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Deryaguin's Approximation

Deryaguin (1934) identified that in colloidal particles, interaction become significant when particles are very close. In that case, radius of curvature of the particles can be taken large in comparison with the distance of separation. With the help of this approximation, the interaction energy between two spheres or cylinders by integrating the interaction energy between the corresponding flat plates can be evaluated.
This approximation can be applied for large particles with thin double layers at small separations as compared with the particle size. It should also be mentioned that Deryaguin's approximation can be implemented to the electrostatic interaction between colloidal particles as well as to the van der Waals interaction between particles at small particle separations.

For better understanding of this concept, consider two particles as shown in the figure below. Assumptions are as follows:

Surface area as $ds = \pi\, 2y\, dl$,
Radius of surface ring = y,
Radius of particle = R,
Minimum distance of separation = H,
Separation at any point on the curved surface which is a function of $y = D$.
We approximate that this surface is a flat plate, $R = R_1 = R_2 \gg H$

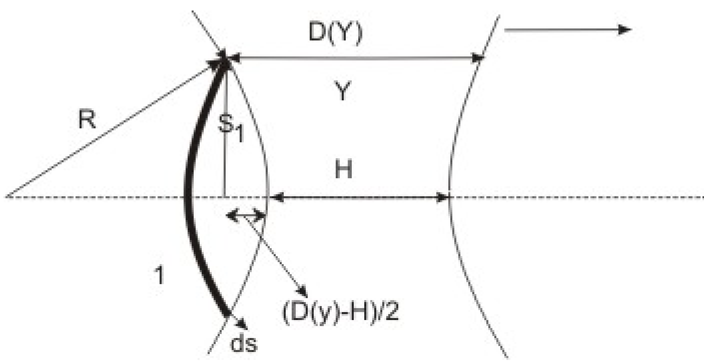

Fig 8.18:

Consider a ring like element of area ds, shown in the figure by bold line. Under this approximation we can take ring element and particle are parallel to each other and thus writing the energy of interaction between them as

$$d\emptyset = G(D)ds$$

Where, G is the energy per unit area. Total energy of interaction between these two particles can be written in integration form as

$$\emptyset = \int_{S_1} G\ D\ ds \qquad (8.23)$$

In the above expression we can write area $'\mathrm{ds}'$ as

$$ds = \pi\ 2y\ dl$$

$$ds = \pi\ 2y\ \sqrt{(dz)^2 + (dy)^2}$$

or

$$ds = \ \pi\ 2y\ \sqrt{1 + \frac{(dz)^2}{(dy)^2}}\ dy$$

Since we have assumed that curvatures are small we can take $\frac{dz}{dy} \to 0$. Thus we can write ds' as

$$ds = 2\pi y dy$$

Substituting this value of $'ds'$ in equation (8.23) we get

$$\emptyset = \int_{S_1} G\, D\, 2\pi y dy \tag{8.24}$$

For this integration, we have to know D as a function of y. From Pythagoras theorem we get

$$R^2 - y^2 = \left[R - \left(\frac{D-H}{2}\right)\right]^2 \tag{8.25}$$

Differentiating above we get

$$2\, ydy = \left(R - \frac{D-H}{2}\right) dD$$

Using this and equation (8.25) we have,

$$2\,ydy = \sqrt{R^2 - y^2}\,dD$$

$$2\,ydy = R\sqrt{1 - \frac{y^2}{R^2}}\,dD \approx RdD \tag{8.26}$$

Combining equations (8.24) and (8.26) we have

$$\emptyset = \pi R \int G\;D\;dD$$

This equation can be changed when particle have different radius by replacing R by $2\mathrm{R}_1\mathrm{R}_2/(\mathrm{R}_1 + \mathrm{R}_2)$. Thus

$$\emptyset = \frac{2\pi R_1 R_2}{R_1 + R_2} \int_H^\infty G(D)dD \tag{8.27}$$

Limits of this integral have been approximated from H to infinity. We know that van der Waal interaction energy per unit area for flat plate is given by-

$$G(D) = \frac{-A}{12\pi D^2} \tag{8.28}$$

So using Deryaguin's approximation we can write van der Waal interaction energy of two spherical particles with radius R_1 and R_2 as

$$\emptyset = \frac{2\pi R_1 R_2}{R_1 + R_2} \int_H^\infty \frac{-A}{12\pi D^2}\, dD$$

Integrating above we obtain

$$\emptyset = \frac{-AR_1R_2}{6R_1 + R_2} \left[\frac{-1}{D}\right]_H^\infty$$

or

$$\emptyset = \frac{-AR_1R_2}{6\ R_1 + R_2\ H}$$

This result is similar to the expression of energy of two large spherical particles derived in earlier section.

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Module 6: "Forces in Colloidal Systems"

Lecture 31:

In broad sense, we can say that the force or energy between two bodies is dependent on the properties of material, shape and on the distance. Now it is possible to divide the force (or energy) between two solids into purely geometric factor, a material and distance dependant term.
Furthermore, there occurs two main problems to compute interaction energy through this approximation, which are as follows:

1. Determination of particle surface fraction above and below the interface which must be considered to calculate the interaction.
2. Expression of interaction potential per unit area between half spaces.

Both problems can be solved with the help of flat meniscus approximation and use of dependency of immersed part with contact angle respectively. Amount of emergent and immersed part depends on the value of contact angle used. Immersed part increases as the contact angle decreases.