

## Module 6: "Forces in Colloidal Systems"

### Lecture 28: "Van der Waal forces between macroscopic bodies"

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## Van der Waal forces between macroscopic bodies

So far, we have studied how the Lifshitz - van der Waals potential ( $\phi$ ) between two atoms varies with distance ( $r$ )

$$\phi = \frac{\alpha}{r^{12}} - \frac{\beta}{r^6} \quad \alpha, \beta > 0 \quad (8.1)$$

The physical origin of LW forces is the instantaneous creation of dipoles due to distortion of electron clouds of neighboring atoms. The resulting time averaged attractive force gives rise to a negative contribution to the potential  $\phi$  which is captured by the second term in Eq 1, while the positive term comes from the repulsive interactions between positively charged nuclei at very small distances. A schematic plot of  $\phi(r)$  is shown in Figure 8.5. In order to simplify our analysis in further steps, we assume the following form of  $\phi(r)$  (See figure 8.6)

$$\begin{aligned} \phi &= -\frac{\beta}{r^6} & r > d_0 \\ \phi &= \infty & r \leq d_0 \end{aligned} \quad \text{where } d_0 \sim 0.159 \text{ nm} \quad (8.2)$$

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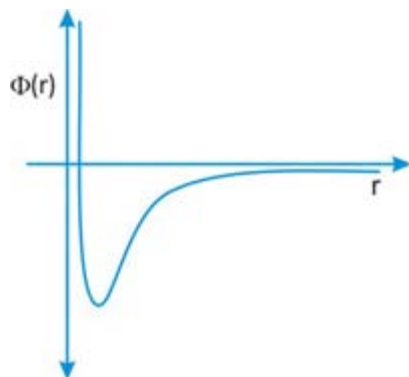


Fig. 8.5:

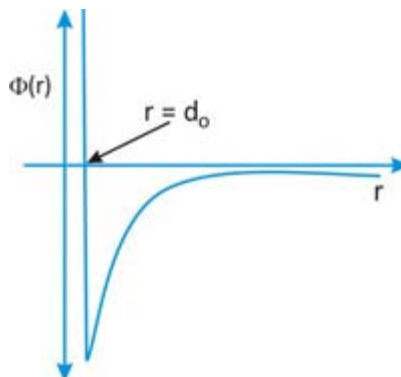


Fig. 8.6:

In this section, we will analyze how the van der Waals potential between two macroscopic particles varies with distance. To do this, one must think of each particle as being made up of a large number of molecules (atoms) of one kind. The total energy of a system comprising two particles is the sum of the respective self energies arising due to the intermolecular (interatomic) interactions within the particle, and a third term which comes from molecules (atoms) in one particle interacting with those in the other. Generally, we are interested in finding out the force between particles; since force is the negative gradient of energy, while calculating the total LW energy potential for a two particle system, we only consider cross interactions because they vary with inter-particle distance. Also, as it turns out, one can use this expression for cross interaction potential to determine the self energy terms, something that would be dealt with later on.

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Consider two flat, parallel slab-like particles of thicknesses  $d_1$  and  $d_2$  separated by a distance  $d$  in vacuum (see Figure 8.7). Van der Waals interactions are short range, and are generally effective for  $d \sim 10\text{-}100\text{ nm}$ . Particle dimensions in the  $x$  and  $y$  directions are much larger than this, of the order to a few  $\mu\text{m}$ . Therefore, one can safely assume an infinite extent in both these dimensions, thereby ignoring finite size end effects.

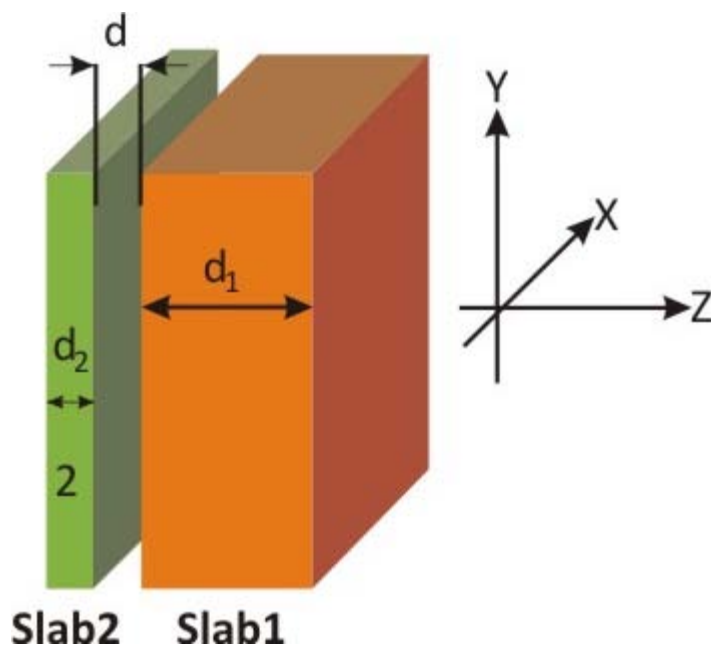


Fig. 8.7:

In order to calculate the total LW interaction potential, first a molecule (atom) from slab 2 is taken (see figure 8.8) and interaction energies with all molecules (atoms) from slab 1 are summed up one by one. It is to be assumed during this summation that the presence of surrounding molecules (atoms) does not affect the interaction potential between the two molecules (atoms) under consideration.

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As the LW potential is a function of the distance  $r$  between the molecules (atoms), one must choose an integrating volume in slab 1 which is the locus of all equidistant points from the chosen point in slab 2. Clearly, this is a thin annular cylindrical disc (see Figure 8.8)

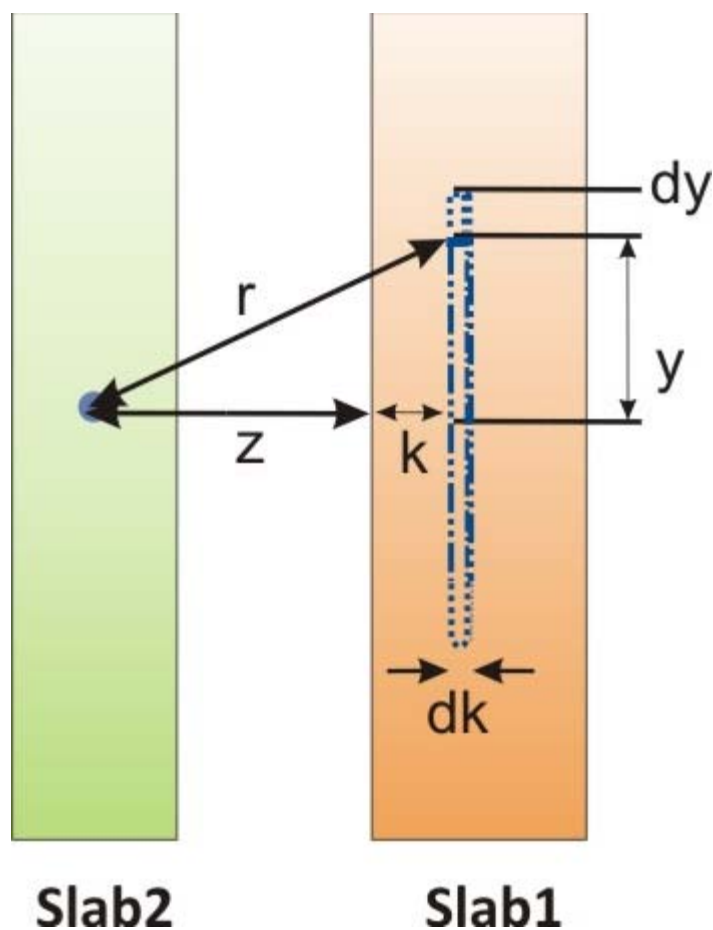


Fig. 8.8:

Let  $dV$  represent the volume of the element

$$dV = 2\pi y(dy)(dk) \quad (8.3)$$

and let  $\rho_1, \rho_2, M_1, M_2$  be the densities and molecular weights of materials 1 and 2 respectively. Then, the number of molecules (atoms) per unit volume in slab 1 is given by

$$\frac{\text{molecules (atoms)}}{\text{volume}} = \frac{\rho_1 N_A}{M_1} \frac{g}{\text{cm}^3} \frac{\text{atoms}}{\text{mol}} \frac{\text{mol}}{g} \quad (8.4)$$

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Using the simplified form of the LW potential between two molecules (atoms) from Equation 8.2, and multiplying with the number of molecules (atoms) present in the integrating volume, one gets the interaction potential  $d\phi''$  between a single molecule (atom) in 2 with the annular element in 1:

$$d\phi'' = -\frac{\rho_1 N_A}{M_1} (dV) \frac{\beta_{12}}{r^6}$$

$$d\phi'' = -\frac{\rho_1 N_A}{M_1} (2\pi y \cdot dy \cdot dk) \frac{\beta_{12}}{r^6} \quad (8.5)$$

From the Pythagorean Theorem,

$$r^2 = y^2 + (z + k)^2 \quad (8.6)$$

Using Equations 8.5 and 8.6, and integrating  $d\phi''$  between appropriate limits ( $k$  from 0 to  $d_1$  and  $y$  from 0 to  $\infty$ ) one gets the net interaction potential  $\phi''$  between the selected molecule (atom) of 2 with the entire slab 1:

$$\begin{aligned} \phi'' &= \int d\phi'' = -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1} \int_{k=0}^{d_1} \int_{y=0}^{\infty} \frac{y}{\{y^2 + (z + k)^2\}^3} dy \cdot dk \\ &= -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1} \int_{k=0}^{d_1} \frac{1}{4(z + k)^4} dk \\ &= -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1} \frac{1}{12} \left[ \frac{1}{z^3} - \frac{1}{(z + d_1)^3} \right] \\ &= -\frac{\rho_1 N_A \pi \beta_{12}}{6M_1} \left[ \frac{1}{z^3} - \frac{1}{(z + d_1)^3} \right] \quad (8.7) \end{aligned}$$

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Now, to get the total interaction potential between slabs 1 and 2, one must integrate over all points in slab 2. To do this, the integrating volume would be one in which every point has the same value of  $z$  (See Figure 8.9) which is a thin slab extending from  $z$  to  $z + dz$

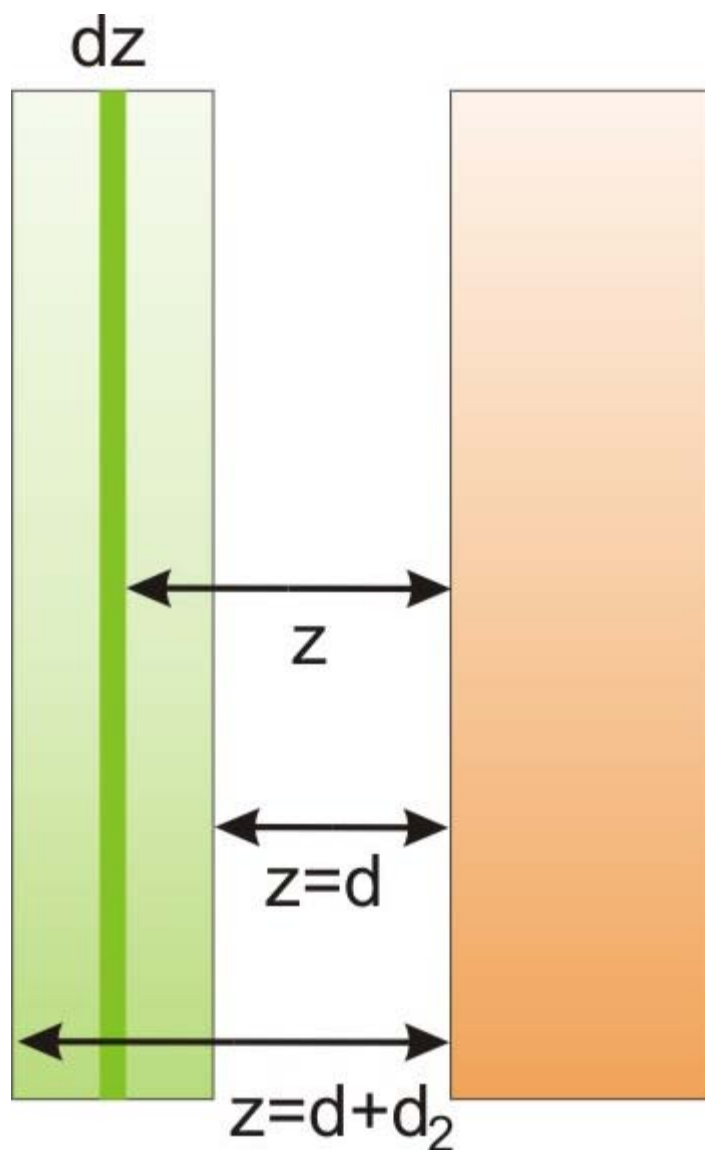


Fig. 8.9:

If  $dG$  is the potential of interaction (per unit area) between the thin integrating volume in 2 and the entire slab 1, it is given by:

$$dG = \phi'' \frac{\rho_2 N_A}{M_2} dz \quad (8.8)$$

Using Equation (8.7) in (8.8) and integrating over the complete slab 2 (from  $z = d$  to  $z = d + d_2$ ) one gets the final expression for the energy of interaction between slabs 1 and 2 (per unit area)

$$G = \int dG = \int_{z=d}^{z=d+d_2} \phi^n \frac{\rho_2 N_A}{M_2} dz$$

$$= \int_{z=d}^{z=d+d_2} -\frac{\rho_1 \rho_2 N_A^2 \pi \beta_{12}}{6 M_1 M_2} \left[ \frac{1}{z^3} - \frac{1}{(z+d_1)^3} \right] dz \quad (8.9)$$

$$G = -\frac{A_{12}}{12\pi} \left[ \frac{1}{(d+d_1+d_2)^2} + \frac{1}{d^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2} \right] \quad (8.9)$$

Where  $A_{12}$  is the Hamaker's constant whose value is given by:

$$A_{12} = \frac{\rho_1 \rho_2 \pi^2 N_A^2 \beta_{12}}{M_1 M_2} \quad (8.10)$$

It has units of energy, i.e., that of ergs or joules. For two bodies placed in vacuum, the value of this constant varies from  $10^{-19}$  to  $10^{-21}$  J or  $10^{-14}$  to  $10^{-12}$  ergs (0.1 to 10 kT).



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It is to be noted that this is the LW energy of interaction per unit area. In reality, if there were two slabs of areas  $A_1$  and  $A_2$  such that  $A_1 < A_2$  one would multiply  $G$  with  $A_1$  to get the total LW energy of interaction (ignoring end effects, and assuming that the LW forces decay fast enough in order to be able to ignore the contribution from the remaining area  $A_2 - A_1$ ).

What is interesting to note here is that the rate of decay of the LW potential between two molecules (atoms) goes as  $r^{-6}$  (Equation 8.2), while the decay is as  $z^{-3}$  (Equation 8.7) for the interaction between a single molecule (atom) with a macroscopic body and as  $d^{-2}$  (Equation 8.9) between two bodies. Thus, these are called long range van der Waals forces.

From Equation 8.9, it is clear that if  $d_1$  and  $d_2$  are larger than the order of 100 nm (i.e. effectively tending to infinity), the expression reduces to that for two semi-infinite slabs placed in vacuum:

$$G = -\frac{A_{12}}{12\pi d^2} \tag{8.11}$$

The force between two such bodies is then given by the negative gradient of the potential  $G$ :

$$F = -\frac{dG}{d(d)} = -\frac{A_{12}}{6\pi d^3} \tag{8.12}$$

As the semi-infinite bodies come closer, the value of  $G$  becomes more negative. However, at very small distances, repulsive forces must take over. From the simplified model from Equation 8.2, we understand that 'contact' between two bodies would be defined as  $d=d_0$ . This is because there is an infinitely large repulsive barrier at that point, due to which the bodies cannot come any closer. Thus, at contact we have:

$$G(d_0) = -\frac{A_{12}}{12\pi d_0^2} \tag{8.13}$$

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In order to relate what we have derived so far with macroscopic observables, recall that the LW energy of adhesion is defined as:

$$\Delta G^{LW} = G(d_0) - G(\infty) = -\frac{A_{12}}{12\pi d_0^2} = \gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW}$$

$$A_{12} = -12\pi d_0^2 (\gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW}) \quad (8.14)$$

Thus, one can use Equation 8.14 to relate  $A_{12}$  which is a molecular parameter (as it depends on the coefficient  $\beta_{12}$ ) to surface tension values, which can be measured from experiments such as contact angle measurement etc.

Putting 1=2 in Equation 8.14,

$$A_{11} = 24\pi d_0^2 \gamma_1^{LW} \text{ and } A_{22} = 24\pi d_0^2 \gamma_2^{LW} (\gamma_{11}^{LW} = \gamma_{22}^{LW} = 0)$$

If the following mixing rule holds:

$$\beta_{12} = \sqrt{\beta_{11}\beta_{22}}$$

$$\Rightarrow A_{12} = \sqrt{A_{11}A_{22}} = 24\pi d_0^2 \sqrt{\gamma_1^{LW} \gamma_2^{LW}}$$

$$\gamma_{12}^{LW} = \left( \sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}} \right)^2 \quad (8.15)$$