attractive the any every system will actually collapse to a point or near nearly to a point and or a very small volume at very close at very low temperature and which never happens, which means actually there is also an repulsion, which actually happens at a very short distance, so that short distance thing was modeled in various ways. And one of the very used potentials are one is hard sphere potential, the other one is the Lennard-Jones potential, but a more realistic is the x 6 potential.

So, we gave you an overview of how the intermolecular interactions work and will give you some problems it. So, when you work it out, you will get a more clear picture about the real life experience of basically intermolecular interactions work, which actually give rise to some give rise to basically formation of liquid state and solid states.

Thank you.