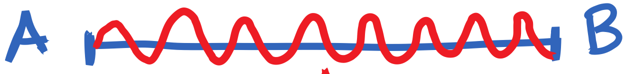
10th March 2022

Lecture 24

A_1 = Area when Flat

A_2 = Area when Fluctuating



Total Surface Area increases. (because of fluctuation)

Liquid Surface :-

(1) There are fluctuations — due to KE of the molecules.

(2) These fluctuations are very high frequency and low amplitude (few nm)

(3) As a flat Surface becomes corrogated the total Surface Energy of the Surface goes up and so Surface Tension flattens these fluctuations.

So at the Free Surface - it's a dynamic Steady State!

Total Energy ascribed at the Surface $(\gamma_s A_2) > (\gamma_s A_1)$ $\boxed{\gamma_s (A_2 - A_1)}$ *

Fluctuations on Any Liquid Surface

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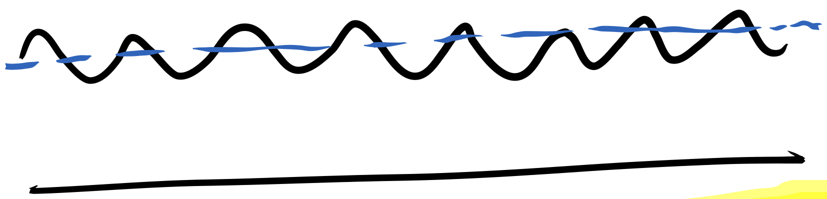
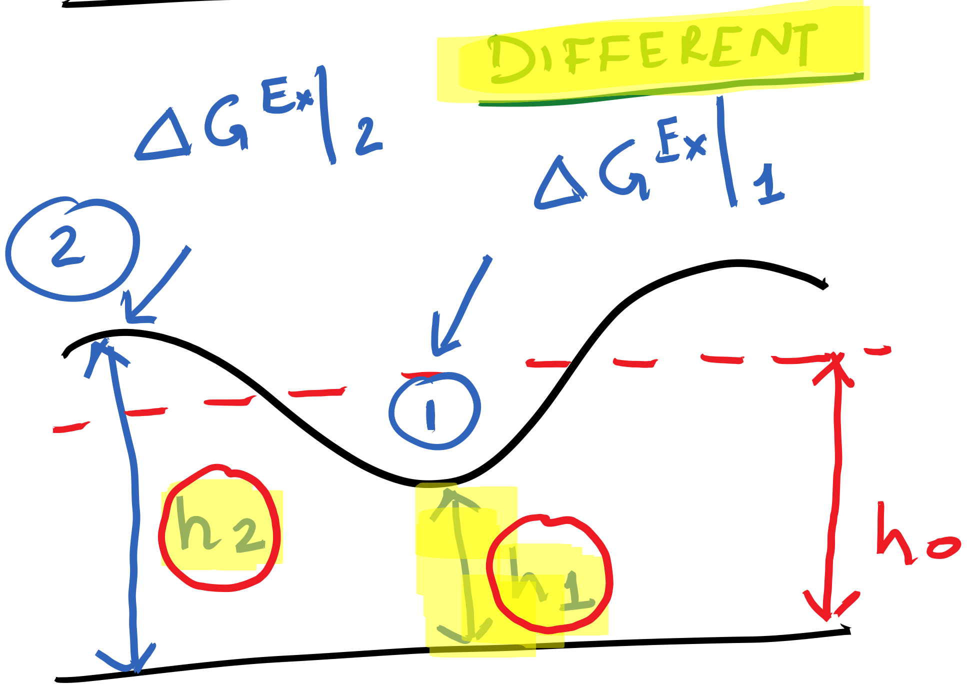
High Frequency → Low amplitude (few nm)





One Fluctuation in detail.

↑
ΔG^{Ex}

Consequence of the Fluctuation at the nano Scale:-

(1) The fluctuation amplitude is of the order of the film thk.

(2) The Strength of ΔG^{LW}_{Local} is different at 1 and at 2.

Amplitude is few nm
Variation in the Local thk is Significant (Compared to film thk).

$$\Delta G^{LW}_{system} = -\frac{A_E}{12\pi h^2}$$

$$\phi^{LW} = \frac{\partial(\Delta G^{LW}_{system})}{\partial h} = \frac{A_E}{6\pi h^3}$$

$$\Pi = -\phi^{LW} = -\frac{\partial(\Delta G^{LW}_{system})}{\partial h} = -\frac{A_E}{6\pi h^3}$$

Disjoining Pressure.

$$\phi^{LW} = \frac{\partial(\Delta G^{LW}_{system})}{\partial h} =$$ How ΔG^{LW}_{system} changes as h changes.

$\phi^{LW} \rightarrow$ Effective Interface Potential

$$\Delta G^{LW}_{System} = -\frac{AE}{12\pi h^2}$$

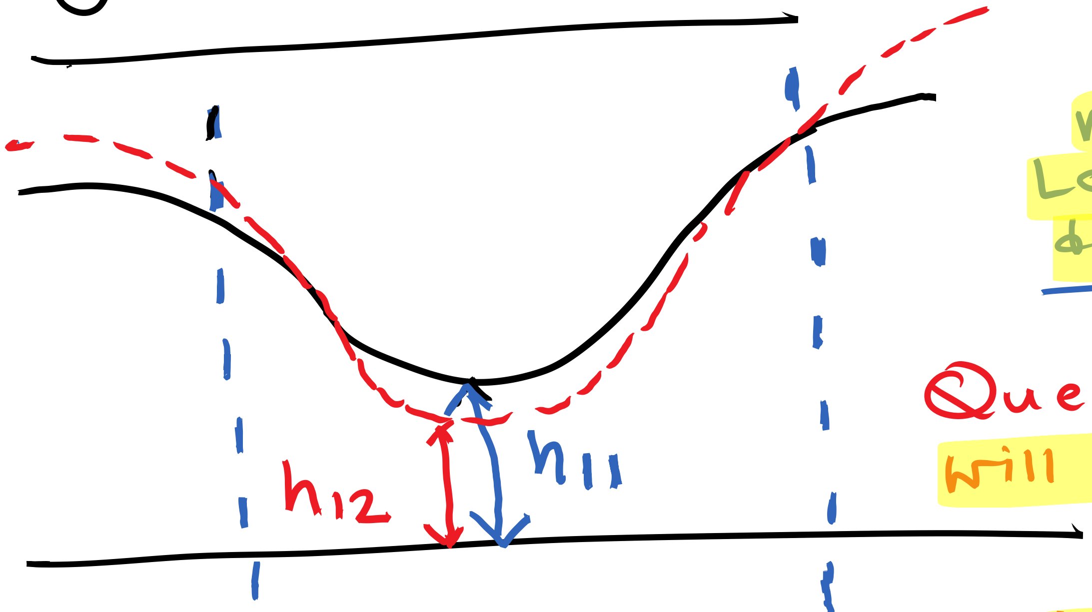
$$\Pi = -\phi^{LW}$$

Effective Interface Potential

$$\phi^{LW} = \frac{\partial(\Delta G^{LW})}{\partial h} = \frac{AE}{6\pi h^3}$$

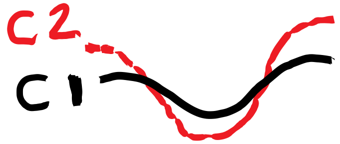
Thick Layer

One Fluctuation



For a thk Film / macroscopic Layer: they don't grow!

Surface Tension Opposes the growth!



Restored / Flattened due to Surface Tension.

Question is will the Fluctuations grow in Amplitude with time?

Whether the Free surface will go from C1 to C2 or not? NO

There is no driving force for this growth

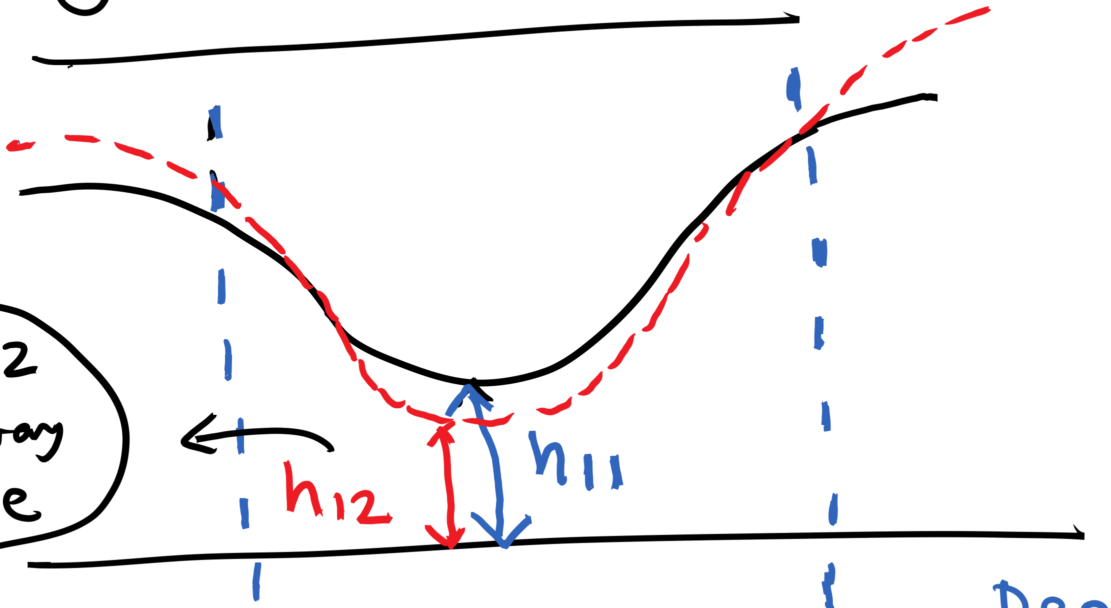
$$\Delta G^{LW}_{System} = -\frac{AE}{12\pi h^2}$$

$$\phi^{LW} = \frac{\partial(\Delta G^{LW})}{\partial h} = \frac{AE}{6\pi h^3}$$

Question:

Will the fluctuations grow in amplitude in a thin film.

One Fluctuation



h_{12} always +ve

As the Thk changes from h_{11} to h_{12}, $\Delta h = h_{12} - h_{11}$

Negative

$$\frac{\partial(\Delta G^{LW})}{\partial h} = \frac{\left[\Delta G^{LW}\big|_{12} - \Delta G^{LW}\big|_{11}\right]}{(h_{12} - h_{11})}$$

Denominator = -ve

If $\Delta G^{LW}_{12} > \Delta G^{LW}_{11} \rightarrow \phi^{LW} = -ve$

$$\Delta G^{LW}_{System} = -\frac{AE}{12\pi h^2}$$

$$\phi^{LW} = \frac{\partial(\Delta G^{LW})}{\partial h} = \frac{AE}{6\pi h^3}$$

We are examining one Growing Fluctuation

$$\phi^{LW} = \frac{AE}{6\pi h^3}$$

h is always positive

→ Denominator is always +ve

$\therefore \phi^{LW}$ Can be negative ONLY when AE is Negative

And

$\phi^{LW} > 0$, when $AE > 0$

$$\frac{\partial(\Delta G^{LW})}{\partial h} = \frac{[\Delta G^{LW}]_{12} - \Delta G^{LW}]_{11}}{(h_{12} - h_{11})}$$

Denominator = −ve

Two Possibilities

$\Delta G^{LW}|_{12} > \Delta G^{LW}|_{11}$

Numerator = +ve

$\phi^{LW} = -ve$

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Or

$\Delta G^{LW}|_{12} < \Delta G^{LW}_{11}$

→ Numerator is −ve

$\therefore \phi^{LW} = +ve$

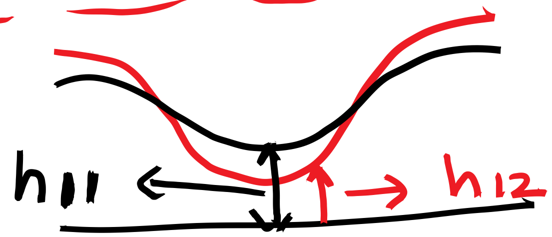
$$\phi^{LW} = \frac{\partial(\Delta G^{LW})}{\partial h} = \frac{A_E}{6\pi h^3}$$

ϕ^{LW} can be -ve only when A_E is Negative

ϕ^{LW} is +ve when A_E is +ve

ϕ^{LW} Negative

$$\frac{\partial(\Delta G^{LW})}{\partial h} = \frac{\Delta G^{LW}|_{12} - \Delta G^{LW}|_{11}}{h_{12} - h_{11}}$$



$h_{12} - h_{11} = -ve$

$\Delta G^{LW}|_{12} > \Delta G^{LW}|_{11}$

ϕ^{LW} Negative → Numerator positive

Physical Consequence?

If the Fluctuation grows, it will Lead to increase in the Excess Free Energy of the System.

When ϕ^{LW} is negative or ΔE is negative

The growth of the Fluctuations is NOT FAVORED.

due to (Active) Interfacial Interactions

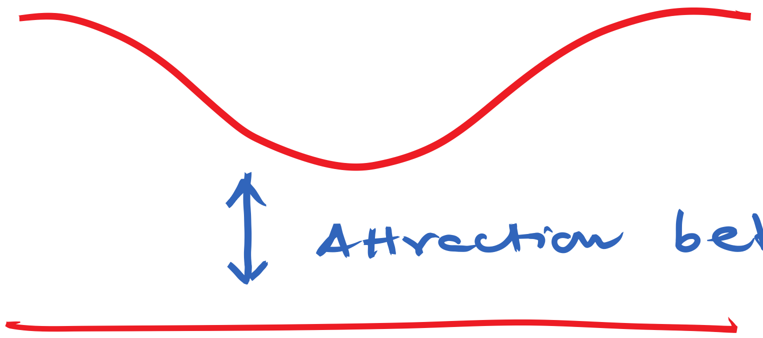
ϕ^{LW} is Positive $\longrightarrow$ ΔE positive

$$\underline{\Delta G^{LW}\big|_{12} < \Delta G^{LW}_{11}} \longleftarrow \text{Consequence.}$$

As the Fluctuation grows → The Excess free Energy of the system decreases. → Growth of the Fluctuation is favored by Interfacial Interaction.

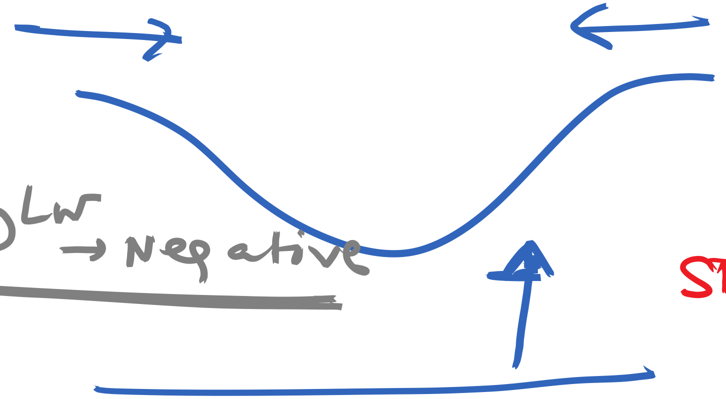
ϕ^{LW} positive would mean that growth of fluctuation due to interfacial Tension is favored.

But → Surface Tension still opposes the growth.



Uniqueness
ϕ^{LW} is +ve

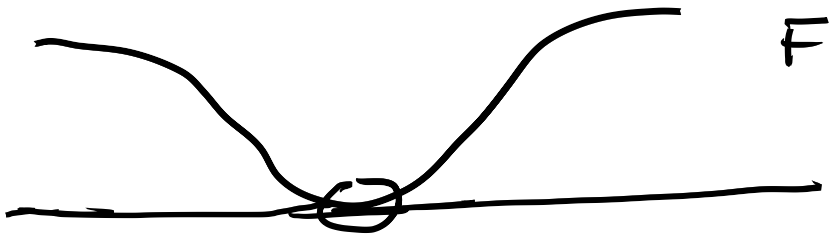
Attraction between these two interfaces



ϕ^{LW} → Negative

STABLE

(1) Surface Tension flattens
(2) Int- Interaction favors growth.



Film Eventually ruptures spontaneously

If ϕ^{LW} is Negative
(1) Surface Tension Stabilizes/ Flattens film
(2) Interfacial Tension does the same