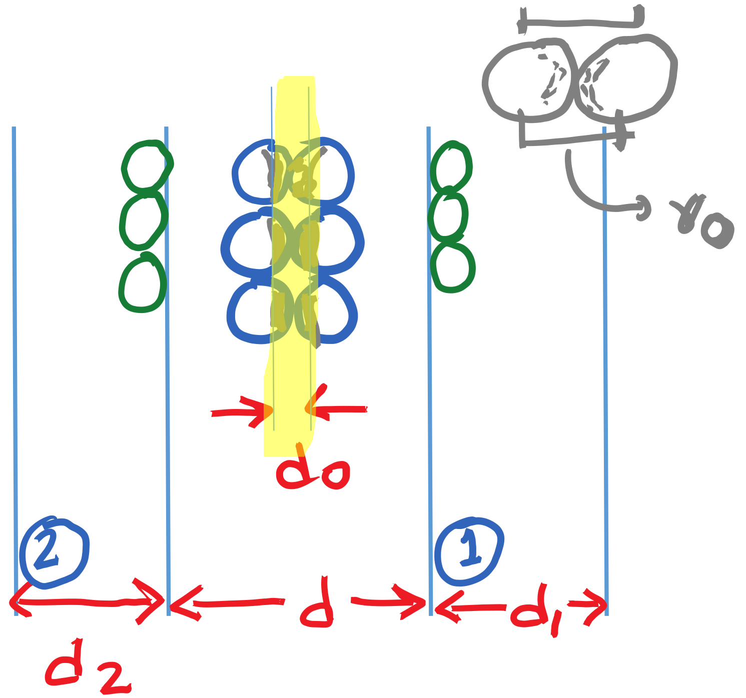


$$\boxed{w_a(x) = -\frac{A}{x^6}}$$

Date: 02.03.2022

Lecture # 20

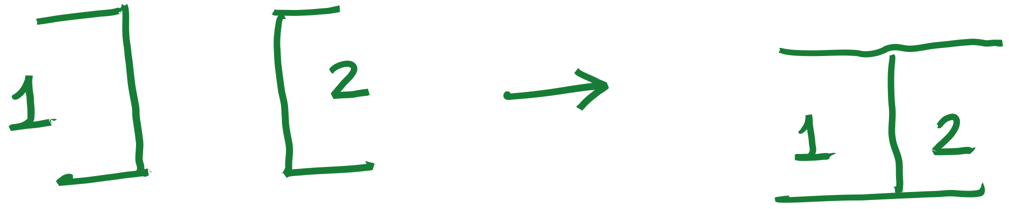
LW interaction only

Interaction between two blocks

→ We also take into consideration the thickness (finite thk) of the blocks

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

Where $A_{12} = \frac{\rho_1 \rho_2 \pi^2 N_A^2 \beta_{12}}{M_1 M_2}$ Hamaker constant

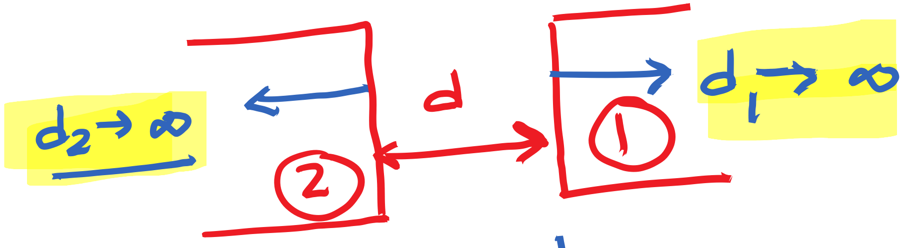


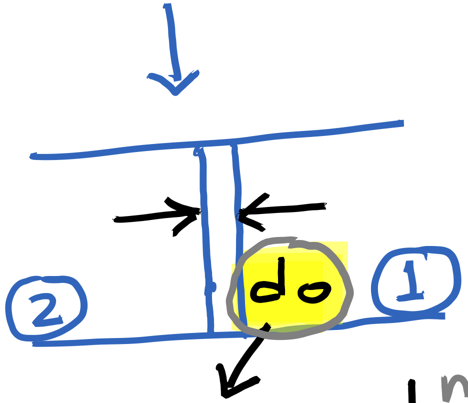
$$\Delta G_{12} = \gamma_{12} - (\gamma_1 + \gamma_2)$$

When the two blocks are very thk / or Semi-infinite

$$(*) \quad G_{12}^{LW} = -\frac{A_{12}}{12\pi}\left[\frac{1}{d^2} + \cancelto{0}{\frac{1}{(d+d_1+d_2)^2}} - \cancelto{0}{\frac{1}{(d+d_1)^2}} - \cancelto{0}{\frac{1}{(d+d_2)^2}}\right]$$

$$\Rightarrow \quad G_{12}^{LW} = -\frac{A_{12}}{12\pi d^2}$$





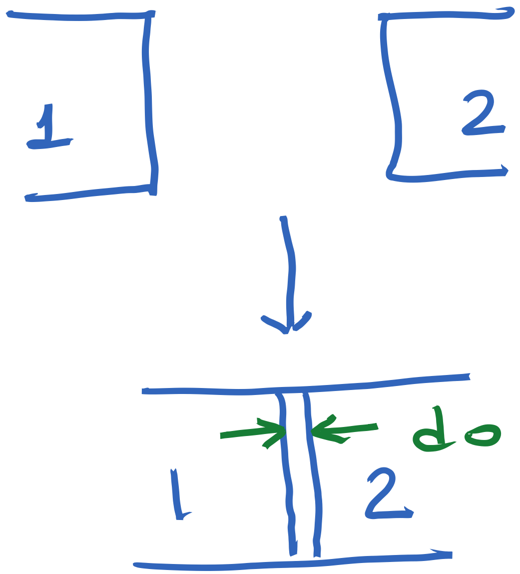
Change in G_{12}^{LW} as the two Semi-infinite blocks, initially far away come in contact:

$$\Delta G_{12}^{LW} = G_{12}^{LW}\Big|_{d=d_0} - G_{12}^{LW}\Big|_{d\to\infty}$$

$$\Delta G_{12}^{LW} = -\frac{A_{12}}{12\pi d_0^2} \quad (*)$$

Collective manifestation of the electronic cloud of all surface mol. coming in contact.

When the two blocks come in contact, the min. sepn. distance is d_0. (NOT = 0)



$$\Delta G_{12}^{LW} = -\frac{A_{12}}{12\pi d_o^2}$$

(LW interaction only)

↑

$d_{min} = d_o$

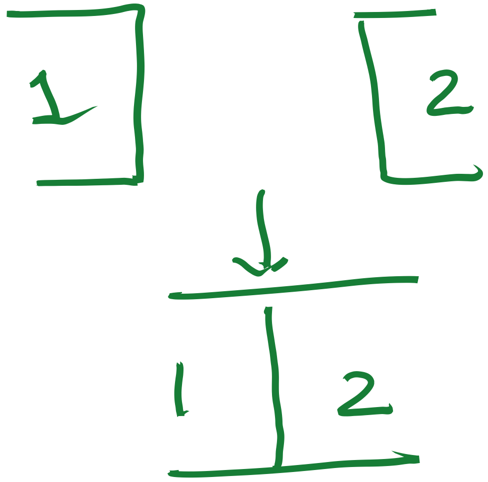
Same*

* T&C apply

If both 1 and 2 are a-polar

↓

Then they are same



Consider Complete Contact

$\gamma_{11} = 0$

$$\Delta G_{12} = \gamma_{12} - (\gamma_1 + \gamma_2)$$

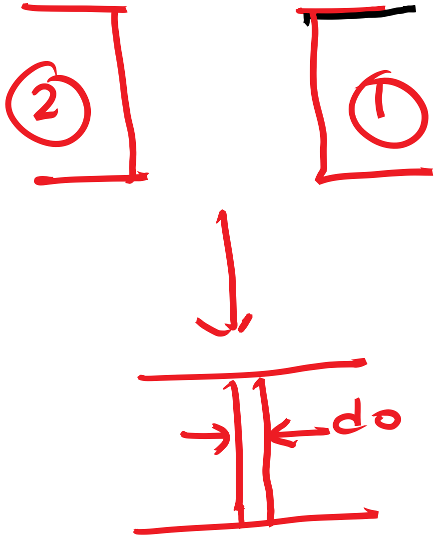
(Includes all Interaction)

$$\Delta G_{12} = \Delta G_{12}^{LW}$$

(If both 1 and 2 are a-polar)

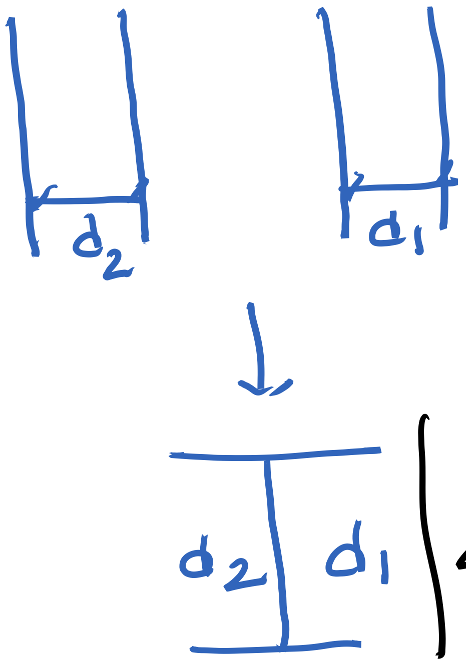
$$\Delta G_{12}^{LW} = \gamma_{12}^{LW} - (\gamma_1^{LW} + \gamma_2^{LW})$$

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



$$\Delta G_{12}^{LW} = -\frac{A_{12}}{12\pi d_0^2}$$

*



$$\Delta G_{12}^{LW} \to 0$$

$$= G_{12}^{LW}\Big|_{d=d_0} - G_{12}^{LW}\Big|_{d=\infty}$$

$$\Delta G_{12}^{LW} = -\frac{A_{12}}{12\pi}\left[\frac{1}{d_0^2} + \frac{1}{(d_1+d_2+d_0)^2} - \frac{1}{(d_1+d_0)^2} - \frac{1}{(d_2+d_0)^2}\right]$$

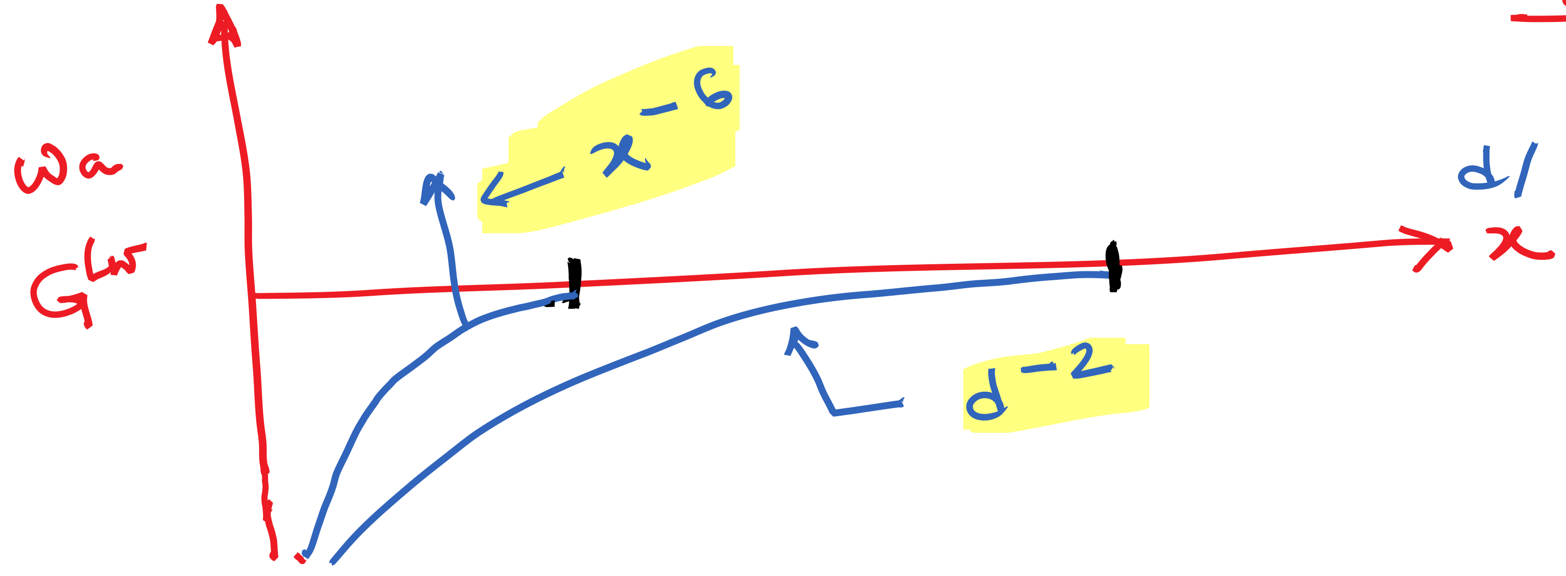
*

Additional terms

Free Energy Landscape gets Influenced by the Finite size of the blocks.

$$\simeq -\frac{A_{12}}{12\pi}\left[\frac{1}{d_0^2} + \frac{1}{(d_1+d_2)^2} - \frac{1}{d_1^2} - \frac{1}{d_2^2}\right]$$

$d_1 \gg d_0, \quad d_2 \gg d_0$



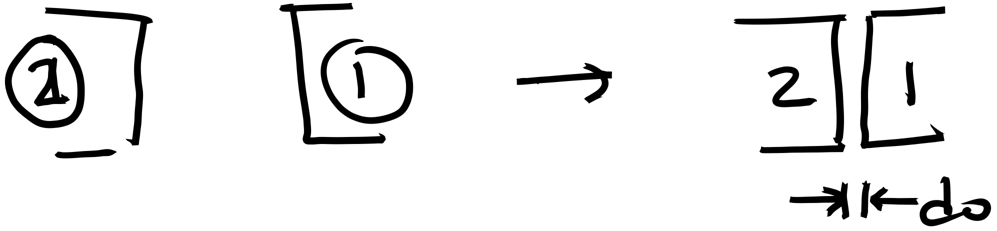
$\rightarrow$ $\underline{\underline{W_a}} = -\frac{B_{12}}{x^6}$

$\rightarrow$ $\underline{\underline{G^{lw}_{12}}} = -\frac{A_{12}}{12\pi d^2}$

They are related

As the sepn distance between particles (x) and two Surfaces (d) increases, $W_a \rightarrow 0$ much more rapidly than G_{12}^{lw}.

* Whatever is the distance upto which the presence of vdw Interaction between two atom/molecule can be felt (~ 10 nm)
The presence/existence of the same vdw interaction between two Surfaces can be felt over much longer distance (~ 100 nm).



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

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

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

$$\Rightarrow A_{12} = -12\pi d_0^2 \left[\gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW}\right]$$

↳ Considered to be material Independent.

$\simeq 0.157$ nm

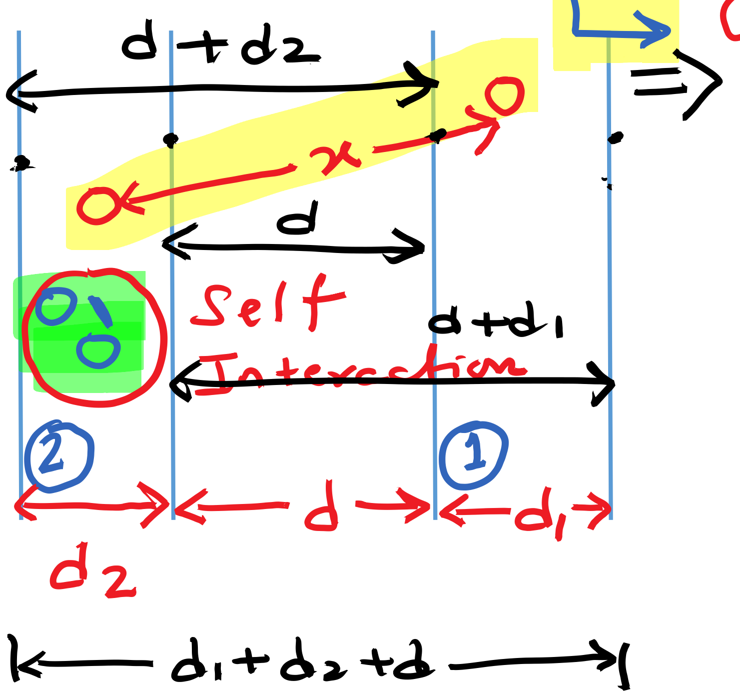
material independent Constant.

If 1 and 2 are of the same material, $\gamma_1^{LW} = \gamma_2^{LW}$, $\gamma_{11}^{LW} = 0$

$$A_{11} = 24\pi d_0^2 \gamma_1^{LW}$$

A_{12} → LW component of surface & Interfacial Tension.

Interfacial Interaction



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

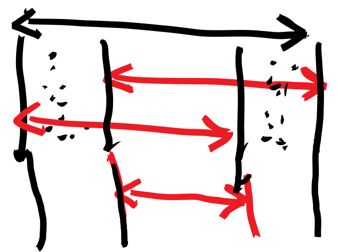
Have we considered all interactions?

Does not include the Self Energy of Interaction of the molecules

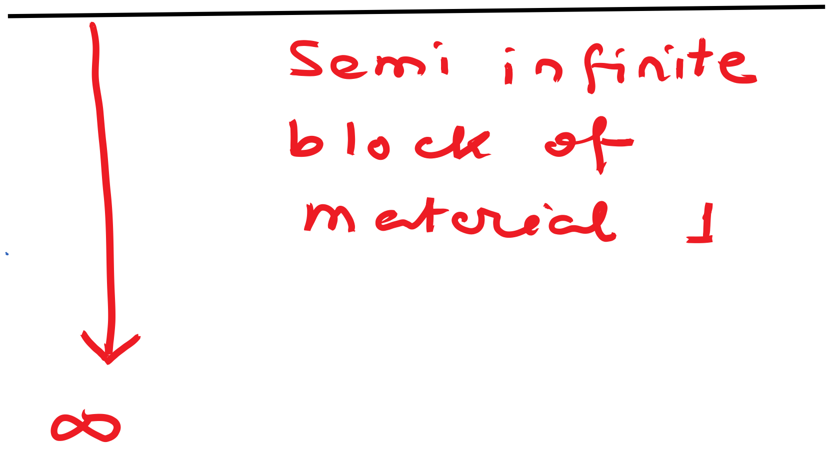
1 – 1 and 2 – 2 interactions are not considered.

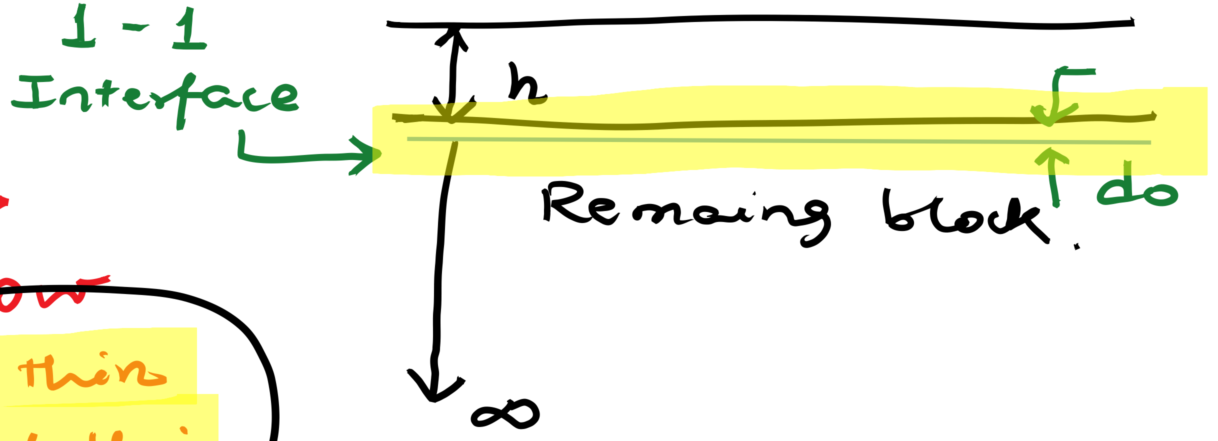
Total Free Energy of the system due to VDW interaction would include the interfacial interaction ✓ + Self Interaction with each block. ✗

Next: How do we consider the Self Interaction



Self Interaction of the molecules:-





We now cut a thin slice of this block, and place it over the remaing block.

Total Energy (Final)

= Energy of molecules between $(0, h)$

+ Energy of molecules between (h, ∞)

+ Interfacial Interaction between the slice and the block.

= Total Energy (Initial)

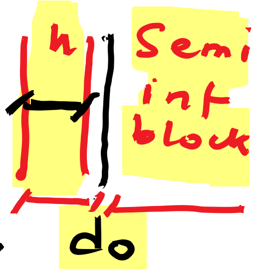
= Energy of molecules $(0, \infty)$ + Energy reqd for Creating the Slice

Creating the interface

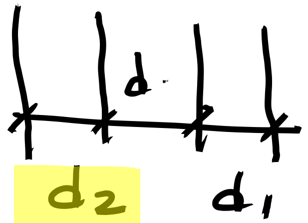
$d_2 = h$

$d = d_0$

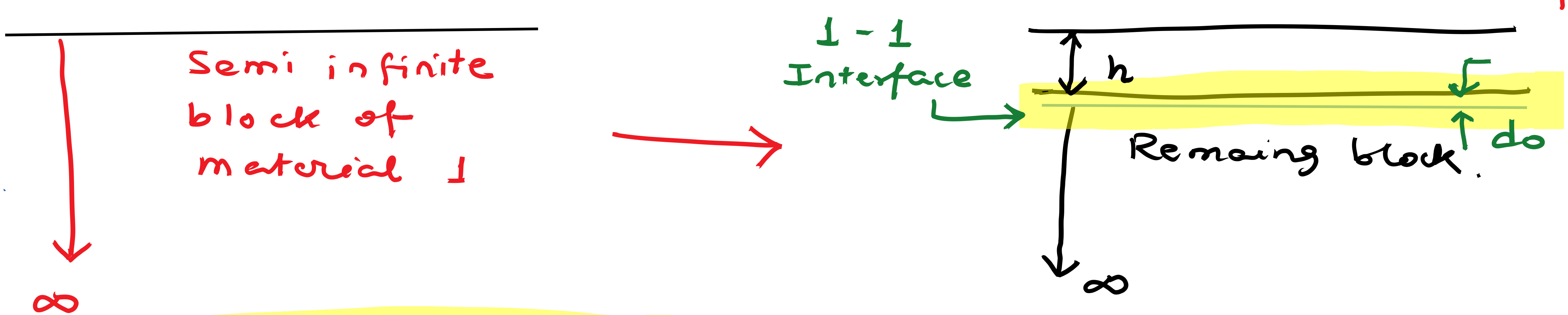
$d_1 = \infty$



1 and 2 one both 1



Self Interaction of the molecules:-



$\cancel{\text{Energy of molecules }(0,\infty)}$ + Energy reqd. for Creating the interface

= Energy of molecules $(0,h)$ + $\cancel{\text{Energy of molecules }(h,\infty)}$

+ Energy due to interfacial interaction

$h + d_0 \approx h$

Energy of molecules $(0,h)$ = (Energy reqd. for creating the interface)

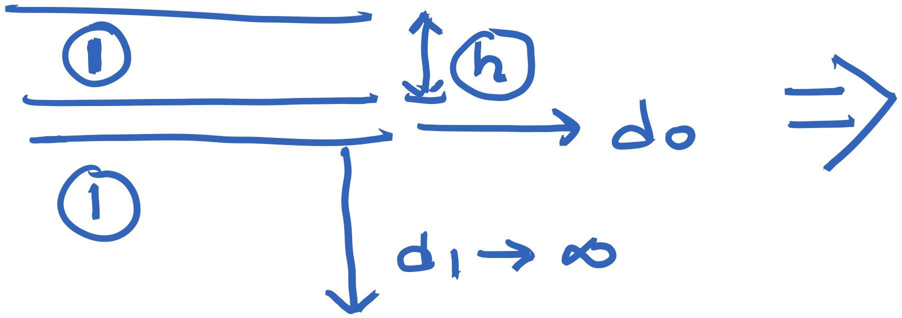
− Energy due to Interfacial Interaction

$$\Rightarrow G^{LW}_{Film} = 2\gamma_1^{LW} - G^{LW}_{11}$$

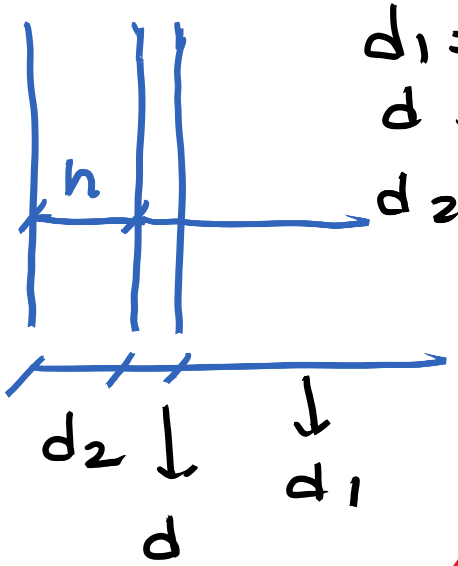
1 - 1
Interface

G_{11}^{LW}

To be Calculated



$\Rightarrow$



$d_1 = \infty$

$d = d_0$

$d_2 = h$

$$G_{12}^{LW} = -\frac{A_{12}}{12\pi}\left[\frac{1}{d^2} + \cancel{\frac{1}{(d+d_1+d_2)^2}} - \cancel{\frac{1}{(d+d_1)^2}} - \frac{1}{(d+d_2)^2}\right]$$

$\to 0$, $d_1 \to \infty$ $\qquad$ $\to 0$, $d_1 \to \infty$

$\downarrow$

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

$\underline{h + d_0 \approx h}$

$$= -\frac{A_{11}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{h^2}\right] = -2\gamma_1^{lw} + \frac{A_{11}}{12\pi h^2}$$

$A_{11} = 24\pi d_0^2 \gamma_1^{lw}$.

$-\frac{A_{11}}{12\pi d_0^2} = -2\gamma_1^{lw}$.

$$G^{Lw}_{Film} = 2\gamma_1^{lw} - G^{Lw}_{11}$$

$$= 2\gamma_1^{lw} - \left(-2\gamma_1^{lw} + \frac{A_{11}}{12\pi h^2}\right)$$

$$= 4\gamma_1^{lw} - \frac{A_{11}}{12\pi h^2} = C - \frac{A_{11}}{12\pi h^2}$$

$$G^{Lw}_{Film} = C - \frac{A_{11}}{12\pi h^2}$$

G^{Lw}_{Film} changes as a function of film thk

If thk of film changes from $h = h_1$ to $h = h_2$,

$$\Delta G^{Lw}_{Film} = G^{Lw}_{Film}\Big|_{h_2} - G^{Lw}_{Film}\Big|_{h_1} = -\frac{A_{11}}{12\pi h_2^2} + \frac{A_{11}}{12\pi h_1^2}$$

$$\Delta G^{LW}_{Film}\Big|_{h} = -\frac{A_{11}}{12\pi h_2^2} + \frac{A_{11}}{12\pi h_1^2}$$

Film thk changed from h_2 to h_1

If h_1, and h_2 both are large,

$$G^{LW}_{Film}\Big|_{h=h_1} \rightarrow C \qquad G^{LW}_{Film}\Big|_{h=h_2} \rightarrow C$$

If h is small $\quad G^{LW}_{Film} = -\frac{A_{11}}{12\pi h^2}$ becomes $f(h)$

Is non zero for small value of h.