

Bio-Physical Chemistry
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Lecture - 10
Dipole-Dipole Interaction

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$$V = - \frac{\mu_1 \mu_2}{2\pi\epsilon_0 r^3}$$

General Case

$$V = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{4\pi\epsilon_0 r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{4\pi\epsilon_0 r^5}$$

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So, in today's class will go on with our interactions with regards to Dipole Dipole alright and in the last class what we actually derived was this expression where. So, V is equal to μ_1 , μ_2 , by $2\pi\epsilon_0 r^3$ right where these are the respective dipole moments of the interacting dipoles. Let us take a very general case. What I mean by general case is, the dipoles can be oriented with orientated with respect to each other at specific angles. So, what I mean by that?

For example, I have a dipole moment μ_1 in this case right and I have another dipole moment say μ_2 , now this is if I take it from the center of these two dipoles let this be the distance between the two centers which is r . So, you can understand what is going to happen.

With respect to the distance between the two dipoles these dipoles are not parallel right. So, they are maintained at a certain angle. Say, this is angle θ_1 which μ_1 makes with this radius vector and if you look at this dipole, then this mix with this one an angle θ_2 ok.

So, this is the very general case now, we do not know what the angle it is we just trying to derive it for two dipoles oriented at certain angles. So, here we will not look at the derivation, but we will just write down the actual form.

The actual form is or the potential energy is can be written as V is equal to $\mu_1 \cdot \mu_2$ by $4\pi\epsilon_0 r^3$ that is the first term minus. Now this remember there is a dot product $\mu_1 \cdot \mu_2$; that means, we are talking about vector quantities now right minus $3\mu_1 \cdot r$ times $\mu_2 \cdot r$ over $4\pi\epsilon_0 r^5$ ok.

So, this interaction energy can be derived and we will not go into the derivation. I can keep in mind the term on the right hand side we can see $\mu_1 \cdot r$ $\mu_2 \cdot r$ and we have r^2 the power 5 term at the bottom ok. These are essentially your dot products of a dipole moments with respect to the radius vector r which is the distance in between μ_1 and μ_2 .

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Handwritten notes on a grid background:

$$\vec{\mu}_1 \cdot \vec{\mu}_2 = \mu_1 \mu_2 \cos \theta_{12}$$
$$\vec{\mu}_1 \cdot \vec{r} = \mu_1 r \cos \theta_1$$
$$\vec{\mu}_2 \cdot \vec{r} = \mu_2 r \cos \theta_2$$
$$V = \frac{\mu_1 \mu_2 \cos \theta_{12}}{4\pi\epsilon_0 r^3} - \frac{3\mu_1 r \mu_2 r \cos \theta_1 \cos \theta_2}{4\pi\epsilon_0 r^5}$$

$\theta_{12} \Rightarrow$ the angle between the 2 dipoles

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Now you know this definitely there I can write $\mu_1 \cdot \mu_2$ now these are the vectors I am talking about is equal to what? $\mu_1 \mu_2$ then the angle between the two dipoles right. So, I can write cosine of θ_{12} that means, this is the angle between the two dipoles and remember this when I am writing this like μ_1 and μ_2 these are absolute magnitudes I am talking about So, now these are scalar quantities.

Similarly, if I can write $\mu_1 \cdot r$ what should I be writing? I should be writing $\mu_1 r$ then cosine of θ_1 right. So, all these again are vector quantities please remember and if I am writing $\mu_2 \cdot r$ then this is equal to $\mu_2 r$ cosine of θ_2 . So, again these are your absolute magnitudes. So, from now on ward what I will do is, I will not represent them like this form I will just write $\mu_2 r$ and all these things straightaway.

See if I am having this and if I am put this back, if I am putting this back into my original expression then I have V is equal to you can write $\mu_1 \mu_2 \cos \theta_{12}$ over $4\pi \epsilon_0 r^3$ and the next term then becomes $3\mu_1 r \mu_2 \cos \theta_1 \cos \theta_2$ over $4\pi \epsilon_0 r^5$

So, again I will just plugged in these dot products right this θ_{12} is what? θ_{12} is the angle between the two dipoles now please keep that in mind. So, θ_{12} is the angle between the two dipoles and obviously, θ_1 and θ_2 are the angles that these dipoles make individual with respect to the.

Student: Separating them.

r which is separating them the distance and just there is an over writing here. So, this is essentially $\cos \theta_1$ and $\cos \theta_2$ ok. Now this thing can be further simplified as you can see. So, this remains like this you can see throughout you have a μ_1 by μ_2 , μ_1 times μ_2 $4\pi \epsilon_0$ term common I can take out and not only that you see now you what you have out here? You have r and r which is essentially what? r^2 you have r to the power 5 term here.

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Handwritten notes on a grid background:

$$V = \frac{\mu_1 \mu_2}{4\pi\epsilon_0 r^3} [\cos\theta_{12} - 3\cos\theta_1 \cos\theta_2]$$

Diagram showing two dipoles, μ_1 and μ_2 , separated by a distance r . The angle between the dipole moments is θ_{12} . The angle between μ_1 and the line connecting the centers is θ_1 . The angle between μ_2 and the line connecting the centers is θ_2 .

For the case where both dipoles are aligned along the same axis (the z-axis), the angles are defined as:

$$\theta_1 = \theta_2 = \theta$$

$$\theta_{12} = 0$$

The potential energy simplifies to:

$$V = \frac{\mu_1 \mu_2}{4\pi\epsilon_0 r^3} [1 - 3\cos^2\theta]$$

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So, what I can write this one as further simplification. So, V is equal to $\mu_1 \mu_2$ by $4\pi\epsilon_0 r^3$ then what should I be writing here? Cosine of θ_{12} minus

Student: (Refer Time: 06:50).

$3 \cos$ of θ_1 times cosine of θ_2 right. So, this is the most general expression you can have for two interacting dipoles making you know certain angles θ_{12} , θ_1 and θ_2 respectively the definitions as we have discussed. Now let us take a very specific case let us take a very specific case.

For example, let us take a case where I have two dipoles like this these are two dipoles right. So, I can have this one as say q_1 minus q_1 and this is.

Student: q_2 .

q_2 .

Student: Minus q_2 .

Minus q_2 and you can understand. So, this dipole has its orientation such that the positive end is closed to the negative end of the other dipole right. So, this is your μ_1 and this is your.

Student: μ_2 .

μ_2 again the length is given as.

Student: (Refer Time: 07:57).

Same for here the length is given as l . Now remember what distance we were talking about. So, this distance is again from the mid point of the dipole. So, if I can extend if I can extend my r . So, this is your r right. So, this one makes an angle θ and this one if you can understand this one also makes an angle θ do you get that?

So, this one makes an angle θ ; that means, μ_1 makes an angle θ with the radius vector r or the distance vector r and this one also makes an angle θ ; that means, θ_1 is equal to θ_2 . So, here I can say θ_1 is equal to θ_2 that is one. Now, tell me what happens to θ_1 θ_2 θ_1 θ_2 ?

Student: 0 (Refer Time: 08:51).

0. So, θ_1 θ_2 is 0 now and if you put these; if you put these here what are you going to get?

Student: $1 - 3$.

That means, I can get now I can simplify my V further by writing as V is equal to $\frac{\mu_1 \mu_2}{4\pi\epsilon_0 r^3} \cos\theta$ right then what is my first term? $\cos 0$ is 1 minus 3.

Student: $3 \cos$.

Cosine square of.

Student: (Refer Time: 09:21).

Theta. Have you ever seen an expression like this before? Where we seen?

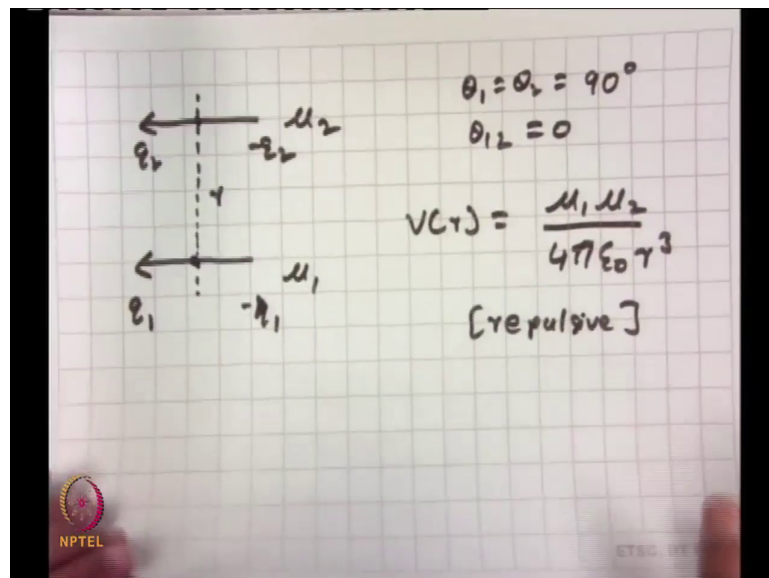
Student: (Refer Time: 09:32).

But anyway this is one of the places you can see the expression and this expression also comes in a very important feature in fluorescence spectroscopy which is called faster resonance energy transfer. There also we talk about you know interacting dipoles which are point charges and there this orientation also comes in ok.

But again keeping this orientation in mind right where θ_1 and θ_2 is θ_1 and θ_2 equal these are parallel, $\theta_1 - \theta_2$ is equal to 0 you have this ok. Now this is an expression guys you will have to remember. The base expression which is the one we started with.

This base expression; that means, the expression we want to start with this you do not have to remember at least I will provide this with you in the exam ok, but any further simplifications based on this expression, you will be able to you will have to be able to do that now what do I mean by that? Let us take another case now.

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So, just simplifying this further we can take another case, where we can have the dipoles like this right. I can have the dipoles like this. So, this is say μ_1 , this is μ_2 again r is from the center right you can have this it does not matter what it is and this is your r this is your r . Now tell me what is θ_1 equal to θ_2 here?

Student: 90 degrees.

90 degrees ok. What is θ_{12} ? Same again parallel 0 now. So, what does V of r become now? Let us look at this expression.

Student: (Refer Time: 11:45).

3 cosine of theta 1 cosine of theta 2 what is $\cos 90^\circ$?

Student: 0.

0 this is also 0. So, this term cancels out I mean this term goes away what is this?

Student: 1.

1 good now.

Student: (Refer Time: 11:58).

Now, think about this, now think about this I just be careful about the sign now. You see these are like charges right I can have q_1 minus q_1 right. I can have q_2 minus q_2 because I am keeping the convention of this sign of the dipole moment where what direction dipole moment will be going. So, if that is the case what should the sign V should this be attractive or repulsive you tell me?

Student: Repulsive.

It should be repulsive yeah it should be repulsive right because you see q_2 is close to q_1 which are both positively charged ions and then q_2 is close to q_1 which are again negative charge the negative ones. So, this one would be μ_1, μ_2 times over $4\pi\epsilon_0 r^3$ and the interaction is repulsive in nature because your like charges are just on top of each other.

So, think about the different orientations you can have now think about the different orientations you can have. So, I can take some other orientation examples right. So, one of the other orientation is this one this flips to give you a very stable interaction potential, when this

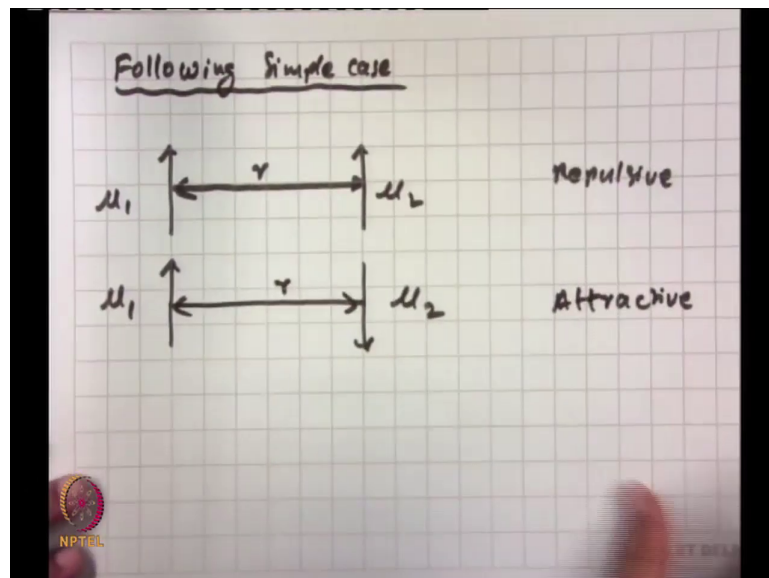
one reflect; that means, minus q_2 would come here and this plus q_2 would go there what would you get? You would be getting a.

Student: Minus.

Same thing with a negative sign because it is a.

Student: Attractive.

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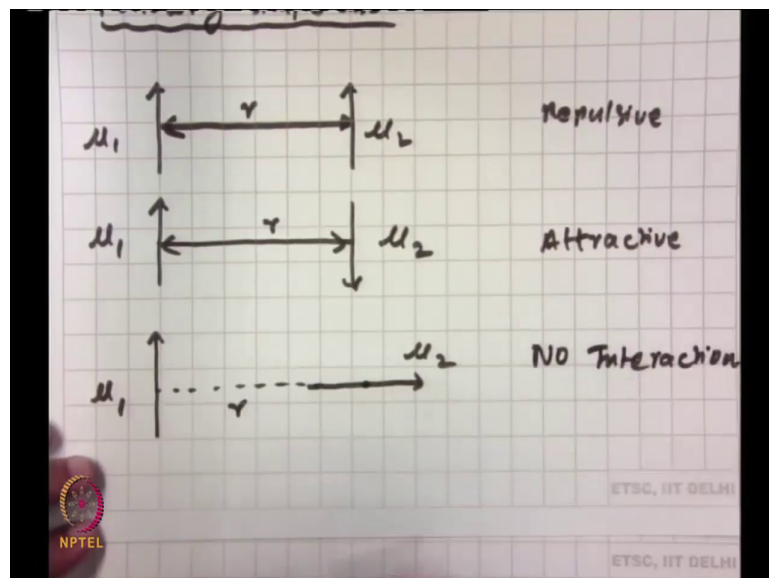


Attractive potential it is an attractive potential that is why. So, you know based on this I can have the following I can have the following simple cases. So, what are the cases? I can have 2

dipole moments aligned like this right what we just saw. So, this is μ_1 , this is μ_2 and this is again r .

So, this we saw is what repulsive right you can see both are pointing in the same direction. The next one I can have is something like this μ_1 , μ_2 again separated by distance r this is attractive ok. I can have another orientation like this which is I have something like this which is one dipole μ_1 right.

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And then I have another dipole which is like this, this is μ_2 and again. So, distance to the centre is r . Now, here you have to tell me would this be attractive would this be repulsive?

Student: (Refer Time: 14:44).

My answer is and this you have to figure it yourself there would be no interaction.

Student: (Refer Time: 14:54).

You understand why right there would be no interaction what is θ_{12} here?

Student: (Refer Time: 15:05) 90.

What is θ_{12} here?

Student: (Refer Time: 15:07).

It is not 0 its 90 degrees right.

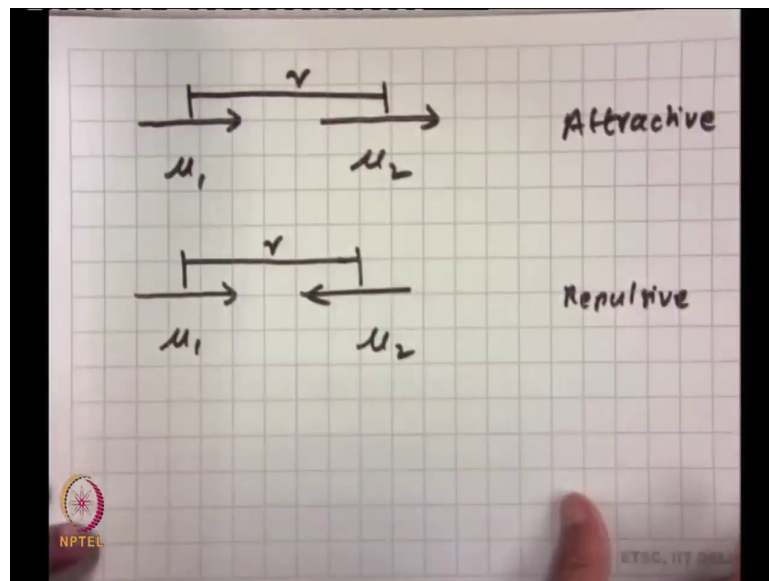
Student: 90 degrees.

Because you extended like this its 90 degrees. So, what is cosine of 90?

Student: 0.

0 and then you can figure out how it comes out right. So, I have already given a hint these things in the exam you should be able to figure out by yourself and write down the respective interactions right.

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So, what are the two other simple cases we can have? So, continuing with our cases we can have two dipoles like this right. So, this is μ_1 this is μ_2 . So, would this be attractive or repulsive this would be?

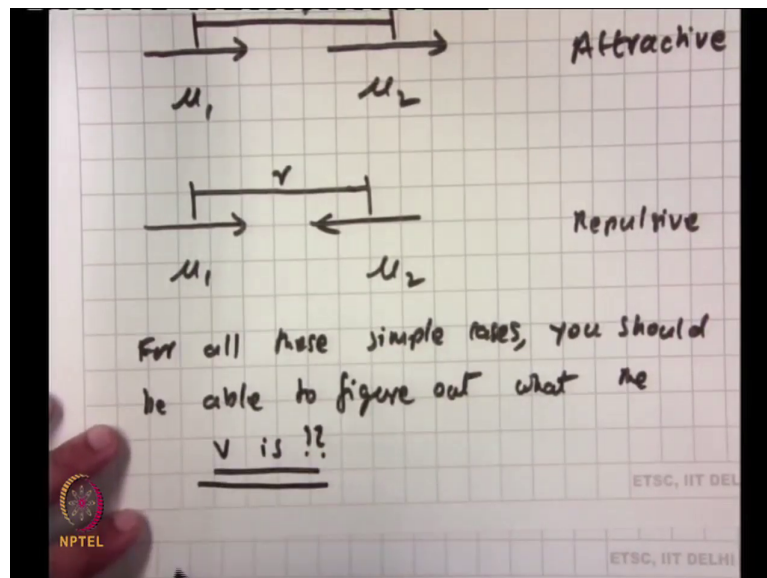
Student: (Refer Time: 15:45).

Attractive right.

Student: Yes.

Or I can have this one this one again μ_1 μ_2 . So, r is essentially from the middle this is r again here this is r . So, this would be repulsive ok.

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So, the bottom line is for all these simple cases you should be able to figure out what the interaction potential V is ok. This you should be able to figure out. So, let us move on now.

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$$V = \frac{\mu_1 \mu_2}{4\pi\epsilon_0 r^3} [1 - 3\cos^2\theta]$$
$$V \rightarrow 0 \quad 1 - 3\cos^2\theta = 0$$
$$\cos^2\theta = \frac{1}{3}$$
$$\cos\theta = \sqrt{\frac{1}{3}} \quad \leftarrow \quad \cos\theta = \pm \sqrt{\frac{1}{3}}$$
$$\theta = 54.7^\circ$$

Consider the situation where V is equal to $\mu_1 \mu_2$ which we just derived $4\pi\epsilon_0 r^3$ $1 - 3\cos^2\theta$ or $\cos^2\theta$. Now, just looking at this under what conditions can V or a V tends to 0? What can I say about this? Can you tell me any factor I can say tends to 0?

Student: (Refer Time: 17:28) can be 0. (Refer Time: 17:30).

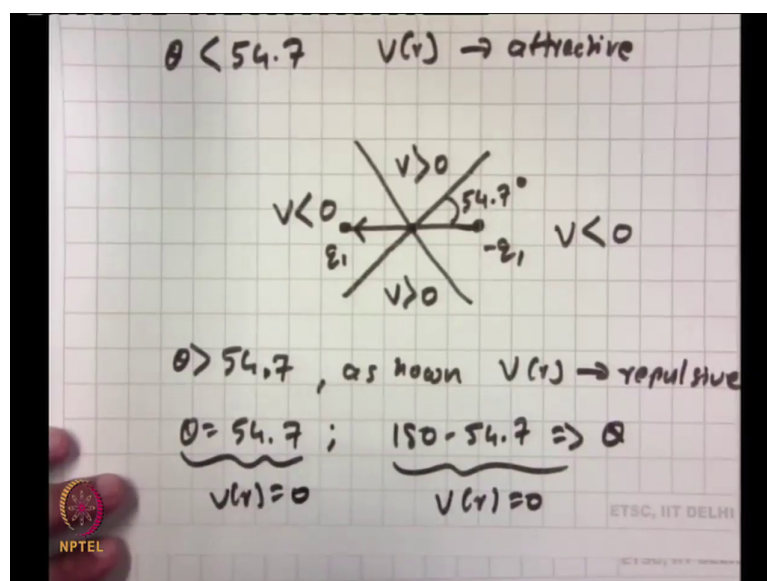
1 minus. So, see μ_1 and μ_2 cannot be 0 right because we know they have dipoles that was given if μ_1 is 0 then obviously, we are not going to talk about anything else. So, when it is.

So, this one; that means, $1 - 3\cos^2\theta$ should go to 0 so; that means, what you are trying to find out is at what angle; that means, at what angle you would not be having

any interactions between the dipoles that essentially what you are saying right; that means, if V is going to 0. So, here I can write cosine square theta is equal to $1/3$ or cos of theta is equal to plus minus $1/\sqrt{3}$.

Now, based on this if cosine of theta is equal to $1/\sqrt{3}$ then theta comes out to be 54.7 degrees ok. See in some sense this will come back to later in the course when we talk about fluorescence, but in some sense you can realize one thing. If we have two dipoles which are orientated at this angle, its essentially a magic angle right; that means, it do not have any interactions. So, there are how can how does the potential picture look like? What I mean is suppose I have a dipole like this.

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Again let me start from centre of the page, I have a dipole like this right and I am trying to find out regions where they are attractive and repulsive in terms of your V .

So, let this be the centre and these are two lines, I am drawing these are two lines I am drawing ok. Now this angle is 54.7 degrees and say this is your dipole this is q_1 , this is minus q_1 . So, you can understand one thing, if θ the θ you are talking about if θ is less than 54.7 ; that means, if θ .

So, in this region in this region from here to here your V actually is less than 0 in this region your V is less than 0 why? Because 54.7 is very interaction is 0 right when you start from here your interaction was attractive. You move like this, you move like this, you move like this, you go to 0 then beyond that you will go into the repulsive regime.

So, between these two crosses or between these two lines, I can say this is V is greater than 0 right similarly here V is greater than 0 and then again you come on to the other side, you have V which is less than 0 ok.

So, these are very nice picture which tells you how the dipoles if they are oriented, what you know they are respective nature of attractions or repulsions would be nature of potential energy would be whether attractive or repulsive?

Now to explain it; that means, if θ less than 54.7 then V of r or V essential is attractive right. If θ is greater than 54.7 is greater than 54.7 as shown V of r because it depends upon r is repulsive is repulsive and what about the angles at which you will be not having any interaction?

Student: Equal.

So, one is θ is equal to 54.7 what is the other angle?

Student: 180 minus.

180 minus this right 180 minus this. So, the other one is at 180 minus 54.7 at 180 minus 54.7 right this is another case where if this is your θ here again V of r is equal to 0 like V of r is

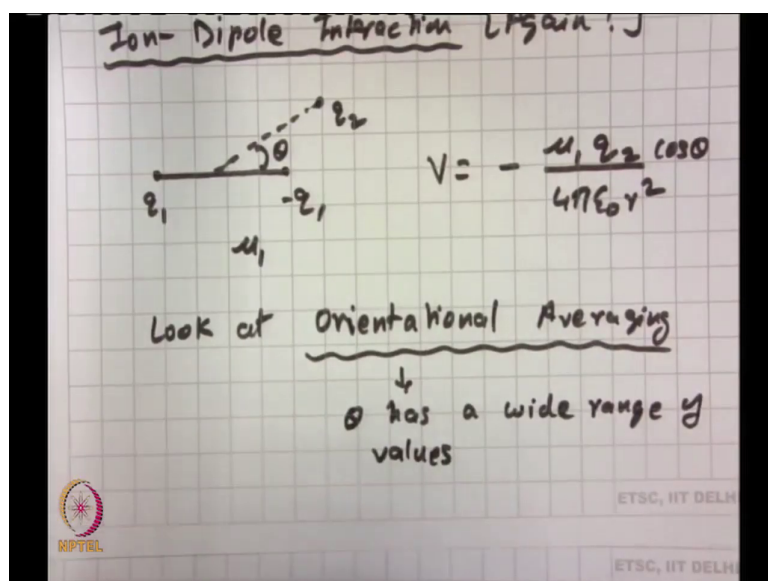
equal to 0. So, essentially this line and this line are what? Your lines of 0 interaction that you can understand now right this line and this line essentially the lines of 0 interaction.

So, what it means is now start looking here, if I have; if I have say a charge which is say plus q_2 here right now q_2 is close to minus q_1 . So obviously, if you are in this regime, this q_2 is closer to its opposite charge hence; obviously, your interaction is attractive.

Now, the moment you come here in the middle what happens? This was the 0 line by the moment you come here you are coming slowly closer to what q_1 , now these are like charges hence your repulsive interaction comes in. So, that is how you can think about it. So, this was about you know the; you know the regions of your attractive and repulsive interactions and also please keep in mind the different alignments you can have.

So, if you would know that formula then based on θ_1 , θ_2 and θ_3 you should be able to drive your interaction potential you know that you should be able to do. And the significance is if anyone gives you a system like that and because you would know V of r for any given angle you would be easily able to calculate because you know V of r right ok.

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Now, moving one step further let us think about this. We will go back to an ion dipole interaction and I will tell you why. You are looking at it again yeah the reason is this.

See when we if we were remember we had a dipole like this right say q_1 minus q_1 right this was l the length of the dipole and we had a charge out here say q_2 which was making a certain angle θ right and for this one what was the V ? Do you remember it was. So, if this is the dipole moment of μ_1 then it is minus μ_1 times q_2 right then we had a factor cosine of θ , then we had $4\pi\epsilon_0$.

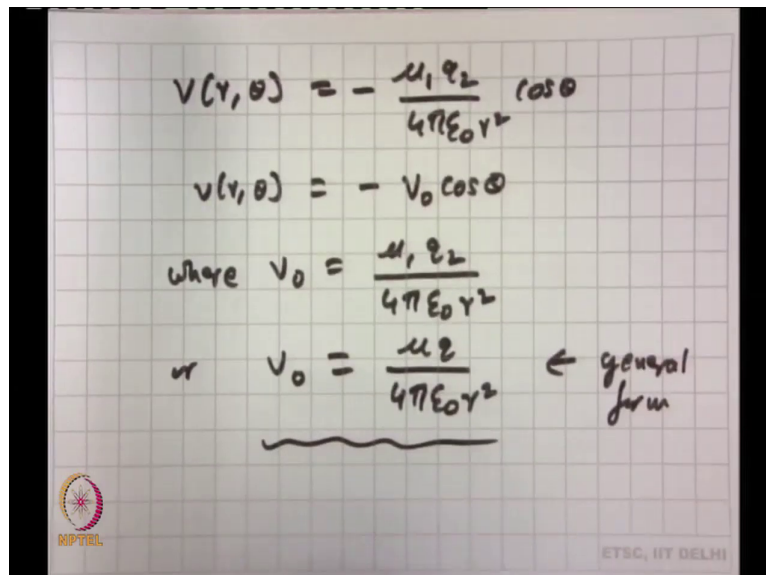
Student: r square.

r square and this is again squared because we are talking about a dipole interacting with an ion or vice versa, but think about real life situation. If you have a freely tumbling dipole, would

you be would you be maintaining a single theta? You will not be maintaining a single theta what you would instead be maintaining is a range of theta values a range of theta values.

So, what I am what we are going to do now is we are going to look at we are going to look at something known as orientational averaging. We are going to look at orientational averaging; that means, theta has a wide range of values and I will just tell you what the range is, tell you what the range is. So, this what are you going to look at and you will be surprised what this orientational averaging can what this orientational averaging can do interaction just wait for this.

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$$V(r, \theta) = - \frac{u_1 u_2}{4\pi\epsilon_0 r^2} \cos\theta$$
$$V(r, \theta) = - V_0 \cos\theta$$
$$\text{where } V_0 = \frac{u_1 u_2}{4\pi\epsilon_0 r^2}$$
$$\text{or } \underline{V_0 = \frac{u_2}{4\pi\epsilon_0 r^2}} \leftarrow \text{general form}$$

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So, look at this equation again and let me write this equation again just to make the connection. I can write the previous equation as V of r theta because it depends upon theta it

also depends upon r to be equal to $-\frac{q}{4\pi\epsilon_0 r^2} \cos\theta$ and this.

I can simplify further by writing $V(r, \theta)$ is equal to $V_0 \cos\theta$, where V_0 is equal to $\frac{q}{4\pi\epsilon_0 r^2}$ or for a general case I can write or for a general case I can just write V_0 I will remove the subscript 1 and 2 q by $4\pi\epsilon_0 r^2$ right this is a very general form right.

So, remember out here since we are involved in only the angular orientational averaging our radial part does not come in. So, it essentially comes into the constant V_0 because we are doing an orientational averaging with respect to θ now what do you mean by that? To find this; to find this orientational averaging; that means, the potential coming from orientational averaging we will solve an integral like this we will solve $V(r)$ we will solve V of r .

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$$\langle V(r) \rangle = \frac{\int_0^\pi V(r, \theta) e^{-V(r, \theta)/kT} \sin \theta d\theta}{\int_0^\pi e^{-V(r, \theta)/kT} \sin \theta d\theta}$$

$$V(r, \theta) = -V_0 \cos \theta$$

$$\frac{V(r, \theta)}{kT} \ll 1 \quad \leftarrow \text{assumption}$$

$$e^{-V(r, \theta)/kT} = e^{V_0 \cos \theta / kT}$$

$$= 1 + \frac{V_0 \cos \theta}{kT} + \dots$$

See I am not writing r θ anymore the reason is because I am doing an orientational averaging I am essentially integrating θ out right there is no longer any θ dependence that is what I am doing.

So, this is equal to now this you have to remember ok. Let us look at the limits 0 to π 0 to π V of r θ e to the power minus V r θ over kT then you would be having $\sin \theta d\theta$ and in the denominator you have this minus V of r θ kT $\sin \theta d\theta$. So, again.

So, this is your average V of r . So, this its like your expectation value this is your average value V of r is equal to the numerator is V of r θ which you know e to the power minus V of r θ kT $\sin \theta d\theta$ right. So, this is your integration you know that is integration variable.

Now, look at what θ varies θ varies from what? 0 to π . So, you can think about a dipole and an ion. So, dipole can see this is the angle θ , then the charge can go from here to here if you go the other way you just essentially repeating that is what you are doing, but the charge can go from here right any θ θ θ θ and it can go to the other side right covering an angle of π which is 180 degrees.

So, this is what we will have to solve guys and actually we are going to do that right we are going to do that. So, how? We will make an approximation first of all we know that V of r θ is equal to what? Minus $V_0 \cos \theta$ we know from before right. We will also do one thing we will see V of r θ by kT is much less than 1 is much less than 1 right.

Do you understand the significance of kT here? You can realize this term has a temperature dependence; that means, these forces would be dependent upon on your thermal energy and here thermal energy is reflected by what? The kT term or r t whichever way you want to look at.

So, based on these two and specially this is an assumption we are making specially this is an assumption we are making say if V of r θ by kT is much less than 1 is much less than 1, then what I can write is look at e to the power minus V of r θ over kT .

So, what is this equal to? This is equal to I can write e to the power $V_0 \cos \theta$ over kT right because V of r θ is equal to minus $V_0 \cos \theta$ and I already had a negative sign here and I know this one is much less than kT . So, what I do is, I do an expansion of this Taylor expansion of e to the power x if I do a Taylor expansion e to the power x what do I get? I get $1 + V_0 \cos \theta$ over kT and so on right.

So, I am making this assumption and based on this assumption, I am simplifying my problem or we are simplifying our problem by expanding this in terms of the Taylor series expansion and just we take the first two terms. $1 + V_0 \cos \theta$ by kT . So, this is something you know by this term you are familiar right with did it for the ion dipole too remember $1 + l$ by r over $1 - l$ by r and we do not consider the other terms essentially the same thing we

are doing. So, take this and put it back in the integral ok, but what we will do is now, we will look at the numerator and denominator separately right.

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The image shows a handwritten derivation of the denominator integral on a grid background. The text is as follows:

Denominator:

$$\int_0^\pi e^{-V(r,\theta)/kT} \sin\theta d\theta$$

$$= \int_0^\pi e^{V_0 \cos\theta / kT} \sin\theta d\theta$$

$$= \int_0^\pi \left(1 + \frac{V_0 \cos\theta}{kT}\right) \sin\theta d\theta$$

$$= \int_0^\pi \sin\theta d\theta + \int_0^\pi \frac{V_0 \cos\theta}{kT} \sin\theta d\theta$$

At the bottom left of the grid, there is a logo for NPTEL. At the bottom right, the text "ETSC, IIT DELHI" is visible.

So, let us look at the denominator. So, let us look at the denominator of your integral. So, the denominator is 0 to pi again I am writing, e to the power minus V r theta by k T sin theta d theta ok.

So, this is essentially again 0 to pi e to the power V 0 cosine of theta over k T sin theta and d theta and using the assumption; using the assumption which we have already done in the previous sheet we can write this 0 to pi 1 plus what? V 0 cosine of theta over k T right times sin theta d theta. And this I can further simplify as 0 to pi I can write what is the first term? Sin theta d of theta plus 0 to pi V 0 cosine of theta k T then I can write sin theta d theta.

So, you can see what we done is for complicated exponential integral, we have split it into 2 very easy to do sum of integrals ok. So, let us take these two integrals (Refer Time: 33:21) 1 this one and this one. So, 0 to pi sin theta d theta is equal to what?

(Refer Slide Time: 33:25)

Handwritten mathematical derivation on grid paper:

$$\int_0^{\pi} \sin \theta d\theta = -[\cos \theta]_0^{\pi}$$
$$= 2$$
$$\int_0^{\pi} \frac{V_0}{kT} \cos \theta \sin \theta d\theta$$
$$= \frac{V_0}{kT} \int_0^{\pi} \cos \theta \sin \theta d\theta$$

let $x = \cos \theta$ $dx = -\sin \theta d\theta$
at $\theta = 0$, $x = 1$
 $\theta = \pi$, $x = -1$

ETSC, IIT DELHI

Student: Minus cos theta.

Minus cos theta in the range 0 to pi now tell me what the value is thank you. So, the value is 2 does everybody realize that?

Student: Yes.

This is cosine of pi minus cosine of 0 minus 1 minus 1 plus 2 great. Now this was the easy one right let us look at the other one, the other one is also very easy. See the other one I am looking at 0 to pi V_0 by kT cosine of theta sin theta d theta. V_0 by kT is a constant right because we are integrating over theta right.

So, though V_0 has the term r it does not matter to us because we are not even integrating over d of r , we are doing an angular orientation averaging right. So, r essential is a constant. So, I can write it has V_0 by kT obviously, kT is also a constant, 0 to pi cosine of theta sin theta d of theta and let us do a trick I am sure you guys know.

Student: (Refer Time: 34:41).

Let x equal to I can do that or I will also do this [FL]. Let x is equal to cosine of theta right then what is $d x$ equal to? What is $d x$ equal to?

Student: (Refer Time: 35:00) minus (Refer Time: 35:03).

Minus.

Student: (Refer Time: 35:04).

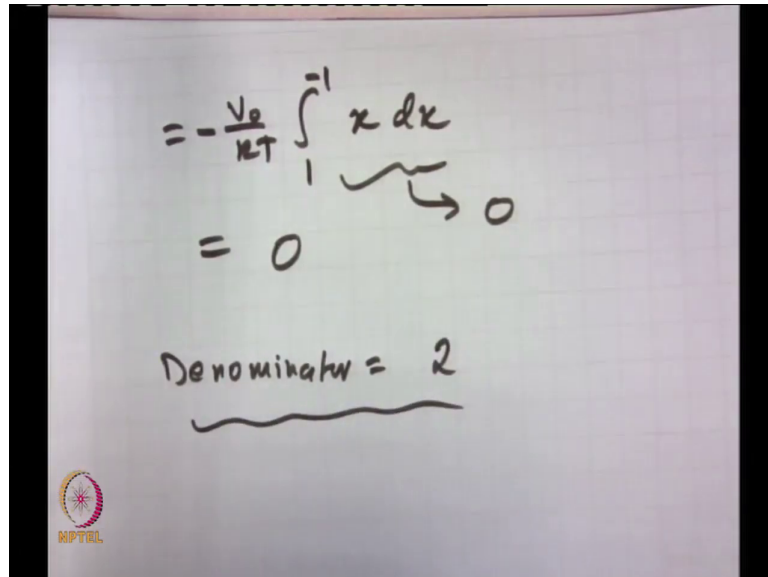
Sin theta d theta ok. So, this one this integral ok. So, one more thing. If x is equal to cosine of theta at theta equal to 0 sorry theta equal to 0 because I have to change the limits of x what is x equal to? 1 right at theta is equal to pi what is x equal to?

Student: 1.

Minus 1 right, there are many ways of doing this integral. So, I am just showing one of the ways you can even do it has as I said, we can write; we can write this one as is been look for

new page. So, we can write this one now as is equal to V_0 by kT right I have a negative sign coming here then what do I have?

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$$= -\frac{V_0}{kT} \int_1^{-1} x dx$$
$$= 0$$

Denominator = 2

I have 1 to minus 1 I do x and look at this $\sin \theta d\theta$ what is $\sin \theta d\theta$? This is essentially d of x right I already have d of x . So, I can put.

Student: dx .

d of x , now there is an extremely similar integral is not it and what is the value of this integral?
What is $x dx$?

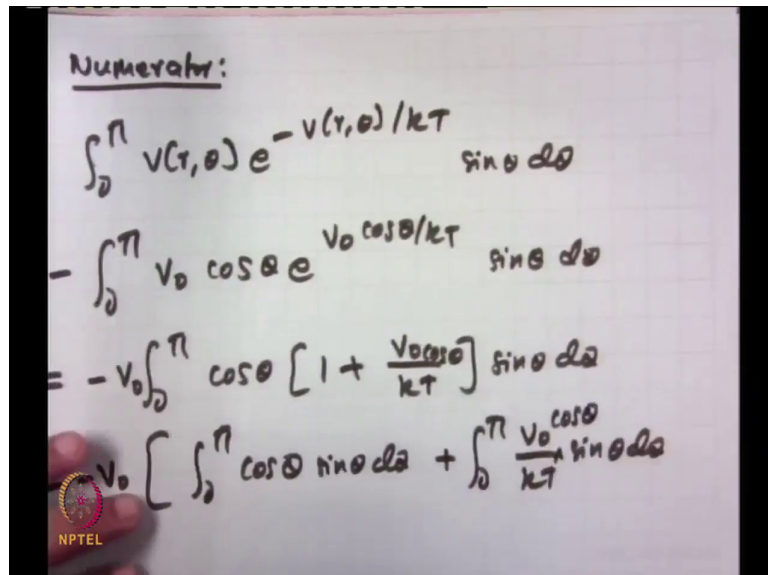
Student: x square by 2.

x square by 2 and then what will you get?

Student: 0.

0 good. So, this is 0. So, this one goes to 0 simple right. So, see a very intimidating integral which was down at the denominator gives what a value of 2 essentially. So, the denominator is equal to 2, the denominator is essentially equal to 2 right good. If you are done with the denominator what did we have in the numerator?

(Refer Slide Time: 37:01)



The image shows a handwritten derivation of the numerator integral on a grid background. The text is as follows:

Numerator:

$$\int_0^\pi v(r, \theta) e^{-v(r, \theta)/kT} \sin \theta d\theta$$

$$= \int_0^\pi v_0 \cos \theta e^{v_0 \cos \theta / kT} \sin \theta d\theta$$

$$= -v_0 \int_0^\pi \cos \theta \left[1 + \frac{v_0 \cos \theta}{kT} \right] \sin \theta d\theta$$

$$= -v_0 \left[\int_0^\pi \cos \theta \sin \theta d\theta + \int_0^\pi \frac{v_0 \cos^2 \theta}{kT} \sin \theta d\theta \right]$$

An NPTEL logo is visible in the bottom left corner of the slide.


So, let us look at the numerator now. The numerator is 0 to pi V of r theta right e to the power minus V r theta by k T sin theta d theta right that is what we have for the numerator.

Now, this what was $V_r \theta$? I can write this as 1 as 0 to π $V_r \theta$ was minus $V_0 \cos \theta$ of θ . So, I can take the negative out sign out here and I do $V_0 \cos \theta$ e to the power what should I write here? I can write $V_0 \cos \theta$ over $k T \sin \theta d \theta$ ok.

Going step by step. Now this is equal to guys this is equal to minus 0 to π I can keep the V_0 outside I have $\cos \theta$, but this one is already simplified form is not it? 1 plus V_0 over $k T$, then $\sin \theta d \theta$ and I do a further simplification I can write it has minus V_0 , then open large brackets here is 0 to π $\cos \theta \sin \theta d \theta$ right plus 0 to π V_0 by $k T \sin \theta d \theta$.

I missed one is not it what did I missed did I miss anything? Just check ok. So, what I missed in this case is, I missed in this case is $\cos \theta$ ok. Now these are the two integrals we have to solve essentially these are the two integrals we have to solve. If you are going to solve these two integrals what are you going to get?

(Refer Slide Time: 39:09)

$$\begin{aligned} & \int_0^\pi V(r, \theta) e^{V_0 \cos \theta / kT} \sin \theta d\theta \\ &= - \int_0^\pi V_0 \cos \theta e^{V_0 \cos \theta / kT} \sin \theta d\theta \\ &= -V_0 \int_0^\pi \cos \theta \left[1 + \frac{V_0 \cos \theta}{kT} \right] \sin \theta d\theta \\ &= -V_0 \left[\underbrace{\int_0^\pi \cos \theta \sin \theta d\theta}_0 + \int_0^\pi \frac{V_0 \cos^2 \theta}{kT} \sin \theta d\theta \right] \end{aligned}$$


So, for the first one what is it? The first one is 0 we already know we did previously. So, the first one is already going to 0.

(Refer Slide Time: 39:21)

Numerator:

$$= - \frac{V_0^2}{kT} \int_0^\pi \cos^2 \theta \, n \, n_0 \, d\theta$$
$$= \frac{V_0^2}{kT} \int_{+1}^{-1} x^2 \, dx \quad x = \cos \theta$$
$$= \frac{V_0^2}{kT} \left[\frac{x^3}{3} \right]_{+1}^{-1}$$

So, then for the numerator; for the numerator we left with. So, the numerator again we left with is equal to my minus I can write V_0 squared because I have a V_0 out here I can write V_0 squared, then what I am what am I solving now?

Student: (Refer Time: 39:39).

Right, but if you go back to this again actually I missed another term.

Student: (Refer Time: 39:46) cos (Refer Time: 39:47).

I meet I missed a cos theta. So, I can just write cosine square theta here otherwise it will also go to 0 if you do not want, yeah, so that is my mistake ok. So, coming again back from here.

So, minus V_0^2 then I have 0 to π cosine square theta, sin theta d theta by $k T$. How do I solve this one? I actually do the same principle again I allow cosine of theta to be x right and this would become what?

Student: (Refer Time: 40:23).

I can write V_0^2 over $k T$ right then I can write minus 1 sorry.

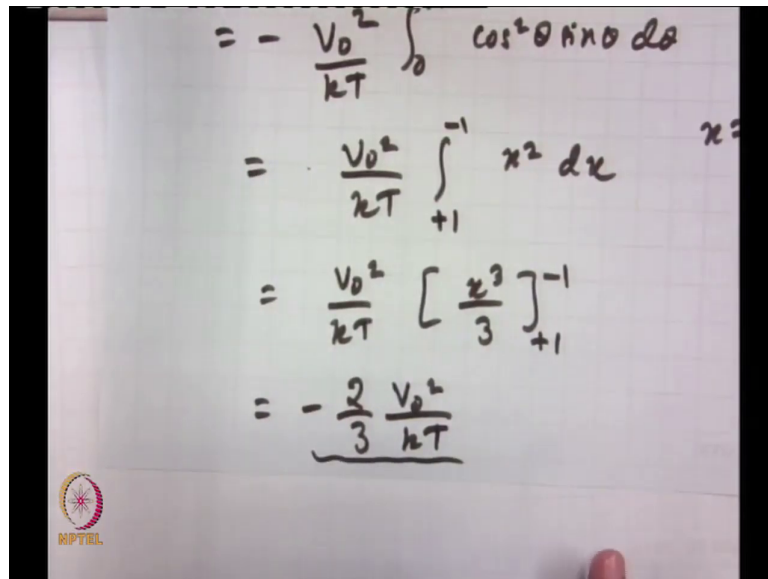
Student: (Refer Time: 40:33).

Plus 1 to minus 1.

Student: x square.

x square then d of x again putting x is equal to cosine of theta right. See we are a negative out here right and this is negative is cancel from here because of this. What do we get from here? V_0^2 by $k T$ now I have its not x square by 2 anymore right what is it? x^3 over 3 plus 1 minus 1.

(Refer Slide Time: 41:10)


$$\begin{aligned} &= - \frac{V_0^2}{kT} \int_0^{\pi} \cos^2 \theta \sin \theta d\theta \\ &= \frac{V_0^2}{kT} \int_{+1}^{-1} x^2 dx \quad x = \cos \theta \\ &= \frac{V_0^2}{kT} \left[\frac{x^3}{3} \right]_{+1}^{-1} \\ &= \underline{-\frac{2}{3} \frac{V_0^2}{kT}} \end{aligned}$$


What I am going to get tell me? This is minus 1 by 3 minus 1 by 3 again anyway. So, I would be getting minus 2 by 3 V_0 squared over.

Student: k T.

k T ok. You should be feeling happy now see what you started from? You started from a very fearful integral right and what did you get the denominator was 2 and the numerator is minus 2 by 3 V_0 square over k T and no more V_0 as its a constant.

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COMBINING NUMERATOR AND DENOMINATOR

$$\begin{aligned}\langle V(r) \rangle &= -\frac{2}{3} \frac{V_0^2}{kT} \cdot \frac{1}{2} \\ &= -\frac{1}{3} \frac{V_0^2}{kT} \\ &= -\frac{1}{3} \left(\frac{\mu_0 q}{4\pi\epsilon_0 r^2} \right)^2 \cdot \frac{1}{kT} \\ &= -\frac{1}{3kT} \left(\frac{\mu_0 q}{4\pi\epsilon_0} \right)^2 \cdot \frac{1}{r^4} \leftarrow Z_{H_1}\end{aligned}$$


So, let me combine. So, combining numerator and denominator then average of V of r is equal to minus 2 by 3 V_0 squared over k T and what did I have in the denominator? 2. So, its essentially minus 1 by 3 V_0 squared over.

Student: k T.

k T what was V_0 equal to? So, I can write minus 1 by 3 then I can write μ_0 this is this one was q right I can just write $\mu_0 q$ let us take out the subscript, I can just write $\mu_0 q$ then what did I have in the bottom? 4 pi.

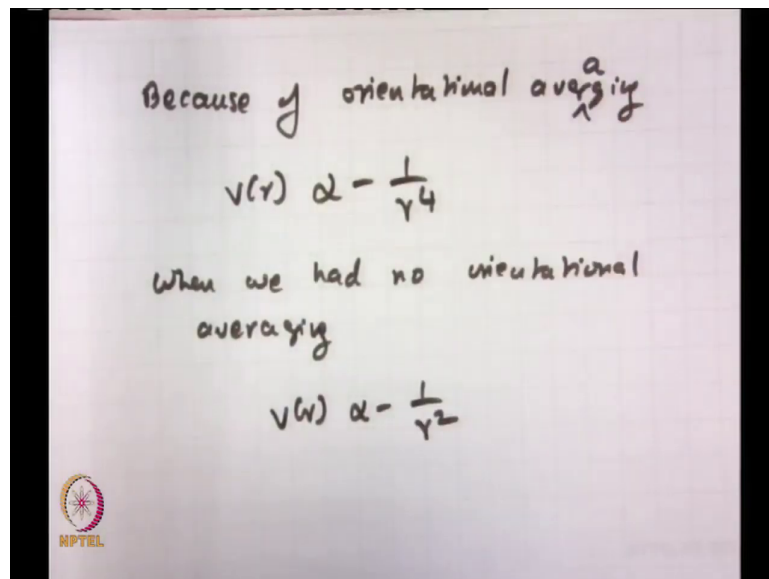
Student: Epsilon (Refer Time: 42:44).

Epsilon 0 r squared. So, this is essentially what? Whole squared over k T I am just plugging in V 0 right. You follow that right I am just plugging in V 0 look at this or you can further write this as minus 1 by 3 k T ok, then I can write mu q over 4 pi epsilon 0 squared what happens to r squared now? It goes to r to the power.

Student: 4.

4 it goes to r to the power 4 and this is important goes to r to the power 4 and this is extremely important. So, there two important aspects one is you can see this is V of r is going to depend upon t because obviously, your thermal energy is going to going to have an effect on your potential energy of interaction ok.

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And the second point is because of orientational averaging because of orientational averaging, now V of r is proportional to $1/r^4$. When we had no orientational averaging then V of r was proportional to what? $1/r^2$. So, again guys please understand the implication of this or the implication of this rather.

The implication is one your V of r definitely depends on the temperature because your temperature is too high, you are going to disrupt all potential energies of interaction right thermal energy is too high. Second is the moment you bring in orientational averaging you essentially just square this term which was initially obtained from a constituent value of θ ok.

Now those should be I will I probably this is you know where we are going to stop for the class today, but I mean let me tell you this, the one we derived for this dipole dipole interaction what was it? It was $1/r^3$ right for a fixed angle θ . So, you in that case also if you bring in this orientational averaging where will it go to?

Student: (Refer Time: 45:30).

It go to $1/r^6$. Take this $1/r^6$ and extend it to what you know in the case of Van der Waals interaction the attractive forces, what was the last term?

The last term was also r^6 do you remember the attractive term? You have say a/r^{12} minus b/r^6 that also has an r^6 and the Van der Waals forces are essentially what? Induced dipole dipole forces right and because you have induced dipole dipole see its still essentially dipole dipole and because you have an dipole dipole their attractive term is still r^6 .

So, hopefully, I have not put you off to much by the derivation, but you know in some cases the moment you do the derivation you have a much better feeling what actually what is going

on, then just looking at the formula and that is why we did this rigorously and if any point of time you would have to do a derivation like this, you would be able to do it ok.

So, this derivation the last derivation you know you do not have to remember for the exam, I am not going to ask you this derivation, but what you should be remembering is the effect of this orientational averaging and for iron dipole dipole dipole what are the different dependencies on r ok. How the range changes from columbic r to r square to r cubed and then also r to the power 4 and r to the power 6 because of orientational averaging good.