

Interfacial Engineering

Dr Manigandan S.

Department of Chemical Engineering

Indian Institute of Technology, Ropar

Lecture-36

Derjaguin approximation; DLVO forces of interaction

Electrostatic repulsive energy between spherical double layers; DLVO forces of interactions

Welcome back. So in this video lecture, we are going to look at what is known as the Derjaguin approximation and DLVO forces of interactions. In the previous lecture, we looked at the electrostatic repulsive forces between 2 planar interfaces, planar surfaces. We considered the overlapping of a double layer between 2 planar surfaces. Right. So, in this video lecture, we will look at the electrostatic repulsive forces of interaction between 2 spherical double layers, right.

So, how will the electrostatic repulsive force be when two spherical, the electrical double layer overlaps, and the electrical double layer of 2 spherical particles overlap? That is precisely what the electrostatic repulsive force of attraction is. Sorry, the electrostatic force of repulsion between 2 spherical particles is what we will look at in this video lecture. Apart from that, we will also see what is known as the DLVO forces of interactions, right? So, DLVO interaction forces are nothing but some total of, you know, the Van der Waals force of attraction and the electrostatic repulsion, right? So, a combination of these 2 is nothing but the DLVO forces of interactions. So, we will look at these two things in detail in this video lecture.

Let us begin.

Time: 2.05 mins

Interaction between spherical double layers



Flat surface

$$\Pi_{EDL} = 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-k\delta)$$

$$F_{EDL} = A \times 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-k\delta)$$

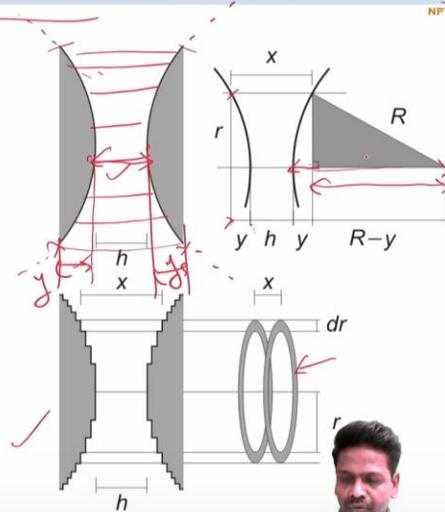
Spherical particles

$$\int \Pi(x) dA \rightarrow 2\pi r dr \quad (1)$$

$$x = h + 2y \quad (2)$$

According to Pythagorean theorem on the grey triangle

$$R^2 = (R - y)^2 + r^2 \quad (3)$$



Creative commons, Derjaguin approximation*
licensed under CC-F

INTERFACIAL ENGINEERING

The interaction between two planar surfaces is described using the disjoining pressure $\pi(x)$, a function of the separation distance x .

$$\pi(x) = (\epsilon\psi^2/\lambda_D^2) * e^{(-x/\lambda_D)}$$

Here, ψ is the surface potential, ϵ is the permittivity, and λ_D is the Debye length.

The electrical double layer force F between two planar surfaces is calculated by multiplying the disjoining pressure by the effective area A .

$$F = \pi(x) * A$$

We cannot use the same equation directly for spherical particles due to curvature effects. The separation distance varies along the curved surface.

The Derjaguin approximation is used to handle this. It breaks the curved surface into infinitesimal flat disks.

For each flat disk:

$$dF = \pi(x) * dA$$

$$dA = 2\pi r * dr$$

The total force F between spherical particles is given by integrating over all such disks:

$$F = \int_0^R \pi(x) * 2\pi r dr$$

The separation distance x in terms of geometry is:

$$x = h + 2y$$

Using the triangle relation (Pythagorean theorem):

$$R^2 = (R-y)^2 + r^2$$

$$\Rightarrow r^2 = 2Ry - y^2$$

The final expression for total force is:

$$F = \int_0^\infty \pi(h + 2y) * 2\pi r(y) dy$$

Substitute $r^2 = 2Ry - y^2$ into the integral.

Time: 16.04mins

Interaction between spherical double layers

objectstore.e2enetworks.net - To exit full screen, press Esc

Flat surface

$$\Pi_{EDL} = 64k_B T n_\infty \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-kx)$$

$$F_{EDL} = A \times 64k_B T n_\infty \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-kx)$$

Spherical particles

$$dA = 2\pi r dr \quad (4)$$

$$2\pi r dr = 2\pi R dy = \pi R dx \quad (5)$$

From Eq. 1, $F(x) = \int \Pi(x) dA$

$$F(x) = \pi R \int \Pi(x) dx = \pi R Z \int_h^\infty e^{-kx} dx \quad (6)$$

Creative commons, Derjaguin approximat' licensed under CC-F

We will see why this is useful for us. Now we need to get the change in area, which is $2\pi r dr$, but this is not desirable for us. We need to convert r to dr , as r is unknown.

It is not always easy to compute $r \, dr$ directly. Therefore, we convert $r \, dr$ into $r \, dx$, where r is the particle's radius, and dx is the separation distance (x). This allows us to calculate the area as a function of x , based on the change in area. This geometric relation will be crucial.

Geometric Relation:

From the triangular property:

$$R^2 = r^2 + (R-y)^2.$$

Rearranging for r^2 :

$$r^2 = R^2 - (R - y)^2.$$

Differentiation:

Differentiating r^2 concerning y :

$$2r \, (dr/dy) = 2(R - y).$$

Simplifying:

$$r \, dr = (R-y) \, dy.$$

Assumption:

We assume $R \gg y$, which is usually valid since the radius (R) is typically much larger than y . With this assumption:

$$R - y \approx R.$$

Thus:

$$r \, dr \approx R \, dy.$$

Conversion to x :

To express y in terms of x , we use the geometric relation:

$$x = h + 2y.$$

This relation connects the separation distance (x) with the geometric parameters.

Substituting this, we complete the conversion of $r \, dr$ into $r \, dx$.

Time: 19mins

Interaction between spherical double layers



Flat surface

$$\Pi_{EDL} = 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-kx)$$

$$F_{EDL} = A \times 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-kx)$$

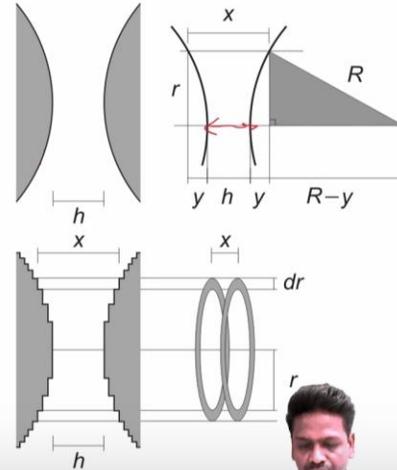
Spherical particles

$$dA = 2\pi r dr \quad (4)$$

$$2\pi r dr = 2\pi R dy = \pi R dx \quad (5)$$

From Eq. 1, $F(x) = \int \Pi(x) dA$

$$F(x) = \pi R \int \Pi(x) dx = \pi R Z \int_h^{\infty} e^{(-kx)} dx \quad (6)$$



Creative commons, Derjaguin approximation
licensed under CC-BY



INTERFACIAL ENGINEERING

In this case, we substitute to convert the terms.

We know that:

$$dx = 2 dy, \text{ or equivalently, } dy = dx / 2.$$

Substituting dy into the equation:

$$2\pi R dr \text{ becomes } \pi R dx.$$

Thus, we have successfully converted $2\pi R dr$ into $\pi R dx$.

Now, we substitute this into the differential area (dA) and integrate. The equation becomes:

$$\pi(x) dA.$$

Since the equation is now expressed in terms of x, we can rewrite:

$$\pi R \int f(x) dx.$$

Here, π and R are constants and can be factored out of the integral:

$$Z = \pi R.$$

The integral becomes:

$$Z \int e^{(-kx)} dx.$$

The limits of integration are defined as:

- Lower limit: h (minimum separation distance, representing the overlap of the electrical double layer).
- Upper limit: ∞ (far-field distance).

We integrate:

$$\int [h \text{ to } \infty] e^{(-kx)} dx.$$

This yields the final equation for the disjoining pressure as a function of the separation distance.

Time: 20.54mins

Interaction between spherical double layers

Flat surface

$$\Pi_{EDL} = 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-kx)$$

$$F_{EDL} = A \times 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-kx)$$

Spherical particles

$$\frac{d\Phi}{dh} = F(h) = \pi R k^{-2} Z e^{-kh} \quad (7)$$

$$\int_{\Phi=0}^{\Phi} d\Phi = -F(h) dh = -\pi R k^{-2} Z \int_{\infty}^h e^{-kh} dh \quad (8)$$

$$\Phi(h) = \pi R k^{-2} Z e^{-kh} \quad (9)$$

$$Z = 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right)$$

Creative commons, Derjaguin approximation licensed under CC-B

INTERFACIAL ENGINEERING

So $kx \ll 1$.

So, if you integrate this, you will get: $\int kx dx = e^{(-kx)}$.

So, $\int [h \text{ to } \infty] e^{(-kx)} dx = [-1/k * e^{(-kx)}]$ from h to ∞ .

This becomes: $0 - (-1/k * e^{(-kh)}) = (1/k) * e^{(-kh)}$.

So k^{-1} is the screening length. This is the equation for the electrical double layer force.

You can also convert this electrical double-layer force into repulsive energy.

We know that: $F = -d\pi/dh$.

Or: $\pi = \int F dh = \int f(h) dh$.

So, $\pi = -\int[0 \text{ to } \pi] d\pi/dh dh$.

This indicates a negative gradient, meaning energy π decreases as h increases.

So, plotting π vs h gives a negative slope: $-d\pi/dh$.

Now, integrating, we get: $\pi = r * k^2$.

Or in denominator form: $\pi = r / k^2$.

Check the units:

- z : Boltzmann constant, k_b [J/K]

- T : Temperature [K]

- n : Number density [molecules/m³ /m³/m³/m³]

So, energy density: [J/m³], multiply by $[1/k^2] \sim m^2$ and $[r] \sim m \Rightarrow$ final unit is [J].

Thus, the final compact energy equation has units of Joules.

This matches the interaction energy for the planar electrical double layer.

Time: 25.02 mins

Interaction between spherical double layers



Flat surface

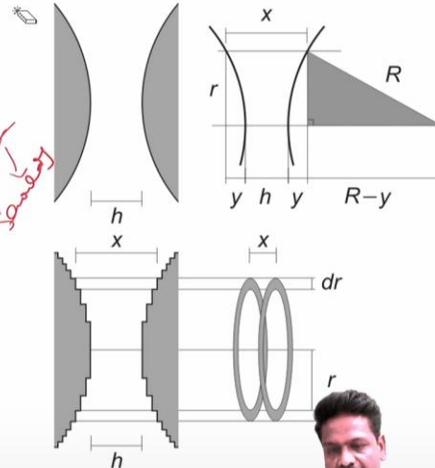
$$\Pi_{EDL} = 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-kx)$$

$$F_{EDL} = A \times 64k_B T n_{\infty} \tanh^2 \left(\frac{ze\psi}{4k_B T} \right) \exp(-kx)$$

DLVO force

$$\Phi(h) = \pi R k^{-2} Z e^{-kh} - \frac{A R_s}{12h}$$

Refer to Table 10.4 for the details



Hiemenz, P. C., & Rajagopalan, R. (2016). *Principles of Colloid and Surface Chemistry, revised and expanded*. CRC press.

Creative commons, Derjaguin approximation is licensed under CC-B

INTERFACIAL ENGINEERING

Here, you have the additional term, like k minus 2. So this is there already. So otherwise, the rest of the thing is pretty much the same, right? Right. So now we have to look at what is known as the DLVO force. You understand that the DLVO force is nothing but a total of electrostatic repulsive plus Van der Waals attractive force.

This is the electrostatic repulsive force for a spherical double layer and two spheres of the same radius.

Let $r_1 = r_2 = R$.

The equation for the Van der Waals force in this case is:

$$F_{vdw} = (A * R) / (12 * h)$$

Where:

- A is the Hamaker constant,
- R is the radius of the spheres,
- h is the separation distance between the spheres.

This can be verified using Table 10.4 in the referenced textbook, which provides equations for various configurations.

It is given in the form of a table. And this one is for the spherical particle having the same radius, right? So this equation is obtained. This is for the Van der Waals equation. Van der Waals attractive energy, you know, beautiful, I mean, Van der Waals energy, right, between 2 spherical particles. And this one is electrostatic repulsive energy between 2 spherical particles.

The total of this is going to be your DLVO. If you plot this as a function of distance, you will get something like this.

Okay. You will get something. Okay. Yeah. So maybe I have not drawn. Maybe. So this is something. So you can also verify the textbook. Hence, this is there's a slight fluctuation here this is the secondary minima okay this is due to weak dipolar interactions right and this one is the primary maxima this is the barrier right a repulsive barrier and this one is the you know, primary minima, Okay, so this is due to the Van der Waals term and this is due to the repulsive term. This one is due to the bond repulsion. So when you plot this DLVO, this, you know, equation, okay, as a function of the edge distance, separation distance, you will obtain a profile like this, you know, the way I have shown here, okay? For more details, you can refer to this textbook, okay? I think you can also refer to this table for other configurations.

Okay. Yeah. So we'll stop here. We will continue from the following lecture. Thank you.