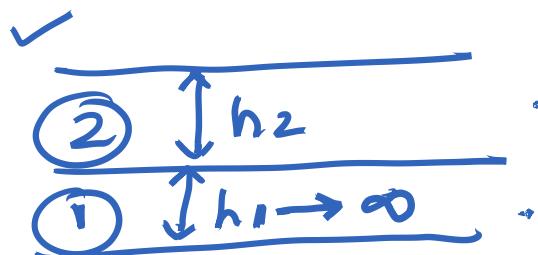


Supported Thin Film

( $\text{thick } d \rightarrow \infty$ )

Substrate (semi infinite)



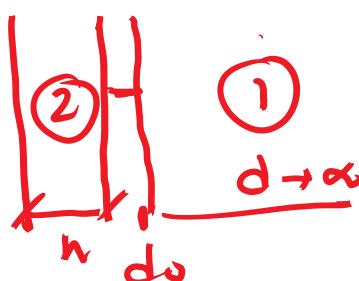
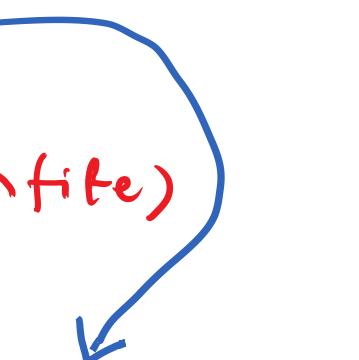
s

$G^{\text{LW}}$   
System

$$= G^{\text{LW}}_{\text{Film}} + G^{\text{LW}}_{\text{Substrate}} + G^{\text{LW}}_{\text{1-2 Interface}}$$

$$= C - \frac{A_{22} - A_{12}}{12\pi h^2}$$

$$= C - \frac{AE}{12\pi h^2}$$



$\Delta G^{\text{LW}}$   
System

$$= G^{\text{LW}}_{\text{System}}|_{h=h} - G^{\text{LW}}_{\text{System}}|_{h=\infty}$$

$$= - \frac{AE}{12\pi h^2}$$

2

1

?

$G_{\text{System}}^{\text{LW}}$  ( Supported Thin Film)

$$= C - \frac{AE}{12\pi h^2}$$

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

only LW int.

Interaction between  
the (Liq - Air) and  
(Liq - Solid) Interface Leads  
to some additional Energy

Excess Free Energy

(Interfacial Energy Due to VW  
interaction)

$$\Delta G_{\text{System}}^{\text{LW}} = G_{\text{System}}^{\text{LW}} \Big|_{h=h} - G_{\text{System}}^{\text{LW}} \Big|_{h \rightarrow \infty}$$

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

Excess of what?

"In addition to" what? →

For a Supported THIN film, there is excess interfacial interaction that depends on the thickness of the system:-  $\Delta G_{\text{sys}}^{\text{LW}} \uparrow$  as  $h \downarrow$

In a supported thin film  
there excess interfacial  
interaction due to the "THINNESS"  
of the film

②

①

$$h_1 > h_2$$

$$\Delta G_{\text{System}}^{\text{Lw}} \rightarrow 0$$

As  $h$   
increases

$$\Delta G_{\text{System}}^{\text{Lw}} = - \frac{AE}{12\pi h^2}$$

What is the Genesis of  
this Interaction:-

VdW interaction between  
(Liquid-Air) and (Liquid-  
Solid) Interfaces.

Case A

Case B

$\Delta G_{\text{System}}^{\text{Lw}}$  is higher.

②

①

$\Rightarrow$  Active interaction between  
the Free surface & The  
interface of the FILM.

$\Delta G_{\text{System}}^{\text{LW}}$  will be **NON ZERO** if

LIQUID

"**h**" is small.

→ Which means there is active Interaction between the two Surfaces / Interfaces - - - - -

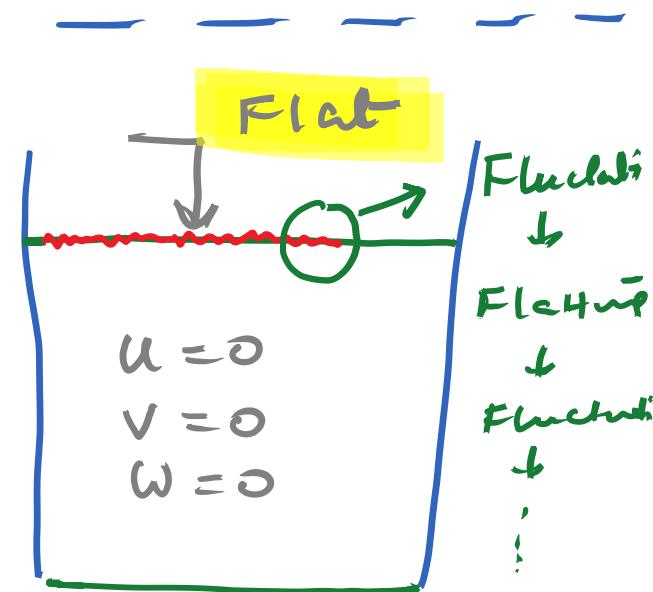


The growth of these Fluctuations is opposed by Surface Tension  
→ Macroscopic manifestation of the PE / cohesive

\* Every Flat Stationary liquid Surface is at a dynamic equilibrium (It Explored at the nano Scale)

Try to understand the Free Liquid Surface at the Nano Scale .

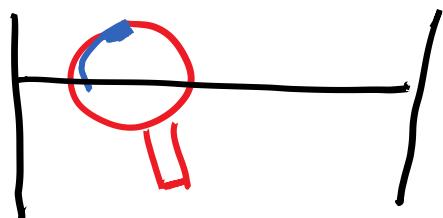
Resolution



Glass of Water  
at the nano Scale)

# Understand a free Liquid Surface at a nano scale

Resolution → Would you still see a flat. surface?



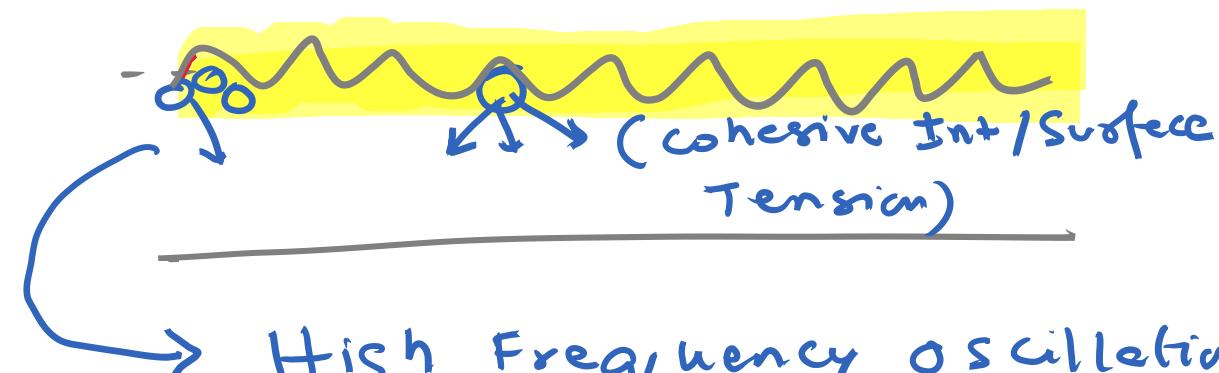
Liq Surface

Flat. macroscopically

Due to a competition between  
KE mediated tendency of the  
molecules to escape and PE  
mediated tendency of other molecules  
to hold it back → Leads to  
Fluctuation at the  
Free Surface.

Low vap.  
pr, Evap. is  
Less →

The fluctuation will be MORE  
if vapor pressure is Low.



High Frequency oscillation  
or fluctuation (random)  
at the free surface.

\* Amplitude → Few nm  
(Low freq Oscillation)

$k_B \rightarrow$  Average translational K.E.

(Molecules  
Do not interact)

$$\text{Int. Energy} = \text{Int. P. E.} + \text{Int. KE} + (\text{Rotation} + \text{Vibration})$$

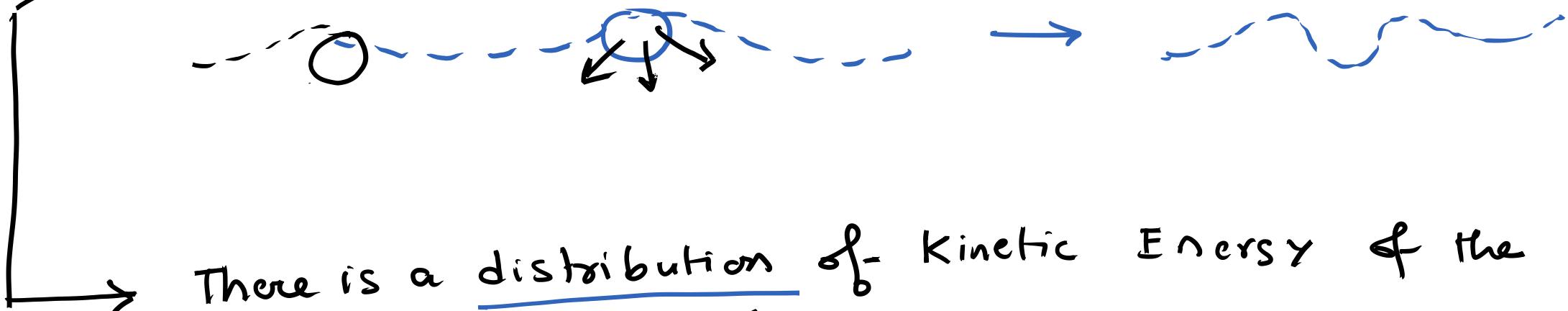
molecule  
+ other  
molecule

Ideal Gas:

Internal Energy / ideal gas constitutive  
of Internal K.E. only.

Inside the  
molecule

Evaporation: [Some Liquid molecules go to vapor phase at Room Temp.]



→ There is a distribution of Kinetic Energy of the molecules in the liquid.

$k_B T \rightarrow$  Average translational KE.

The molecules with higher KE try to escape to the vapor.

All molecules with higher KE can't Evaporate

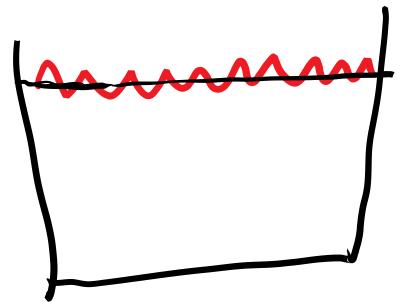
In order to evaporate, the molecule has to overcome the cohesive Interaction.

The Surface fluctuations on the Free Surface of a Liquid has no consequence / Implication for a Macro-sized.

Liquid Pool.

=

W



→ Dynamic  
Steady  
State.

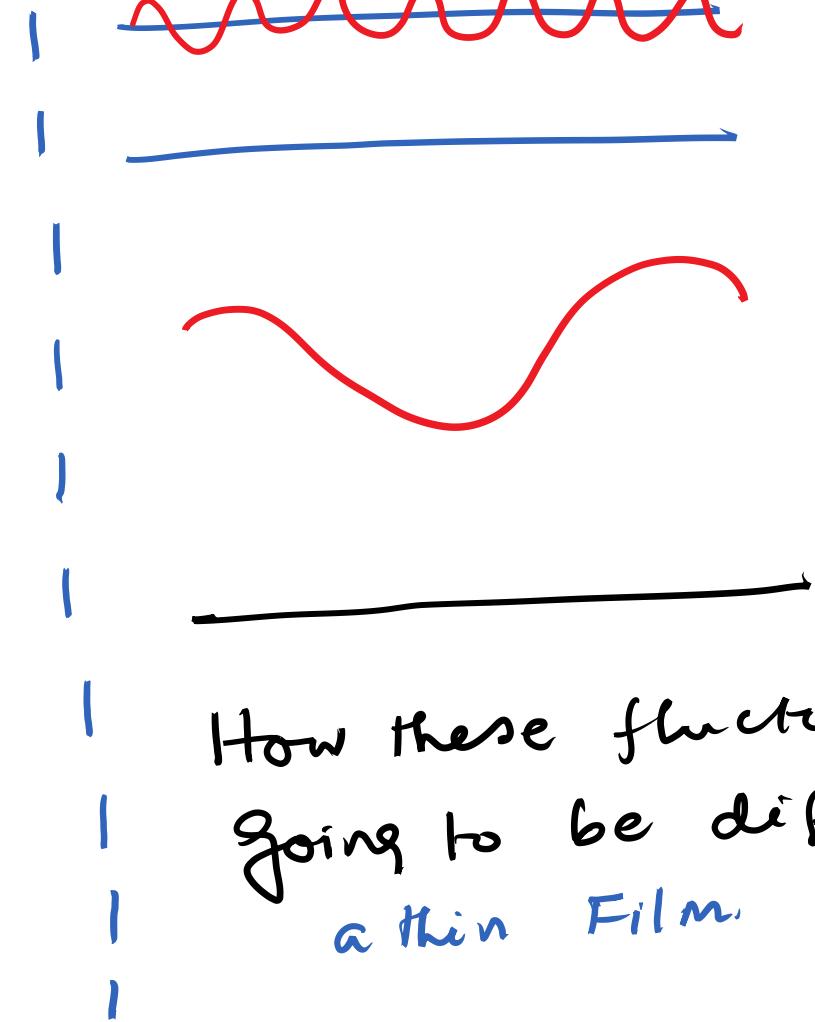
Fluctuation →  
Flattening (PE / Cohesive Int /  
Surface Tension)



Fluctuation

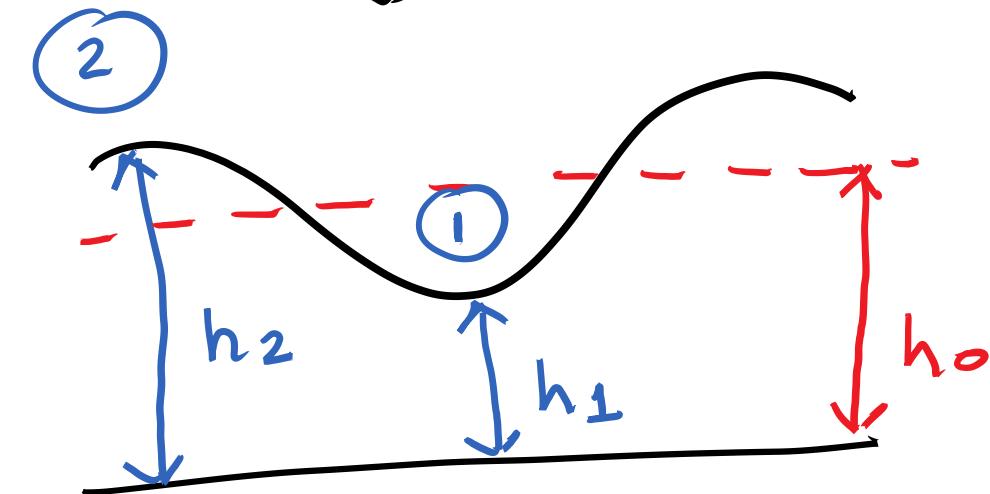
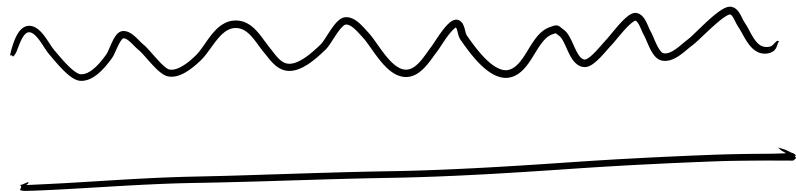
+  
Flattening

; cont eternily



Similar.  
Fluctuation  
present  
there too!  
=

How these fluctuations are  
going to be different for  
a thin Film.



One Fluctuation in detail.

Consequence of the Fluctuation at the nano Scale:-

- (1) The fluctuation amplitude is of the order of the film thk.
- (2) The Strength of  $\underline{\Delta G_{lw}}_{\text{Local}}$  is different at ① and at ②.

$$\Delta G_{\text{system}}^{\text{Lw}} = - \frac{AE}{12\pi h^2}$$

$$\Pi = - \frac{\partial (\Delta G_{\text{system}}^{\text{Lw}})}{\partial h} = - \frac{AE}{6\pi h^3}$$

↳ Disjoining Pressure.

$\frac{\partial (\Delta G_{\text{system}}^{\text{Lw}})}{\partial h} =$  How  $\Delta G_{\text{system}}^{\text{Lw}}$  changes  
as  $h$  changes.