Advanced Chemical Thermodynamics & Kinetics

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Lecture - 09
Molecular Interactions 04

Hello everyone. So, in the previous lecture we discussed about the molecular interactions. And then we talked about what will be the energy of a dipole in an external field. And we talked about the we ended our discussion on this section discussing what is dipole interaction, I mean giving rise to the Debye equation, what is the expression for the macroscopic polarization. And if we combine these two how will we get the Clausius Mossotti equation.

Now we will continue on this, and today we will be discussing what happens what is the origin behind the intermolecular interactions. Now we have actually our background ready, because you already discussed; what is the expression for electric dipole interacting with an external field.

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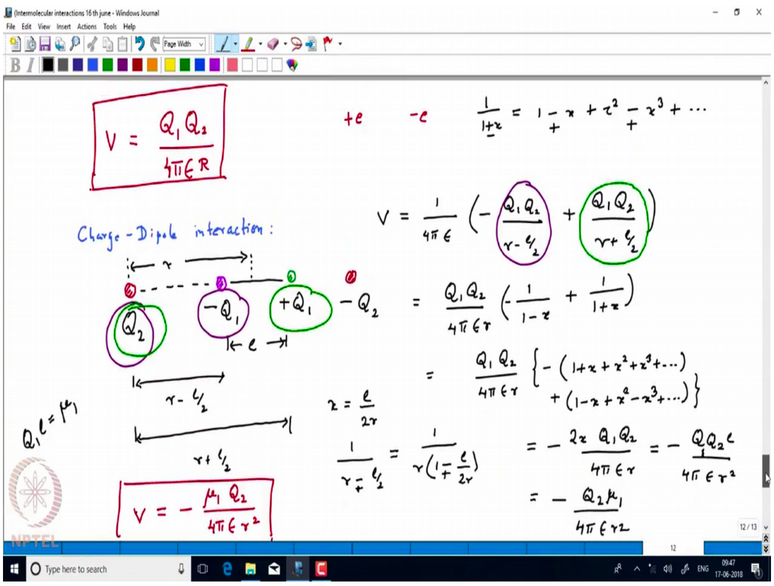

So, the interaction potential for 2 charges already you know that if I write the interaction potential as V, and if the charges are Q 1 and Q 2. So, then the interaction potential will be Q 1 Q 2 by 4 pi epsilon, where epsilon is the permittivity of the medium, which will be epsilon 0 if it is in vacuum, or it will be epsilon 0 times the epsilon R, the reality permittivity, if it is in some medium. And times the R where R is the inter charge separation distance; now what that is already known. So, this is basically between 2 mono poles ideally.

Now the question is if I have a monopole and if I have a dipole, how the interaction potential is going to look like. Now for that we have to know that; what is the location of the monopole with respect to the dipole. When you talk about monopole the usual convention is that you take the monopole to be as a positive charge. And let us now work on it. So, we can actually write it as a leave it as Q 1 Q 2. For example, suppose if Q 1 Q 2 are one of them is a positive charge something like say plus c the other one is minus c.

So, automatically the interaction potential will be negative because it is Q 1 times Q 2 and in this case it is plus c times minus c, which will give you a minus c square. So, that is basically tells so, the interaction potential is negative or the system is a bound system. Similarly, now we can talk about the ion dipole interaction. Let me use some other colour for that. Ion dipole or more specifically we can call it as a charge dipole dipole interaction.

So now, it will depend at what orientation the charge is located with respect to the dipole. For example, suppose I have the dipole like this, we have a positive end and we have a negative end. So, we have basically minus Q 1 charge, and here I have a minus plus Q 1 charge. And what I am going to put? This third charge, which is say Q 2 and we are not telling anything about the sign of the charge right now whether it is a positive charge or a negative charge we are just simply saying that it is a Q 1.

And then who can say that suppose the Q 1 or the Q 2, sorry is located at a distance R from the centre of this dipole, and along the axis of the dipole. So, suppose this is Q 2 which is the new charge it is magnitude is Q 2. And then already for the dipole we are using some convention where we are writing capital R notation. Here actually I will just change the notation a little bit I am using that this is l or l is basically the length of the dipole. And from the center of the dipole, the distance of the charge of the new charge is basically small r. So, this is small r, and this charge is located on the same axis as the dipolar axis.

Now, this is a very particular geometry of course, now the question is what will be the interaction potential that we can easily figure out. So, this charge Q 2 will have interaction with either of the charges Q 1 plus Q 1 and minus Q 1. And that will give rise to basically addition of potential. So, what I am saying is if I want to write it, suppose I have the potential as V, and then I have to first consider the interaction between Q 2 and minus Q 1.

So, every interaction as we know will have a term which is 1 by 4 pi epsilon. And then the first term will be interaction between the Q 2 and minus Q 1. So, will have minus Q 1 Q 2 divided by the distance. And in this case as you can see the distance will be r minus l by 2. Because this distance we are not talking about, this distance between the Q 2 charge which I have denoted as the red sphere, and the Q 1 charge which is basically the pink circle. So, that distance is basically r minus l by 2. It is very obvious from the geometry.

And similarly there will be an interaction between this Q 2 we can actually mark it. So, this is the term first term is basically this term. And then there will be another interaction with Q 2 and the plus Q 1 which we are going to write and the distance for that as you can see is up to here. So, this is r inter nuclear so, the distance from the charge to the centre of the dipole. So, it will be an additional l by 2 distance so, the distance is r into l plus 2. And this time it is between Q 2 and Q 1 so, we are writing Q 1 Q 2 divided by r plus l by 2. So, this interaction is basically between the new charge and the positive end of the dipole. And then we can actually summarize it. So, as you can see that we can actually write it cleverly so, I can take Q 1 Q 2 common.

So, if I do that I will write at Q 1 Q 2 by 4 pi epsilon times I will have, as you can see here will have r minus l by 2. And then if I just make a substitution let say x equal to l by 2 R. Then we can actually take the r common also here. So, in the denominator we have 1 divided by r minus l by 2 or r plus l by 2 something like that. And that I am writing cleverly as 1 divided by r and then we can actually write it as 1 minus l by 2 r. So, these r I am taking common so, I am writing 4 pi epsilon into r divide and then I have 1 divided by the first term is basically there was a minus, and I have 1 minus x. Because x is l by 2 r and the second term I have plus 1 divided by 1 plus x.

Now, we have to expand 1 plus x and 1 minus x, 1 upon 1 plus x or 1 minus x, that we already know 1 by 1 plus x the expansion goes like 1 there will be a minus sign 1 minus x plus x square minus x cube and so on. Similarly, if we had a minus sign here; so we will just replace the x with minus x. So, this will be plus, the second the third term will be again plus x square the 4th term will be again plus something like that.

So, you get a plus series for the 1 minus x and we will get a minus series the odd series basically if it is for 1 plus x. So, together if we write, then it will be something like this. I will have Q 1 Q 2 by 4 pi epsilon r times I will have, let us look carefully I will have a minus sign here. And first term is 1 by 1 minus x. So, I will have 1 plus x plus x square plus x cube, that way it is a series. And then the second term is the 1 by 1 plus x. So, I will have 1 minus x plus x square minus x cube plus this way, this is also another series.

So, what we see here is that we will have basically from here as you can see that we can take the leading order term. And the leading order term this one will cancel the first term the leading order term will be minus x minus x which is basically minus 2 x. So, what will have is will have a minus of x, and then will have plus minus x. So, overall I will have a minus sign. And it will be just multiplied by minus 2 x Q 1 Q 2 by 4 pi epsilon R. And then we can actually substitute the value of x x was l by 2 r. So, you can just write it. So, it will be minus Q 1 Q 2 and it is l by 2 r. So, 2 x will be l by r l divided by 4 pi epsilon. And then instead of r I will have r square, because it is l by r and then we know that this Q 1 times l is nothing but the dipole itself. And then we can actually replace it by mu.

So, this term will be nothing but minus, this will be Q 1, Q 2 into mu in divided by 4 pi epsilon r square. So, we can just write the final expression. So, what we got for the dipole or with a charge interaction that we are getting as minus the interaction potential is minus, we can just rewrite it, instead of writing it as mu I can actually write it as a mu 1, because mu 1 actually denotes the dipole due to charges plus Q 1 and minus Q 1. So, I am just using the mu 1 notation for that. So, I will have overall minus mu 1 into Q 2 divided by 4 pi epsilon into r square. So, these will be interaction for an dipole with a charge, like we had an interaction of between the 2 charges.

Now, we see that here we have a very specific arrangement of the test charge which is a Q 2 with respect to the dipole. Now of course, if Q 2 is positive the interaction will be negative, because as you can see the physical reason for that is Q 2 is actually closer to the negative end on the dipole.

That is why it is a favorable position, but if Q 2 is negative for this geometry will have the potential energy as positive; which means actually it will be a repulsive interaction, because in that case the Q 2 will be a positive charge which will be close, which will be a negative charge which will be close to the negative end on the dipole which is unfavorable position. So, in that case actually Q 2 the most favorable orientation will be along the axis, but closer to the other charge where actually the Q 2 should be here.

So, for that position will be favorable for a charge which is a minus Q 2. Now we will move on. And then in the next section we are going to discuss what will be the interaction between the 2 dipoles. Because we are basically now combining our previous ideas of the interaction between how basically the dipole interacts or the dipole interacts with the field what are the interaction potential. Now we are talking about basically intermolecular interaction where actually molecules may possess permanent dipole moment. And then we are basically bringing up this idea that what will be the interactions between 2 permanent dipole moments.

So, we have first talked about charge interaction which is already known to you. And then what I will happen with a monopole and the dipole kind of interaction which we just described. And then we are going to discuss the most important thing which is basically interaction between 2 dipoles. So, we will now discuss about dipole interaction.

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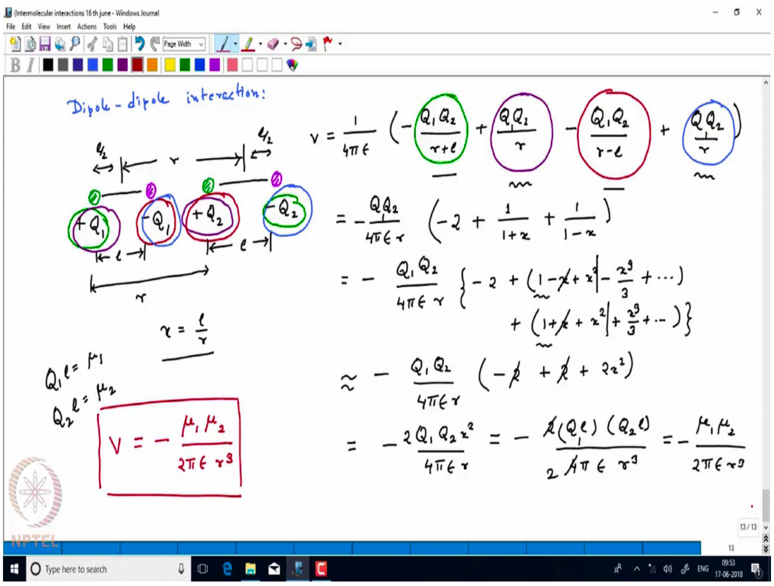

Now, before we go to that you, remember that we often talk about something like a point dipole. Now what is a point dipole? Point dipole means suppose I have a dipole which is something like this, which has a dimension like this. But if you view the dipole of your or you are doing an experiment where actually the dimensions of the experiment have fairly large compared to the dimension of the length of the dipole which is l.

Then actually the dipole will kind of appear like these 2 charges the distance between the 2 charges will appear very very small. And for an observer who is far away or for a observer who is doing a macroscopic experiment, this dipole will appear as if the 2 charges are coalescing are already coalesced. So, it will the observer will think that these charges are basically on top of each other, but still there will be a effect of the dipole because it is not free charge. So, we for that actually use a term which we call as a point dipole. So, that is the meaning of the word point. So, it is basically as if the dipole is behaving as a point, there is no physical length of the dipole. Now the question is, what will be the interaction between 2 dipoles.

But again we have to consider a favorable geometry, and let us consider that we have a positive end like this. And then we have a negative end of the first dipole as like this. So, this is our first dipole where we can choose the charges as let us say plus Q 1. So, this is dipole 1 and minus Q 1, and then I am bringing the second dipole to it. Obviously, the most favorable orientation will be where actually the positive end faces the negative end of the other dipole. So, a position like this; where I have for the second dipole plus Q 2 and minus Q 2, these are the charges.

And let us also consider the lengths of the dipoles are same. Meaning this is l, this is also l. This is just for the; I mean keeping the calculation simple. And as before let us also consider the dipole dipole distance which is a measure from the center of the dipole to the center of the dipole distance is r, small r.

Now, again as before we are going to basically carry out the calculation for the interaction potential, and we know that this interaction potential now will have basically 4 times, because that plus Q 1 will interact with plus Q 2 plus Q 1 interact with minus Q 2 and so on. So, we can actually do work out the maths one by one so, let us all follow. So, will have 1 by 4 pi epsilon 0, and then the first thing will be let us say I am talking about Q 1 minus Q 1 and Q 2. So, the nearest neighbors so, it will be minus Q 1 Q 2 divided by the length. And the length in this case will be as you can see if we can do the Q 1 Q 2 kind of notation, then I have r here. And then it will have plus Q 1 let us say, let us first do this interaction let me use a different colour.

So, I am first interact, I am plus calculating the plus Q 1 with say, minus Q 2 which is the farthest ones ok. So, it will be plus Q 1 minus Q 2 so, that term will be minus Q 1 Q 2 divided by the distance. And the distance in this case as you can see it will be r plus this distance which is l by 2 plus this distance. So, it will be overall r plus l. Then let us consider the second term, and second term we are considering let say so, this was our first term between the 2 charges. Now let us consider the second term and for the second term let us consider that I have Q 1. And then also take that other one as say Q 2. So, we are first calculating that potential due to plus Q 1.

So, I am taking this plus Q 1, and asking what will be the interaction potential between this plus Q 1 and this plus Q 2 so, let us write it. So, in this case it will be plus Q 1 plus Q 2. So, I will have Q 1 Q 2 kind of term. And then divided by look at the distance so, I have r here. So, this distance will be basically r itself. Because this is r minus l by 2, and this is actually r plus l by 2. So, we are basically adding and subtracting l by 2 from both side s, this will be just R. Similarly, now we can actually work out for the interaction potential of the third term. So, this was basically our second term, where actually considered the Q 1 o r plus Q 1 and the interaction with plus Q 2. Or let us focus on minus Q 1 which is this and say first will be plus Q 2.

So, that term will be; since this is a minus and plus so, I will have overall a minus sign, I will have minus Q 1 Q 2 divided by, now what will be the distance? As you can see this is basically overall distance is r and then it is basically the center to center distance which is r. And then we have to subtract l by 2 from both sides. So, will have basically r minus l, and this is basically this interaction. And then we are left with only one interaction which is basically from with this charge how it is interacting with this charge minus Q 1 and minus Q 2. So, obviously I will have a plus term which is Q 1 Q 2 divided by now let us see the distance. So, the distance will be in this case r minus l by 2 plus l by 2. So, it will be basically r and this is interaction is between the minus Q 1 and minus Q 2.

So, now we can actually arrange the terms and as you can see here it is again very straightforward calculation. But in this case we have taken we can actually take the r common, but in the denominator in this case see that it is not r plus l by 2 or r minus l by 2. It is just r so, we can actually write it down. So, if I look at it carefully these 2 terms are basically same terms. So, this is between the (Refer Time: 23:21) ends of the dipole; like, plus Q 1 is interacting with plus Q 2 and minus Q 1 is interacting with minus Q 2. So, these 2 terms if I take the Q 1 Q 2 by r common 4 pi epsilon r let us actually write here epsilon, because we are just considering the general medium of permittivity epsilon. And then these 2 terms will give me a factor which is a basically factor of 2 so, will have 2 here.

And then let us work out on this term and this term. So, first the first term minus Q 1 Q 2 by divided r plus l. So, if I take r common, then I will have 1 divided by 1 plus x; where, x is nothing but l by r, it is not l by 2 r. And similarly for the second term Q minus Q 1 Q 2 divided by r minus l will have minus 1 divided by 1 minus x. And then you see the beauty here that in the earlier case we can actually take it to be instead of taking 2 common or Q 1 Q 2 by r common we could have taken actually the minus common, then actually this will be minus this will be plus, this will be plus. Now unlike the previous plus this is actually addition. In the previous case as you can see this was a subtraction, because there was a negative sign which is here. This is minus 1 over 1 minus x divided by 1 plus 1 by 1 plus x.

So, we can actually write down the series once again it is not necessary, but I will do it just for your convenience. So, I will have Q 1 Q 2 by 4 pi epsilon into r I have a minus 2. And then will have a series for 1 plus x, and that series goes as you know it is 1, and then I will have minus x plus x square minus x cube by 3 like this. And it is a series I should write in the series form. And then I have a plus 1 by 1 minus x which is 1 plus x plus x square plus x cube by 3 and so on. So, overall what I can see here, I will just have a term which is just 2.

And then I mean if you want to include the effect of x, we have to include the up to third term. So, basically I am truncating the series up to here both the serieses. And then what I see this x actually gets cancelled, and I will have basically 2 here, and then I will have twice x square. So, if I just truncate up to the second term the x cancels and then will get a 2 here, let me write here, Q 1 Q 2 by 4 pi epsilon into r. And this is an approximation we are making right now.

And then I have minus 2, and then plus, this one and this one gives me 2, and these 2 will cancel. And then the x is also canceled. So, I have to consider another term; which is basically plus 2 x square and this is again an approximation. So, these 2 now gets cancelled. And then in the final expression I will have twice x square into Q 1 Q 2 by 4 pi epsilon r. And then I know that x is nothing but l by r so, I will just replace it. So, it will be minus Q 1 Q 2, 2 times x square by 4 pi epsilon r, and then I am again replace x as l by r. So, it will be twice Q 1 l.

So, x square will be l square by r square; so one l an attaching with Q 1, and the other l an attaching with Q 2. This will be l square divided by 4 pi epsilon r cube. And then what we have is Q 1 into l, and we know that Q 1 into l is basically the dipole moment of the magnitude of the dipole moment for the first dipole. Similarly, Q 2 into l is basically magnitude of the second dipole.

So, overall what we are getting is mu 1 mu 2 with a negative sign, and these 2 gets cancelled with these 2 to give me 2 overall, and 2 pi epsilon r cube. So, thus we got interaction potential for dipole dipole interaction. It is basically the interaction potential between 2 dipoles, if the dipoles are oriented in a favorable condition, where actually the positive end of one dipole faces the negative end of the other dipole. So, this is one of this is the most favorable geometry. You can have actually the 2 dipoles. So, which are actually have a tilt handle, but that we are not considering right now.

So, we will keep the discussion simple. So, the dipole dipole interaction will be something like minus mu 1 mu 2 divided by 2 pi epsilon r cube. And now you can review what we have just done. So, if it is between 2 charges as you can see, if you write the distance between the 2 charges as smaller. So, it will be Q 1 Q 2 by 4 pi epsilon 0 epsilon r, and then if it is between 2 between a dipole and charge, then we see that actually it goes as 1 over r square. And then it if it is between 2 dipoles actually it goes as one of over r cube.

Thus, we see basically how the interactions are or if I actually increase the polarity of these multiple, how the interactions are basically going to look like.