Module 6: "Forces in Colloidal Systems"

Lecture 29: ""

The Lecture Contains:

- Self Energy of a thin film
- Thin film on a semi-infinite solid substrate
- Two semi-infinite blocks placed in a medium

Previous Next

Self Energy of a thin film

As promised earlier, we now find the self energy of a film of material of thickness h. To do this, first consider a semi-infinite slab as being divided into two parts: $(0 \text{ to } h)$ and $(h \text{ to } \infty)$ as shown in Figure 8.10:

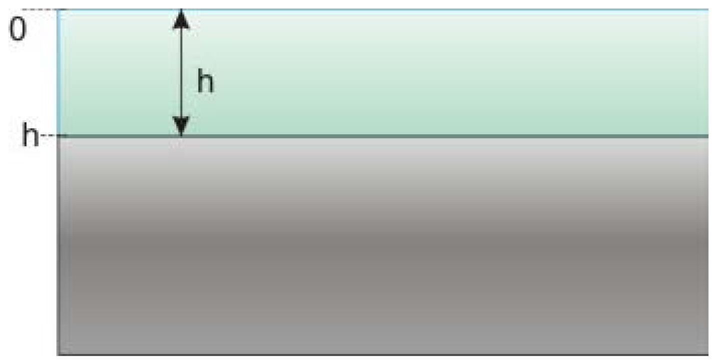

fig 8.10:

Total energy of semi-infinite slab from $(0-\infty)$ = Energy of film from $(0-h)$ + Energy of semi-infinite slab from $(h-\infty)$ + Energy of interaction between molecules (atoms) residing in the film $(0-h)$ and those residing in $(h-\infty)$.

We realize that the term on the left side of the above equation and the second term on the right side equal the same quantity, as both slabs are semi-infinite. Therefore,

Energy of film from $(0-h) = (-1)^{*}$ Energy of interaction between molecules (atoms) residing in the film $(0-h)$ and those residing in $(h-\infty)$

Previous Next

We can use Equation 8.9 to find the LW interaction energy between $(0-\mathrm{h})$ and $(\mathrm{h}-\infty)$ by replacing d by d_0, d_2 by ∞ and d_1 by h. Doing so, we have,

Energy of film of thickness $\mathrm{h} = G^{LW} = \frac{A_{11}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{(h+d_0)^2}\right]$ (8.16)

One can approximately write $\mathrm{h}+\mathrm{d}_0$ as h to get a simplified expression:

$$G^{LW} = \frac{A_{11}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{h^2}\right] \quad (8.17)$$

Where, one can use $\mathrm{A}_{11} = 24\pi \mathrm{d}_0^2 \gamma$ to write the equation in terms of macroscopic parameters:

$$G^{LW} = 2\gamma_1^{LW} - \frac{A_{11}}{12\pi h^2} = 2\gamma_1^{LW}\left(1 - \frac{d_0^2}{h^2}\right) \quad (8.18)$$

A note of caution is in order here: while using Equation 8.17 instead of Equation 8.16, the condition for ‘no film’ is $\mathrm{h} = \mathrm{d}_0$ and not $\mathrm{h} = 0$.

Previous Next

Thin film on a semi-infinite solid substrate

We now calculate the energy of a thin film of thickness h on a semi-infinite solid substrate (Figure 8.11)

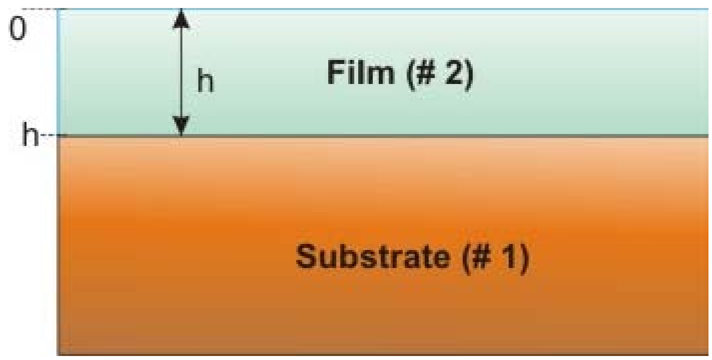

Fig. 8.11

Total Energy of the system = Energy of film + Energy of Substrate + Interaction Energy

$$G^{LW}_{INTERACTION} = \frac{-A_{12}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{h^2}\right]$$

$$G^{LW}_{FILM} = \frac{-A_{22}}{12\pi h^2} + 2\gamma^{LW}_{22}$$

$$G^{LW}_{SUBSTRATE} = constant \text{ (independent of h)}$$

Sum of all three terms gives the total energy:

$$G^{LW}_{total} = \frac{-A_{12}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{h^2}\right] + \frac{-A_{22}}{12\pi h^2} + \text{Constant}$$

$$G^{LW}_{total} = \frac{A_{12} - A_{22}}{12\pi h^2} + \text{Constant}$$

$$G^{LW}_{total} = \frac{A_e}{12\pi h^2} + \text{constant} \tag{8.19}$$

where A_e is the effective Hamaker's constant which is defined as

$$A_e = A_{22} - A_{12}$$

Replacing A_{22} and A_{12} in terms of interfacial tensions using Equation 8.14:

$$A_e = 12\pi d_0^2(2\gamma_2^{LW} - \gamma_1^{LW} - \gamma_2^{LW} + \gamma_{12}^{LW})$$

$$A_e = 12\pi d_0^2(\gamma_2^{LW} - \gamma_1^{LW} + \gamma_{12}^{LW}) \tag{8.20}$$

Note that the effective Hamaker's constant can be positive or negative depending on the values of and . In order to evaluate the constant term, we note that as approaches , the value

A_{12} A_{22} h d_0

of G_{TOTAL}^{LW} must approach γ_1^{LW} (because $h \rightarrow d_0$ is the condition for no film). Using this condition along with Equation 8.14, we conclude that the constant must be equal to $\gamma_2^{LW} + \gamma_{12}^{LW}$.

A_e can also be written in terms of the spreading coefficient which is defined as:

$$S_{12}^{LW} = \gamma_1^{LW} - \gamma_2^{LW} - \gamma_{12}^{LW} \quad (8.21)$$

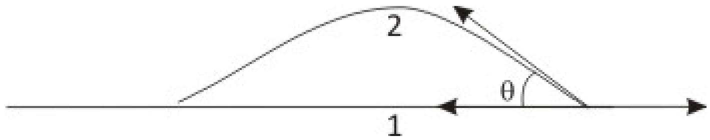

Fig. 8.12:

Using Young's equation (in cases where it is valid) one can also write (see Figure 8.12):

$$\cos\theta = 1 + \frac{S}{\gamma_2} \text{ or } \frac{S}{\gamma_2} = \cos\theta - 1$$

From Equations 8.20 and 8.21, the effective Hamaker's constant, A_e is related to the Spreading coefficient as:

$$A_e = -12\pi d_0^2 S_{12}^{LW}$$

so,

$$A_e < 0, if, S_{12}^{LW} > 0$$

$$A_e > 0, if, S_{12}^{LW} < 0$$

Physically, a positive value of the spreading coefficient (and a correspondingly negative value of the effective Hamaker's constant) implies a case of complete wetting of the solid substrate by the liquid film $(\theta = 0)$ while $S < 0 (A_e > 0)$ relates to the case of an unstable film that eventually breaks up into droplets (De-wetting; see Figure 8.13) . As has been shown earlier, the condition for instability of a thin liquid film under the influence of van der Waals forces with the substrate is precisely that the value of Ae be positive. Thus we see that the results we have obtained are consistent to our earlier knowledge, and that they make physical sense!

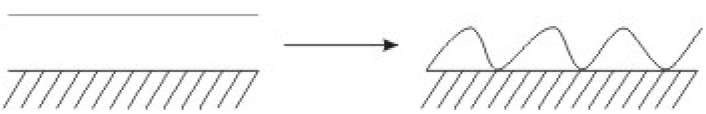

Fig 8.13:

Previous Next

Two semi-infinite blocks placed in a medium

Now let's consider the case where two semi-infinite blocks 1 and 2 are separated by a distance 'd' in a medium 3 (not vacuum; See Figure 8.14).

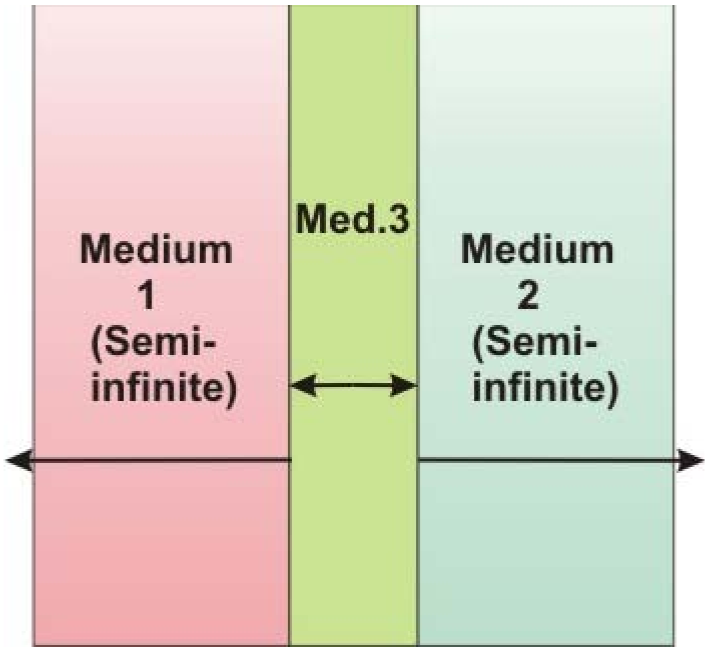

Fig 8.14:

The total van der Waals energy of the system (only that part which depends on 'd') is the sum of the following components:

= Self energy of film of medium 3 (thickness d) + Interaction energy between semi-infinite blocks spaced d apart + Interaction energy between the film and semi-infinite medium 1 + Interaction energy between film and semi-infinite medium 2

Summing over all these components:

$$G^{LW} = \frac{-A_{33}}{12\pi d^2} - \frac{A_{12}}{12\pi d^2} + \frac{A_{13}}{12\pi d^2} + \frac{A_{23}}{12\pi d^2} + \text{Constant} \qquad (8.22)$$

$$G = \frac{-A_{e132}}{12\pi d^2} + \ Const$$

$$A_{e132} = A_{12} + A_{33} - A_{23} - A_{13}$$

Where A_{e132} is the Effective Hamaker's constant. In order to determine the value of the constant term in Equation 8.22, we use a similar approach as in the section above, except that we take the limit of the energy as d approaches infinity. Its value comes out to be $= \gamma_{13}^{LW} + \gamma_{23}^{LW}$

Previous Next

From Equation 8.22 it is evident that the variation of G with d is purely monotonic, and its sign does not change over the entire range of separation distances.

Also, using an earlier result, $A_{ij} = \sqrt{A_{ii}A_{jj}}$ in the above expression for the effective Hamaker's constant we get,

$$A_{132} = \sqrt{A_{33}} - \sqrt{A_{11}}\,\sqrt{A_{33}} - \sqrt{A_{22}}$$

Force between particles are attractive or repulsive depending on whether A_e is positive or negative, respectively. In other words, if A_{33} has a value intermediate between those of A_{11} and A_{22}, the two semi-infinite bodies will repel each other in the presence of a medium 3. We have also shown that A_{ii} scales linearly as γ_{ii} which means that in terms of macroscopic parameters, the condition for repulsion is

$$\gamma_{11} < \gamma_{33} < \gamma_{22} \;\; or \; \gamma_{22} < \gamma_{33} < \gamma_{11}$$

$$A_{ii} = 24\pi d_0^2 \gamma_i^{LW}$$

$$\Rightarrow A_{132} = 24\pi d_0^2 \left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_1^{LW}}\right)\left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}}\right)$$

Attraction =>

$$\gamma_1^{LW}, \gamma_2^{LW} < \gamma_3^{LW}$$

$$\gamma_1^{LW}, \gamma_2^{LW} > \gamma_3^{LW}$$

As a corollary, if 1 and 2 are the same media, one can never have repulsion as A_{e131} comes out to be a negative quantity.

$$\Delta G^{LW} = G(d_0) - G(\infty)$$

$$= \frac{-A_{132}}{12\pi d_0^2}$$

$$= \gamma_{12}^{LW} - (\gamma_{13}^{LW} + \gamma_{23}^{LW})$$

Previous Next