

## Electrical double layer (EDL) interaction (Helmholtz)

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Lecture-32

### Electric double layer models; capacitor (Helmholtz) model

Welcome back. In this video lecture, we will look at the electrical double layer interaction. So far, we have looked at the Van der Waals force of interaction between two macroscopic objects. Now, in this video lecture, we will look at the force due to electrical double layer or electrostatic force of interaction. So this electrostatic force of interaction is purely coming from the coulombic interaction between two charged systems. If two oppositely charged systems interact, there will be electrostatic attraction. If two like charged systems interact, there will be electrostatic repulsion. Okay, we will look at them in detail. Let's begin. Right,

(Time: 1:13 min)

van der Waals force constant

Verify the units

$$\Phi_A = -\frac{1}{(4\pi\epsilon_0)^2} \left( 2\alpha\mu^2 + \frac{2\mu^4}{3k_B T} + \frac{3}{4} h\nu\alpha^2 \right) x^{-6} = \beta_{11} x^{-6}$$

Debye                      Keesom                      London

$\alpha$  - Polarizability =  $C^2 m^2 J^{-1}$   
 $\mu$  - Dipole moment =  $C.m$   
 $\epsilon_0$  - Vacuum permittivity =  $\frac{F}{m}$  or  $\frac{C}{m}$                        $C = \frac{J}{V}$

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So as we described, before we, yeah, so before we begin, let us first understand, you know, the Van der Waals force constant, okay, from where we left, right, right.

So it is very important that you should know that the  $\beta$ , which is the Van der Waals force constant, uh you know carries unit with it right so there is unit right so which means that the  $\beta$  is uh uh is nothing but the  $J/m^6$ , right? So eventually you will have the unit of the interaction potential energy as joule, okay? So because this  $\beta$  carries with it three distinct terms, okay? So depending on the situation, sometime all three terms exist, right? Sometime one of two terms exist, right? But it is very important to check the unit consistency always, right? So sometimes you may deal with, you know, depending on the situation, you might deal with all three also. So it is very important that you need to look at the consistency of the unit, verify the unit first, right? Before, you know, computing the pairwise interaction potential energy. All right. So in this case, we have got three terms within this bracket. One is Debye, Keesom and London dispersion force. So it is important for us to check that each term will have a unit of, you know,  $J/m^6$ , right? Then ultimately one would have the energy, total energy as joule. So I have also listed the important microscopic parameters like polarizability which is  $\alpha$ , dipole moment and vacuum permittivity. The unit of all are also given here. Now, let's first take the Debye interaction, right? So, the unit of this Debye, must be  $J/m^6$ . Let's first analyze that. The rest of the terms can be done by yourself as an exercise, okay?

$$\Phi_A = -\frac{1}{(4\pi\epsilon_0)^2} \left( 2\alpha\mu^2 + \frac{2\mu^4}{3k_B T} + \frac{3}{4} h\nu\alpha^2 \right) x^{-6} = \beta_{11} x^{-6}$$

$$C = \frac{J}{V}$$

Where

- $\alpha$  is the polarizability,  $C^2 m^2 J^{-1}$
- $\mu$  is the dipole moment, C.m
- $\epsilon_0$  is the vacuum permittivity, F/m or C/v.m

$$\frac{C^2 m^2 J^{-1} C^2 m^2}{C^4 J^{-2} m^{-2}}$$

$$\frac{C^4 m^4 J^{-1}}{C^4 J^{-2} m^{-2}}$$

$$\frac{J}{m^6}$$

(Time: 6:00 min)

**van der Waals force constant**

**Verify the units**

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Debye                      Keesom                      London

$\alpha$  - Polarizability =  $C^2 m^2 J^{-1}$   
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$C = \frac{J}{V}$

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Right. So, this is, I think the unit consistency is verified for the case of Debye. You can verify yourself for the case of Keesom and London. Okay. Right. Right. So now, let us look at,

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**Understanding some fundamentals**

1. Electric charge.
2. Electrostatic force.
3. Coulomb's law.

An **electric field** surrounds an electric charge, and exerts force on other charges in the field, attracting or repelling them.

Electric field

Coulomb's law

$$F \propto \frac{q_1 q_2}{r^2} = \left( \frac{1}{4\pi\epsilon_0} \right) \times \frac{q_1 q_2}{r^2}$$
$$F \propto \frac{m_1 m_2}{r^2} = g_c \times \frac{m_1 m_2}{r^2}$$

Electric force between charged bodies or atoms at rest is called electrostatic force and quantitatively the same is described by Coulomb's law.

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Before going into the details of the electrical double layer interaction, let us look at some important fundamentals behind the Coulomb's law or Coulombic interaction, electrostatic force, right? So we'll understand what electric charge, electrostatic force, is and Coulomb's law in this slide, right? So, let us say whenever you deal with, right, say whenever there is charge systems, right, okay, there will be electrostatic force, right. So, let us say we have a subatomic particle, okay, and subatomic particle will have electrons and protons in it. Okay, depending on the number of electron and the number of, I mean, the protons. So one would get the charge, the subatomic particle will gain negative charge or positive charge, right? Okay, now the same thing you can also extend it for two macroscopic objects, okay? It can be negatively charged macroscopic object or positively charged macroscopic object. So whenever there is a charge system, the electric field will emanate from the charge system and that electric field will interfere with the other charge system.

So due to which the electric force will be created. So that is what exactly we have shown in the schematic. Right, so when such a electric force is created, depending on whether two charge systems are like, I mean, whether both are negatively charged or positively charged, you will have electrostatic repulsion or electrostatic attraction. So what is, what governs this, you know, force, electrostatic force, right? That is nothing but the Coulomb's law, okay? So whenever there is a two point charge, okay, let's say the magnitude of the point charge is  $q_1$  and  $q_2$ , okay, and they are kept at a distance of  $r$ , it is nothing, the Coulomb's law describes, says that the force, that is electric force here,

$$F \propto \frac{q_1 q_2}{r^2} = \left( \frac{1}{4\pi\epsilon_0} \right) \frac{q_1 q_2}{r^2}$$

- $q_1, q_2$  - Electric charges
- $r$  - Distance between the charges
- $\epsilon_0$  - Vacuum permittivity of free space

When I say vacuum permittivity, which means that there is no medium exists. So, you just keep this charge system in the vacuum as it is and how the interaction takes place. That is exactly you study. In such case, you will use this proportionality constant that is nothing but  $1/(4\pi\epsilon_0)$ . But sometime you will keep this or you will study these systems, right, in a medium, okay, which might contain some electrolyte and all that. So in such case, how do we deal with? In such case, there is something called. .. you know, relative permittivity which is nothing but  $\epsilon_m/\epsilon_0$ , okay  $\epsilon_m$  is the permittivity of the medium,  $\epsilon_0$  is the vacuum permittivity so see it is difficult to you know always describe in a different you know parameter right for example Whenever you define a

Coulomb's law, you cannot say for vacuum permittivity, this is the equation. For the case where this medium is considered, the Coulomb's law will be different. You cannot have two different equations or multiple equations. So to generalize this equation, what you know it has been proposed was you can actually multiply this  $\epsilon_0$  with the  $\epsilon_r$  okay. Remember  $\epsilon_r$  has got no unit because it is a ratio you know between  $\epsilon_m$  and  $\epsilon_0$  correct. Right this has no unit

Now let's say if you're dealing with uh you know medium instead of vacuum what you will be getting finally is the  $\epsilon_m$  itself because  $\epsilon_0$ ,  $\epsilon_0$  will cancel with each other you will have  $\epsilon_m$  itself okay Right. So, r, if you are dealing with only vacuum  $\epsilon_r$  is 1. For vacuum permittivity  $\epsilon_r$  is 1. In that case you will have this equation as it is intact. This equation will be intact. So irrespective of whether you are dealing with vacuum. or whether you are dealing with medium you ,you need not worry so you can always use this generalized equation

$$F \propto \frac{q_1 q_2}{r^2} = \left( \frac{1}{4\pi\epsilon_0\epsilon_r} \right) \frac{q_1 q_2}{r^2}$$

So in that case, so for water, you will be using the, you know, instead of  $\epsilon_0$  alone, you will be using  $\epsilon_0\epsilon_r$ . Okay, right. So, this equation, if you look at, this is in analogous to the, you know, the gravitational Newton's, you know, force, right, gravitational force.

$$F \propto \frac{m_1 m_2}{r^2} = g_c \times \frac{m_1 m_2}{r^2}$$

- $m_1, m_2$  - Masses
- $r$  - Distance between the masses,
- $g_c$  (often written as  $G$ ) - Gravitational constant

Here, if you look at, this is also proportional to the masses, right, mass of the two objects, which is  $m_1, m_2$ . and it is also inversely proportional to the square of the distance right so something like this the coulomb's law is also described something in a similar fashion whereas here the proportionality constant will be uh you know  $1/(4\pi\epsilon_0\epsilon_r)$  whereas here the proportionality constant is the gravitational constant But the unit of these two equations is Newton. Because we are talking about the force, the unit of this will be Newton. You can also verify this.

$$\frac{C^2 Vm}{m^2 C}$$

$$\frac{VC}{m} = \frac{V \frac{J}{V}}{m} = \frac{Nm}{m} = N$$

(Time: 14:52 min)

### Understanding some fundamentals

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$$F \propto \frac{m_1 m_2}{r^2} = g_c \times \frac{m_1 m_2}{r^2}$$

Electric force between charged bodies or atoms at rest is called electrostatic force and quantity is the same is described by Coulomb's law.

So you can see for yourself that the unit of this will be simply newton okay right so now we will move on to

(Time: 15:04 min)

### Electrical double layer potential

- When ions are present in a system that contains an interface, there will be a variation in the ion density near that interface that is described by a profile like that shown in figure.
- Suppose that it was possible to separate the two bulk phases, then, each of the separated phases would carry an equal and opposite charge. These two charged portions of the interfacial region are called the *electrical double layer*.

Due to thermal agitation.

What is known as electrical double layer interaction or potential So whenever you deal with electrolyte medium, okay, let's say you have the, you know, a container where you

have the electrolyte medium. Let's say you have salt, like NaCl salt, like you have  $\text{Na}^+ \text{Cl}^-$ , like that entire solution will be distributed with this counter ions and co-ions of salt. Now, the question is, what is the charge of the entire solution that will be neutral? Because Na and Cl will be distributed such a way that the electroneutrality condition is achieved, which means that the charge of the solution will be always neutral, okay?

(Time: 15:54 min)

**Electrical double layer potential**

> When ions are present in a system that contains an interface, there will be a variation in the ion density near that interface that is described by a profile like that shown in figure.

> Suppose that it was possible to separate the two bulk phases, then, each of the separated phases would carry an equal and opposite charge. These two charged portions of the interfacial region are called the *electrical double layer*.

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Now, this is one scenario. Let's say in this case, in this medium, okay? containing counter ions, co-ions in the solution, let's say I introduce another system, solid system, which is charged, which is not neutral, but charged, which is negatively charged. Okay. whenever you introduce the negatively charged system it actually disturbs the electro neutrality right so suddenly what will happen so there will be a change in the ion density near the surface whereas far away from the surface there will be no change so this far away from the surface the electroneutrality is naturally attained so there will not be any change but near the surface there will be change in the distribution of the ion density okay so why is it happening because whenever you suddenly introduce the charge system into the electrolyte medium uh you know there will be uh a counter ions will uh you know because it is negatively charged this system the solid system is negatively charged you can expect the uh you know binding right uh counter and binding on the surface of the charge i mean charge the system for example uh you know the counter ions can bind the surface in a three possible way it can bind the surface Or it can hold the counter ions. For example, you will have a strongly bound counter ion or weakly bound counter ion or diffuse counter ions. So, this diffuse counter ions are held by the electrostatic attraction. Whereas this is actually strongly bound these the electrostatic attraction. Whereas this

one weakly adsorbed, weakly bound counterion is due, you know, attached to the surface by physisorption, which is weakly bound. Okay. So in this way, you can expect that there will be change in the ion density across this surface, right? Potential variation will be there.

Again, so again, if I consider these two as two bulk phases, let's say this is one bulk phase, solid is one bulk phase, and the liquid medium is another bulk phase. If I separate these two bulk phases, right, from this then you can see that both this bulk phase carry equal and opposite charge okay that is because of the electroneutrality condition okay so this process is called electrical double layer and attraction interaction based on this electrical double layer is called electrical double layer interaction

(Time: 18:58 min)

**Electrical double layer potential**

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- When ions are present in a system that contains an interface, there will be a variation in the ion density near that interface that is described by a profile like that shown in figure.
- Suppose that it was possible to separate the two bulk phases, then, each of the separated phases would carry an equal and opposite charge. These two charged portions of the interfacial region are called the *electrical double layer*.

Due to thermal agitation.

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Let's say you've got a medium where you have two charges system in the medium. So this will have electrical double layer and this will have electrical double layer. So when both interact with each other, there will be electrical double layer interaction. so, in a nutshell, the electrical double layer means whenever ions are present in the medium okay and and and suddenly when interfaces charged interfaces introduced into the medium there will be variation in the ion density near the interface right and the profile of that will vary something like this, will exist. The profile will be something like this. Okay, right. That is exactly what we call it as an electrical double layer. So this electrical double layer will be something like whenever you separate these two bulk phases, they will carry equal and opposite charges in it, right, such that the electroneutrality condition is achieved. Okay, so here I have listed various models for double layer interaction. As you

can see there are three models Helmholtz model, Guoy-Chapman model and Guoy-Chapman Stern model. Okay,

(Time: 20:30 min)

Various models for double layer interaction

1. Helmholtz (H)
2. Guoy-Chapman (GC)
3. Guoy-Chapman-Stern (GCS)

20:30 / 26:51

we look at them one by one in detail as we move along. So let us first consider the Helmholtz model. which is nothing but a capacitor model proposed by Helmholtz, right? And in this model, the model considers the parallel plate assumption, which means that, let's say you have the charged interface, right? You have a charged interface, and you introduce this charged interface into the medium, electrolyte medium, you have negative charge, right? And there will be counter ions, right? There will be counter ions, like there will be three types of counter ion. One is strongly bound, weakly bound, and diffuse counter ion, okay? And Helmholtz considers only the strongly bound counter ions, which means that if you take out this, you know, counter ion phase and the solid rigid phase into two separate plate, both will have equal and opposite charge, right?

So, that means both will carry equal and opposite charge. In such cases, the distribution of the potential, the variation of the potential will be linear. So, that is exactly what we have shown in the schematic, okay? That is exactly what we have shown in this schematic. So, which means that if you separate this, you know, the entity that is the solid surface and the counter ion, if you assume that counter ion is also a rigid layer, and then if you separate them into two, you will have both, both will be carrying equal and opposite charge. The distribution of potential in such case will be linear, right? So this model based on capacitor model is nothing but Helmholtz model.

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**Capacitor model (Helmholtz)**

The variation of electrochemical potential in the vicinity of the interface between two phases

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So here our starting point so our point of departure will be we want to see how this potential variation is linear so we know that our point of departure will be coulombic force right right this comes from the coulombic law itself coulomb's law itself which means that this is nothing but

$$F = \left( \frac{1}{4\pi\epsilon_0\epsilon_r} \right) \frac{q_1q_2}{r^2}$$

So, this is exactly what we know, Coulombic force, right. But we are not just interested in the Coulombic force, but we are interested in the potential variation. So, we want to determine what electrochemical is or we want to know what is the variation of potential across the you know in the vicinity of the interface okay so for that we want explicitly the potential variation, so we know that electric field can also be defined by

$$E = \frac{F_c}{q} = \frac{V}{m}$$

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Capacitor model (Helmholtz) 

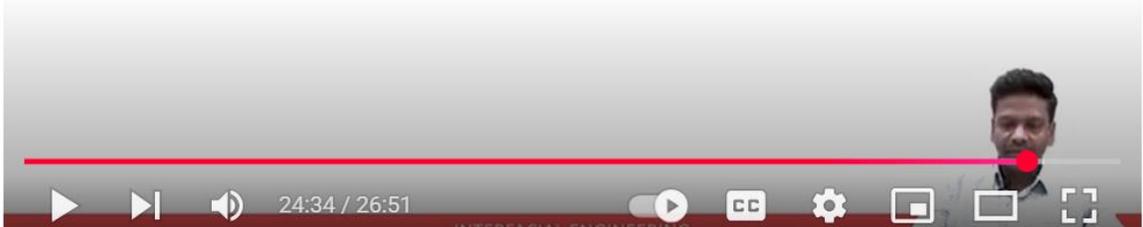
$$F_c = \frac{1}{4\pi\epsilon_0\epsilon_n} \left( \frac{q^2}{r^2} \right)$$
$$E = \frac{F_c}{q} = \frac{V}{m}$$


So you know that  $F_c$  can be expressed, how it is coming you know  $F_c$  can be expressed as

$$E = \frac{F_c}{q} = \frac{N}{C} = \frac{NV}{J} = \frac{NV}{Nm} = \frac{V}{m}$$

(Time: 24:34 min)

Capacitor model (Helmholtz) 

$$F_c = \frac{1}{4\pi\epsilon_0\epsilon_n} \left( \frac{q^2}{r^2} \right)$$
$$E = \frac{F_c}{q} = \frac{N}{C} = \frac{NV}{J} = \frac{NV}{N \cdot m} = \frac{V}{m}$$


So this is nothing but volt per unit length, okay? So this is also nothing but

$$E = \frac{F_c}{q} = \frac{-d\Psi}{dx}$$

$\Psi$  – potential

Potential is usually expressed as volt. So you get the same unit, right, as we just now obtained for  $F_c/q$ , right? So here the sine negative indicates that the potential decreases as  $x$  increases, right? So this is nothing but a negative slope, okay, right? So now if you just simplify this,  $E$  is nothing but a slope here and so what you will get is, let's say you will get  $\Psi$ , which is nothing but

$$\Psi = -E x + C$$

If you apply the boundary condition that

$$x = 0$$

$$\Psi = \Psi_0.$$

$$\text{Thus, } C = \Psi_0$$

So, you will have,

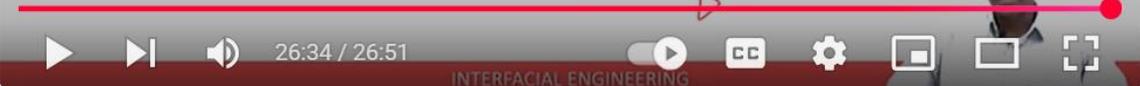
$$\Psi = \Psi_0 - E x$$

$$\Delta\Psi = -E x$$

So, which means that  $\Psi$  is varying as a function of  $x$ , okay, as proposed by the Helmholtz, right? Yeah.

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Capacitor model (Helmholtz) 

$$f_c = \frac{1}{4\pi\epsilon_0\epsilon_m} \left( \frac{q_1 q_2}{r^2} \right)$$
$$E = \frac{F_c}{q} = - \frac{d\phi}{dx}$$
$$\phi = -E x + C \quad x=0; \phi = \phi_0$$
$$C = \phi_0$$
$$\phi = \phi_0 - E x$$
$$\Delta\phi = -E x$$


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So, we'll stop here. We will continue from the next lecture. Thank you. Thank you.