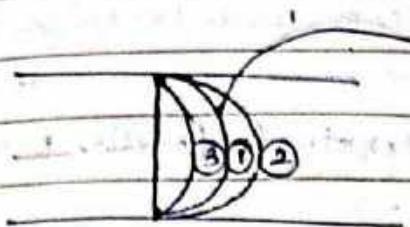


Thin Polymer film

boundary layer - zone where effects of viscosity are felt.



follow Newton's Law of Viscosity

- ① Parabola  $\rightarrow$  Newtonian fluid.
- ② & ③ are Power Law fluids.

Non Newtonian fluid

$$\textcircled{4} \rightarrow n > 1$$

$$\textcircled{5} \rightarrow n < 1$$

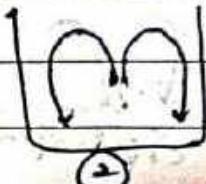
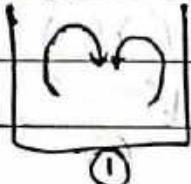
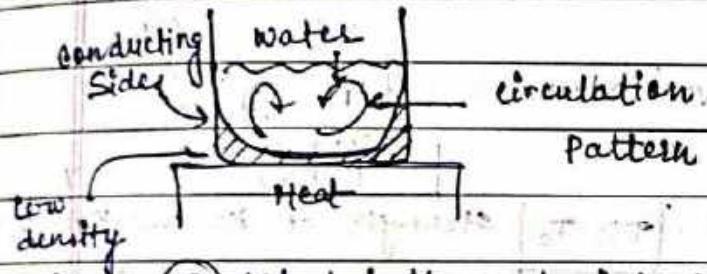
$$\tau_{yx} = \mu \left( \frac{\partial u}{\partial y} \right) \quad \tau_{yx} = \mu \left( \frac{\partial u}{\partial y} \right)^n$$

$$n = 1$$

$$n > 1 \text{ or } n < 1$$

Newtonian

Natural convection  $\rightarrow$  a flow triggered by density difference



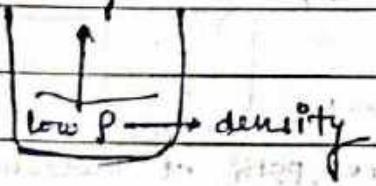
(Q) What is the material of the container for ① & ②

non metallic  $\rightarrow$  ②  $\rightarrow$  bottom heats first and the rest is uniform

viscous shear stress leads it to go to the core

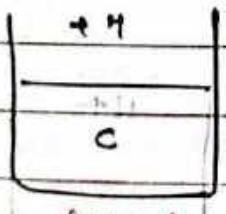
metallic  $\rightarrow$  ①  $\rightarrow$  (center)

$\rightarrow$  does not have the resistance due to viscous shear forces.

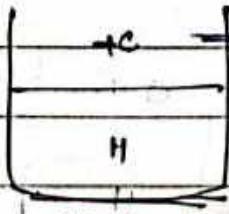


C  $\rightarrow$  cold Water

H  $\rightarrow$  Hot Water



Case 1



Case 2

faster homogenization

hot water will have a better tendency to go up.

Nanoscale

What is special about the nano scale?

not limited to 1 nm only

Diameter of human hair  $\rightarrow$  50 - 70  $\mu\text{m}$ .

1 - 10 nm  
or

Typical size of an organic molecule  $\approx 1 \text{ \AA} = 10^{-10} \text{ m}$  in some cases  $1 - 100 \text{ nm}$ .

at 10  $\text{\AA}$   $\rightarrow$  semi-crystallized nanoparticles  $\rightarrow$  Quantum Dots

quantum dots → nanoparticles made from semiconducting materials.



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Gold → surface plasmon resonance.

UV-rays are thrown at quantum dots

→ jump from valence bands to conduction bands

when UV light is switched off they come back & emit light

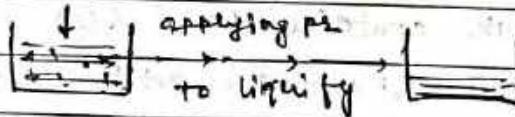
band structure becomes fn of size → leads to change in colour

→ Nanoscale is that scale where intensive properties become extensive  
(e.g. conductivity changes)

finite size effect → when studying any microscopic system with a very large no. of degrees of freedom, invariably makes an approximation and simulate a smaller and/or discretized model system. This introduces systematic errors called finite size effects.

$T_c$   
critical T

↳ liquification is not possible



$T \geq T_c$  strength of KB becomes so high

that PE can never exceed it.

if PE strength of PB  $\geq$  KB → liquidity.

if  $T$  is ↑ KB ↑ PE  $\neq$  f( $T$ ) → does not ↑ =

condensed phase (liq, solid)

non zero intermolecular forces,

non zero internal PE.

mean free path →

Non condensed phase (gas)

$\approx 0$ .

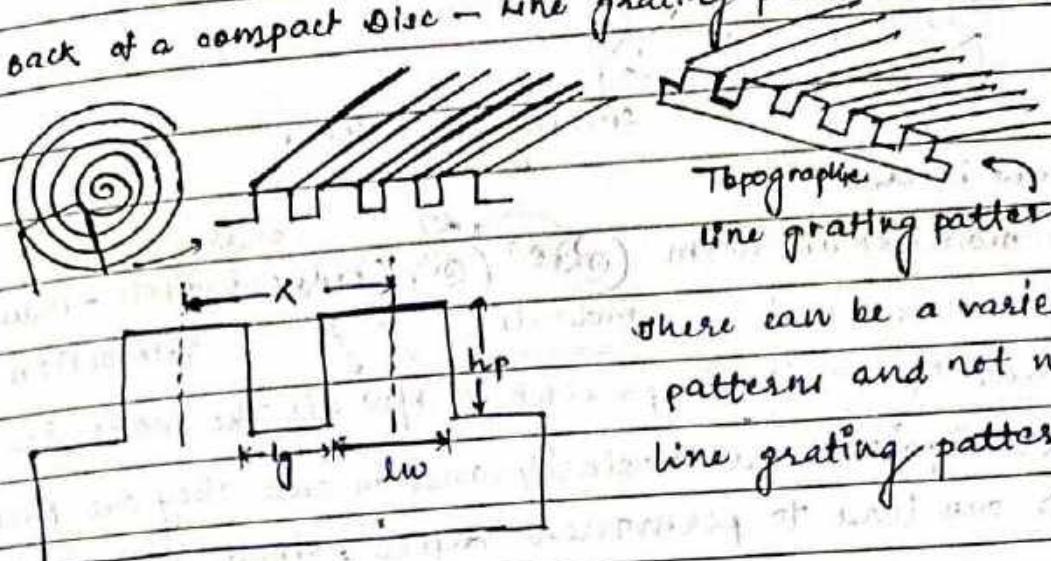
mean free path of molecules  $\rightarrow \infty$

intermolecular forces

mean free path of molecules

Visible light - 400 to 700 nm.

Back of a compact disc - Line grating pattern?



There can be a variety of topographic patterns and not necessarily only line grating pattern.

① Topographic  $\rightarrow$  physical / Relief.  
"everything is a pattern."

② Chemical Patterns: Patterns with different practical property.

Nanopatterns: Lines of 5 nm width separated by 10 nm gaps.

Structural colours: Colours that we see behind the CD due to structure and diffraction happening through them.

Surface Tension of water -  $72 \text{ mJ/m}$ .

forms a hemisphere for minimization of surface energy  $\rightarrow$  Water drop

Surface Tension  $\rightarrow$  Young's eq  $\rightarrow$  contact Angle

Dispersion forces  
Surfactants.

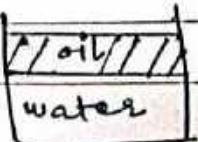
Thin-film Types -

Supported

very stable

support is a liquid or a deformable support.

Eg. =

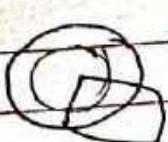


Ellipsometer  
for thick measurement

UnSupported

self standing film

soap containing water film



air

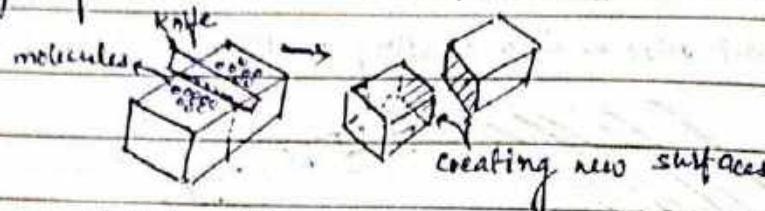
soap containing water film

## Dipole forces - (permanent, induced dipole)

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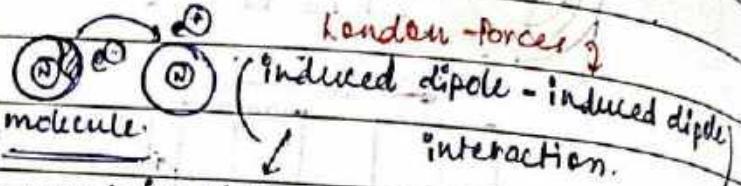
### surface tension (surface energy)

energy reqd. to create unit surface area. of a material



### Vander Waal's interaction

- \* Rutherford model of an atom what was binding the molecules?
- \* Intermolecular Interaction. Is present in b/w all the molecules closely.
- \* lone e<sup>-</sup>s or e<sup>-</sup>O pairs lead to polarity and in case they are present along with 1D - 1D can lead to permanent dipole <sup>perm</sup> dipole interaction (Keenly) forces
- \* The strength of interaction depends only on the separation, not gravity (Hooke's law). London forces are omnipresent but the condition is  $S^- S^+$  should be in range of roughly 10 nm.



- \* Monoatomic gases are closest to ideal gas because they don't have rotational & vibrational Energy.
- \* Ideal gas is a gas whose internal Energy (U) consists of only Kinetic Energy and no potential Energy which is the other name for intermolecular interactions (London forces).

- \* Necessity of a gas molecule to come & heat the wall  $\rightarrow$  gas pr. (gas molecule) moving with its own vel.  $\rightarrow$  starts experiencing (v<sub>1</sub>) more attraction towards wall

leads to enhanced pressure  
vel. while moving ↑ → extent of pr. ↑  $(P + \Delta P) \rightarrow$  Vander waal's

$$\left( \frac{P + \alpha}{V} \right) (V - b) = RT$$

$\alpha$   $\rightarrow$  1D - 1D interaction

$$(v_1 + \Delta v_1) 1D - 1D$$

- \* strength of interaction b/w steel molecules is more than that b/w butter molecules.

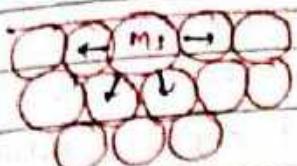
Internal energy = [Internal PE] + Internal  $kT$

[energy associated with rotation & vibration intramolecular interac]

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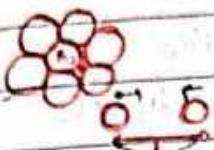
what happens at the surface?



- Net force  $\neq 0$

- coordination No. is less for surface molecules.  
aka [undercoordinated].

- force is acting towards the bulk.



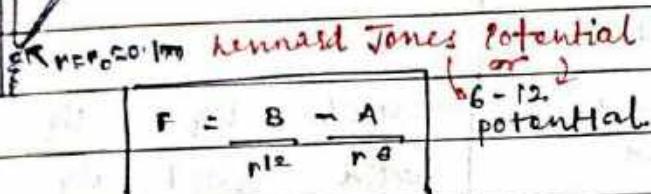
$F_{\text{tot}} = -A/r^6$  vanderwaal interaction b/w 2 molecules.

$\rightarrow \sigma$  will be 0 in the cond<sup>n</sup> of nuclear fusion and nothing else.  $r_{\text{min.}} = 2r_A + 2r_B$  where  $r_A$  and  $r_B$  represents radii of 2 molecules A and B respectively.

2. Attraction forces  $\rightarrow$  till they touch.

Then repulsion

total  
repulsion  
BETN  
Repulsion



Attraction  $\rightarrow$  repelling

Bond repulsion.

If sep<sup>n</sup> distance is more than  $r_0$  (10 nm) then only interaction. (which is active).

When  $r$  is very small, repulsion dominates aka  $r^{-12}$  term dominates

$\Rightarrow$  strength of attractive & repulsive forces is equal.

Liq.	Solid.
molecules can change their rel. position wrt the neighbouring atom. (molecules can reorganise on their own)	molecules cannot change their rel. position wrt the neighbouring atom (deformation is not there)
strength of intermolecular forces is quite less.	more

Liq.	Solid.
$\Delta U = -A/r^6$	$\Delta U = -A/r^12$

\* hydrogen bond is a classic ex. of polar bond (permanent-dipole interaction)

Difference b/w liq. & gas in terms of internal energy

Gas  $k_B T$   
internal  $\rightarrow$  internal Kinetic Energy

Liquid  $-A/r_0$   
internal  $\rightarrow$  Internal PE  
Energy

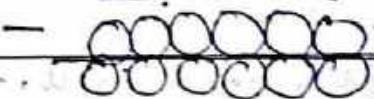
- organic liq.
- vap. pr. is high
  - do not have polar interaction
  - only London forces or LD-LD
  - boiling pt less
  - relatively more volatile
  - surface tension less

- Water
- lower vap. pr
  - polar interaction in addition induced dipole - induced dipole
  - Bpt. more
  - less volatile
  - much higher

- Surface
- when the molecules are exposed to (air, atmosphere or vacuum)
  - collectively called non condensed phase  $\rightarrow$  either no molecules or no interaction b/wenn molecules
  - air/vacuum      air/vacuum  
solid                  liquid

- interface
- condensed phase - interaction b/w the molecules  
(intermolecular interaction  $\neq 0$ )

- solid      liq : liq  
solid      solid : liq



\* Distillation is interfacial mass transfer. However, by the above def. it will be a surface phenomena bcoz mass transfer takes place b/w vapour & liquid

- ① van der waal
- ② polar interaction
- ③ entanglement Effect (Noodles effect)  - because of geometry of molecules. Polymeric material in liquids due to long chains have this force acting on them.

solids  
only potential energy

liquids  
both types of energy

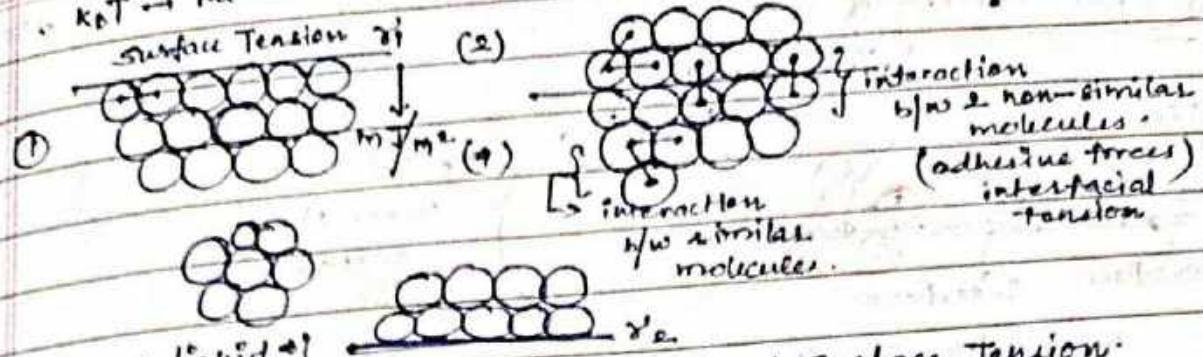
gas  
only translational energy

Surface Tension acts along the surface

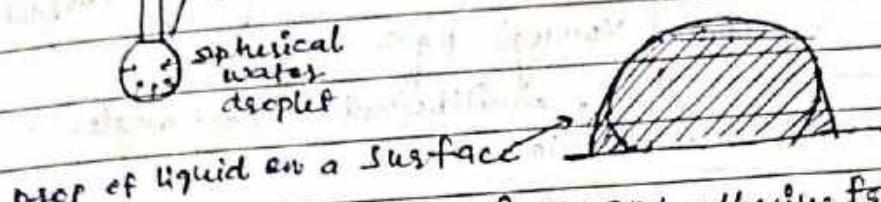
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$k_B T \rightarrow$  internal kinetic energy

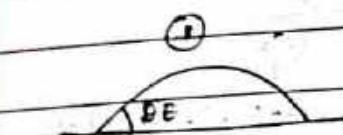


why spherical?  $\rightarrow$  minimal Surface Tension.  
All surface molecules are experiencing inward surface force. manifestation of surface force.



Depends on the cohesive forces and adhesive forces

(rel. strength)



limiting value of  
 $\theta_E$  :-

$$0 < \theta_E < 180$$

$\theta_E = 0$  is an asymptotic limit  
it tends to zero.

However, it cannot reach exactly



-max. cohesive forces  
- higher is the cohesive force, lower will be the tendency of the drop to spread.

( $\theta_E$  is higher) liquid.

molecules want to interact with their own species. So the available molecules for adhesive interaction are less.



-max. adhesive forces  
- higher adhesive force, more spread of the droplet ( $\theta_E$  is lesser)

more molecules want to interact with surface and so more spread.

$$\theta_E = 0$$

complete wetting.

$$0 < \theta_E < 90$$

tilted

very strong Adhesive forces.

Asymptotic Limit

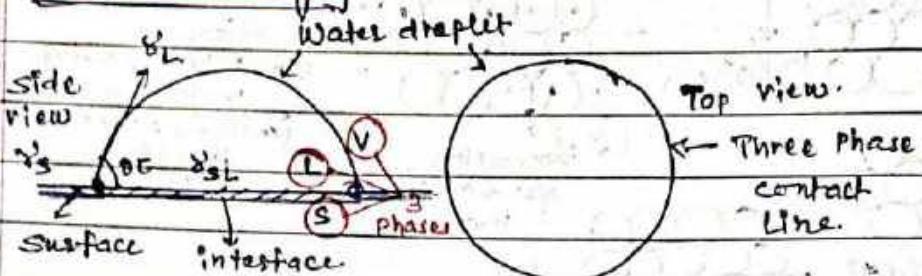
$$\theta_E = 180 \Rightarrow \text{No contact}$$

$\gamma_E$  less implies  $\gamma_S$  more

$\gamma_A = ST \text{ of } A = \text{Always need some energy for creating surface}$  → Date: 10/10/2023  
 $\gamma_{AB} = \text{energy reqd. for creating interface} \Rightarrow \text{may be +ve or -ve}$  Page: 1/4

① ② & ③ are similar in the fact that they form a finite droplet.

↓ Partial wetting?



$\gamma_S$  - Surface Tension

$\gamma_L$  - Liquid surface Tension

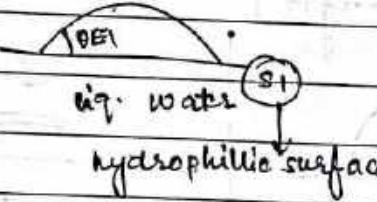
$\gamma_{SL}$  - Surface Tension of the Lig-Solid interface / Interfacial tension.

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta_E \quad \text{Young's Eqn.}$$

equilibrium contact angle.

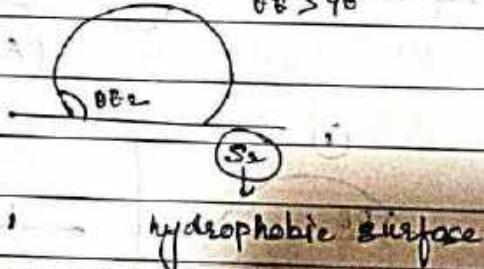
$\theta_E \rightarrow$  solid-vap interaction

$$\theta_E < 90^\circ$$



$$\gamma_{S1} = \gamma_{SL1} + \gamma_L \cos \theta_{E1}$$

$$\theta_E > 90^\circ$$



$$\gamma_{S2} = \gamma_{SL2} + \gamma_L \cos \theta_{E2}$$

$$\gamma_{SL1} \leq \gamma_{SL2}$$

$$\gamma_{S1} = \gamma_L \cos \theta_{E1} = \gamma_{S2} - \gamma_L \cos \theta_{E2}$$

$$\frac{\gamma_L}{\gamma_S} (\cos \theta_{E2} - \cos \theta_{E1}) = \gamma_S - \gamma_{S1}$$

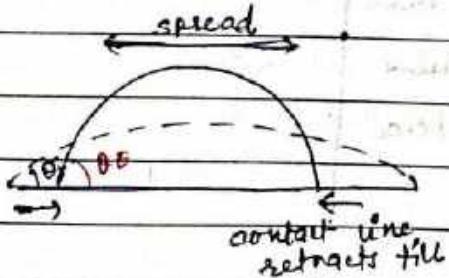
$$\frac{\gamma_L}{\gamma_S} = 1$$

$$\gamma_{S2} = \gamma_{S1} \cos \theta_{E2} - \cos \theta_{E1}$$

13/01/23

Conclusion  $\gamma_{S2}$  is lower | Surface Tension for hydrophobic is lower naturally

(1)



on spreading a drop with your finger:-

① It will spread more

② When  $\theta_E$ , the drop is in

Mechanical equilibrium

$$\theta_E \leq \theta_E^*$$

$E_g = \text{Mech} + \text{Chem} \rightarrow \text{Thermal} + RXN$

$E_g$

$E_g$

$E_g$

$E_g$   
(for chem)  
eq

Reduction in  $\gamma_s \rightarrow$  reduction in  $\cos\theta_E \rightarrow \uparrow$  in  $\theta_E$



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- (3)  $\theta_i < \theta_E$  where  $\theta_i$  is intrinsic contact angle.

The vertical force does not cause any change as the surface on which it lies is solid. Young's eq<sup>n</sup> is not valid for liquid-liquid interface and there is a similar pull downwards.

- (4)

The droplet tries to restore its original shape and tries to retract back till  $\theta_i \approx \theta_E$  (reaches equilibrium)

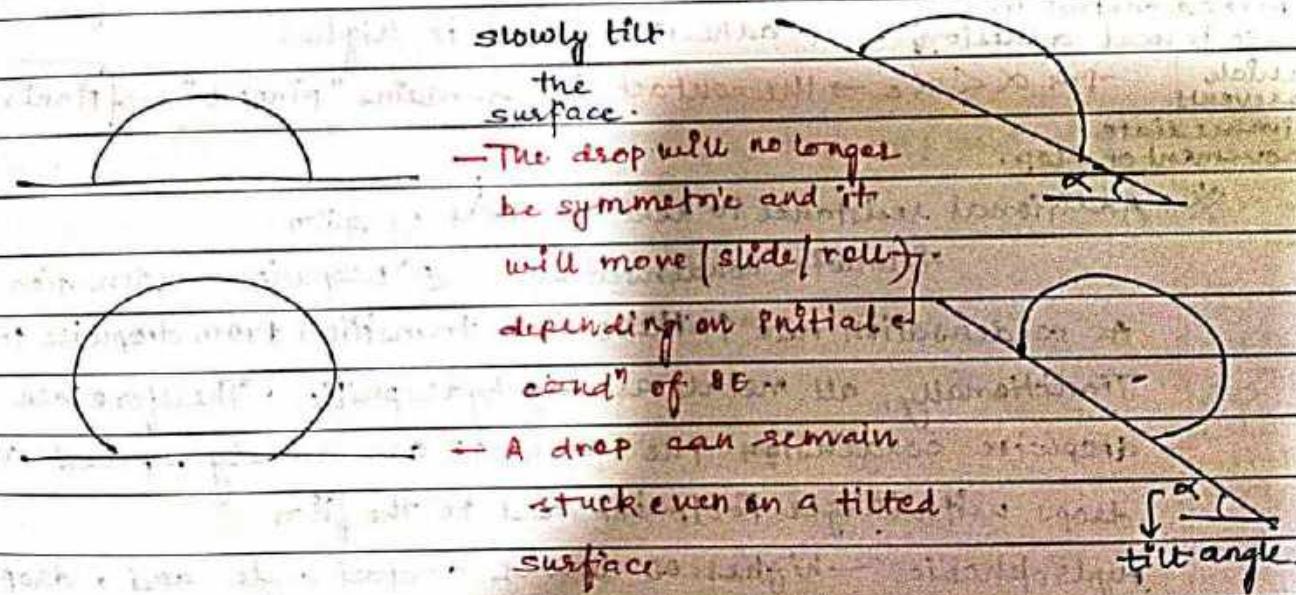
(5) As  $\theta \downarrow \cos\theta \uparrow$ . So there is net inward force and there is no equilibrium because of imbalanced forces for a period of time.

(6) A flow (retraction) triggered by surface tension.

(7) This phenomenon is known as Dewetting.

(8) This dewetting motion violates no-slip boundary condition ( $\text{vel.} = 0$  b/w liquid-plate interface).

(a)



why will the drop move?

There is a body force ( $g \sin \alpha$ ) working on the drop.

A liquid will deform when subject to a stress whatever that is.

Any finite value of  $\alpha$  actually leads to a non-zero body force and movement should be there if there is a net body force. The higher or lower value of  $\alpha$  only dictates the velocity of the droplet.

On most practical surfaces, when the tilt angle is small, the drop may not move but it will deform where  $\theta_A \neq \theta_E$ .  $\theta_A > \theta_E \Rightarrow \theta_A > \theta_E$  and  $\theta_A < \theta_E$ . If tilt angle  $\uparrow$  further then it is likely it will move at some tilt angle due.

surface energy higher lower contact angle.

for a drop remaining stuck on the tilted surface.

① The contact angles it will be different



$\alpha_A \rightarrow$  advancing contact angle

$\alpha_R \rightarrow$  receding contact angle

$\alpha_A > \alpha_R$

$\theta_A > \theta_R \quad \theta_R < \theta_E$

why does it sticks?

Manifestation of no slip condn.

friction is used for solid-solid surfaces.

→ how strong are the adhesive forces

→ contact angle hysteresis gives no idea of the strength of the adhesive forces.

$\Delta\theta = \theta_A - \theta_R \uparrow$  implies we are applying more force

along a pinned contact line these is local adhesion coeff. of static fr. is  $\uparrow$  and strength of adhesive forces is higher.

which prevents immediate movement of drop.

for  $\alpha < \alpha_c \rightarrow$  the contact line remains "pinned"  $\Rightarrow$  pinning

filowise condensation  $<$  droewise condensation

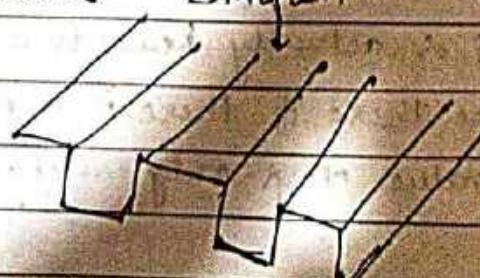
As condensation rate  $\uparrow$  there is a transition from droewise to filowise

Traditionally, all metals are big hydrophilic. Therefore even during droewise condensation the droplets are widely spread and drops with larger footprint add to the film

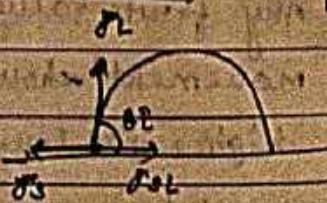
hydrophobic — higher  $\theta_E$  lower contact angle and, droplets have freedom to move and have smaller footprints.

Topographic patterns. — Simplest

wire grating pattern



Young's eqn



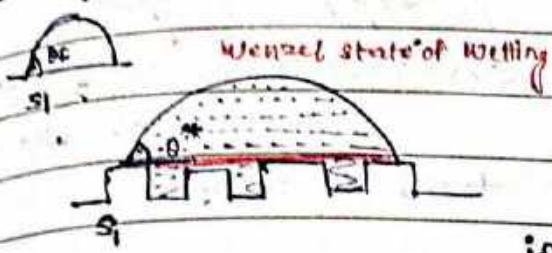
Hydrophilic surface  
only if  $\theta_E$   
is water

$$r_S = r_L + r_L \cos \theta_E$$

\* We assume pinning force constant but on  $\uparrow$  of wetted body forces. (for a droplet on incline)

Wetting on a patterned (Topographically) surface.

$\theta^*$  is same in both cases.

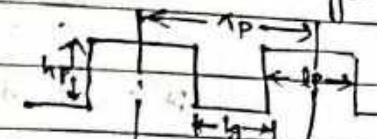


$\theta^*$  → apparent equilibrium contact angle.

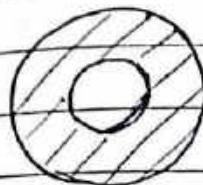
$$\cos \theta^* = k_p \cdot \cos \theta_B$$

$k_p$  = Line roughness.

If line width, line height



$$\text{Hydraulic radius} = \frac{\text{Cross sectional area}}{\text{wetted Perimeter}} = \frac{\pi(r_2^2 - r_1^2)}{2\pi(r_1 + r_2)} = \frac{r_2 - r_1}{2}$$



$$k_p = l_p + 2h_p$$

geometric  
cannot  
be defined

$h_p$  → ht. of pattern / pattern depth

$l_p$  → distance b/w 2 consecutive  
heights.

Suppose there are  $n$  no. of patterns below the drop and depth is  $d$ .

$n h_p d$  → area below the drop

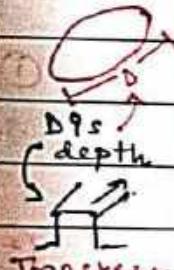
→ footprint (projected area)

actual area of contact or wetted area =  $n \pi (l_p + 2h_p) D$

Line roughness = actual area

$k_p > 1$  always

projected area



$\theta^* < \theta_B$  &  $\theta_B < 90^\circ$  if the surface is hydrophilic

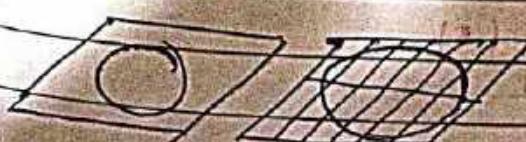
$\theta^* > \theta_B$  &  $\theta_B > 90^\circ$  if the surface is hydrophobic

↑ hydrophobicity by patterning

Where does the contact line actually rest?



In a line patterned surface, the droplet will not be hemispherical but the footprint will become elliptical. (in case of Wenzel state of wetting the droplet becomes elliptical)



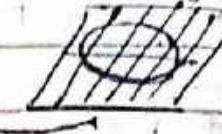
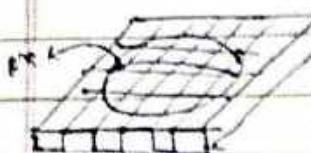
Aspect ratio  $\Rightarrow \frac{h_p}{l_p} = \text{af difference}$ .

Duty ratio  $\Rightarrow \frac{l_p}{l_p + h_p} = \frac{\text{length of 1 pattern}}{\text{dist. b/w 2 consecutive pattern heads}}$ .



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Contact is defined in the region where the minor axis is major or angle the edges are parallel to the major axis  
in an ellipsoidal, the curvature changes, at every point

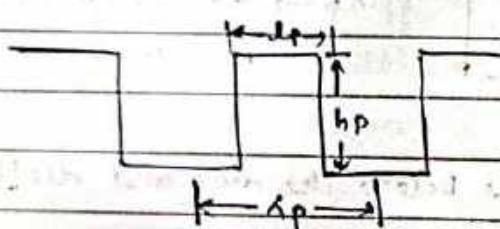


The exact contact angle or the line where it lands does not exist.

curvature is changing as a function of coordinates. aka distance from the centre.

- Preferential spreading of droplet along the dip of patterns - Anisotropic
- Shape ellipsoidal
- Exact location of contact line

Wetting

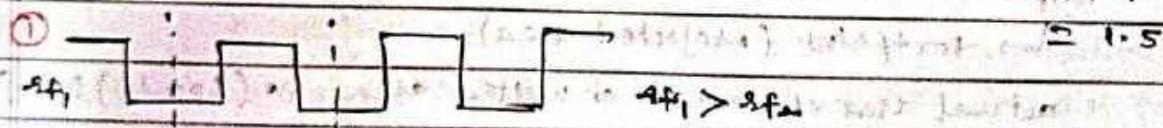


$$h_p = 250\text{nm} \quad \text{af} \geq l_p + 2h_p$$

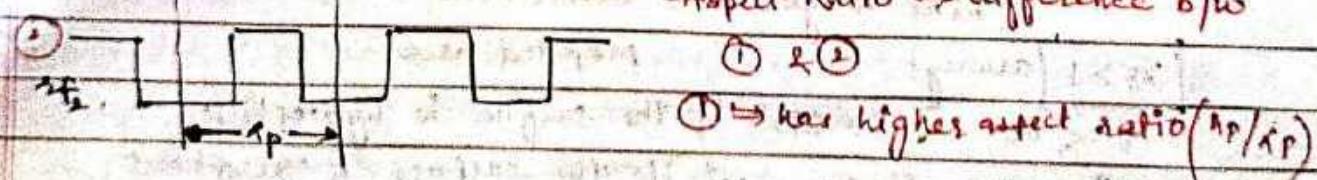
$$l_p = 1000\text{nm} \quad l_p$$

$$h_p = 400\text{nm} \quad \text{af} > 1000 + (2 \times 400)$$

With all rounded corners height 1000

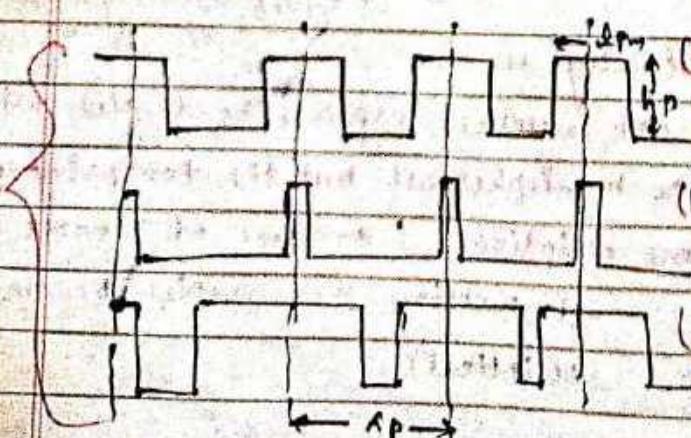


Aspect Ratio  $\rightarrow$  difference  $b/w$



① & ②

①  $\Rightarrow$  has higher aspect ratio ( $l_p/h_p$ )



Difference in ①, ② & ③

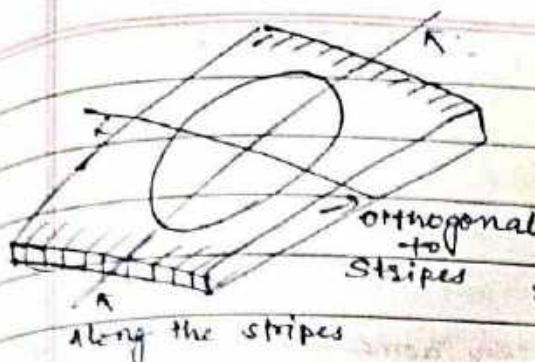
Duty Ratio ( $l_p/l_p + h_p$ )

① has less duty ratio and

③ has more.

- \* ratio of flat projection of solid liq. contact area to the total flat geometrical area (projected area) under the drop.

(P)  
Date : / /  
Page :



Presence of grooves (grooves facilitate flow)

⇒ if tilted in direction of stripes —

on a topographically patterned surface,

the guiding grooves lead to easier flow

⇒ The tilt in different dirns gives the max/min. CAH (contact Angle Hysteresis)

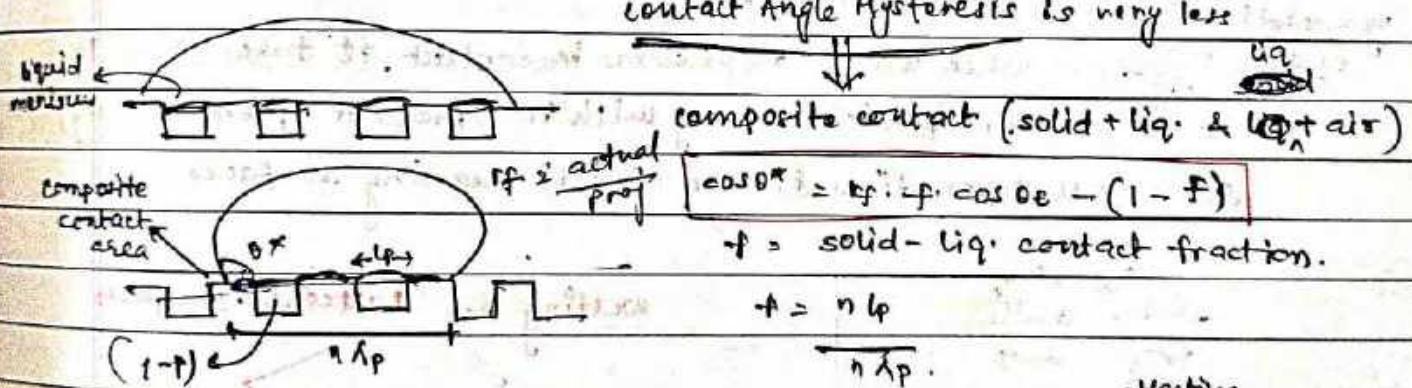
point of aspect ratio ↑ the CAH along the transverse dirn also ↑. However, in the dirn of patterns it (CAH) reduces.

$CAH | \text{orthogonal} \uparrow$  ] for a stripe patterned surface. ↑ Higher Aspect Ratio  
 $CAH | \text{along } \downarrow$  ] ↓ (?) for Higher Aspect Ratio

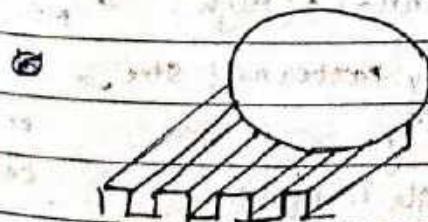
comparison - same periodicity, higher feature ht. & one has lower feature ht.  
 More ht. So CAH more & opposite, in case of lower feature ht.

### Cassie State of wetting (1946) → Lotus leaf

contact Angle Hysteresis is very less



# in case of Cassie state it is possible to achieve hydrophobicity even in case of hydrophilic surface as the base



for Cassie state of wetting, what will be the shape of water droplet?  
 closer to hemispherical structure.

Liquid is not entering the lines/striper. Apparently the liq. base is flat as its not entering the grooves. some places its resting on solid and at some places its resting on air cushions.

Since it is close to hemispherical, its directional dependence is similar to the liq. lying on flat surface.

$\eta \cdot f > 1 \rightarrow$  trying to  $\uparrow \theta^*$  than  $OB$   
 $\eta \cdot f < 1 \rightarrow$  trying to  $\uparrow \theta^*$  than  $OB$

P Date: / /  
 Petals Page:

\*  $f = 1$  means "flat surface",  $\eta \cdot f > 1 \rightarrow \cos \theta^* = \cos OB$   
 no pockets  $\rightarrow$

$$\cos \theta^* = r_f \cdot f \cdot \cos OB - (1-f)$$

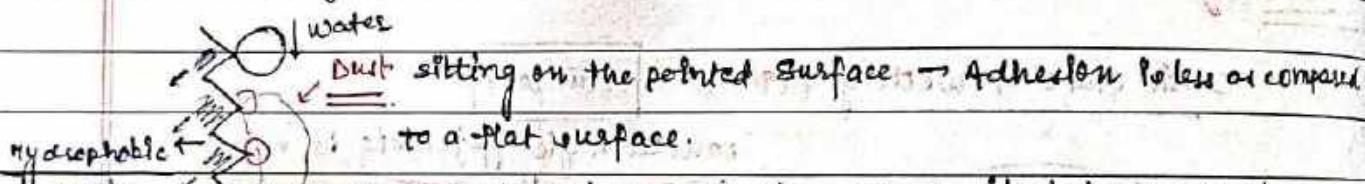
$$(>1) (<1) \rightarrow$$

when some  $\theta^* < 90^\circ$ , if  $\cos \theta^*$  can come out to be  $< 0 \rightarrow$  the surface becomes hydrophobic / effective hydrophobicity is achieved.

for castle state of wetting!:-

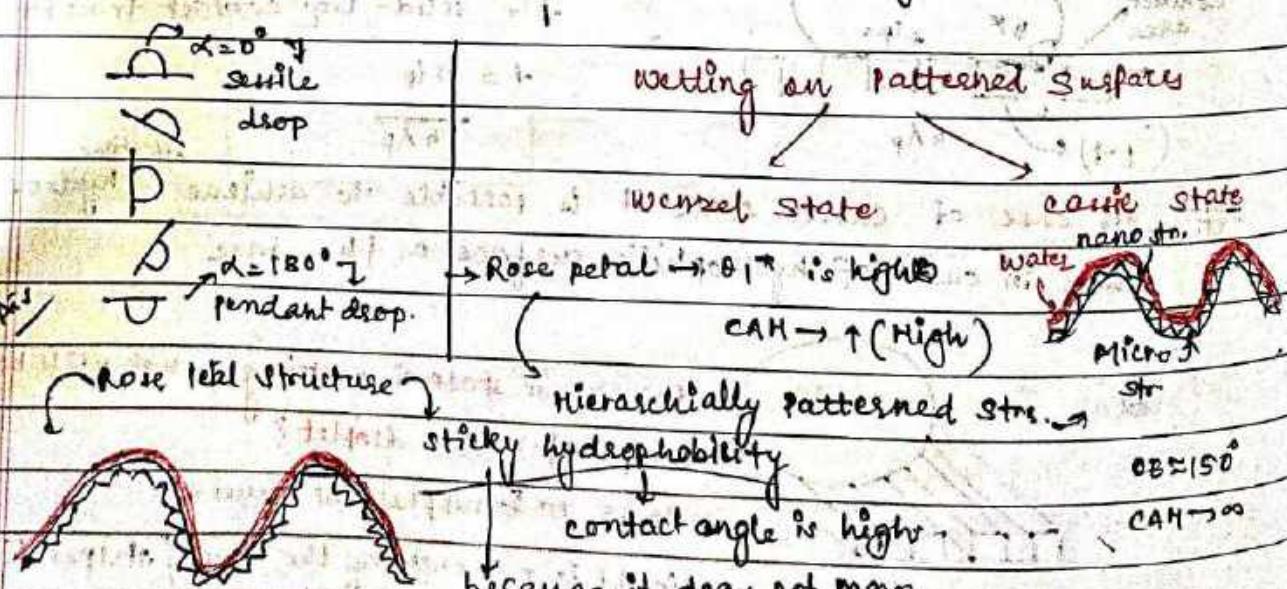
The sliding angle & CAH is  $\downarrow$ , the net adhesion is less due to the presence of air pockets.

self cleaning surfaces!:-



when water drops come in contact, it takes away the dust particles along with it (picks it up on its way)

Solar cell covers find the use of self-cleaning surfaces.



castle impregnated wenzel state  $\rightarrow$  castle state of wetting on nano structure. Wenzel state of wetting on micro structure.

super hydrophobic, i)  $OB > 150^\circ$   
 surfaces ii)  $CAH < 10^\circ$

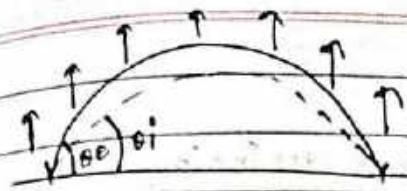
## Evaporation of a Drop

-friction  
(S-S) - pinning  
(S-L)



Data : / /

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High int. Energy molecules evaporate by overcoming cohesive forces.

EVP → loss of mass → change in shape

change in contact angle

longer balanced or intrinsic angle  $\theta_i$  decreases  $\Rightarrow$  disturbed.

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta_i$$

Net inward force  $\rightarrow$  contact line  $\rightarrow$  until becomes  $\theta_i$  again acting on the drop retracts and forces are balanced

continuously?

[consequences]  $\Rightarrow$  a decreased drop size  $\Rightarrow$  finally no drop (complete evap.)

[CCA] mode of drop evaporation

constant contact angle

$\rightarrow$  Retraction of contact line continuous

Eventually we get a flat surface

ie Retraction  $\theta_i \rightarrow 0^\circ$   $\rightarrow$  imbalance acts  $\Rightarrow$  force is capable of overcoming pinning force

$\rightarrow$  No pinning.

surface with pinning (of contact line):— Drop flattens with time

complete pinning  $\rightarrow \theta_i$  progressively  $\downarrow$  & eventually becomes 0.

strength of adhesive

force b/w  
molecules  
liquid &  
vapour

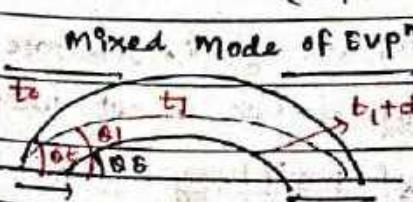
CCA mode

$\rightarrow$  cont. contact radius mode

As  $\theta_i \downarrow$  imbalance  $\uparrow$ . So practically !—

mixed mode

contact line remains pinned.



Mixed mode of EVP

The contact line retracts suddenly at some  $\theta_i$

Then again pinned

Nature of motion of contact line

(discrete)

pinning followed by rapid retraction of contact line till  $\theta_i$  becomes  $0^\circ$

Nature of contact line motion is given the

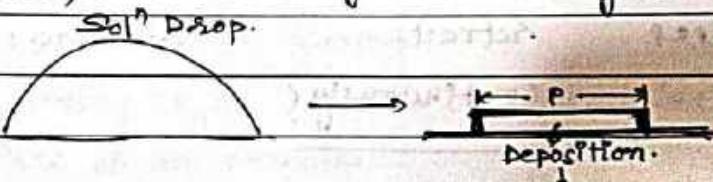
name  $\rightarrow$  stick-slip motion

$$\text{Strength of pinning force} = \text{Loose} - \text{Bead}$$

Mixed mode  $\rightarrow$  sequential pinning & depinning  
contact line is not retracting uniformly but in bursts.

instead of a liq. lets talk about sol' :-

(Dilute)  $\rightarrow$  To prevent change in  $\eta$  & viscosity -



Non-Uniform  $\rightarrow$  Unless it is a completely pinned drop, the drop shrinks or retracts

when will solute start depositing on surface?

[leaching]

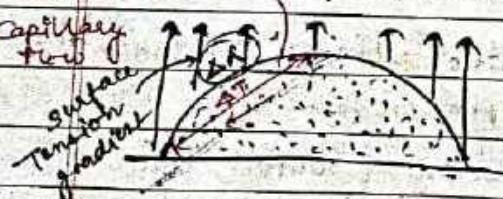
As the solvent evaporates, intrinsic conc of solute keeps on  $\uparrow$ . Ideally, deposition happens only when intrinsic conc reaches saturation conc

Ideally  $\rightarrow$  central deposition

actually  $\rightarrow$  coffee stain effect / coffee ring effect! - 1997

ring-like peripheral deposit

Thermo  $\rightarrow$  deposit in the central part



(1) Due to curvature effect, the rate of evaporation across the drop surface is not uniform

\* It's max. at periphery and min. at apex.

implicit cond' is isothermal.

for fluid dynamics problem

*practical  
surface  
some pinning*

9  
Rohit

Date : 7/4  
Page :

Under practical cond'ns : → slight difference in eq. & vessel surface.

consequences of more evapn at periphery :—  
rate

conc at periphery is higher.

local saturation at periphery will be attained faster.

bcoz of rapid evapn & higher conc at periphery !—

(c) A quicker dropping Temperature (Thermal effect)  
higher. (Dropping T along periphery is lower)

(d) Local viscosity along the periphery also ↑ favouring the process of pinning even more

(e) Surface Tension at the periphery and bulk will be different bcoz of conc difference. Surface Tension depends on nature of particles and surface.

(f) we have a Temp. gradient from surface to periphery due to dropping Temp. (natural convection) → convective flow field, bcoz lead to accumulation of solute to the periphery even more

Thermo Capillary Flow.

Due to high viscosity at the periphery diffusive flow due to conc gradient does not happen. Viscosity makes the soln stick to the periphery.

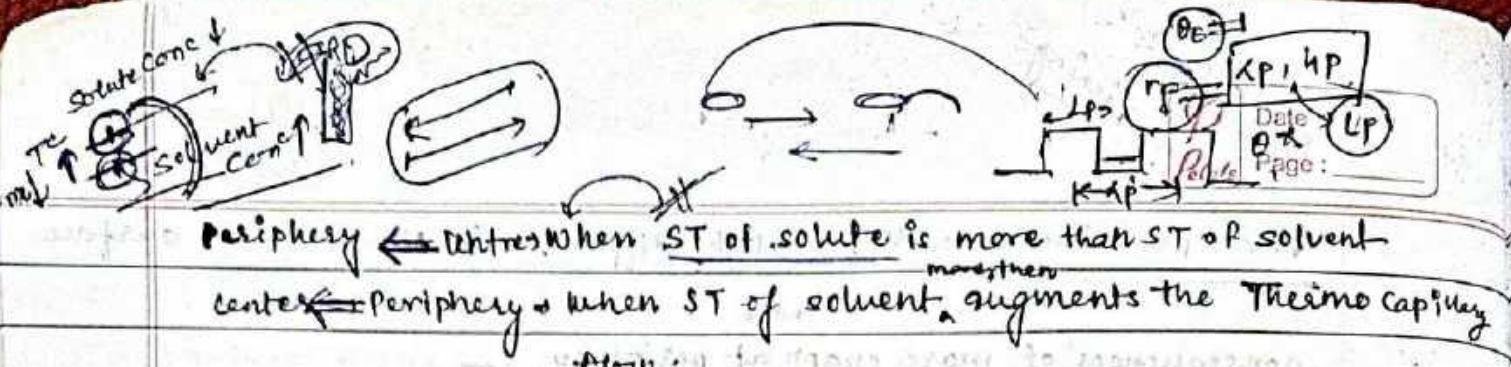
Solutal Marangoni flow → flow that takes place due to surface tension gradient.

⇒ Marangoni flow is a flow that is triggered by surface Tension grad. and it takes place flow low Surface Tension to high surface Tension.



Osmosis. ⇒ When the conc in the 2 chambers become equal, it stops. Osmosis is a special class of diffusion where you forcibly stop the movement of particles.

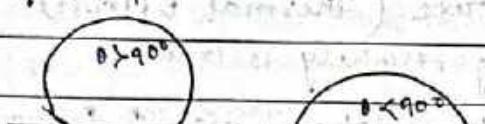
The dir<sup>n</sup> of marangoni flow is going to depend on ST of solute & solvent.



~~spray painting → opposing flows thermocapillary & marangoni flow to prevent coffee stain effect~~

↓ the ST  $\iff$  small form<sup>n</sup> / No form<sup>n</sup> of coffee stains stain effect

→ 02/23 1) liq. drop:



→ limiting case → complete pinning  $\rightarrow$  film form<sup>n</sup>. can't define θE

Young's confign.

2) liq. sol?



base substrate

surface over which we form a film or for coating

after film formation.

θL

(area where interfacial energy is manifested)

$$S_{SL} = \gamma_S - (\gamma_L + \gamma_{SL})$$

spreading coeff

Total interfacial energy

$$\text{Unit area. } S_{12} = \gamma_1 - (\gamma_{12} + \gamma_2)$$

$S_{12}$  → net

\* The film formation is ( $S_{12} - \text{net}$ ) i.e.

thermodynamically not favoured.

If  $S_{12} + \text{net} \rightarrow$  thd. favoured.

The film coated  $\Rightarrow$  can be solid/liquid

Si wafer  $\rightarrow$  covered with a surface oxide covered with (1.5-2.0 nm)

thin layer called the native oxide layer. It is advantageous as well as problematic while making chips. Si forms the layer as soon as it comes in contact with atmosphere.

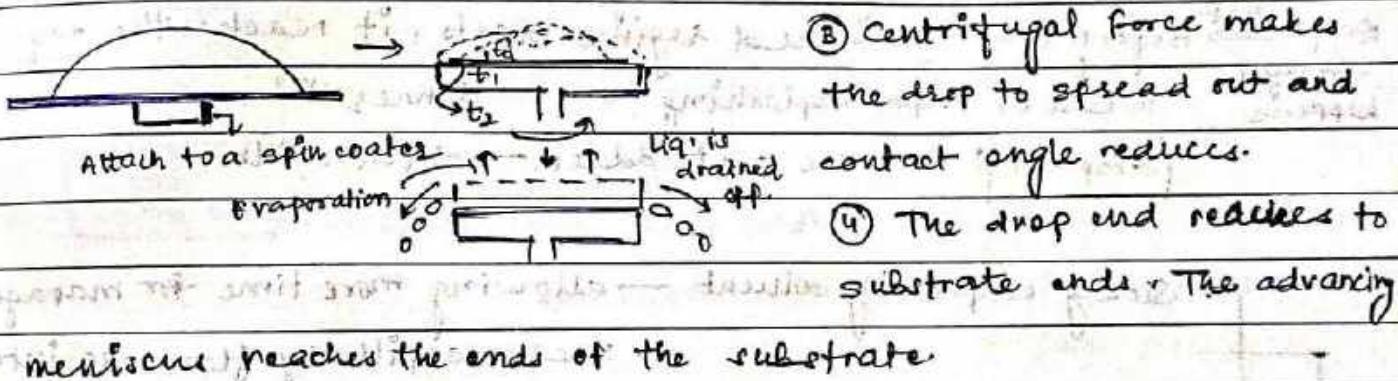
Si has very high surface energy. Lot of interfacial energy & unbalanced interactions form bonds with O<sub>2</sub>. Si surface energy is highly ~~low~~ and spreading coeff is ~~large~~ highly ~~the~~ favouring the ~~not~~ thermodynamically.

uniform thin  
film of  
solute.

- for having a thin uniform film of solute! —
- Drop should spread completely for uniform thin film formation.
- If you apply additional thermal force, it is possible to reduce the contact angle (favours spreading)
- To apply a film coating, the solvent used should be able to! —
  - should dissolve the solute.
  - evaporates after film formation.

Spin coating! — Before rotating : — ① Dispensing. (add the drop)

② start Rotation.



meniscus reaches the ends of the substrate.

Does it ensure complete coating?

Right now, we have a rotating liq. pool of the soln.  
Since it is still rich in solvent, it will retract back if the rotation is stopped in b/w the process. The drop will retract back to its original geometry but not to the same size as some amt. of solvent has already been evaporated as well as splashed out.

⑤ Quasistatic pool with simultaneous evapn. → solvent evaporates intrinsic concentration increases → gradual increase in solute conc.

⑥ Saturation limit / Saturated soln

→ Pt. where solute conc = saturation limit, deposition starts, film formation (solute) to form.

⑦ If dil soln not taken, even when we apply the centripetal force as the viscosity is higher, rate of spreading ↓.

Rate at which contact line spreads is a kinetic parameter dependent on viscosity.

Once spreading is done (soln loses solvent)

95% of solution is lost due to splashing.

Page: \_\_\_\_\_

low viscosity

high vapour pressure

solubility of the solute

spreading coeff should favour

→ reqd. characteristics of a solvent.

intrinsic solute conc<sup>↑</sup> when becomes equal to saturation the film form starts.

"form" of a film which may not be thermodynamically stable but the solute particles are now stuck

if we vary the initial conc of solute in the dispense drop what happens?

Thickness of film varies if in. conc<sup>↑</sup> thickness twice vice versa.

or. can be varied by increasing RPM. (thickness  $\downarrow$ )

Evapn but Before evapn governed regime starts, it reaches the edge substrate always happens in case of ↑ spin → splashing more → thinner film.

(drop vol.  $\uparrow$  → more solute added → thicker film.)

Slowly evaporating solvent → allowing more time for maragoni &

thermocapillary flows aka internal flows

Evaporating too fast → even before meniscus reaches substrate

something that is edge solvent would have evaporated (partial either too fast or too slow in coating): hair will be fine

evaporating → does not directly affect thickness (slightly but not much)

2/02/23 hydrophilic surface like water Hydrophobic surface does not like H<sub>2</sub>O.

Surfactants: — a surfactant molecule is a composite of artificial spatial variation molecule which variation in hydrophilicity in its structure one part is hydrophilic and one is hydrophobic long chain

Head group (inorganic)

Tail group

(Hydrocarbon) (hydrophobic)

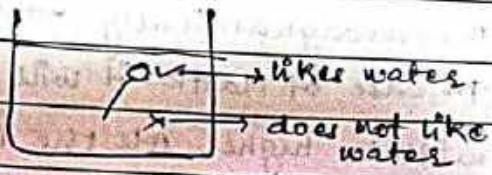
\* Surfactants are classified on the basis of nature of head group.

4 types of Surfactants :-

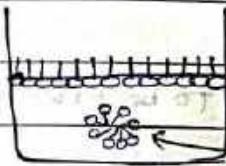
(1) cationic (2) Anionic (3) Zwitterion (4) Non-ionic.

in general glass - Hydrophilic

plastic - Hydrophobic (Perspex)



hydrophilic part is satisfied & hydrophobic is not satisfied,  
surface active molecules  $\rightarrow$  Surfactants

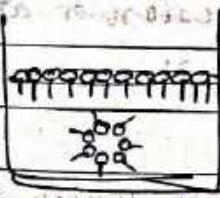


Eventually free surface gets filled up after continuous addition of surfactant molecules.

After some more addition  $\rightarrow$  micelle formation.

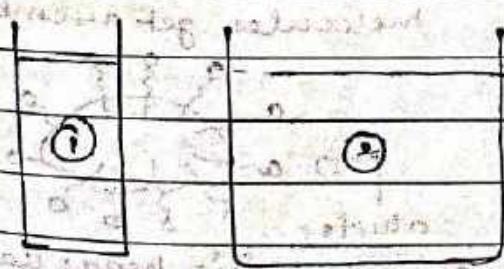
critical micelle conc  $\rightarrow$  CMC  $\rightarrow$  The conc at which first micelle forms  
(formation  $\rightarrow$  \* self assembly process - driving force for of first micelle) self assembly is energy minimization.

This is thus a thermodynamically favoured process.



Reverse Micelle:-

$\rightarrow$  micelle formation in a hydrocarbon or organic solvent



CMC depends on the containers in which surfactants are being added.  
because of availability of surface  
CMC is a f<sup>n</sup> of vessel geometry.  
CMC formation takes place faster in ①



Stage ①: interface gets filled up

Stage ②: - hydrophilic head group will like hydrophilic walls.

So hypothetically if the molecule attaches to the wall, it becomes thermodynamically unstable not favoured for glass. In case of Plastic "it will get favoured and CMC in case of plastic will be higher. All the interfaces get filled & then micelle form" takes place.

Q. Why molecules go to the wall first & then form micelle in a plastic interfacial assembly happens at molecular level and it is favoured over micelle form" because micelle form" requires a large no. of surfactant molecules roaming later.

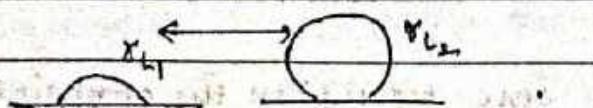
Detergents! — Typically, dirt is considered to be oil.

water  $\gamma_L$   $\rightarrow$  presoak  $\rightarrow$  Rub  $\rightarrow$  Rinse.

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta$$

\* Hydrophilic surfaces are higher energy surfaces  $\rightarrow$  (Young's eqn)

after assembly drop is no longer free & covered by higher energy hydrophilic surfaces.  $\gamma_L \uparrow$ ,  $\theta \downarrow$ . so the adhesion or attachment between the dirt or surface. [Assuming  $\gamma_{SL}$  does not change]

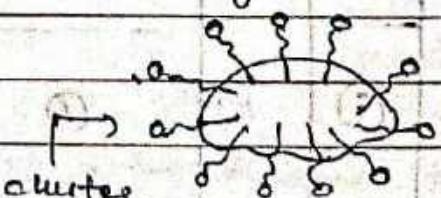


oil or dirt over which surfactant molecules, get assembled.

surface energy  $\gamma_{L1}, \gamma_{L2}$

$\theta \downarrow$  footprint  $\downarrow$

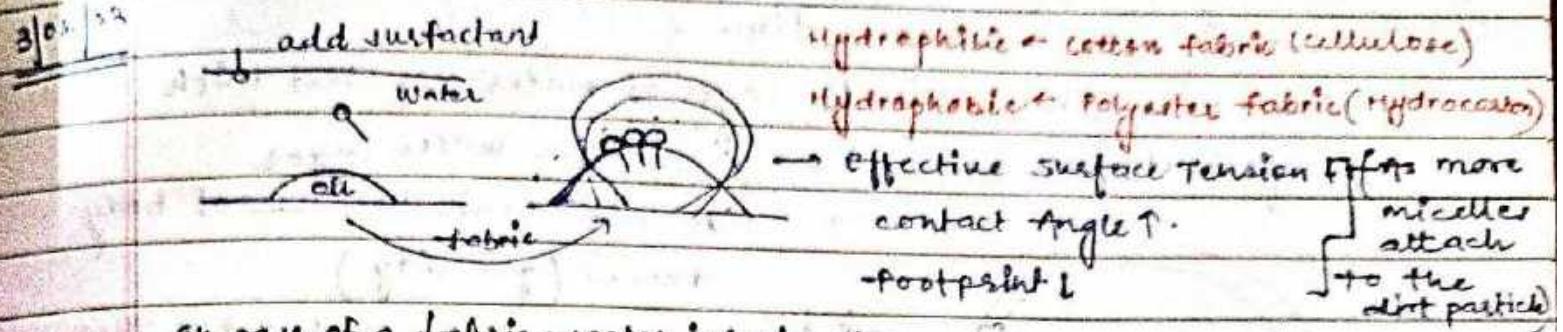
By brushing or rubbing  
it becomes easy to detach.



of hydrophilic heads leads to  $\uparrow$  surface energy. Thus  $\theta \uparrow$

\* water is needed for the molecules to move. Rinsing is done because the

micelle-attached dirt remains in water. Some want to remove it by rinsing.



In case of a fabric-water interface:-

- ① addition of more surfactant leads to additional adsorption of surfactants on the fabric → attraction of head group towards fabric is strong → hydrophilic drop surface tension ↑ → fabric ST ↑ (due to hydrophobic tails)
- The interaction b/w head group and fabric is more than b/w head group and water. After washing, cotton cloth remain slippery due to these rods.
- Since there is surfactant adsorption on the surface contact angle θ ↓

What is dry cleaning?

- instead of water, organic chemicals are used.
- used for non cotton based fabric which are hydrophobic in nature
- In hydrophobic fabric → surfactant + water mixture will lead to ↓ in contact angle spreading the oil even more.

Shampoo:-

Some surfactant molecules get adsorbed &

makes our (hair strands) → some proteins which favours hair fluffy and smooth.



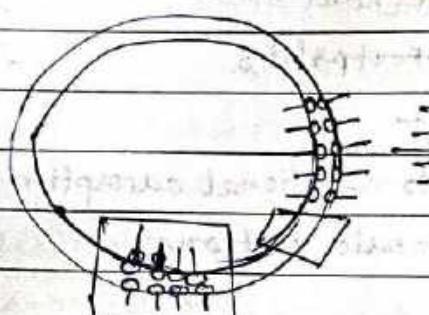
Herbal shampoos → no ionic ends.

So this doesn't happen  
- Hair becomes fluffy because the like charges repel each other.

adsorption of tails towards it.

Conditioner:- surfactant with opposite charge. Neutralizes the charge. (cationic shampoo → Anionic conditioner)

- ① Soap Bubbles :— self standing Thin Films  
During the lifetime of a soap bubble, why does it remain intact/stable for some time?

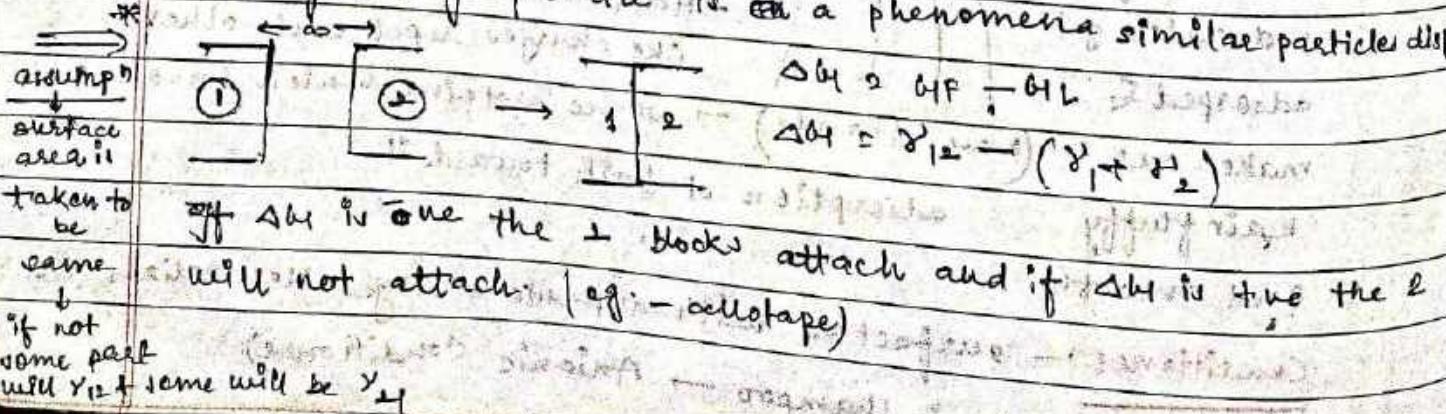
- ② Soap bubble is a thin layer of water covered with surfactant molecules. → If only water layer  
It will drain because of body forces (gravity)
- 
- However, when these are surfactant molecules when fluid tries to drain out the molecule heads stick some closer and charges repel. Head groups gives a spring effect and does not allow water to drain easily.
- Spring effect b/w molecules stuck in opposite interfaces at the bottom and adjacent interfaces at the sides.

particulate Detergents → not to dislodge oil but somehow to encapsulate particulate matter & remove them out.

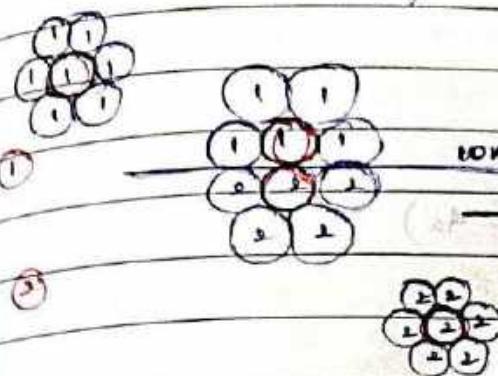
The fading or discoloring of white clothes is due to the particulate matter present along with dirt in atmosphere

### Interfacial Tension:

\* Shaking of a syrup bottle is a phenomena similar to particles dispersing



$\gamma_{12} \rightarrow$  interfacial Tension  $\rightarrow$  energy reqd. to create ~~new~~ interface (unit interface  $\Delta H^{\circ}$ )



$\gamma_{12} = (\text{energy of interaction of a pair of molecules at the interface}) - (\text{energy of interaction of the same pair in bulk})$

Excess energy of interaction due to interaction of the interfaces.

$$\gamma_{12} = E_s - E_b$$

surface      bulk

$N = \text{No. of molecules (molecular pair) per unit area of the interface}$

$$\gamma_{12} = N(E_s - E_b)$$

$\gamma_1 = \text{Vanderwaals} + \cancel{\text{London}} \text{ Polar} + \text{steric}$  very specific

$\gamma_1^{LW}$  depends on  $\gamma_1^{AB}$  only between  
emipresent atomic structure  $AB \rightarrow$  Acid Base Long chain polymers  
or molecules.

$$\gamma_1 = \gamma_1^{LW} + \gamma_1^{AB} + \gamma_1^S$$

$$\gamma_{12} = N(E_s - E_b)$$

$$E_b = -\gamma_{11} V_{11} - \gamma_{22} V_{22}$$

interaction  
 $(LW, AB(\text{may}), S(\text{may}))$

$\rightarrow V_{11} \rightarrow$  interaction b/w 2 molecules of 1 vapour or Boiling Pt. Surface Tension

$\rightarrow \gamma_{11} \rightarrow$  co. ord no. of 1.

$\rightarrow (-ve)$  sign represents attraction.

3 interconnected properties.  
(having same reason)

$$E_s = \gamma_{11s} V_{11} - \gamma_{12} V_{12} - \gamma_{21} V_{21} - \gamma_{22s} V_{22}$$

intermolecular interactions

$\gamma_{11s} =$  surface coordination no. of ①

$\gamma_{12} =$  No. of molecules of ① surrounding ② at the interface

$\gamma_{21} =$  No. of molecules of ② surrounding ① at the interface

$\gamma_{22s} =$  surface coordination no. of ②

$\gamma_{21} \neq \gamma_{12}$  can be different.

### Assumptions:-

① Coordination nos. are same in both the phases.

$$\gamma_{11} = \gamma_{22} = \gamma$$

$$\gamma_{12} = \gamma_{21} = \gamma_{112} = \gamma_{221} = 0.5\gamma$$

② The eq" becomes:-

$$\text{So, } \underline{\underline{E_S}} = -\frac{\gamma}{2} (V_{11} + V_{22} + 2V_{12})$$

$$E_b = -\frac{\gamma}{2} (V_{11} + V_{22})$$

$$\text{So, } \gamma_{12} = N (\underline{\underline{E_S}} - E_b)$$

$$\Rightarrow N \frac{\gamma}{2} \left( \underbrace{V_{11} + V_{22}}_{\text{cohesive interaction}} - \underbrace{2V_{12}}_{\text{adhesive interaction}} \right)$$

(intermolecular)

Let's say, Phase ① is non-condensed  $\rightarrow V_{11} = 0, V_{12} = 0$

$$\gamma_2 = \frac{N \gamma}{2} V_{12}$$

Considering ② to be Non-condensed.

$$V_1 = \frac{N \gamma}{2} V_{11}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{N \gamma}{2} V_{12}$$

$$\therefore N \gamma V_{12} = (\gamma_1 + \gamma_2) - \gamma_{12}$$

$$-N \gamma V_{12} = \gamma_{12} - (\gamma_1 + \gamma_2)$$

$$\therefore \Delta H = -N \gamma V_{12} = \gamma_{12} - (\gamma_1 + \gamma_2)$$

\* Surface Tension is always +ve

$\gamma_{12}$  is always +ve because energy is always required to form new surfaces.

\* What is the implication of interfacial tension being +ve or -ve?

→ Agreeing to the fact  $\gamma_{12}$  can be +ve or -ve.

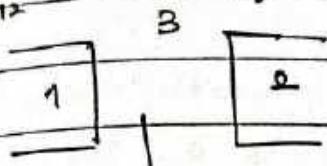
→ Depends only on magnitude of  $V_{12}$ .

There can be net repulsion b/w dissimilar molecules. Therefore  $\gamma_{12}$  can have different signs. There is a contradiction, as both vanderwaals and polar interactions are attractive.

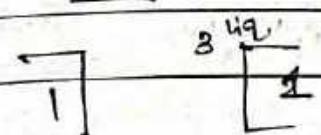
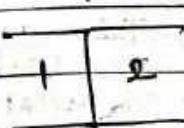
$\rightarrow$  the interfacial tension is the energy required to destroy an interface.

Eg: Dissolution of sugar & water

\*  $\gamma_{12}$        $\gamma_{13}$



$$\Delta H_{132} = \gamma_{12} - (\gamma_{13} + \gamma_{23})$$



$$\Delta H_{131} = \gamma_{11} - 2\gamma_{13}$$

Assumption  $\rightarrow$  If 2 similar materials come in contact, there is no interface.

$$\therefore \gamma_{11} = 0$$

$$\Delta H_{131} = -2\gamma_{13}$$

$\gamma_{13} \leftarrow$  adhesion -

so, the necessary cond<sup>n</sup> for having stable colloid  $\gamma_{13}$  ~~for~~ for colloid formation  $\Delta H_{131}$  ~~+ve~~.

$\gamma_{11} = 0$   $\leftarrow$  assumption  $\rightarrow$  behave like a bulk  $\rightarrow$  coordination no same.

colloid :- Dispersion of small particles.

stable :- Particles remain dispersed.

Unstable :- Particles coagulate.

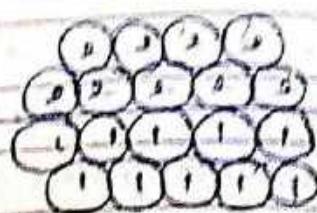
Interact b/w ① & ③.
is favoured $\approx$ compared to ② & ①

Blood is a colloid  $\rightarrow$  inside capillaries  $\rightarrow \Delta H$  ~~+ve~~

if there is bleeding  $\rightarrow \Delta H$  ~~-ve~~  $\rightarrow$  for clotting.

6/2/23  $V_{12}^{\text{ext}} = V_{12}^{\text{LW}} + V_{12}^{\text{AB}} + V_{12}^{\text{ST}}$  neglected in this course

always may not talk, outside the



$$\Delta G_{12}^{\text{ext}} = -N \cdot Z \cdot V_{12}^{\text{ext}}$$

$$= -N \cdot Z \left( V_{12}^{\text{LW}} + V_{12}^{\text{AB}} \right)$$

$$= \Delta G_{12}^{\text{LW}} + \Delta G_{12}^{\text{AB}}$$

3 Assumptions :-

①  $V_{12}^{\text{LW}} = \sqrt{V_{11}^{\text{LW}} V_{22}^{\text{LW}}}$  (Quantum Mechanics)

$$NZ \cdot V_{12}^{\text{LW}} = \left( NZ \sqrt{V_{11}^{\text{LW}} V_{22}^{\text{LW}}} \right) \quad \text{by geometric mean}$$

$$= 2 \left( \sqrt{\frac{V_{11}^{\text{LW}} NZ}{2}} \left( V_{22}^{\text{LW}} \frac{NZ}{2} \right) \right) = 2 \sqrt{Y_1^{\text{LW}} Y_2^{\text{LW}}}$$

The assumption is basically related to interfacial tension

$\Delta G_{12}^{\text{LW}} = -2 \sqrt{Y_1^{\text{LW}} Y_2^{\text{LW}}}$

$Y_{12}^{\text{LW}} = (Y_1^{\text{LW}} + Y_2^{\text{LW}}) - 2 \sqrt{Y_1^{\text{LW}} Y_2^{\text{LW}}}$

$H_{12}^{\text{LW}} = H_1^{\text{LW}} + H_2^{\text{LW}} - 2 \sqrt{Y_1^{\text{LW}} Y_2^{\text{LW}}} = (\sqrt{Y_1^{\text{LW}}} - \sqrt{Y_2^{\text{LW}}})^2$

Hence  $\rightarrow H_{12}^{\text{LW}}$  is always +ve. Therefore  $\Delta G_{12}^{\text{LW}}$  is always -ve.

1 3 1 If ① and ③ are both apolar. That means

$$\Delta G_{131}^{\text{LW}} = \Delta G_{131}^{\text{AB}}$$

If ① & ③ are apolar. So there will be no polar component which also means that  $\Delta G_{131}$  will always be -ve as  $Y_{13}^{\text{LW}}$  is always +ve.

$\Delta G_{131}$  is a better value than  $\Delta G_{132}$  because dispersion usually consists of particles which are of same material (similar).

Stable colloid in an apolar solvent is not stable. Adsorption is favoured. organic / apolar liq. are poor solvent. It doesn't form a dispersion in case only van der waals' forces present.

② Polar component of surface tension ( $H_{12}^{\text{AB}}$ ) - it is defined in terms of two empirical parameters.

$\gamma^- \rightarrow$  e<sup>-</sup> donor / proton acceptor parameter  $\rightarrow$  Lewis Base / Brønsted Base

$\gamma^+ \rightarrow$  e<sup>+</sup> acceptor / proton donor parameter  $\rightarrow$  Brønsted Acid / Lewis Acid.

$$\gamma_{i,AB}^{AB} = 2\gamma_i^+ + \gamma_i^- \quad (\text{of same material})$$

This assumption is related to surface tension.

A ~~polaric~~ material is called apolar if either of  $\gamma^+$  or  $\gamma^-$  are 0. Then the net polar component of surface tension will be 0.

$$\gamma_{i,AB}^{AB} = 0$$

means either

①  $\gamma_i^+ = 0$  or ②  $\gamma_i^- = 0$  or ③  $\gamma_i^+ + \gamma_i^- = 0$ ,

Surface tension will comprise of only the van der Waals surface tension. There is some polarity which ~~is~~ does not get reflected in the surface tension.

$\rightarrow$  monopolar material  $\rightarrow$  either  $\gamma_i^+ = 0$  or  $\gamma_i^- = 0$

$\rightarrow$   $\gamma_i = \gamma_{i,0}$  is not a necessary cond<sup>n</sup> to call a particle apolar

$$\Delta H_{12}^{AB} = -2 \left[ \sqrt{\gamma_1 + \gamma_2^-} + \sqrt{\gamma_1^+ \gamma_2^+} \right]$$

$$\Delta G_{12}^{AB} = \gamma_{12}^{AB} - (\gamma_{1,AB}^{AB} + \gamma_{2,AB}^{AB})$$

$$\gamma_{12}^{AB} = \Theta \Delta H + (\gamma_{1,AB}^{AB} + \gamma_{2,AB}^{AB})$$

$$= -2 \left[ \sqrt{\gamma_1^+ \gamma_2^+} + \sqrt{\gamma_1^- \gamma_2^-} \right] + \left[ \left( \sqrt{\gamma_1 + \gamma_1^-} + \sqrt{\gamma_2 + \gamma_2^-} \right) \right]$$

$$\gamma_{1,0}^{WW} = \sqrt{\gamma_1^{WW} - \sqrt{\gamma_2^{WW}}}$$

$$\gamma_{12}^{AB} = (\sqrt{\gamma_1^{WW}} - \sqrt{\gamma_2^{WW}})^2 + 2 \left[ \sqrt{\gamma_1 + \gamma_1^-} + \sqrt{\gamma_2 + \gamma_2^-} \right] - 2 \left[ \sqrt{\gamma_1 + \gamma_2^-} + \sqrt{\gamma_1^+ \gamma_2^+} \right]$$

③  $\Delta H_{13}^{AB} = -2\gamma_{13}$  Both ① & ③ are fully polar.

Now, Does this ensure a stable colloid?  $\rightarrow$  No.

Now, we need to look into individual components.

$\Delta H_{13}^{AB} \Rightarrow -ve \rightarrow$  ~~Attraction~~, b/w 2 particles of ① in liquid ② is favoured.

Thermodynamically, the process is favoured.

$$\gamma_{13} = +ve$$

colloid is not stable

$$\Delta H_{13}^{AB} = \gamma_{11} - (\gamma_{13} + \gamma_{31})$$

o, (not valid for solids).

Numerically, the ~~attr~~ cohesive part + v/w part - adhesive part can be the

Thus polar solute in polar solvent does not guarantee stable colloid.

colloid  $\rightarrow$  stable when  $\rightarrow \Delta G_{131}^{\circ} < 0$   
 $\gamma_{13}$  has to be  $-ve$

out of ① or ③, 1 is monopolar: —

- ①  $\gamma_1 + \gamma_3 - \gamma_{13} + \gamma_{31}^{\circ}$  all zero  $\rightarrow \Delta G_{131}^{\circ} = -ve$
- ②  $\gamma_1 + \gamma_3 = 0 \rightarrow 1$  term of cohesive and 1 of adhesive will become 0.  
rest Non zero.
- ③ No generic term form

Both ① & ③ are monopolar: —

- ①  $\gamma_1^+ \gamma_3^+ \gamma_{13}^-$ , either 1 is zero  
 $\gamma_1^- \gamma_3^-$  of the 2 combos
- ②  $\gamma_1^+ \gamma_3^-$ , either 1 is zero.  
 $\gamma_3^+ \gamma_1^-$  of the 2 combos

Best possible combination for cohesive stability  $\gamma_1^+ = 0 \quad \gamma_3^+ = 0$

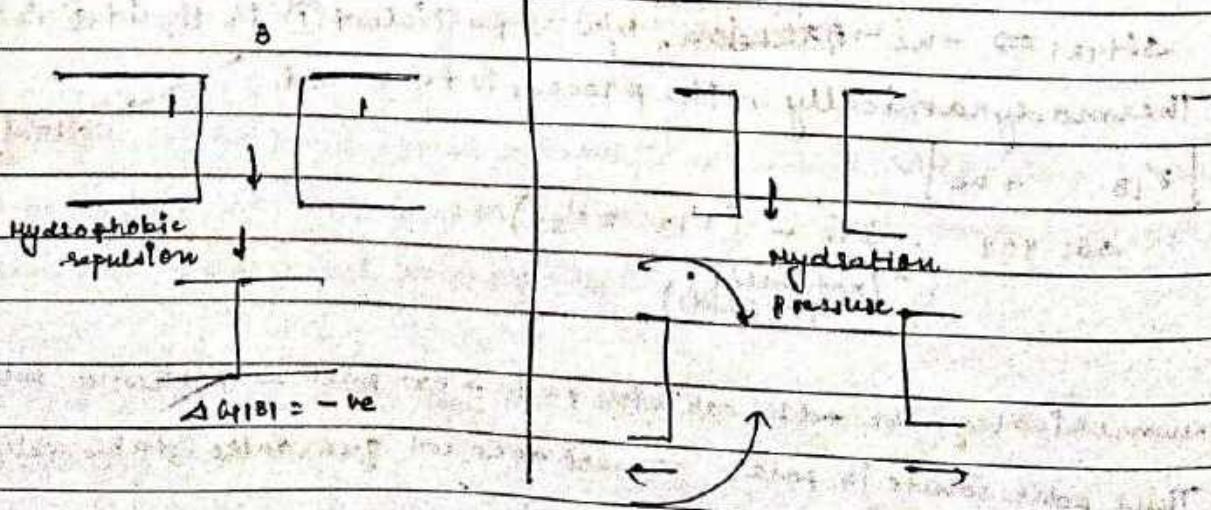
Sets/Kills the cohesive part of polar "interaction" to be zero. So for a colloid and liq. systems the adhesive component had to overcome both the cohesive component as well as the vanderwaals component, to achieve colloidal stability. But in this case, we will only have to overcome vanderwaals component.

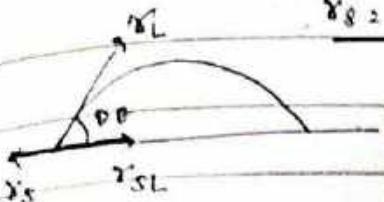
If in T  $\rightarrow$  red in viscosity  $\rightarrow$  so the dynamics of the particles change making the lower part of an ice cream cup taste like ice or more icy.

Storage syrups in cool place to preserve the dispersion because of the above reason.

8/02/23

8





$$\gamma_S = \gamma_{SL} + \gamma_{L} \cos \theta$$

contact angle goniometer to measure contact angle

hydrophobic hydrophilic

$$\Delta H_{SL} = \gamma_{SL} - (\gamma_1 + \gamma_2)$$

$$\Rightarrow \Delta H_{SL}^{\text{tw}} + \Delta H_{SL}^{\text{AB}}$$

$$= -2\sqrt{\gamma_1^{\text{tw}} \gamma_2^{\text{tw}}} - 2\left(\sqrt{\gamma_1 + \gamma_2^-} + \sqrt{\gamma_1^- \gamma_2^+}\right)$$

$$\Delta H_{SL} = -2\sqrt{\gamma_L^{\text{tw}} \gamma_S^{\text{tw}}} - 2\left(\sqrt{\gamma_S + \gamma_L^-} + \sqrt{\gamma_L^- \gamma_S^+}\right)$$

$$\Delta H_{SL} = \gamma_{SL} - (\gamma_S + \gamma_L)$$

$$\gamma_S = \gamma_{SL} - \gamma_L - \Delta H_{SL}$$

$$\gamma_L = \gamma_L - \Delta H_{SL} = \gamma_{SL} + \gamma_L \cos \theta$$

$$\boxed{\Delta H_{SL} = -\gamma(1 + \cos \theta)} \quad \text{Young - Dupre Eqn.}$$

With the help of Young - Dupre eqn & goniometer, we can find out the Surface Tension of an unknown solid.

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_L^{\text{tw}} \gamma_S^{\text{tw}}} + 2\sqrt{\gamma_S + \gamma_L^-} + 2\sqrt{\gamma_S^- \gamma_L^+}$$

3 fully characterized liquids  $\gamma_1, \gamma_1^{\text{tw}}, \gamma_L^+, \gamma_L^-$  Liq 1  $\rightarrow \theta_1$

$\gamma_2, \gamma_2^{\text{tw}}, \gamma_L^+, \gamma_L^-$  Liq 2  $\rightarrow \theta_2$

$\gamma_3, \gamma_3^{\text{tw}}, \gamma_L^+, \gamma_L^-$  Liq 3  $\rightarrow \theta_3$

if we have 3 liq & a goniometer :-

① we get 3 contact angles.

② for Eg., LHS is completely known. R.H.S. 3 unknowns.

Q. equilibrium contact angle of diiodomethane, water and glycerol are  $39^\circ$ ,  $60^\circ$ ,  $68^\circ$  following data is given ! -

- find out the surface tension.

	$\gamma^{\text{tw}}$	$\gamma^+$	$\gamma^-$	$\gamma^{\text{tot.}}$
diiodomethane	50.8	-	-	50.8
water	51.8	25.5	25.5	72.8
glycerol	84.0	57.4	8.2	61.10

$$n(1 + \cos \theta) = 2\sqrt{r_s^{LW} r_s^{LW}} + 2\sqrt{r_s^+ r_s^-} + 2\sqrt{r_s^+ r_s^-}$$

$$\textcircled{a} \quad 50.8(1 + \cos 39.4) = 2\sqrt{50.8 r_s^{LW}}$$

$$1.778 \times 50.8 = 50.8 \times r_s^{LW}$$

$$\rightarrow r_s^{LW} = \frac{50.8 \times 1.778}{4}$$

$$\Rightarrow r_s^{LW} = 39.923.$$

$$72.8(1 + \cos 60.9) = 2\sqrt{21.8 \times 39.923} + 2\sqrt{r_s^+ r_s^-} + 2\sqrt{r_s^+ r_s^-}$$

$$108.205 = 59 + 2 \times 5.05(\sqrt{r_s^+} + \sqrt{r_s^-})$$

$$108.205 = 59 + 10.1(\sqrt{r_s^+} + \sqrt{r_s^-})$$

$$\rightarrow 4.872 = \sqrt{r_s^+} + \sqrt{r_s^-} \quad \text{--- (i)}$$

$$61.10(1 + \cos 63.1) = 2\sqrt{34.0 \times 39.923} + 2\sqrt{r_s^+ r_s^-}$$

$$88.744 = 73.685 + 2.5777\sqrt{r_s^+} + 15.152\sqrt{r_s^-}$$

$$15.06 = 2.5777\sqrt{r_s^+} + 15.152\sqrt{r_s^-} \quad \text{--- (ii)}$$

$$\text{if } r_s^{\text{tot}} = 64.0$$

$$64(1 + \cos 63.1) = 73.685 + 2.5777\sqrt{r_s^+} + 15.152\sqrt{r_s^-} -$$

$$92.956 - 73.685 = 2.5777\sqrt{r_s^+} + 15.152\sqrt{r_s^-}$$

$$19.27$$

$$\textcircled{a} \quad 12.560 = 2.5777\sqrt{r_s^+} + 15.152\sqrt{r_s^-}$$

$$6.71 = 15.152\sqrt{r_s^-}$$

$$0.542 = \sqrt{r_s^-}$$

$$\rightarrow \sqrt{r_s^-} = 0.542 \rightarrow r_s^- = 0.294$$

$$r_s^+ = (4.872 - 0.542)^2 = 18.95$$

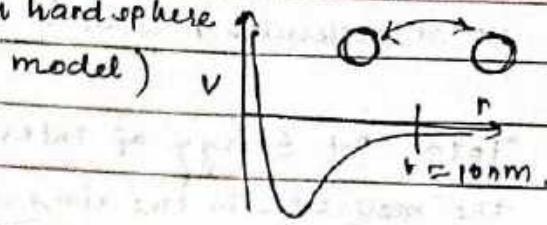
$\Rightarrow$  Using goniometer we can also measure CAH (contact angle hysteresis)

Implicit assumption:— We assume that evaporation is not taking place

$$V_{IJ}(r) = \frac{B}{r^{12}} - \frac{A}{r^6}$$

$r_{12}$   
 $r_6$

(Based on hard sphere model)



Molecular dynamic simulation's basis eqn =  $B/r^{12} - A/r^6$ .

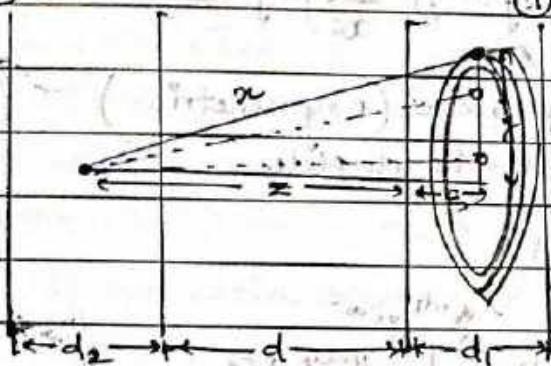
$r^{12} \rightarrow$  physical origin.

$r^6 \rightarrow$  square of ~~into~~ attraction

### Intermolecular interaction between 2 surfaces :-

consequences :-

material ①



"material

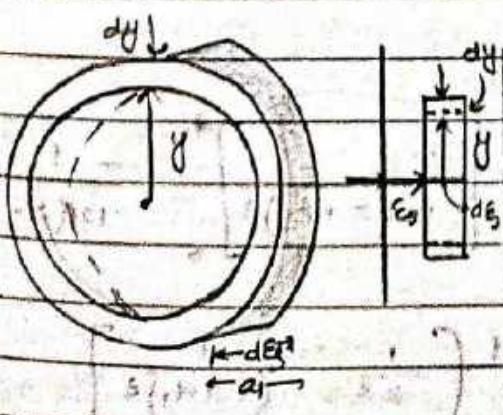
$$V_{LT}(r) = E_S - \frac{\alpha}{r^{12}} - \frac{\beta}{r^6}$$

$\alpha$   
 $\beta$

\* Surfaces are made of molecules. So b/w 2 surfaces there is going to be some kind of minimum distance b/w them. ( $r_s + r_s$ )

\* Effectively, we are going to consider int'n of all molecules of ① with all molecules of ②

\* The expanse of material ② in terms of  $x$  will be in  $x = d$  to  $x = d + d_2$



Vol. of the element

$$dV = \pi r^2 dy d_2$$

No. of molecules present in

$$\text{unit volume} = \text{Nos.} = \frac{\text{No. mol}}{\text{Vol. mol Vol.}}$$

$$= \frac{\text{No. mol} \times \text{mass}}{\text{mol mass Vol.}}$$

$$= N_A \times \frac{\text{density}}{\text{Molecular mass}}$$

No. of molecules present in unit vol. =  $N_A P$ ,

M.

No. of molecules present in the ring =  $(\pi \eta dy d\epsilon_s) \left( \frac{P_1 N_A}{M_1} \right)$

Total Pot. Energy of interact<sup>n</sup> of the chosen molecule of ② with all the molecules in the ring. =  $\left( \frac{P_1 N_A}{M_1} \right) (\pi \eta dy d\epsilon_s) \left( \frac{-B}{r^6} \right)$

We are considering only attractive part because we always see them coming in contact and not merge because for that we'll have to press them against each other.

Total PE of interact<sup>n</sup> of the chosen ② with all molecules in the block ① =  $\int \int \int \left( \frac{P_1 N_A}{M_1} \right) (\pi \eta dy d\epsilon_s) \left( \frac{-B}{r^6} \right) dy$

$$\text{limits: } z=0, y=0, z=d_1, y=\infty$$

why not from  $-\infty$  to  $\infty$   $\Rightarrow$  (symmetric)

The ring stretches in all sides.

$$x^2 = (z + \epsilon_s)^2 + y^2$$

$$= -2\pi P_1 N_A B_{12} \int \int \int \frac{y dy d\epsilon_s}{M_1} \int_{z=0}^{d_1} \int_{y=0}^{\infty} [(z + \epsilon_s)^2 + y^2]^{-3}$$

$$y^2 + (z + \epsilon_s)^2 = r^2$$

$$\rightarrow 2y dy = dr \quad \int_0^d y dy = \int_0^r dr = \frac{1}{2} r^2 = \frac{1}{2} \int_0^r \frac{4[(z + \epsilon_s)^2 + y^2]}{2r^3} dr = \frac{1}{4} \int_0^r \frac{4[(z + \epsilon_s)^2 + y^2]}{r^2} dr$$

inner part = 1

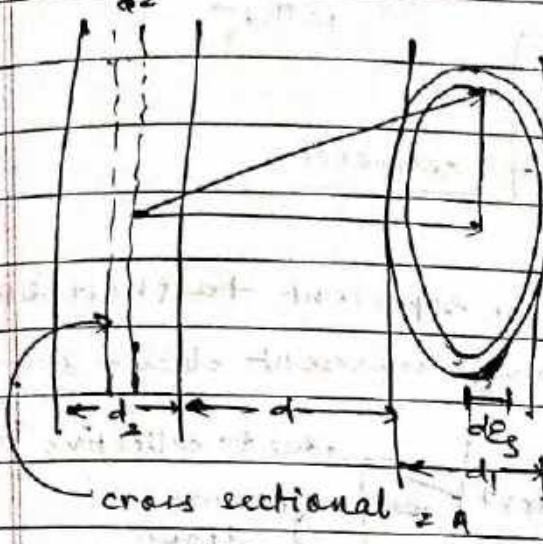
of integral  $= \frac{1}{4} (z + \epsilon_s)^4$

$$= \int_0^{d_1} \frac{1}{4(z + \epsilon_s)^4} d\epsilon_s = \left[ \frac{-1}{12(z + \epsilon_s)^3} \right]_0^{d_1} = \frac{-1}{12(z + d_1)^3} + \frac{1}{12 z^3}$$

$$= \frac{1}{12} \left[ \frac{1}{z^3} - \frac{1}{(z + d_1)^3} \right]$$

$$\text{Interaction of chosen molecule of } \textcircled{1} \text{ with all molecules of } \textcircled{1} = P_1 N_1 \pi \beta_{12} \frac{1}{GM_1} \left[ \frac{1}{z^3} - \frac{1}{(z+d_1)^3} \right]$$

Assuming  $\rightarrow$  forms a monolayer  $\rightarrow$  no interface on contact of  $\textcircled{1}$  &  $\textcircled{2}$



Volume of the strip  $= A d_2$

$$\text{No. of molecules in this block } = \frac{(P_2 N_2) A d_2}{M_2}$$

Interaction of all molecules within the strip with all molecules of  $\textcircled{1}$

$$= - \frac{P_1 P_2 N_1^2 \pi \beta_{12}}{GM_1 M_2} \left[ \frac{1}{z^3} - \frac{1}{(z+d_1)^3} \right] A d_2$$

cross sectional area

per unit Vol.

derivation is based on hard sphere approxm

with sep dist  $= d_0$  & not 0.

$$= - \frac{\epsilon_1 \epsilon_2 N_1^2 \pi \beta_{12}}{GM_1 M_2} \left[ \frac{1}{z^3} - \frac{1}{(z+d_1)^3} \right] d_2$$

per unit cross sectional area.

So, for the entire block of  $\textcircled{1}$   $\Rightarrow$  sum of interactions

$$\text{with molecules of } \textcircled{2} = G_{12}^{lw} = \frac{P_1 P_2 N_1^2 \pi \beta_{12}}{GM_1 M_2} \int_d^{d+d_2} \left[ \frac{1}{z^3} - \frac{1}{(z+d_1)^3} \right] dz$$

$$G_{12}^{lw} = \left( - \frac{P_1 P_2 N_1^2 \pi \beta_{12}}{GM_1 M_2} \right) \int_d^{d+d_2} \frac{1}{z^3} - \frac{1}{(z+d_1)^3} dz$$

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

where  $A_{12}$  = const.

$$A_{12} = \frac{P_1 P_2 N_1^2 \pi^2 \beta_{12}}{12\pi} \left[ \frac{1}{(d+d_1+d_2)^2} + \frac{1}{d^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2} \right]$$

$$A_{12} = + \frac{P_1 P_2 N_1^2 \pi^2 \beta_{12}}{M_1 M_2} = \text{Hamaker constant}$$

$(\epsilon_1, \epsilon_2, r, M_1, M_2)$  material dependent terms

(5 material dependent terms.)

$$P_1, P_2, M_1, M_2, \beta_{12}$$

$$\text{For } G_{12}^{lw} \quad d_1 \rightarrow \infty \quad d_2 \rightarrow \infty \quad A_{12} = \frac{A_{12}}{12\pi d^2} \rightarrow \boxed{1} \boxed{2}$$

At contact there is a min. sep. distance  $d = d_0 \rightarrow \boxed{1} \boxed{2}$

$\rightarrow$  orbitals just touch.

Major Assumption! — irrespective of material ( $d_0$ ) is considered const.  
& its value is taken to be  $0.157 \text{ nm}$ .

for  $d_1 = \infty, d_2 = \infty$

$$\Delta G_{12}^{lw} = \gamma_{12}^{lw} \left| \frac{d_1 = d_0}{d_2 = d_0} - \frac{\gamma_{12}^{lw}}{d_2 = \infty} \right| = -A_{12}$$

→ intermolecular inter<sup>n</sup> b/w

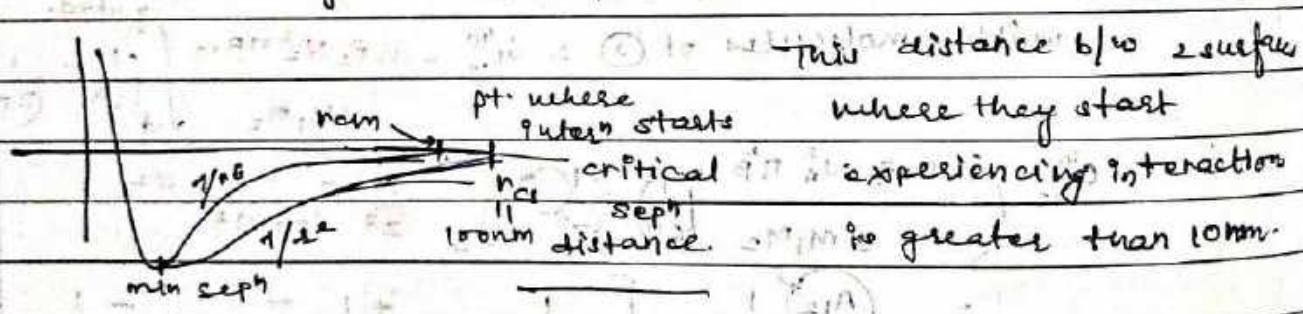
→ blocks of finite thickness

having finite sep<sup>n</sup> b/w them → derivation

In the 4 terms of  $\Delta G_{12}^{lw} \rightarrow$  2 terms represent farthest dist. &  
remaining 2 terms represent closest dist.

between 2 surfaces →  $d^n$  force of "int" due to collective int'nl  
power drops.

The sep<sup>n</sup> distance b/w 2 surfaces where they start experiencing  
the force is greater than b/w 2 molecules.



In practical surfaces the int'nl is much larger

$$\frac{r_{cm}}{r_{ci}} = \frac{10}{100} = 1 \quad r_{cm} \rightarrow \text{critical sep}^n \text{ dist. b/w 2 molecules}$$

$$\frac{r_{ci}}{r_{ss}} = \frac{100}{10} = 10 \quad r_{ci} \rightarrow \text{critical sep}^n \text{ dist. b/w 2 surfaces}$$

$$\begin{aligned} \Delta G_{12}^{lw} &= -A_{12} = \gamma_{12}^{lw} - (\gamma_1^{lw} + \gamma_2^{lw}) \\ \frac{12\pi d_0^2}{12\pi d_0^2} &> (\sqrt{\gamma_1^{lw}} - \sqrt{\gamma_2^{lw}})^2 = (\gamma_1^{lw} + \gamma_2^{lw}) \\ &= \gamma_1^{lw} + \gamma_2^{lw} - 2\sqrt{\gamma_1^{lw}\gamma_2^{lw}} = \gamma_1^{lw} - \gamma_2^{lw} \\ -A_{12} &= -2\sqrt{\gamma_1^{lw}\gamma_2^{lw}} \end{aligned}$$

Assumption →  $A_{12} = 24\pi d_0^2 \gamma_1^{lw} \gamma_2^{lw}$

We are not considering material dependent  $d_0$ .

$A_{12} = \pi P_2 N_A \pi^2 \beta_{12}$  cannot calculate  $A_{12}$  as  $\beta_{12}$  is unknown.

M<sub>1</sub>M<sub>2</sub>

Role / significance of Hamaker Constant: — not talking about the strength of molecule but the strength of two surfaces. (intern)

$\beta_{12}$  = strength of inter<sup>n</sup> b/w 2 molecules.

$$A_{11} = -\frac{1}{12\pi} \frac{24\pi d_0^2 \gamma_1^{lw}}{\text{surfaces}} \quad (\text{b/w 2 molecules of 1})$$

We have nowhere considered the self inter<sup>n</sup> or inter<sup>n</sup> of similar molecules.

$$\gamma_{11}^{lw} = -A_{11} \left[ \frac{1}{d_0^2} + \frac{1}{(d+d_1+d_2)^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2} \right]$$

Self energy of inter<sup>n</sup> of the molecules

→ Total energy of this Block

=  $\sum$  All pairwise inter<sup>n</sup>.

some energy has to be applied to cut a slice of the block & put it back again to create an interface.

Total energy = energy of the surface + energy supplied.

Rotating the surface by  $90^\circ$ ! —

Total Energy of inter<sup>n</sup> of all molecules b/w ( $0, \infty$ ) + Ext. energy applied = Total Energy of inter<sup>n</sup> ( $0, h$ ) + Total Energy of inter<sup>n</sup> ( $h, \infty$ ) + Interfacial interaction b/w molecules confined b/w  $[0, h]$  and  $[h, \infty]$  at  $h$

Distance

Ext. energy = PE of the + interfacial applied film inter<sup>n</sup>.

$$\gamma_{11}^{lw} = -A_{11} \left[ \frac{1}{d_0^2} + \frac{(h, \infty)}{0} + \frac{(d_1, \infty)}{0} - \frac{1}{(d_0+h)^2} \right] \quad h = d_2$$

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

Ext. energy = PE of the film

Total Energy of inter<sup>n</sup> between  $(0, h)$  = -interfacial inter<sup>n</sup> at  $h$

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

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

$$\frac{A_{11}}{12\pi d_0^2}$$

$$\Delta \gamma_{film}^{lw} = -G_{interference}$$

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Page :

$$\text{Excess free energy of the film } \Delta \gamma_{film}^{lw} = \frac{-A_{11}}{12\pi} \left[ \frac{1}{d_0^2} - \frac{1}{h^2} \right]$$

air  
self standing self film/air

Excess free energy  
PE of interaction  
of film due to its  
thickness

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

surface tension term

(Excess energy in the film)  $12\pi h^2$

Excess free  $\rightarrow$  tends to zero as  
film becomes  
Term due to self thickness

$$\text{critical } h \text{ for which PE of interfacial} \\ \Delta \gamma_{film}^{lw} = \Delta \gamma_{film}^{lw} \Big|_{h \rightarrow \infty} = \frac{2\gamma_1^{lw} - A_{11}}{12\pi h^2} \Big|_{h \rightarrow \infty}$$

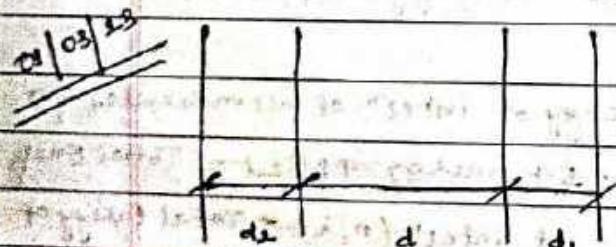
what is a thin film?

# Thin films are films in which PE of interfacial is non zero. (Excess free energy  $\neq 0$ )  
for  $h \rightarrow \infty \Rightarrow$  Excess free energy  $\rightarrow 0$ . ( $h \approx 100\text{ nm}$ )

(c) Based on molecular interac<sup>n</sup> of the similar constituent molecule.  
The thickness below which a film exhibits non-zero PE  
that is a thin film.

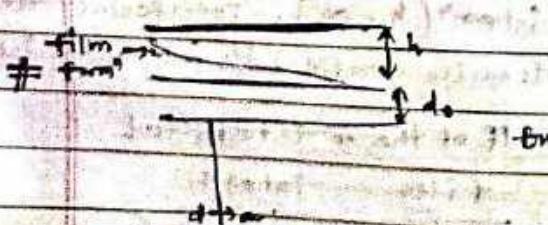
Droplet in case of 2-component soln:

The 2 components have different saturation  $h_s$  so they deposit at different places and the rings might be concentric circles or patchy depositions.



$$\Delta \gamma_{12}^{lw} = \frac{-A_{12}}{12\pi} \left[ \frac{1}{(R+d_1+d_2)^2} + \frac{1}{(R-d_1)^2} - \frac{1}{d_1^2} \right]$$

Based on only 1-2 type interac<sup>n</sup> or adhesive interac<sup>n</sup>. We have not looked at cohesive interac<sup>n</sup> or self interac<sup>n</sup>.



$$\begin{aligned} & \text{Energy of molecules } (0, \infty) + \text{External applied energy} \\ & = \text{Energy of molecules } (0, h) + \\ & \quad \text{Energy of molecules } (h, \infty) + \text{Interfacial energy (due to interaction)} \end{aligned}$$

$$\Rightarrow \text{Ext. energy applied} = \Delta \gamma_{film}^{lw} + \Delta \gamma_{interface}^{lw}$$

Putting  $d_2=h$ ,  $d_1=\infty$  in  $\Delta \gamma_{12}^{lw}$  formula! —



$$\Delta \gamma_{interface}^{lw} = -A_{11} \left[ \frac{1}{d_0^2} - \frac{1}{(h+d_0)^2} \right] = 2\gamma_1^{lw} + A_{11}$$

$$[\Delta \gamma = 2\gamma_1^{lw} + A_{11}]$$

$$C_1 = A_{11} \left[ \frac{1}{d_0^2} - \frac{1}{h^2} \right] \quad h \gg d_0$$

$$C_1 = G_{\text{film}}^{\text{LW}} + 2V_1^{\text{LW}} + A_{11}$$

$$12\pi h^2$$

$$\Rightarrow G_{\text{film}}^{\text{LW}} = C_2 - \frac{A_{11}}{12\pi h^2}$$

$$C_2 = C_1 - 2V_1^{\text{LW}}$$

- As  $h \uparrow$ ,  $G_{\text{film}}^{\text{LW}}$  slowly becomes constant
- As  $h$  is low, the 2nd term becomes active.

- There is some excess energy of interaction if film is too thin.
- There would be some value of  $h$  above which it is inactive & below which the 2nd term becomes active.
- A film is called a thin film if the 2nd term ( $A_{11}/12\pi h^2$ ) is active.

Thick

Thin

$\Delta G_{\text{film}}^{\text{LW}}$  separating  $\Sigma$  interfaces.

"inter" between  
the  $\Sigma$  interfaces.

active interfacial interact'.

$\Delta G_{\text{film}}^{\text{LW}}$  → Excess free energy due to thickness of the system.

$$\Delta G_{\text{film}}^{\text{LW}} = G_{\text{film}}^{\text{LW}} - G_{h=\infty}^{\text{LW}} \Rightarrow \Delta G_{\text{film}}^{\text{LW}} = \frac{A_{11}}{12\pi h^2}$$

$$= \frac{g_2 - A_{11}}{12\pi h^2} = g_2 + A_{11}$$

gets rid of the constant term.

(i) If it's thick → excess energy becomes negligible.

⇒ Excess energy is manifestation of thickness of the film.

∴ The wall with higher magnitude of Excess Energy is the thinner film. Proximity of the interfaces gives rise to interaction.

Q. As far as a film is concerned, what is a more practical situation?

Assumpt' - film of same material resting on block of same material

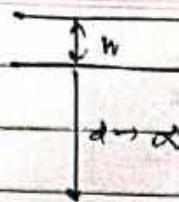
Reality → 2 different materials. Eg. → wall is a substrate & air film

Drop Vol.

- plattening at the center due to  $\uparrow$  mass with  $\uparrow$  in Vol.
- close to the contact line no distortion
- Contact line spreads out but locally  $\Delta G$  same.
- if drop is pinned no spreading.

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②

### Supported Thin films 1 -

①

$$\Delta G_{\text{SYSTEM}}^{\text{LW}} = \Delta G_{\text{FILM}}^{\text{LW}} + \Delta G_{\text{SUBSTRATE}}^{\text{LW}} + \Delta G_{\text{INTERFACE}}^{\text{LW}}$$

$$c_2 = \frac{A_{22}}{12\pi h^2} + c_3 - \frac{A_{12}}{12\pi d_0^2} - A_{12} \left[ \frac{1}{d_0^2} - \frac{1}{(9\pi h)^2} \right]$$

$$\Delta G(h) = c_2 - \frac{A_{22}}{12\pi h^2} + c_3 - A_{12} \left[ \frac{1}{d_0^2} - \frac{1}{(9\pi h)^2} \right] + A_{12}$$

$$= c_2 - \frac{1}{12\pi h^2} (A_{22} - A_{12}) - A_{12} \left[ \frac{1}{d_0^2} - \frac{1}{(9\pi h)^2} \right]$$

Term is const.

$$\Delta G_{\text{SYSTEM}}^{\text{LW}} = -A_e + c_2$$

effective Hamaker constant  $\Rightarrow A_e = A_{22} - A_{12}$

$$\Delta G_{\text{SYSTEM}}^{\text{LW}} = \frac{A_e}{12\pi h^2}, \quad h \rightarrow 0 \quad \Delta G_{\text{SYSTEM}}^{\text{LW}} \rightarrow \infty$$

$$P_1 \neq P_2$$

Air

Position

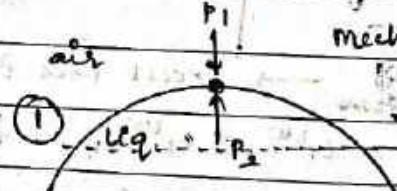
$P_1$

$P_2$

Flat liquid

surface in equilibrium.

mechanical equilibrium



Flat meniscus

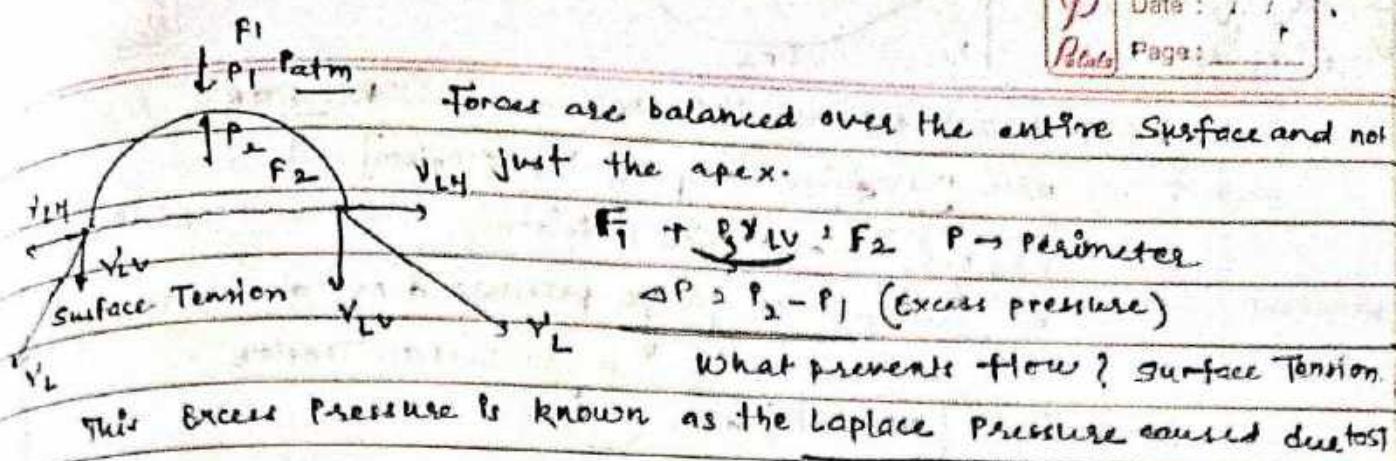
$$P_1 \neq P_2 \Rightarrow P_2 > P_1$$

A curved meniscus forms because of the effect of surface Tension.

① liquid penetrating into domain of air.

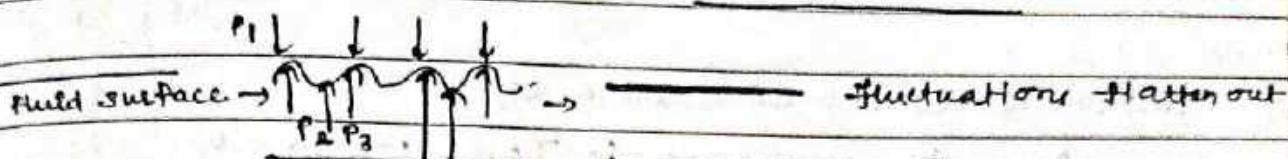
② Air penetrating into domain of liquid.

Note: Cohesive forces acting forward  $\rightarrow$  net inward pull. Meniscus remains stable  $\rightarrow$  some thing balancing this is excess pressure



What prevents flow? Surface Tension

This Excess Pressure is known as the Laplace Pressure caused due to



min. Surface Energy is always spherical

based on curvature  $\rightarrow P_2 > P_1, P_3 < P_1 \Rightarrow P_2 > P_3$  (caused due to ST)

Due to this  $P_s$  gradient, there is flow and the surface flattens out.

If the amplitude of the waves are high, due to different potential gradient between raised part & enclosed part  $\rightarrow$  fluctuations flatten out.

ST & gravity  $\rightarrow$  Boundary factor depends on length scale.

Curvature & Amplitude

Fluctuations on the surface of a lig.  $\rightarrow$  factors  $\rightarrow$  Laplace Pressure &

The 2 factors work together acc. to situation. Gravity Potential Difference.

Laplace Pr.: - If curved lig. meniscus at mechanical eqbm., the liquid side pressure on the concave side is higher than the air side pressure.

$P_2$  curved lig. meniscus at mechanical eqbm.

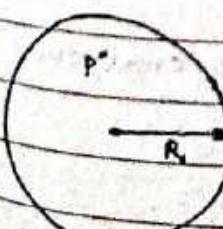
$$P_1 > P_2$$

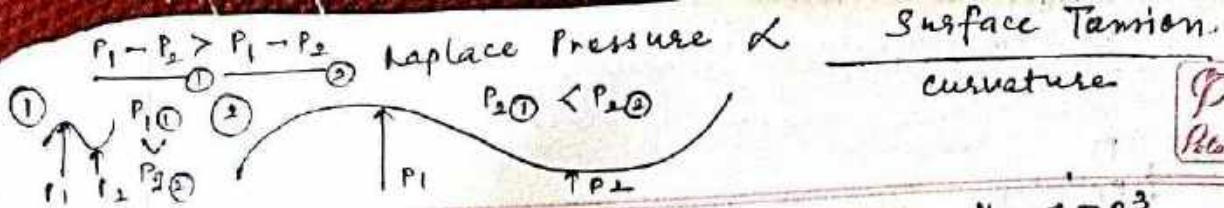
Spherical Liquid Drop with radius  $R$

We want to increase size of the drop from  $R$  to  $R + dR$ . Supply some energy  $\rightarrow$  do work (expand the volume)

$\rightarrow$  At the tip of the needle we'll have a nearly spherical drop.

$\rightarrow$  Drop is dispensed on a contact angle goniometer using a needle.





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Work done to expand the drop :—  $W = \frac{4\pi R^3}{3}$

$$W = PdV \quad [\text{in a typical Thd. problem}]$$

why only  $P$ ?  $\rightarrow$  outside  $P_{atm}$   $dV = \frac{4\pi R^2 dR}{3}$ .

We always take gauge pressure & not absolute  $P_1$   
due to surface tension

$$\text{Here } \Rightarrow SW = (P'' - P') dV = \Delta P dV$$

First Law of Thd. :—  $dE = SW + S\dot{Q} = ?$

Assuming no change in Temp.  $\Rightarrow S\dot{Q} = 0$ .

So because of the expansion done (only by amount  $dR$ )

the manifestation of this work is change in surface energy.

Initial Surface Energy =  $Y A_i$  ( $A_i = 4\pi R^2$ )  
Surface Tension.

Total Energy ascribed at the surface =  $Y 4\pi R^2$

Due to Expansion, change in area  $\Rightarrow dA = 8\pi R dR$

$$\Rightarrow dE_s = 8\pi R dR Y \Rightarrow SW = 8\pi R dR Y$$

Assumptions !— (i) Isothermal & non dissipative system (frictionless)

First Law.

$$\Delta P \cdot 8\pi R^2 dR = 8\pi R dR Y$$

$$\Rightarrow \boxed{\Delta P = \frac{2Y}{R}}$$

(ii) The change in Radius is infinitesimal.

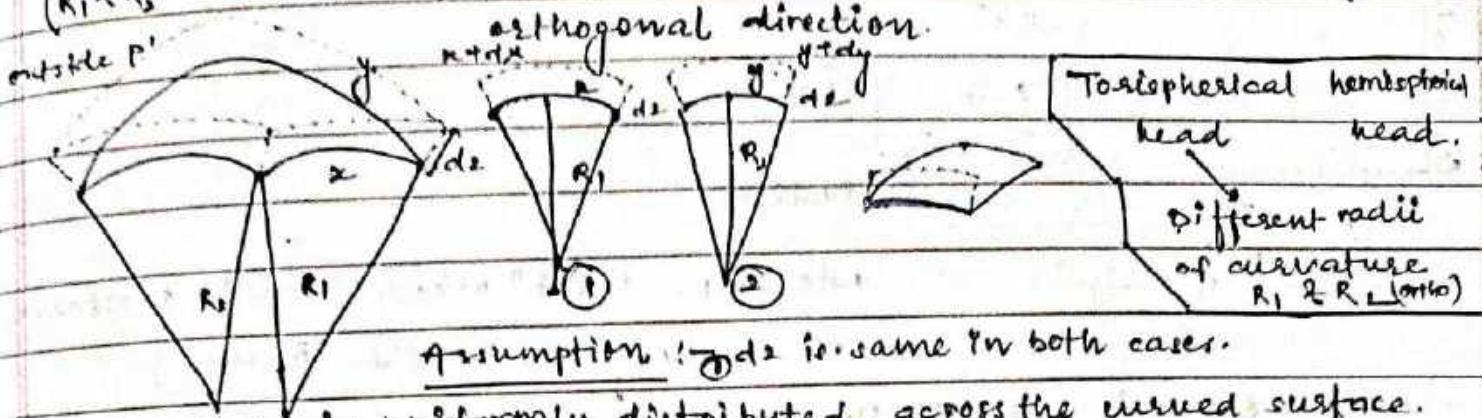
Change in Internal energy is negligible as compared to surface energy. In classical Thd., there is no consideration of time.

# To fully define the geometry of a curvature  $\Rightarrow$  2 radii of curvature  
+ 3 coordinates

# Spherical surfaces are special surfaces where, curvature is same everywhere.

Laplace Pressure for a general curved surface :-

$(R_1, R_2 \rightarrow \text{local curvature})$   $R_1$  and  $R_2$  are the radius of curvature in  $x$  &  $y$  dir.



Assumption :  $d_2$  is same in both cases.

- Assumptions :-
- ② Pressure is uniformly distributed across the curved surface.
  - ④ Isotropic material - expansion is same everywhere.
  - ⑤  $x$  and  $y$  are very small. So their product of higher order is neglected.

$$\text{Initial } A = xy$$

$$(x + dx)(y + dy) - xy$$

$$dx = (x + dx)(y + dy) - xy$$

$$= dy + y dx$$

$$dA = \Delta P dV = \Delta P xy d2 \quad dS = y(dx + dy)$$

$$dV = xy \cdot d2$$

assuming the ① & ② to be triangles :-

Similar :-  $y + dy = R_2 + d_2$  and  $x + dx = R_1 + d_2$

$$\frac{dy}{R_2} = \frac{dx}{R_1}$$

$$dy = \frac{R_2}{R_1} dx \quad dx = \frac{R_1}{R_2} dy$$

$$dA = dS \Rightarrow \Delta P xy d2 = y \left( \frac{xy d2}{R_2} + \frac{yx d2}{R_1} \right)$$

$$\Rightarrow \Delta P xy d2 = y xy d2 \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

Young-Laplace Eqn

$$\Delta P = y \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

" At the surface is very small we treat it as same kind of rectangular surface

in a solid fluctuations are much less - very strong cohesive forces.

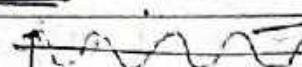
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## Spontaneous Instability in Ultra Thin Polymer films.

①  $\Delta \omega_{12}^{LW} = -\frac{1e}{12\pi h^2}$

②  $\Delta P = V \left[ \frac{1}{R_1} + \frac{1}{R_2} \right] [\text{Laplace Pressure}]$

①   
 $R_1$  ↑  
 $R_2$  ↓  
Liquid

lateral pr. distib<sup>n</sup> which leads to flattening out of fluctuations (Laplace Pressure)

② Cause of such pressures/fluctuations

a) Because of the competition to evaporate, there is dynamic steady state not static causing fluctuations.  
→ Because of KE distribution

~~ there are fluctuations

b) fluctuations happen at very small molecular level:

c) At the molecular level, surface molecules have a distib<sup>n</sup> of KE so there is a competition to leave. As they try to evaporate this leads to fluctuations which look flat at macroscopic level.

Laplace Pressure causes flattening of these fluctuations → 2 reasons curvature & cohesive forces which don't allow the molecule to escape. When evap<sup>n</sup> is min., the macroscopic ss at the molecular level is dynamic.

③ Glass of Water / pool of Liquid

a) flat surface  
 $u, v, w = 0$

b) leaving the liq. for a long time → evap<sup>n</sup>.

c) KE distib<sup>n</sup> (avg.  $KE = \frac{1}{2}kT$ )

higher KE molecules participate in evap<sup>n</sup> ( $KE = f(T)$ )

d) in order to evaporate, the molecule needs to overcome cohesive forces.

↑ overcome these limitations.

if Energy > Limit it, evaporates otherwise not.

e) All surface molecules are potential candidates for evaporation. In some cases, they are successful in some they are not.

Non Planar surface → spatial variation of Laplace Pressure

↓↓↓↓↓↓ ↓ flat surface  
 $u, v, w = 0$

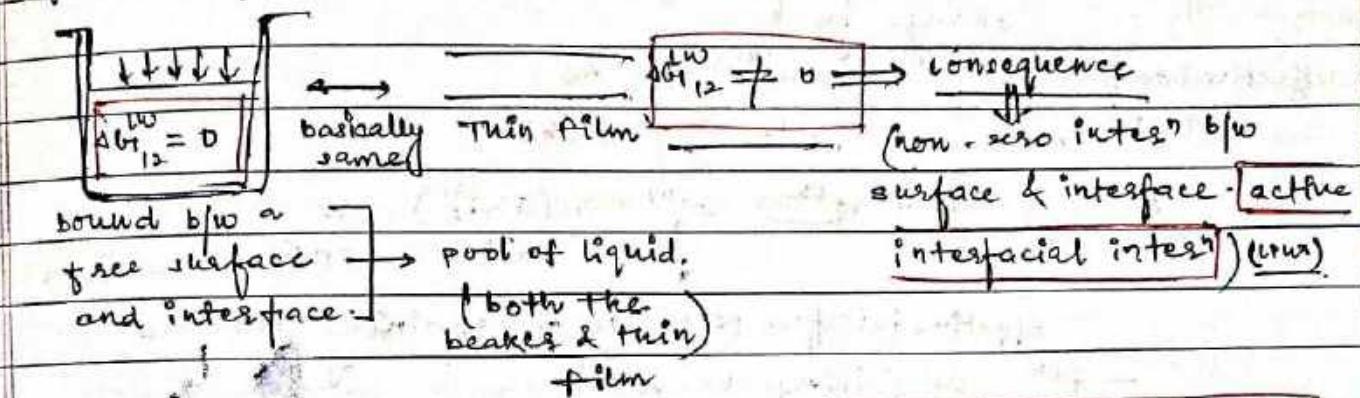
dynamic steady state

fluctuations → flattening

④ anything that may favour the growth of these fluctuations?  
 can there be any physical effect that can ↑ the intensity of these fluctuations?

→ if there is some interfacial interaction between 2 surfaces.

if  $h \rightarrow$  very thin ( $< 100\text{ nm}$ ) a non zero  $\Delta G_{12}^{LW}$  ( $= -4e/127\pi h^2$ )



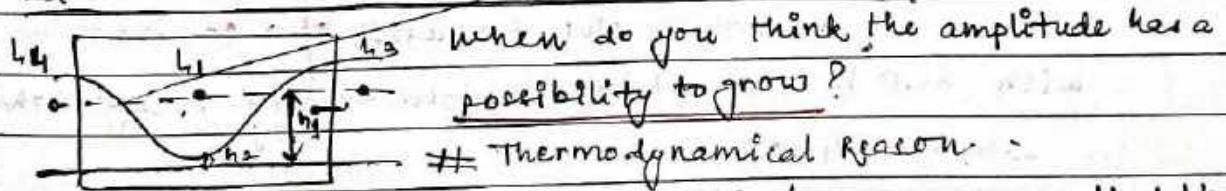
$$\gamma_s - \gamma_L - \gamma_{SL} \quad S_{SL} = \gamma_s - (\gamma_L + \gamma_{SL})$$

spreading coeff

$S_{SL} < 0 \Rightarrow$  Not favoured

A rectangular box represents a thin film. Inside, "50 nm" is written above a horizontal line. Below this line, "5 nm" is written. A bracket groups "50 nm" and "5 nm" with the text "both are predicted to be unfavoured ( $S_{SL}$ )". To the right of the box, "favoured.  $\Leftrightarrow S_{SL} > 0$ " is written.

Let us examine 1 oscillation in a thin film.



If it is possible by some means that these fluctuations are associated with lowering of  $\Delta G_{12}^{LW}$  bcoz of fluctuations,  $h$  reaches  $h_2$ .

if  $\Delta G_{12}^{LW}$  at  $h=h_2$  is lower than  $h=h_1$ ,  $\Rightarrow$  growth will be favored.

$$\Delta G_{12}^{LW}|_{h_2} - \Delta G_{12}^{LW}|_{h_1} \geq 0.$$

initial thk =  $h_1$

$$\text{initial } \Delta G_{12}^{LW} = \Delta G_{12}^{LW}|_{h_1} = \Delta G_1$$

$$\text{At } h=h_2 \Delta G_{12}^{LW}|_{h_2} = \Delta G_{12}^{LW}|_{h_2} - \Delta G_{12}^{LW}|_{h_1}$$

$$\Delta G_{12}^{LW}|_{h_2} \leq \Delta G_{12}^{LW}|_{h_1}$$

Replace pressure works independently.

possibility of change of  $\Delta H$ .  
if  $\Delta H_2 < \Delta H_1 \Rightarrow$  fluctuations thermodynamically favoured.  
if  $\Delta H_1 < \Delta H_2 \Rightarrow$  fluctuations Thd. not favoured.

We are basically checking change of  $\alpha$  with reduction of film thickness ( $h$ )

change in  $h$

$$\text{effective interface potential} \rightarrow \phi^{LW} = \frac{\partial(\Delta H_{12}^{LW})}{\partial h} = \frac{\Delta \epsilon}{6\pi h^3}$$

Intuitively: -  $\phi^{LW} = \frac{\partial(\Delta H_{12}^{LW})}{\partial h} = \frac{\Delta \epsilon}{6\pi h^3}$ .

Effective interface potential or Conjoining Pressure

$-\phi^{LW}$  = Disjoining pressure.

$h_1$  to  $h_2$  ( $h_1, h_2 \rightarrow$  both +ve)

$$, \Delta H_1 \text{ to } \Delta H_2, h_2 - h_1 = +ve$$

$$\frac{\partial(\Delta H_{12}^{LW})}{\partial h} = \frac{\Delta H_2 - \Delta H_1}{h_2 - h_1}$$

if  $\Delta H_2 > \Delta H_1 \Rightarrow$  Num positive

Denom. -ve.

$$\phi^{LW} = -ve.$$

Growth = Not favoured  $\Rightarrow \Delta \epsilon -ve$

with red<sup>n</sup> in film thickness, film energy  $\uparrow$ . So growth not favou

$\Delta H_2 < \Delta H_1 \Rightarrow$  Num -ve

Denom  $\pm ve$

$$\phi^{LW} = +ve \rightarrow \text{favoured} \Rightarrow \Delta \epsilon +ve$$

From the standpoint of interfacial interac<sup>n</sup>, growth is favoured.

(However, it's not a completion for the growth to occur)

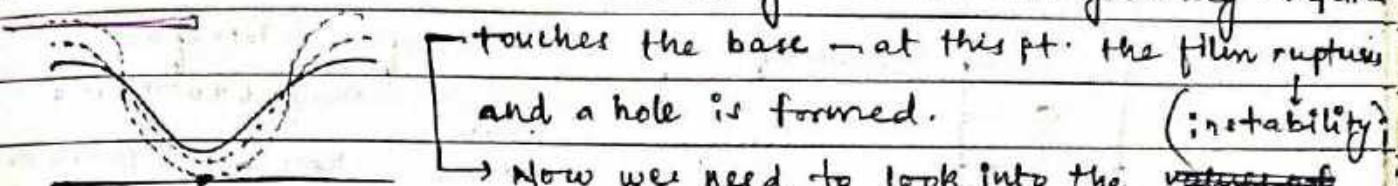


$$\phi^{LW} = \frac{\partial(\Delta H_{12}^{LW})}{\partial h} = \frac{\Delta \epsilon}{6\pi h^3}$$

sign depends only on the Hamaker constant.

\* A system is prone to favouring growth of the oscillations when conjoining pressure is active.

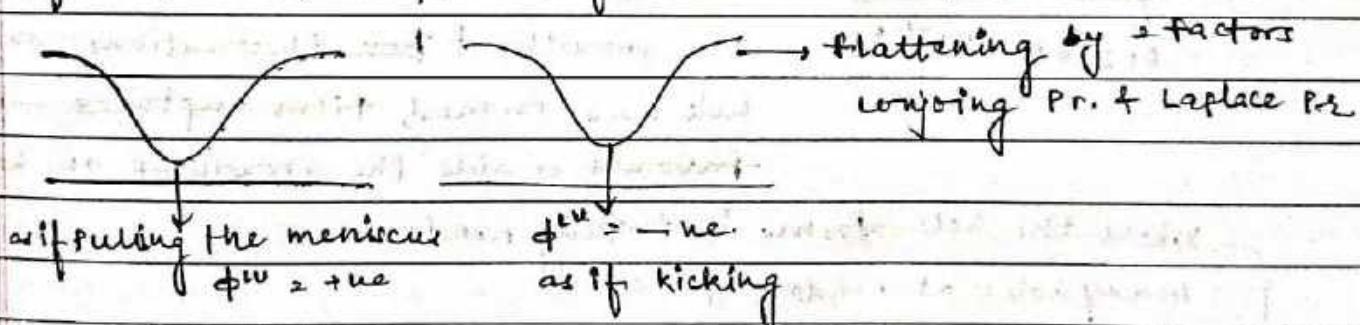
If growth is favoured according to the thd. of the system, what does it mean → Oscillation amplitude grows till the growing amplitude



relative values of Laplace Pressure and conjoining pressure and (stability of film) → compare them.

If  $LP > CP \rightarrow$  film will flatten out. However, it will take longer time to flatten out.

If  $CP > LP \rightarrow$  ruptured film



→ opposing effects of  
conjoining and Laplace  
pr. (competition between 2)

A system where growth of oscillation is favoured  $\rightarrow CP > LP \rightarrow$  film gets ruptured.

$LP \rightarrow$  stabilize the film  $\rightarrow ST \rightarrow$  flattening out

$CP \rightarrow$  destabilize the film  $\rightarrow$  Interfacial inter " → pulling "

~~Top layer - lowest surface energy~~

~~SSL now~~

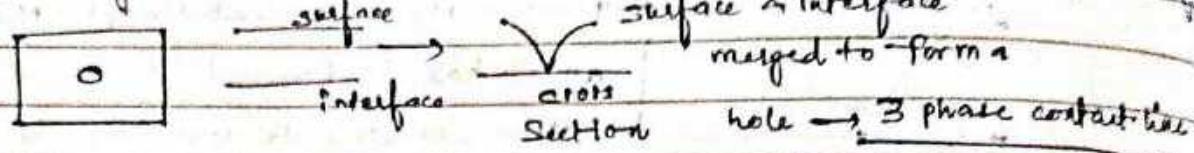
~~Excess free energy will tend to zero.~~

~~No driving force for interfacial coarsening.~~

~~True  $\rightarrow$  ultra-crystalline~~

"hole form" / spontaneous rupture

→ growing oscillation amplitude  $\approx h / \text{the surface \& the interface mass}$



Now we have a contact line which will equilibrate till it reaches  $\theta_E$  (extra eqib. contact angle). Till then, the contact line will recede and hole will grow until  $\theta \approx \theta_E$ .

Hole form<sup>n</sup> is accompanied with hole growth.

Till film has not ruptured, ST tries to oppose  $\dot{\theta} = \theta_E$   $\dot{\theta} \neq \theta_E$ , the growth of hole fluctuations. Once the hole has formed, film ruptures  $\rightarrow$  ST favours or aids the growth of the hole.

Where the hole forms is totally random.

Many holes at random places.

There are ways to avoid the randomness of the hole form<sup>n</sup>.

- film instability → Hamaker const - film will evolve or not is decided by thickness.

Spreading coeff.  $\rightarrow$  doesn't consider film thickness does not tell film will evolve/unstable or not

Spl. coating

If we can somehow create a th. unstable film which is sufficiently thick then nothing will happen (no interfacial int.) → no rupture actual interfacial tension  $= \sigma = 0$  · only Laplace pressure

SSL will not differentiate b/w a film of thickness 50nm and 500nm. However, if we look into  $\phi$  (conjoining pr.), for a higher value of  $h$ , conjoining pr. will be zero, so spontaneous instability is ruled out so for 50nm film CPr. will be true and for 500nm film CPr. will be negligible.

15/03/23  
Bcos of  
KE diff'b  
There will  
be

fluctuations Thick X →  
no interfacial  
interaction

(P) Date : / /  
Flattening out  
Replace Pr.

Film

Thin ↓ active (May)

spontaneous  
instability  
in ultra-thin  
liquid films

interaction/Vanderwaals  
interaction.

Thin films → Order of ~100 nm.

Liq) - what type of liquid are we talking about? → Polymer  
we do not prefer to do these expts. with regular liquids. Why?

any regular liquid is associated with evaporation → bcos of evap'g  
thickness will reduce and go below 100 nm and will show spontaneous  
instability with time. Everything will evaporate in sometime and  
Polymer we will only be looking at bare substrate. So, we  
cannot perform large scale microscopic analysis (high magnification  
or higher resolution). for regular liq., vapour pressure is adequately  
high. The whole physics depends on thickness of the film.

- whether the film will actually evolve (rupture) will be cannot be  
predicted by SL only. we need conjoining pr. to predict  
conjoining pr. → (ne or -ne) → film is thin

stable unstable

(=0) → film is thick.

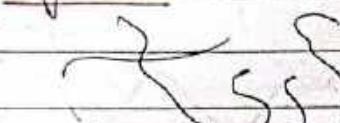
For  $5\ \mu$  film,  $C_{Pr}$  is zero. Check SSL. Then stability & instability  
is decided.

film will not evolve

film will remain  
intact

- Liquid used → Polymer → which almost does not evaporate  
very low vap. pr

Polymer :-



long chain  
mostly hydrocarbon

⇒ at the melting pt  $T_m$  → internal KE overcomes P.E. (cohesive inter)

⇒ Flow or deform' means molecules can change their rel. position.

M.P. of Water = ~~0~~  $0^\circ\text{C}$  at 1 atm. pr.

⇒ at m.pt. → only for crystalline → all arrangements break at the same melting pt.

⇒ at  $T_g$  for amorphous materials → They have a range at which the material melts. (super cooled) → molecules are random and not arranged in lattice.

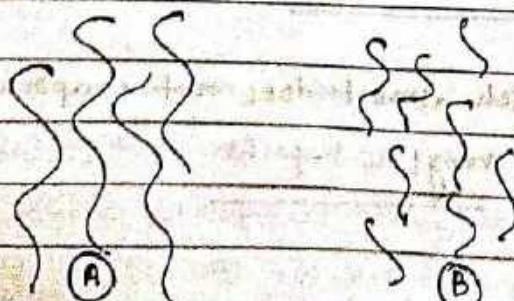
at  $T_g$  ⇒ behaviour → solid film

Solid ⇒  $\infty$  viscosity of material.

⇒ T at which experiments are done should be greater than  $T_g$  for a film polymer.

Quenching → To control disintegration of films above  $T_g$ . Film still ( $\downarrow T$ ) remains stable but what we see is due to the kinetics of the process.

16/03/23



long chain

short chain.

① manifestation will be on the degree of entanglement.  
Longer the chains probability of entanglement is higher.

deformation & solidification of a plastic  
Went up to a T above which its viscosity dropped and deform' may happen.

Then T + viscosity again stabilized

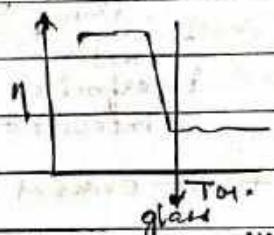
Solid Materials (auto rotation of molecule)

- Amorphous crystalline

glass ↓ mostly all

have a  $T_g$ , metals.

orientation of all molecules repeat



$T_g$  glass

transition Temperature

$\eta_{sp}$  hardly changes as a result of chain length.

- ① Higher the level of entanglement higher will be the opposing forces to flow. As a result, higher viscosity.

- ① How to represent (capture) the chain length?  $\rightarrow$  mol wt.  $\rightarrow M_n$
- ② Whether all chains are of same length?  $\rightarrow$  PDI (Poly Dispersity Index)

①  $M_w \rightarrow$  Weighted avg. molecular wt.

$M_n \rightarrow$  No. avg. molecular wt.

~~now elaborate~~

$$\text{PDI} = \frac{M_w}{M_n}$$

$M_n$

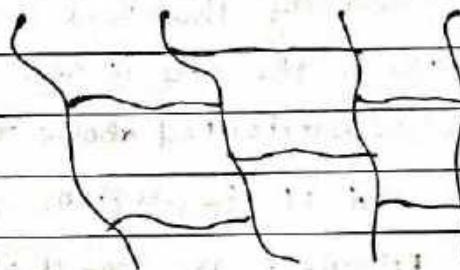
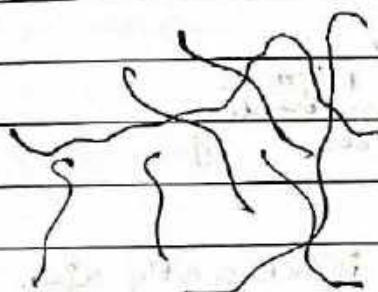
$\frac{1(\text{one})}{\text{closer}} \rightarrow 1.0$

is the PDI

The length of the chains is almost same

There is more variation in the length of chains

most of the chains are of same length. Shows a narrow peak



Glassy / Thermoplastic

→ chains are isolated.

→ on applying energy, the ~~polymer~~ chains break in a way they flow.

→ They have  $T_g$  (Glass Transition Temp.) above which the polymer flows.

Thermoset/ Rubbery

→ chains are cross linked/ attached to each other

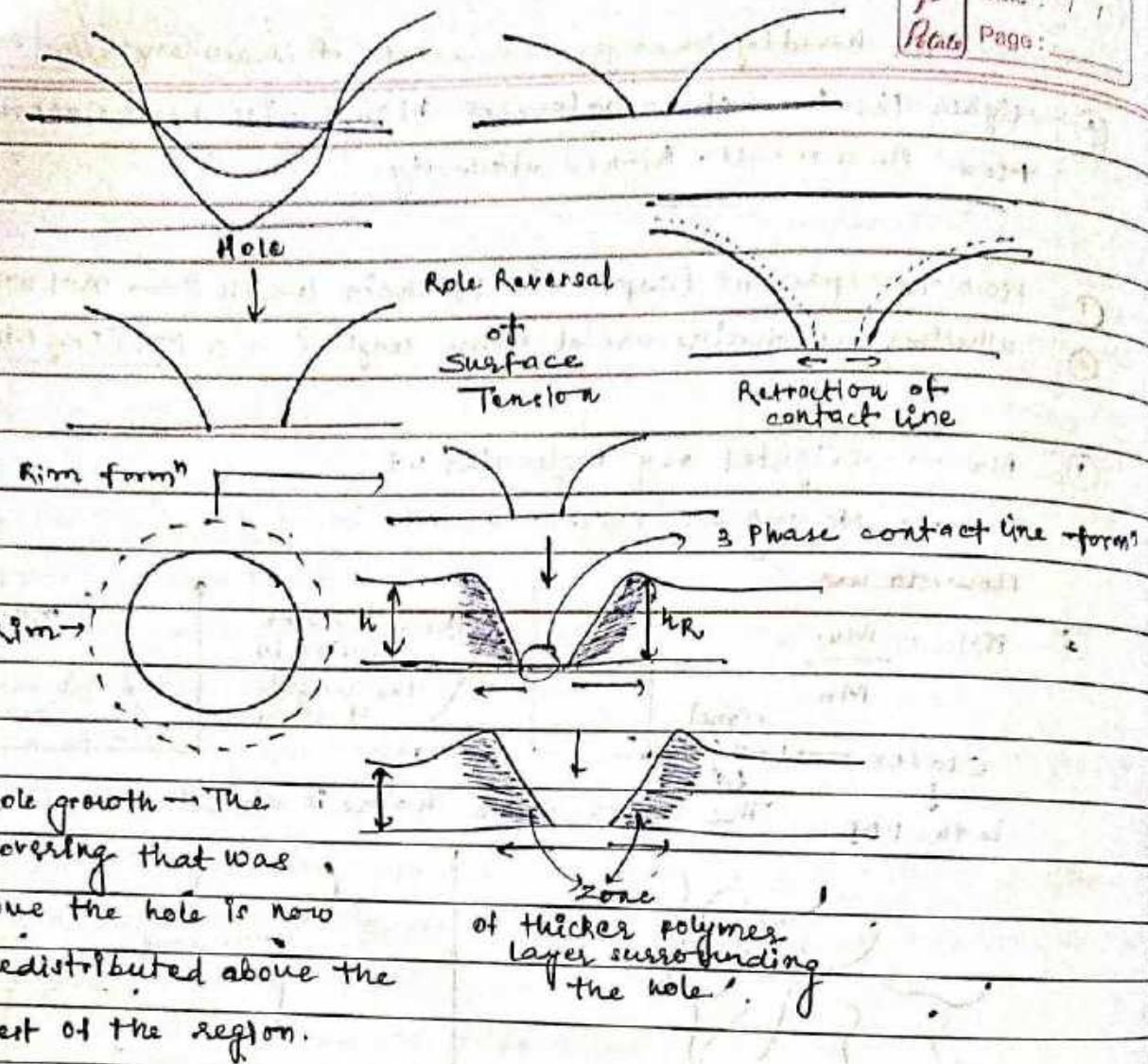
→ When energy is applied the cross links are stretched, then they release energy & go back to their original configuration. Sometimes the links may break. That is basically degradation.

→ Most of the time they don't have  $T_g$  ( $T$  above which a material flows) ~~so~~ they don't flow & just break

A # hole grows because of the retraction of contact line due to Surface Tension

Long chain polymers above  $T_{g1}$  behave as liq. (flow).  
Hole growth is added ST.

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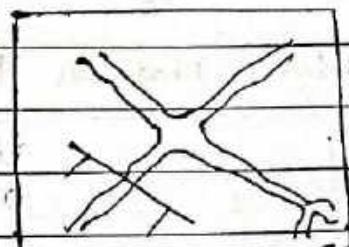
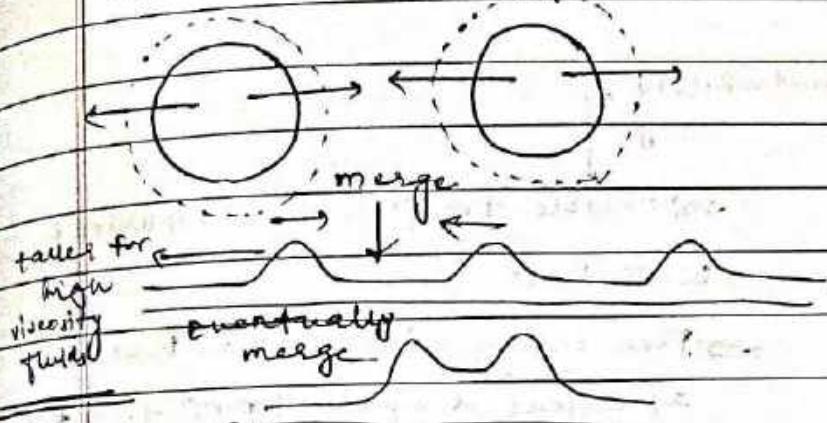


- # Hole growth → The covering that was above the hole is now redistributed above the rest of the region.
- # Polymers are long chain → Viscosity is inherently high.
- # This redistribn<sup>b</sup> is in liq. state & requires involves a high viscosity fluid. (Visc. ps. is low so not evaporating mass is to be conserved. so the liq. has to be redistributed)
- # As viscosity is very high the redistribution does not happen instantaneously. So, rim is a signature of local accumulation.
- # Long chain Polymeric liquids above  $T_{g1}$  behave as non-newtonian fluids with high viscosity.
- # Local accumulation around growing hole due to slow flow as a result of viscosity.
- # Higher is hole grow, rims become taller

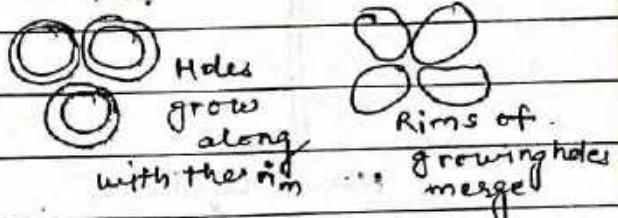
Influence of  $\eta \rightarrow$  on Rim? Higher viscosity ~~higher~~  
Molecular wt. high  $\rightarrow$  long chains  $\rightarrow$  long chain molecules all higher the temperature  $\rightarrow$   $T_{g1}$  behave as liq.

If we have a fluid which is 10 times more viscous and 10 times more dense will fall together.

• kinematic viscosity captures the effect of density along with viscosity



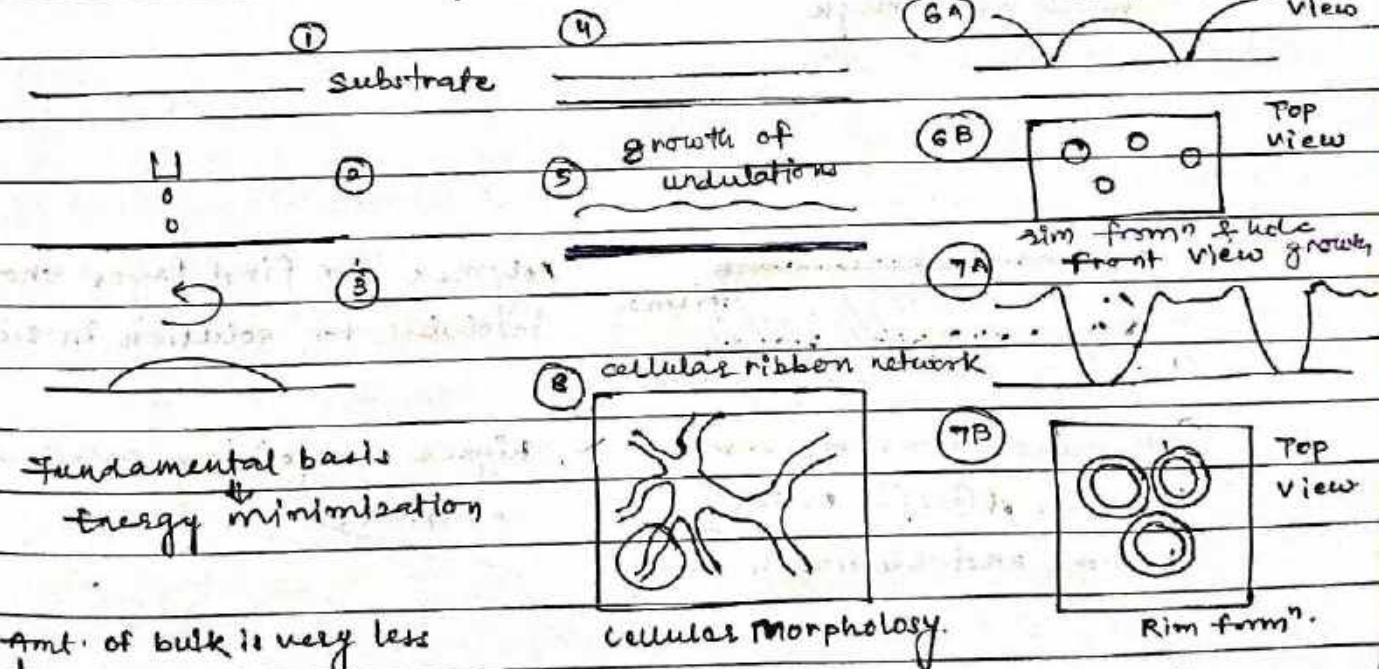
interconnected  
filament threads.  
*Platogallacta*  
Instability



### 17/03/23 Thin-film Dewetting Experiments:-

→ Polymer thin film.

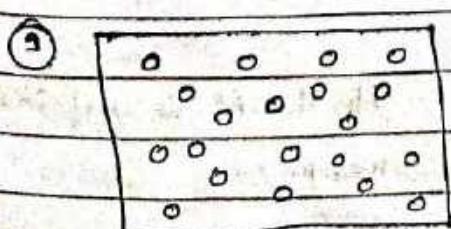
→ Spontaneous instability & subsequent dewetting.



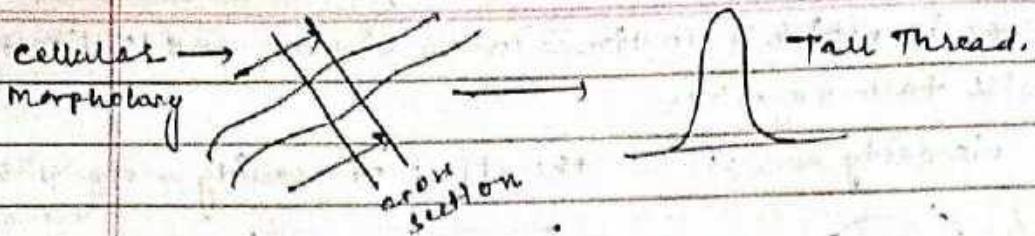
Amt. of bulk is very less

so interface is dominating

bulk IB numerically overshoots interfacial energy



disintegration of the ribbon and droplet formation



### Rayleigh - Plateau Instability



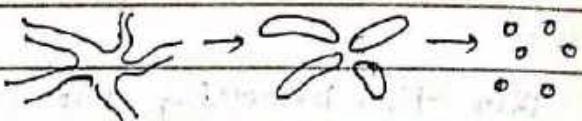
Narrow Liq. Thread

responsible for flowing of tapwater &

Waterfalls.

Free energy minimization leads to

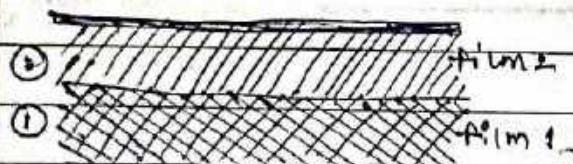
spherical droplet forms from ② to ①



Double coating ← wall painting

thick → To prevent rupture

Walls are rough.

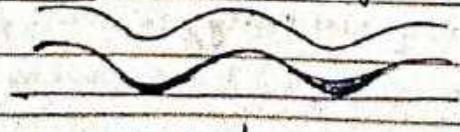


Polymers for first layer should be insoluble for solution in second layer

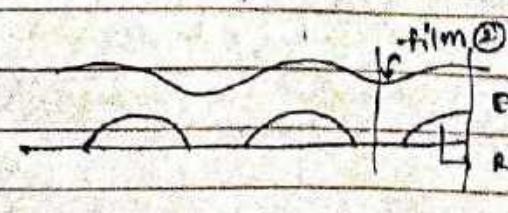
(No reason to assume same thickness of ② & ① as they become unstable simultaneously)

higher conjoining pressure decides rupture

case 1. — Bottom layer becomes unstable:



In phase mode of Instability because the undulations are in phase.



If the  $\pi_1$  is disjoining, nothing happens.



depending on  $P_r$  is higher at  $B_1$  or  $B_2$  there can be 2 pathways,  
rupture takes place acc. to c. pr.

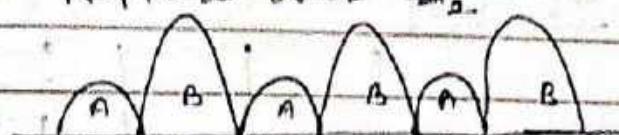
Rupture over  $B_1$ .



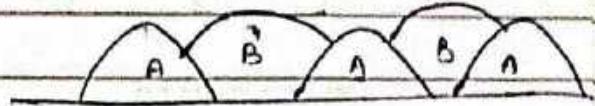
conjoining  $P_r$  is stronger over

$B_1$ : Holes form over the same area.

Rupture over  $B_2$ .



or



film (2) ruptures over film (1)  
and takes some area over  
Ⓐ to some interfacial area

case 2. 1- Top layer becomes unstable

is there any difference in  
the nature of interfaces.



(B) interface is liq-liq so it  
can deform.

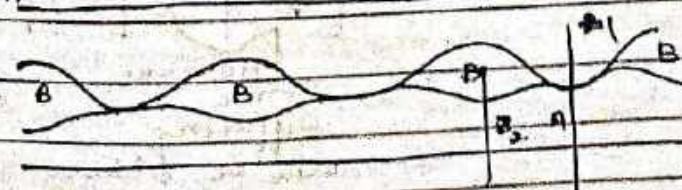
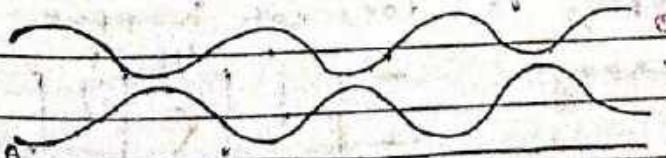
Ⓐ & (B) ?  
film-film  
interface  
surface  
+  
solid-liq.  
liq.  $\downarrow$  liq.  
can deform

if one liq pushes  
another downward rigid. Interface.

3rd law of Newton

Another will be pulled upwards

out of Phase Mode  
⇒ of instability



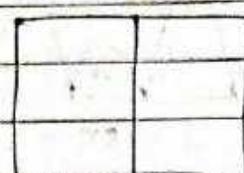
18/03/23

Patterns → somewhere between Micro & Nano.

metamaterials → are refractive index materials which can lead to invisibility.

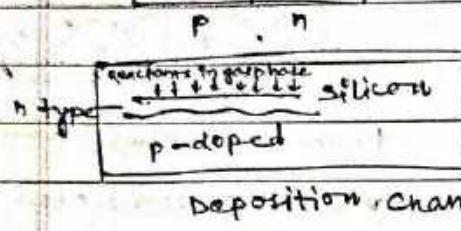
Biggest application area of patterning → micro Electronics industry

Just for knowledge

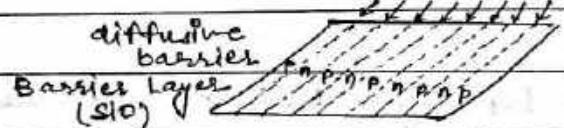
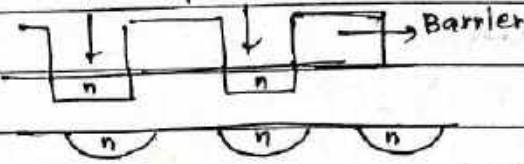


p-n Junction

p-n junction is formed at the boundary b/w p-type and n-type semiconductor



n-dopant



barrier layer should be enough to avoid diffusion to n-dopant

To have a faster process, more no. of p-n jns → add more processes  
 making n-layers narrower → to avoid ↑ size  
 ↑ the no. density of the layers) of devices.

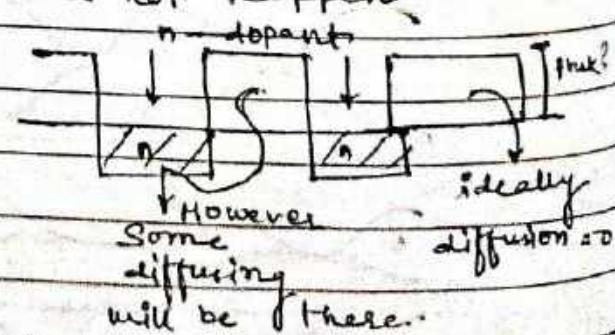
make device bigger

① Take a Si Wafer

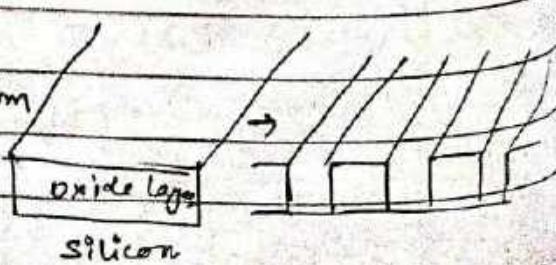
② Growth an oxide layer

Silicon has lower Surface Tension higher Surface energy so oxide just grows when exposed to the surface.

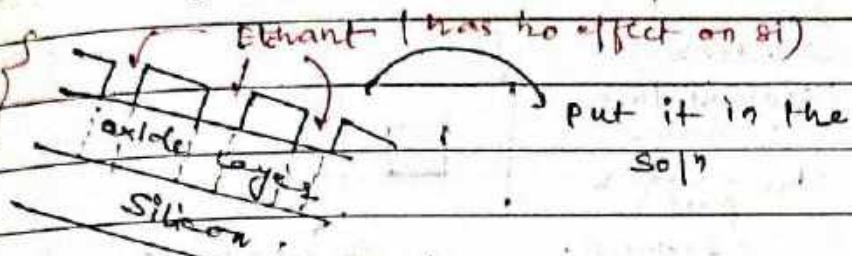
As the natural oxide layer's thickness ( $1.5 - 1.8 \text{ nm}$ ) is enough  
 diffusion of the doping  $\text{F}^{+}/\text{n}^{+}$  does not happen.  
 → No. Unlikely not enough.



③ We want to remove the oxide layer from some places as strips.



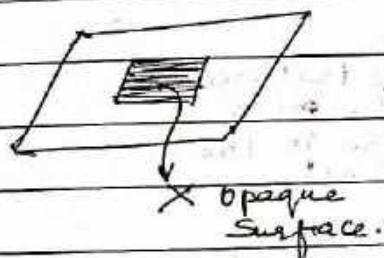
Some chemicals "dissolve" the oxide layers - (Etching)  
If we put the entire wafer - the entire oxide layer will go away. So we need another layer over the oxide layer which we can pattern more easily so that when we take the oxide layer to the chemical soln, only parts of oxide layer gets dissolved.



What is the top layer we have introduced? How are we coating it? Spin Coating. Photo Resist Layer

a chemical that undergoes "changes" in property when exposed to light

Ex. X-Ray Plates



So we introduce photomask so that some areas get exposed to light & some don't (remain opaque)

- ① "Changes"  $\Rightarrow$  photoresist is a generic word.  $\hookrightarrow$  the photoresist
- ② "Light"  $\Rightarrow$  not normal light because we want to perform the experiment somewhere  
 $\Rightarrow$  so we use UV but why not Infrared?  $\hookrightarrow$  wavelength more than that of visible light

- ① For 1 type of photoresist only one thing happens but it depends on the nature of the layer  
If we want to pattern the photoresist layer, we take help of mask and then the UV rays.

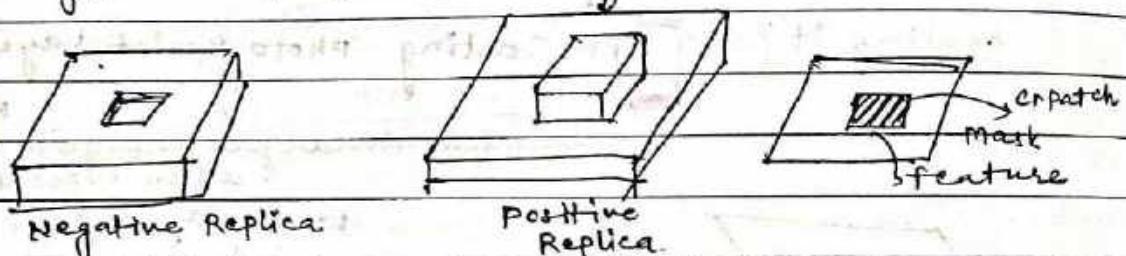
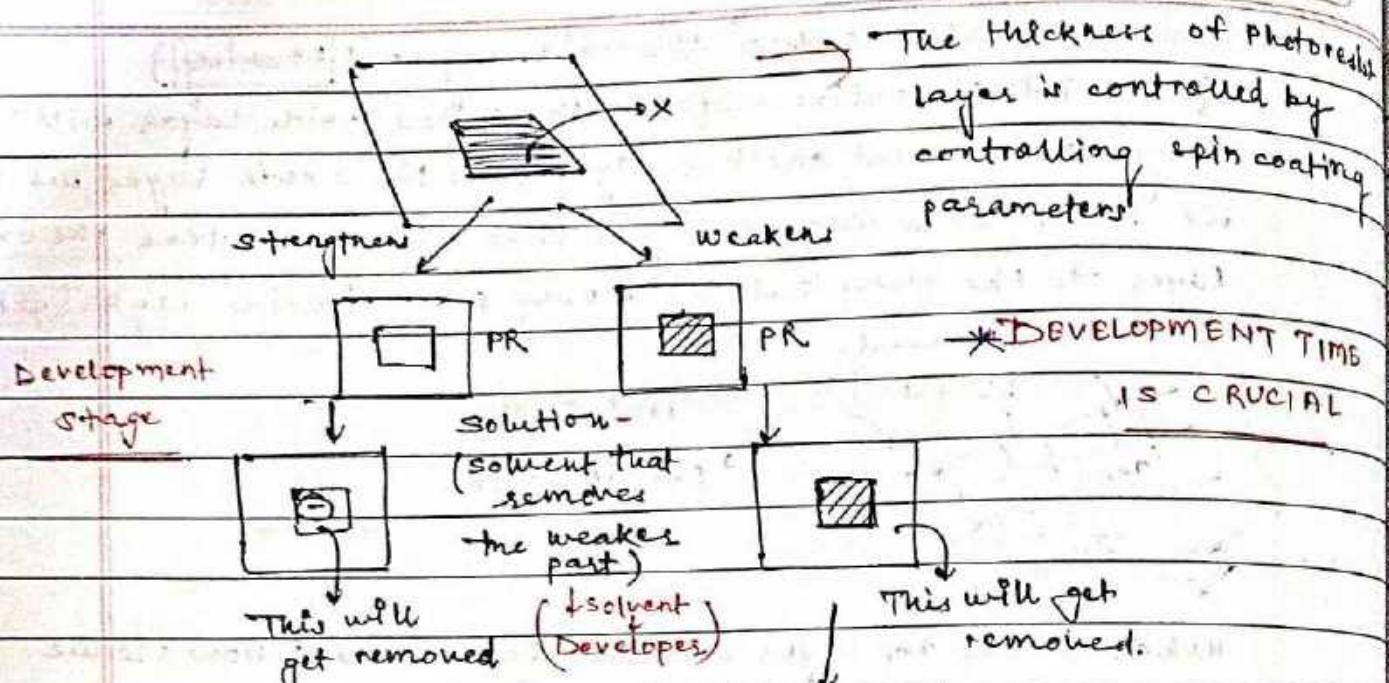
The type of photoresist upon exposure strengthens and the other type degrades.

Now, the photoresist will remove the weaker part in both the cases (the exposed and the masked part).

Mask → Pure silica glass (Quartz) which allows UV rays to pass and have thin layers (patches) of chromium which does not allow UV light. So when UV light falls from a pattern.

Page:

Page:



(wherever the features were in mask they are not there in the pattern)

(where the features were in mask the same are in the patterns)

This determines the type of PhotoResist

A PR that creates the replica is a -ve photoresist

A PR that creates the replica is a +ve photoresist

\* Weakening means as compared to others areas some chemical modifications have happened which will make the exposed part easier to dissolve. (strengthening → difficult to dissolve).

\* Photoresist → Polymer → Long chain

Key difference between the stronger & weaker part

Patch weakens → [Chain length ↓] → hardening  
chains become shorter on exposure

Patch strengthens ↑ chains become longer on exposure  
(viscosity ↑)

Silicon wafer → Photo Resist → Spin coating → Mask → Optical source

Etching ← Developer ← Mask Aligner



Date : / /

Page:

~~oxide~~ → An oxide covered pattern which have photoresist coating.



In the example, one resist has been used.

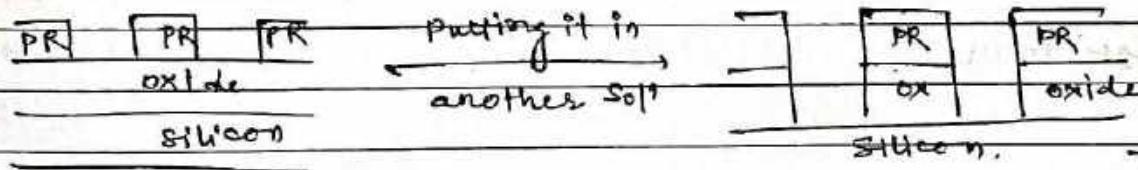
Why is development time crucial?

- \* If the exposure time is too long, the weakened as well as the strengthened part will go away.
- \* If wanna play safe, you may underdevelop. (not letting weakened part to completely wear off).
- \* Development time depends on thickness of photoresist

$$\text{Development Time} \propto (\text{Thickness})_{\text{PR}}$$

mgmt plan (-2)

④ Now our objective is to ~~solve~~ dissolve the oxide. (Etching)

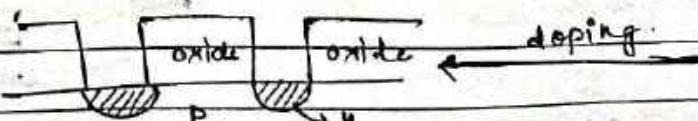


We have created spatial window for access to wafers.

⑤ Now we remove the strengthened photoresist layers.

Again dissolved in development solution. for a longer time

(PR → weak polymer layer → fails to withstand Si  
the harsh cond's of doping rxn. So diffuses with the dopants and forms some useful substance)



⑥ Then doping is done.

In chip we don't need

The oxide layer → so remove it by etching

Etching oxide layer along the contours of the pattern

## Photolithography

- 103/103
- ① Wafer cleaning or surface prep :- wafers are chemically cleaned to remove particulate matter on the surface as well as any types of organic, inorganic and metallic impurities.
- ② Barrier layer or growing an oxide layer :- Si surface  $\rightarrow$  ↑ surface energy and oxidizes immediately in contact with air. This oxide layer is very thin ( $1.5 - 1.8 \text{ nm}$ ). This silica layer itself cannot be used as a barrier. So,  $\text{SiO}_2$  layer is grown on the wafer at this stage.
- ③ Photo-resist processing - we want to remove oxide layer as strips from some places. Some chemicals dissolve the oxide layers (Etching). If we put the entire wafer, complete oxide layer will go away. So we need another layer over oxide layer which can be patterned easily and then only strips of oxide layer gets removed (dissolved).
- So we introduce Photo Resist to be coated on the substrate by the method of spin coating. Photo resist is a special class of photo sensitive polymer which undergoes changes when exposed to light. So we introduce Photomask so that some areas get exposed to light & some don't. We don't use normal light but UV because we want to experiment somewhere and some will require light. We don't use infrared because it is less than visible light. So required magnification / resolution might become a problem.

Step 01 :- ① Dehydration & priming - before resist is coated, wafer must be free from moisture and contaminants both of which cause severe problem in resist processing.

Dehydration baking  $\rightarrow$  eliminate moisture absorbed on wafer surfaces as hydration ~~surf~~ substrates lead to adhesion failures. performed by heating b/w  $400^\circ\text{C} - 300^\circ\text{C}$ .

After this, the wafer is coated with a pre-resist priming layer which enhances the adhesion properties of the wafer.

Resist coating must follow as soon as possible after priming.  
 $\text{HMDS} \rightarrow$  Hexamethyldisilazane  $\rightarrow$  primes.

Hard Bake  
 $(150^{\circ}\text{C} - 160^{\circ}\text{C})$   
 Post Bake  
 $(110^{\circ}\text{C} - 130^{\circ}\text{C})$

P Date : / /  
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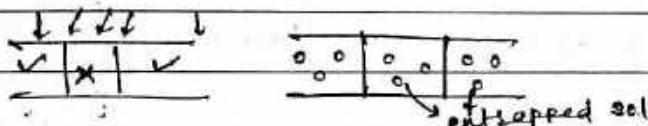
Mark

① spin coating — relatively thin film of a specific thickness  
 resist coating dispense the → molecules traveling → splash drainage → evaporation  
 drop from center to edge from the edges → evaporation  
 parameters affecting film thickness: ① RPM ② dispersed drop vol.

③ choice of solvent ④ duration of spinning ⑤ ambient condition (humidity)  
 rate of evaporation

$(90 - 110^{\circ}\text{C})$

⑥ soft baking — after spin coating, because of long chain structure of polymer there is an internal net formed which cause solvent molecules to remain entrapped and not evaporate. We want entire depth of film to change properties on exposure to UV light. However solvent molecules (10-20%) don't change properties. So, soft baking is the process of heating by which we want to remove solvent molecules which still remain entrapped.



over soft baking — degrades photosensitivity of resists by either reducing developer solubility or actually destroying a portion of the sensitizer.

Under soft baking will prevent light from reaching sensitizer and positive resists are incompletely exposed if considerable solvent remains in the coating & under soft baked the resist is readily attacked by the developer in both exposed and unexposed areas causing less etching resistance.

⑦ exposure ⑧ development ⑨ post development inspection.

photomask — opaque plate with holes or transparent holes that allow light to shine through in a defined pattern. Lithographic masks are typically transparent fused silica blanks covered with a pattern defined with a chrome metal absorbing film. Use ebeam/laser/x-ray to strip off chromium.

⑩ mask alignment → to align features on a substrate to features on a photomask.  
 ⑪ expose to UV ⑫ develop ⑬ hard bake ⑭ etch ⑮ resist strip.

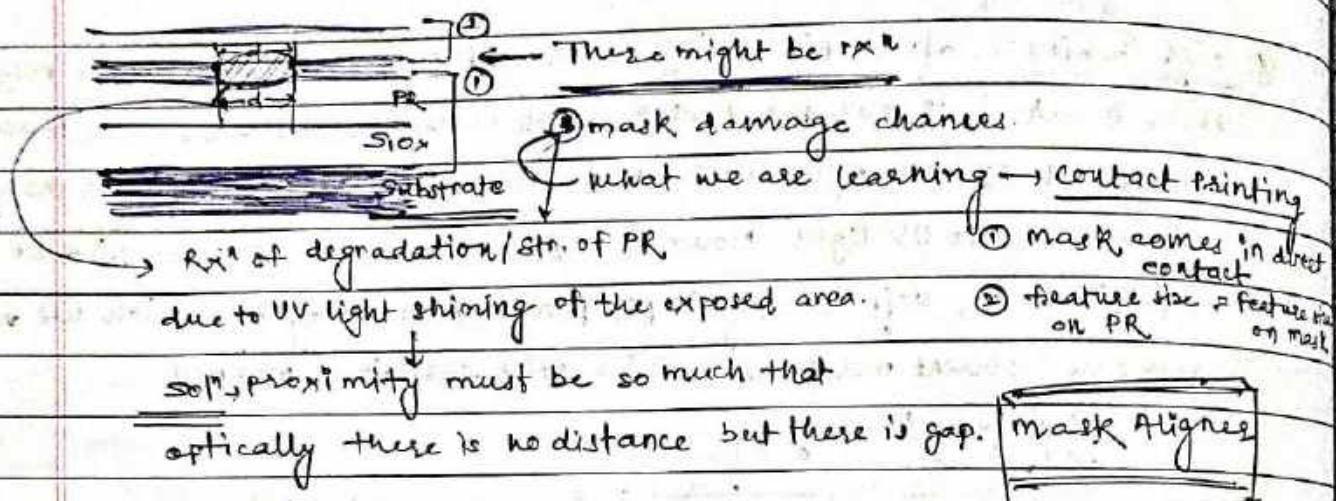
Photolithography is a secondary patterning technique, The primary patterns are formed on the mask, photo lithography just Xeroxes it.

Postbake → performed after exposure, at temps slightly higher than soft baking

Developing → final baking step to ↑ stiffness of the patterned photoresist

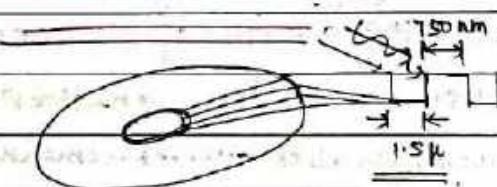
Hard bake → ↑ layer and ↑ adhesion as well.

The pattern on chromium coating is made by bombarding it with  $e^-$ . (electron beam)  $e^-$  beaming technique is not used on oxide layer becoz it takes lots of time and is an expensive method (use multiple times)



29/03/23

### Structural colours.



**size effect** → light with different wavelength gets reflected from different locations on a structure (topographical pattern) (some depth)

For → structures which have length which is comparable to size of the wavelength light reflects the surface

$$\text{diffraction limit} = \lambda/2$$

UV 200 nm (200 nm)

$\rightarrow$  if we have a slit 400 nm. But if we start taking smaller and smaller slit light will stop entering at some  $\lambda \sim 100$  nm and thus no rainbow form (structural colour)

\* If we want to make smaller patterns what can we do?

① Use light of smaller wavelength.

② Using photore sist material which undergo structural changes as a response to the light it is exposed and not any random light

Theoretically,

- B. why we cannot use PR that responds to white light?  
 work in a well lit lab. → so unmanageable to work with  
 labs are lighted well

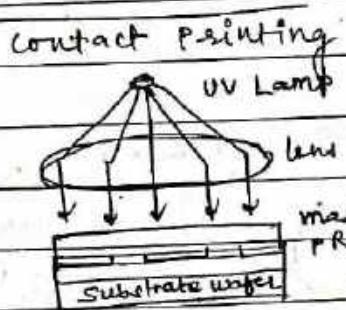
- C. why only UV and not Infrared?

The feature size becomes large:  $\frac{1}{2} \lambda$  for IR. For UV we can make smaller patterns.

Scientifically, we cannot go beyond 100nm.

Iphones / newer ~~different~~ gadgets use linewidth smaller than 20nm? How? It is well below diffraction limit

### Optical Exposure !



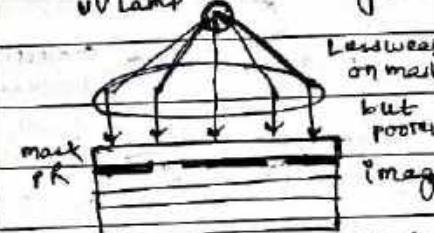
- resist coated silicon wafer
- kept at physical contact with the photomask during exposure

- because of the exposure time resist & mask very high resolution is possible in contact printing (1-micron feature)

- The problem with contact printing is that debris, trapped b/w the resist & the mask can damage the mask and cause defects

#### Proximity printing

no changes of mask damage



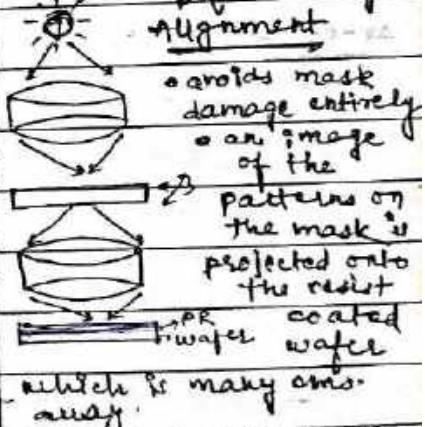
- similar to contact printing except there's small gap
- M/D to 25 microns, i.e. maintained b/w the wafer and the mask during exposure

- gap minimises but does not eliminate mask damage approximately 1 to 4 micron resolution is

- possible with proximity printing

• photoresist exposure is full bottom

#### Projection Printing

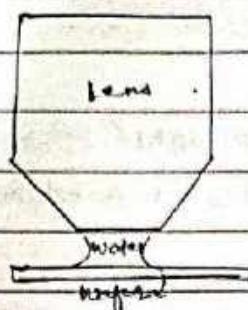


- in order to achieve high resoln, only small portion of mask is imaged

- This small img field is scanned or stepped over surface of wafer. The projection printers that step mask img over wafer surface are called step-and-repeat systems

- capable of approx. 1 micron resolution.

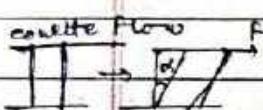
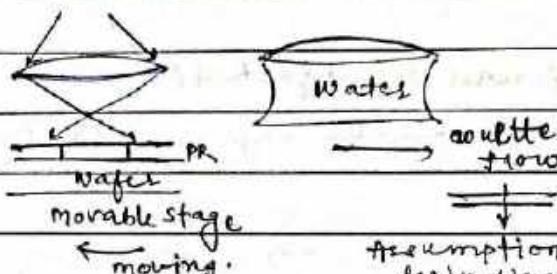
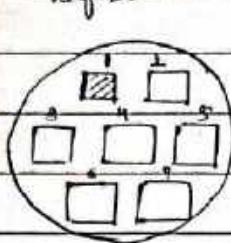
No eq<sup>n</sup> — Newton's 2<sup>nd</sup> Law for flowing system.  
 Valid for Newtonian liq. only. Navier's eq<sup>n</sup> (cauchy Eq<sup>n</sup>)  
 Stokes fluid. for Non Newtonian fluids,  
 Thd Pr. = Mechanical Pr. (Pr. due to Translational KE) Page:



Immersion Lithography — replaces usual air gap w/ fluid  
lens and wafer surface with a liq. med. that has  $RI > 1$

change in numerical aperture  $\rightarrow$  enhancement

Resolution is  $\uparrow$  by a factor equal to  $RI$  of the liq.



to get pattern at different locations (1, 2, 3, 4, 5, 6, 7)

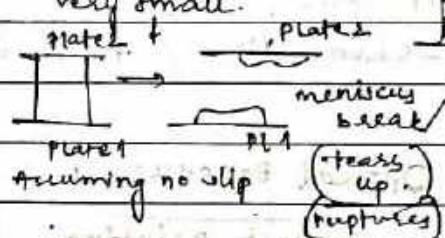
$\rightarrow$  Post-bake ( $110^\circ\text{C}$  -  $120^\circ\text{C}$ )

$\rightarrow$  after development

$\rightarrow$  Hard bake ( $150^\circ\text{C}$  -  $160^\circ\text{C}$ )

Assumption in derivation of Couette Flow + deviations are very small.

To form interface again we need to introduce making up of



assuming no slip

(tears up ruptures)

## 24-03-23 Photo Lithography! —

### Advantages

most of the problems are overcome.

by soft lithography

Objective  
① feature size  
is diffraction limited.

② Technique is directly applicable to the photoresist

### Limitations

③ requires elaborate Etching setup.

(light source cost)

total flat surface

nothing natural is flat

Yellow Room  $\rightarrow$  cutoff several wavelengths of light, where processing occurs.

planar

We want to pattern several other types of polymers, gels & others (planar)  
thermosetting thermoplastic materials.

Sol-gel technique  $\rightarrow$  primarily makes inorganic oxides by soft processing

Photolithography was highly material dependent. We want to achieve patterns on non planar surfaces.

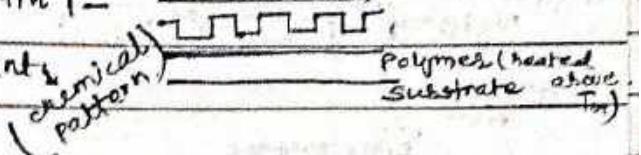
No particular technique called soft lithography  $\rightarrow$  a set of soft collection of different techniques

Photolithography is a specific technique

idea about Soft Lithography

Whatever is the technique we start with:-

example of Soft Lithography → Thumbprint



\* corneal surface & eyelid never come in contact due to lubrication by tear layer/film when a dust particle comes falls the film, ruptures and dust particle comes in direct contact with the cornea and causes irritation. Tear film is not very thin. So there is spontaneous rupture.

by soft lithography we are producing a ~~replica~~ replica! —

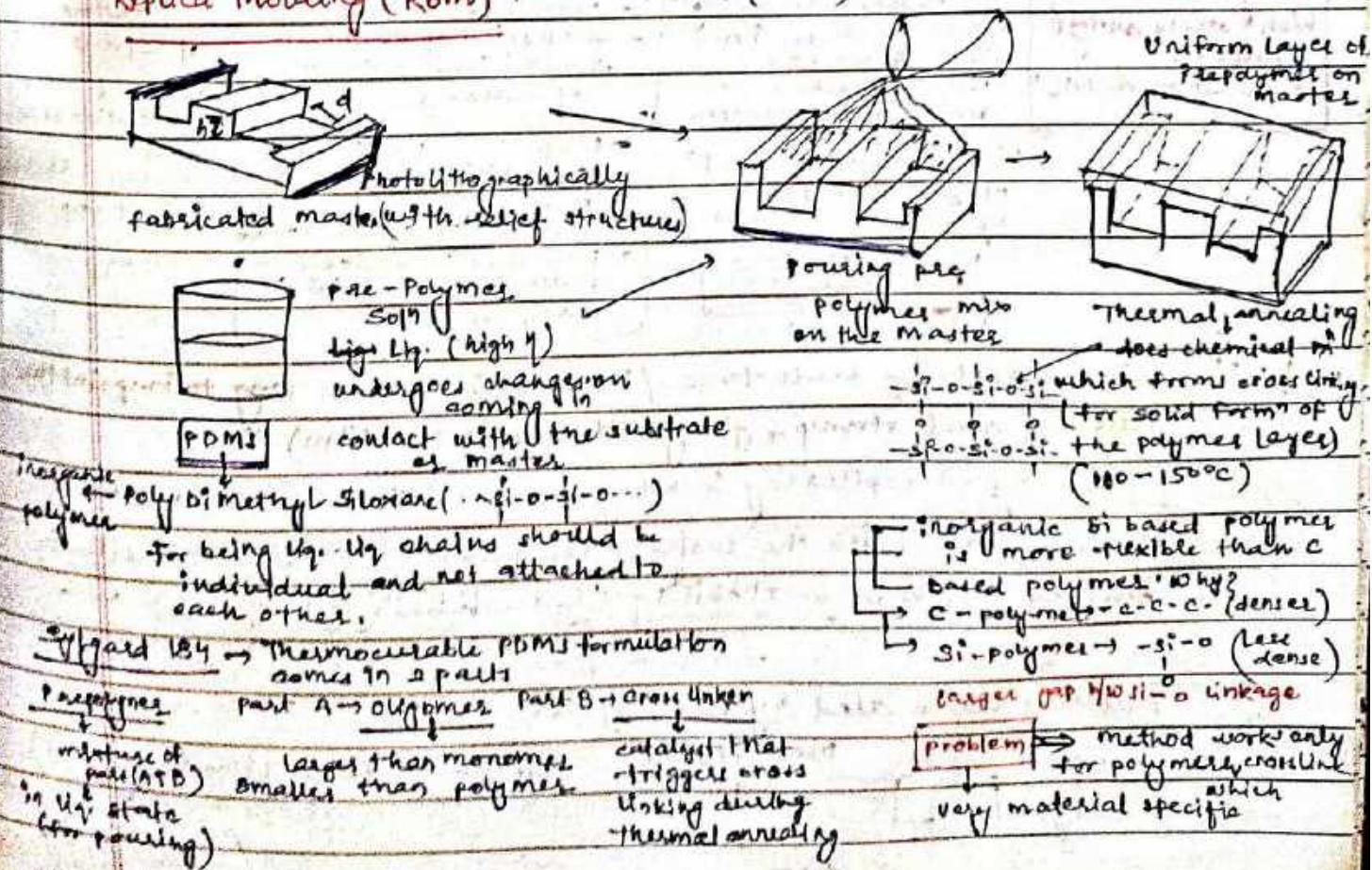
① It is a secondary process, the primary one lies when mold or stamp is pressed onto the polymer-substrate layer.

② It is a parallel process.

Based on the Nature of mold or stamp used

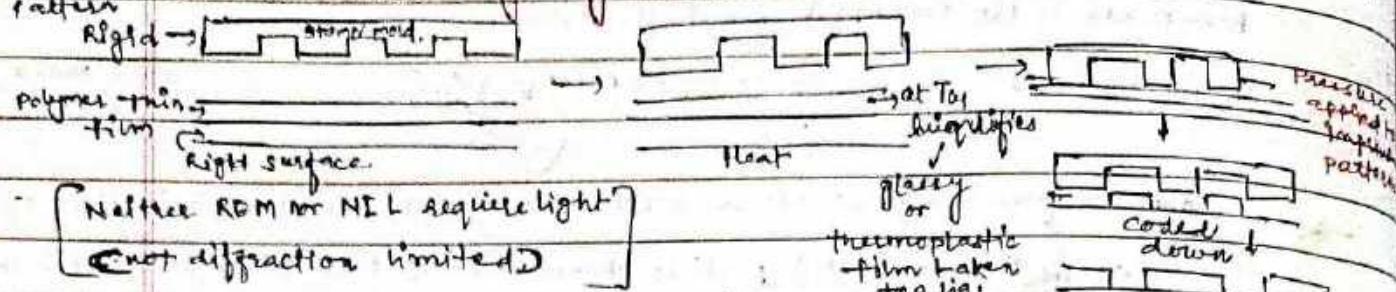
- [Fabricated by RLM] pave the way for
- +flexible → patterning of a non-planar surface
- Rigid → good candidate for rigid stamp?
- Dissolvable → microphotolithography
- pattered Photore sist Layer

Replica Molding (RM) :— Whitesides (1995)

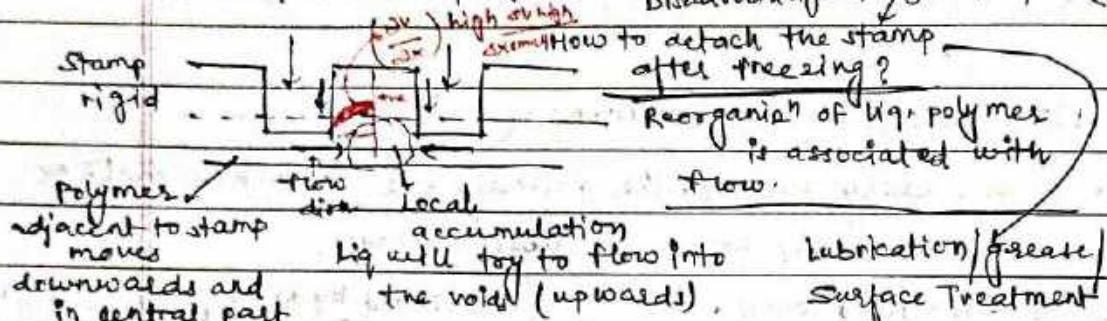


can be used for all thermoplastic polymers (anything that has a Tg)

Master (Nano Imprint Lithography (NIL)) → Stephen Chow (15-30 yrs old) more generic than RIM.



Applied to imprint the patterns Disadvantage of rigid stamp (-ve replica)



Consequences of high shear stress. NIL is associated with very high shear stress.

smaller is the feature size higher is Tg.

Why is there very high stress during pattern replication via NIL?

During freezing we are making viscosity higher. So stress ↑ even more. A workable viscosity which lets alterations to happen

Viscosity changes as a function of Temp.  
So the stress gets stored in the structures as residual stress.  
So increased pressure

- non planar surfaces cannot be patterned using NIL
- critical parallelism w/o mold & film has to be ensured
- high T & high Pn
- adhesion of mold with resin! severe chances of damage

- large area patterning capability
- more generic
- resolution achieved  $\sim 10\text{ nm}$
- possible to achieve patterns over fairly large area.

Slip Boundary Cond<sup>n</sup>

no slip finite vel. Slippery ground

b = slip length

vs = slip velocity

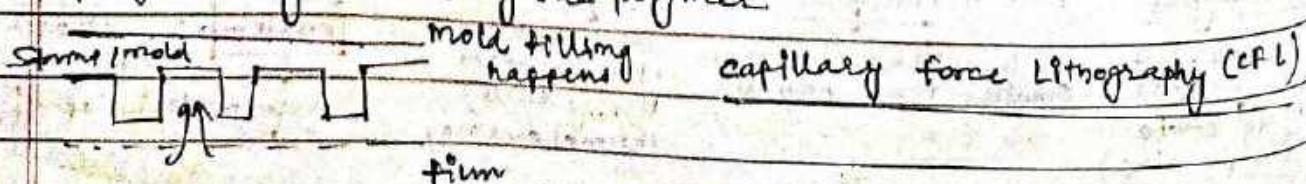
Benefits of slippery surface!

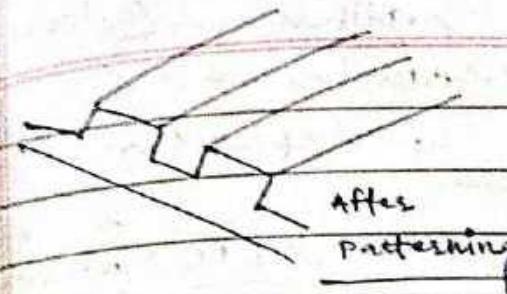
Lubrication/surface treatment of stamp in NIL

→ stress & cost of violation of no slip → easier detachment of stamp

29/03/23 without applying brute-force / pressure is there a way to imprint the patterns (rigid stamp + glass or thermoplastic film)?

Capillarity → capillarity is not guaranteed the moment we bring a lig. in contact with the surface. The necessary cond<sup>n</sup> for capillary rise/depression is wetting (hydrophilic) (hydrophobic), as meniscus face up meniscus goes down preferentially wetted by the polymer





If the geometry of the mold is same we will get the same pattern on both CFL & NIL.

Difference in requirements CFL v/s NIL :-

No need to apply force (CFL)

Stamp may not be rigid (CFL) since it does not need to withstand the pressure. We can easily use a flexible stamp (we get form).

The only req. being wettability of the flexible stamp.

Attachment is easier

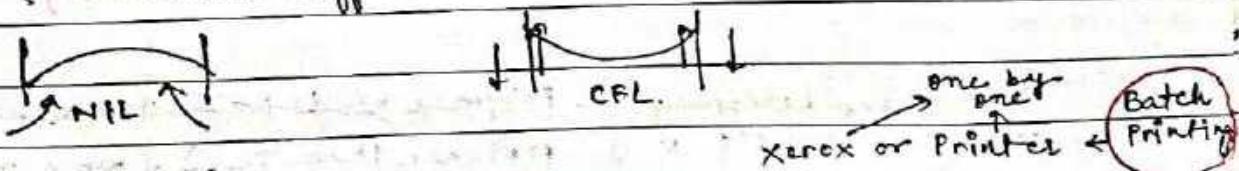
(Q) NIL is a generic technique whereas REM is not  $\rightarrow$  bcoz REM works with a particular class of material (material dependent) + CFL/NIL are material independent.

Once fully patterned we cannot conclude if its done by REM/NIL or CFL  $\rightarrow$  pattern replicated by CFL will not have residual stress but with NIL it will have residual stress.

Both the processes need some finite time (time reqd. for mold filling).

Difference in the intermediate (incomplete structures) of CFL + NIL?

What is it?  $\rightarrow$  Visible difference in meniscus



Can there be any continuous Lithography?  $\rightarrow$  printing of paper in a press

Paper is flexible. So conclusion  $\rightarrow$  continuous lithography is flexi possible provided the surface is flexible.

However we usually see batch process (Lithography) around us.

## Roll-to-Roll Nanoimprint Lithography :-

Nano patterned surface

Imprinting Roller

Speed of the rollers and the moving substrate is critical.

Heating  
(so that viscosity drops)

flexible substrate

How are we ensuring Pr? (Interference?)  
We ensure how close we are going to bring the moving rollers to the substrate  
(stamp) (rolling platform)

Final Pattern  $\rightarrow$  depends on ht. of the stamp

Here pattern height is not going to be governed by ht. of the features.

It depends on how close we are bringing the rollers. The max. ht. we can get is  $h_p$  - of the replicated pattern. So we can adjust the proximity b/w the 2 rollers and we can get structures of different heights by controlling the penetration of the rollers in the Uliquified film.

In normal NIL cooling happened when the stamp was in place

Here, cooling is happening when the stamp is not in place. Just before the heating zone we have a film in the low viscosity zone. So the patterns will have a tendency to flatten out (Laplace Pr.) As we have a patterned surface with different pressure zones around it. So, we will have to do rapid cooling very fast after rapid heating.

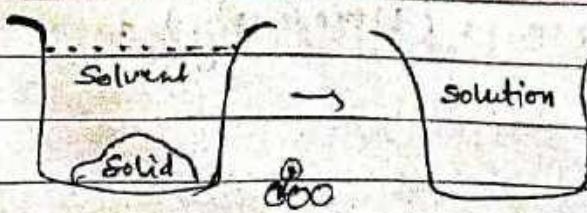
Material dependent as it only happens on flexible surfaces.

How to get same ht. after roller NIL? - (imp. arises)

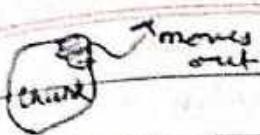
NIL if one necessary for Polymers needs to be taken upto liq. state CFT cond? (Higher than  $T_g$ )  $\rightarrow$  (when molecules have enough energy to overcome entanglement effects & viscosity)

30/03/93

Any other means to Uliquify the polymers? - (Dissolution)

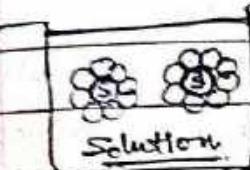


Looking at it from the viewpoint  
① Solid - liq interface gets destroyed  
Why would a solid / solute dissolve in a solvent?

 A diagram showing a solid "chunk" being dissolved by liquid molecules. The liquid molecules are shown as small circles surrounding and interacting with the solid chunk.

chunk disintegrates from solid in the presence of the liquid. The solid would like the liquid to spread over it.

Q spreading coeff. — The necessary bond for dissolution can be related to spreading coeff. Liq. molecule is coming into our system because of its ability to interact (attract). The solid dissolves when solid molecules find it easier to interact with liq. molecules than it is with solid molecules. So the strength of adhesive attraction should be greater than cohesive attraction, then dissolution happens.



Fragmentation → can be due to adhesion or energy ↑ surface area for mole water molecules to attract

mixing removes concentration boundary layer

saturation — power of water molecules to attract solid molecules get exhausted i.e. no more solute can be dissolved. No more saturation near BL

$S_{sl}$  decides the ability of molecule to allow liq. to spread over it. However, it doesn't allow now to other solid molecules to stay close near it bcoz of cluster of liq. molecules surrounding it.

for dissolving a solute, suppose  $n$  molecules of solvent are req. But the available solute molecules have already exhausted available sites.

Solubility — ability of solvent molecules to surround a solute molecule so when no solvent molecules are available saturation limit is reached.

Q How the T affect solubility?

Q Once the solute molecules dissolve does it still have attraction with solid molecules? — No because interactions are short ranged.

Q K.E. So molecules themselves start running away in different directions Brownian dynamics and its effect is more visible in a rarefied system (gaseous system) bcoz mean free path is  $\approx 10\text{ nm}$

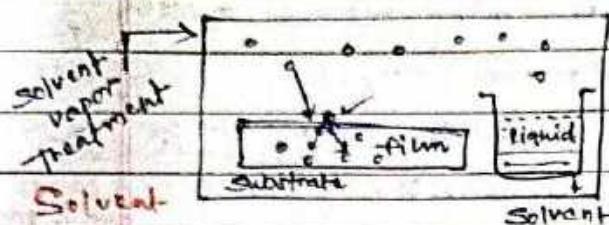
Syllabus  $\Rightarrow$  Inter b/w 2 surfaces + post Q midsem.  
 \* There will be a flask (surprise) test  
 in one of the remaining classes.

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If we take a solvent in very less amount, what happens?

We are keeping the film in an environment which has some solvent molecules but the no. is very less. The container will get filled up

with some liq. vapour because of evaporation. Brownian motion.



will take place and some of these molecules will hit the film surface. The film has a tendency

assisted to spread. So it will adsorb the vapour molecules. This will have

NIL a consequences: — (1) Liq. mol vaporizes & goes to vapour space

(2) water molecules will penetrate into liq. film.

Adhesive inter of liq. molecules with solid is preferred. Within the film the liq. molecules have penetrated. The consequences are:

(1) ↑ the solute - solute space. So. ↓ in viscosity as it is taking the film to a liq. like state. Molecules are more free to move.

(2) The film is accommodating water molecules. So, it will now swell. The solid molecules are now getting surrounded by liq. molecules. But the amount of liq. molecules is less.

This process reduces the glass transition temperature below room T.

$$\text{Flory fox eqn: } \frac{1}{T_g} = \frac{w}{T_{g1}} + \frac{1-w}{T_{g2}} \rightarrow \begin{array}{l} w \rightarrow \text{wt. fraction of polymer in solvent film.} \\ 1-w \rightarrow \text{melting T of solvent} \end{array}$$

room T imprinting

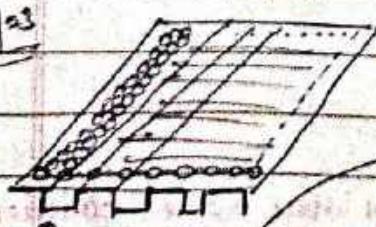
glass transition T of polymers



Pattern Transfer

swelling by taking the film out of the chamber & letting solvent evaporate

5/03/23



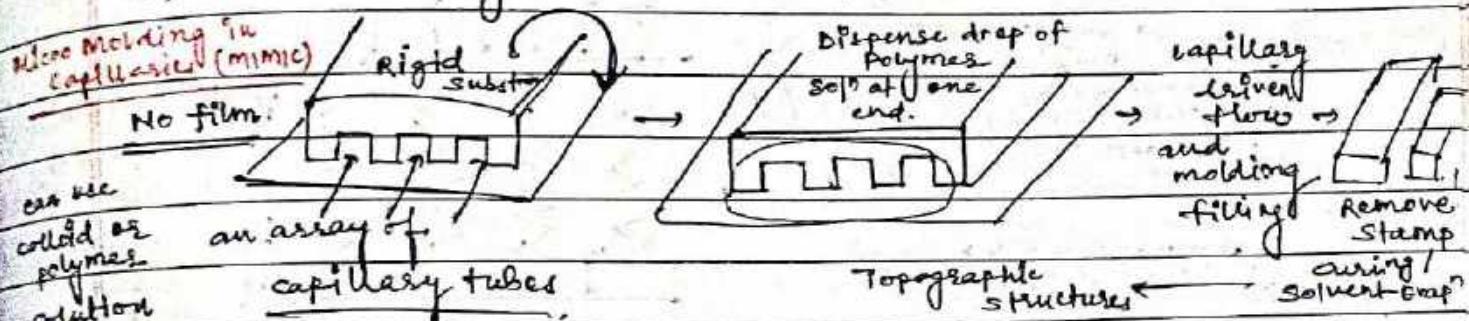
hexagonal closed pack array of monodispersed colloidal particles. → made by spin coating (can b)

How do we make such structures?

Simply imposing any technique is not going to work. Why we cannot do NIL? because the waste portion of the stem will flatten the colloids. can use deep evap but different flows (marangoni & thermal) will lead to coffee ring effect! But if we can mold the system

in such a way that the 2 flows go in opposite dir<sup>n</sup> can generate desired results.

what we actually do?  $\Rightarrow$  To make hexagonal closed mark array  
 $\Rightarrow$  Replica molding flexible stamp.



The technique is based on the spontaneous filling of capillaries formed b/w 2 surfaces in conformal contact, at least one of which has a recess relief structure. MIMIC is a thd. driven process; the liq. fill the capillaries to minimize the free energies of the solid-vapor and the solid-liq. interface rate of fill is ad. by viscosity & ST.

Problems in MIMIC :- ① for long lengths it will be difficult because the rate of capillary filling ( $\frac{dx}{dt} = \frac{R\sqrt{4\pi\rho g\sigma}}{4\eta L} = \frac{R(\gamma_{SV} - \gamma_L)}{4\eta L}$ ) will not

happen as  $2 \uparrow \cdot \frac{dx}{dt} \rightarrow 0$ .

② dilute solution will evaporate  $\rightarrow$  distortion (evap. mediated distortion)

Difference b/w CFL & MIMIC :- ① dir<sup>n</sup> of capillary flow is different (from

② in CFL the capillary rise is of the molten polymer. However here (viscosity is very high) (length)  
the liquid polymer is used (viscosity +) (length ?)

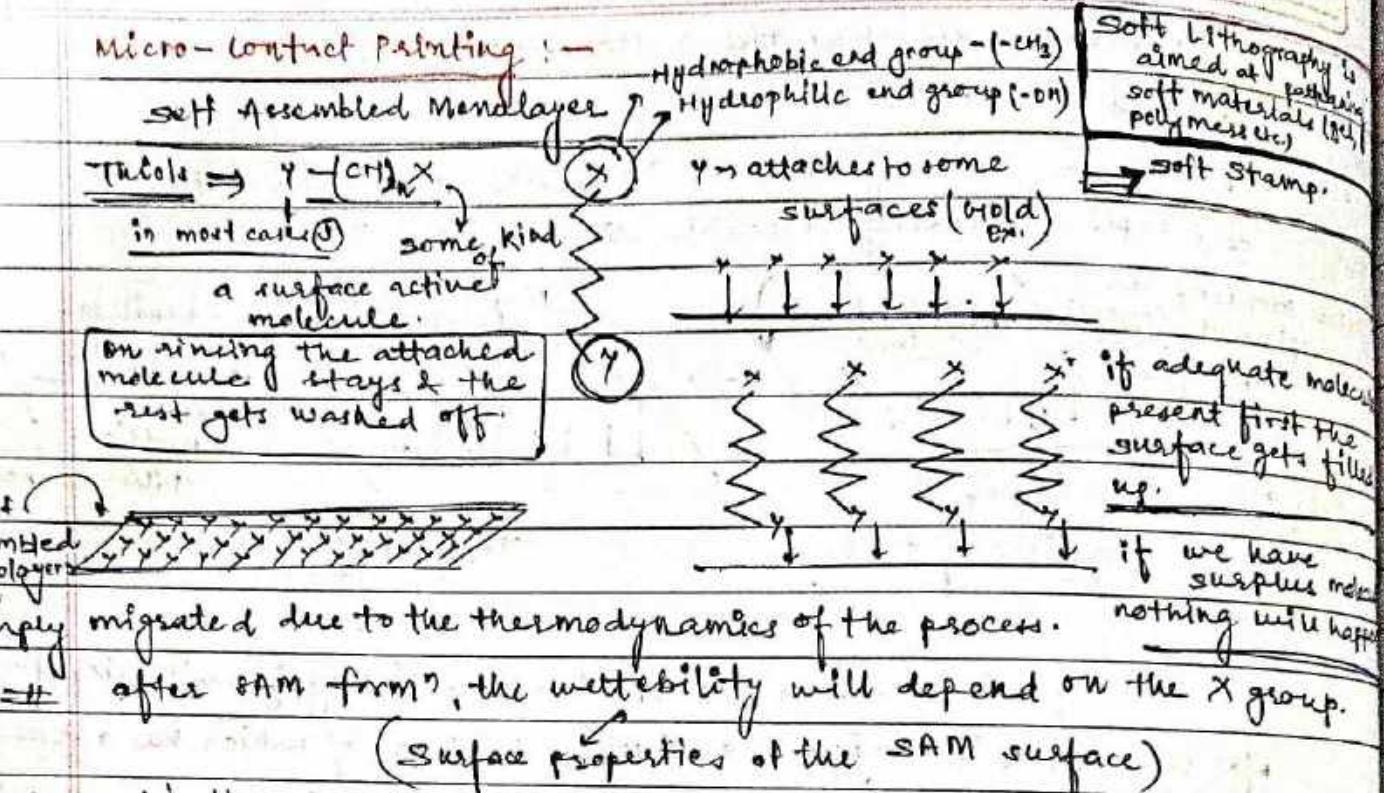
\* if the colloidal diameter is D then the linewidth will be of the order  $\approx D$   
not exactly D.



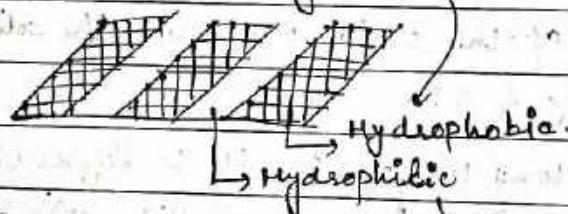
hs will be

# at least of the order greater than D. ( $hs > D$ )

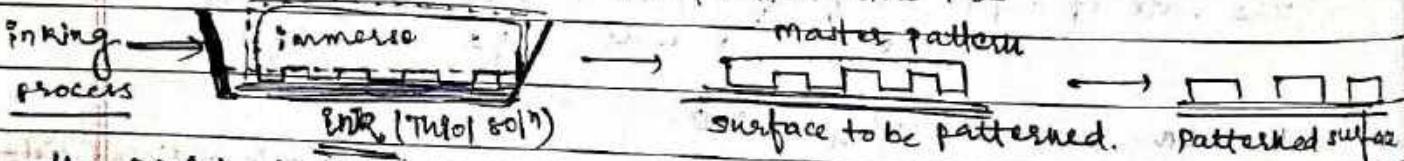
## Micro-contact printing :-



# Objective! — To get alt.

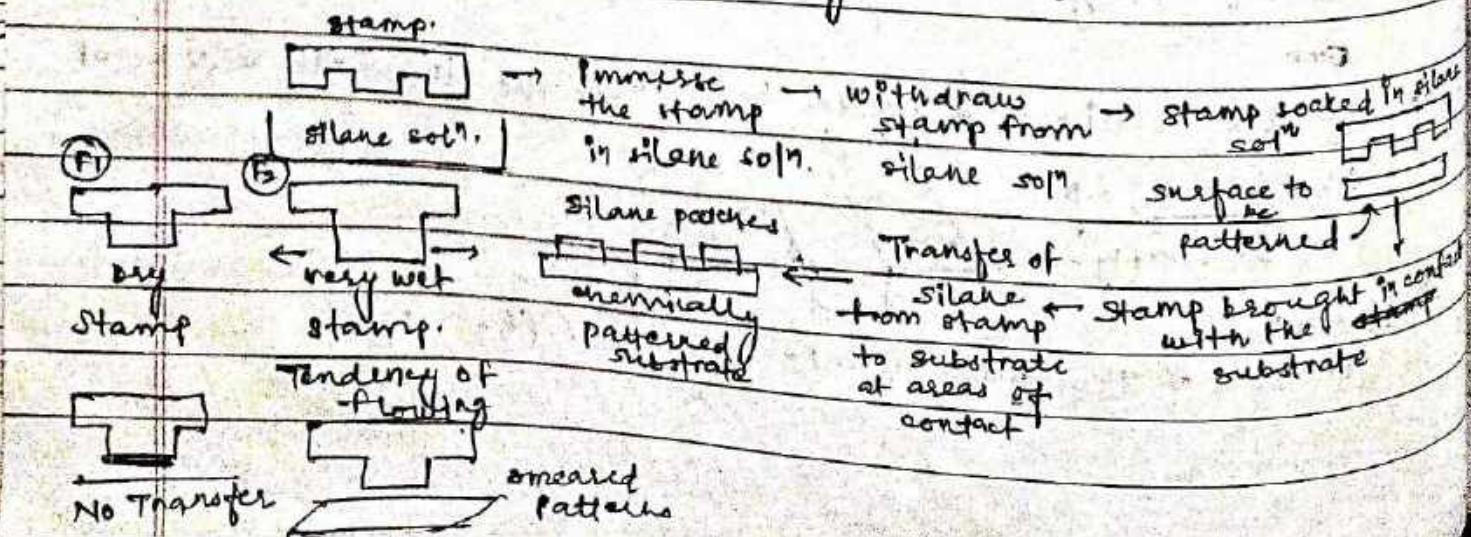


patterns like this



# Thiol should not attach to the master pattern. When patterning transfer no slip could stick with master. patterning on substrate is chemisorption.

Objective! — We want the areas below stamp protrusion to react with each other to not and get chemically patterned domains



Poly(DMS)  $\rightarrow$  Thermo curable polymers  
Silyl-  
Oligo-  
gated.

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Worst Case :- The oil/water meniscus merges and wets a totally hydrophobic surface

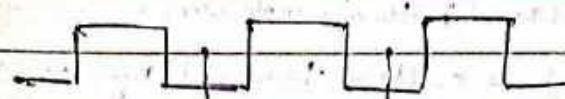
In order to stop spreading in the Ingle : - ~~reduce 1 viscosity~~  
 $\rightarrow$  don't transfer immediately.  
 $\rightarrow$  heating the stamp (with ink) to let the solvent evaporate partially so the solvent allows the particles to swim.



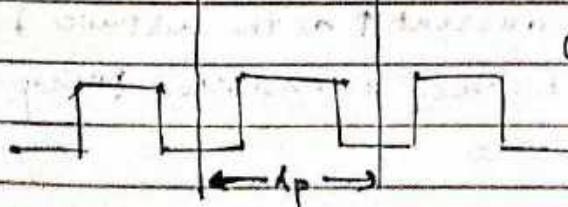
can't take very concentrated thiol soln because then pattern transfer from stamp to surface becomes a problem

as most of the soln will stick to the stamp.

1 limitation / something unachievable by any of the lithography techniques ! - ① Secondary patterning techniques. The original patterns are created somewhere else (mask - photolithography mold / stamp - soft lithography).



how to get different Rs using same stamp ?

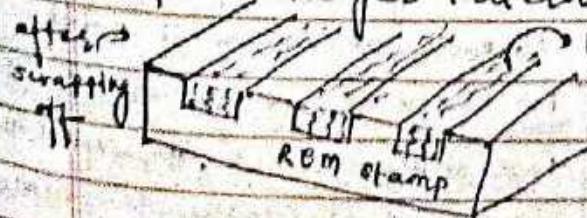


② Whatever structure which we are making is monolayer. There are no multilayer structures.

③ All are batch processes.

Micro Transfer Molding : - UV curable polymers

for multilayer patterns



How do we peel it off ?

(Solvent) vapour exposure

should swell only the stamp material and not the UV curable polymer.

Since only the holding material swells the strips easily get peeled off.

Piezoelectric scanners are made up of piezoelectric material which elongates or contract proportionally to an applied voltage

5/04/23

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## AFM Atomic Force Microscope

Scanning EM microscope (SEM)  $\Rightarrow$

Transmission EM microscope (TEM)  $\Rightarrow$  transmission of e<sup>-</sup>s through sample film  
optical microscope  $\Rightarrow$  uses light beam (white light)

EM microscope - Instead of white light we use e<sup>-</sup> source. (lower, higher resolution)

We need the height in order to determine the structure of patterns.  
No other microscope other than AFM gives info about the depth.

Predecessor of AFM  $\rightarrow$  STM Scanning Tunnelling Microscope was discovered in 1982  $\rightarrow$  Nobel Prize - 1986

Very high tip resolution

Tunnelling current

for sharp metallic tip close to a metallic surface. If we apply a very high voltage, e<sup>-</sup>s will flow through air  $\rightarrow$  tunnelling current

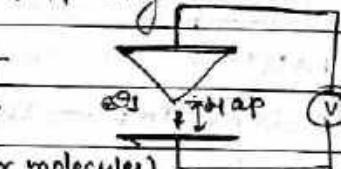
If tip is at a certain height, it creates necessary cond<sup>n</sup> for proper tunnelling,

so occur a very high vacuum bcoz we don't want

to get scattered e<sup>-</sup>s to get collided & scattered (with air molecules)

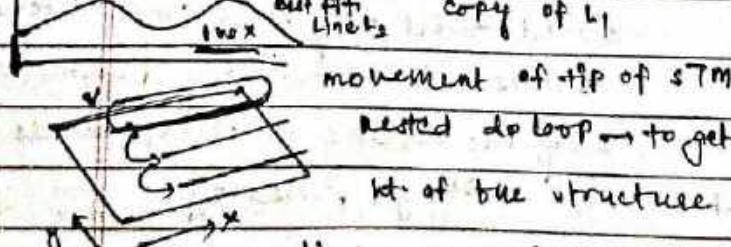
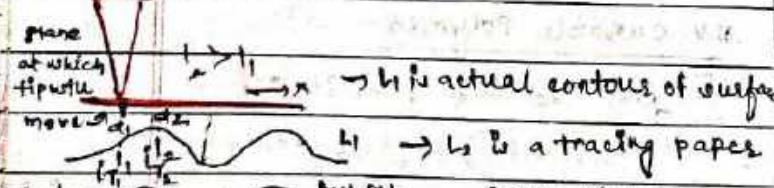
The flow of e<sup>-</sup>s through air is called tunnelling current.

The strength of tunnelling current  $\downarrow$  as the distance  $\uparrow$ . If separation distance becomes zero, it becomes a conductor (very high current if distance  $\uparrow$  current  $\downarrow$  to zero).



### Constant Height Mode

STM Tip



are so much tall that they go beyond red line.

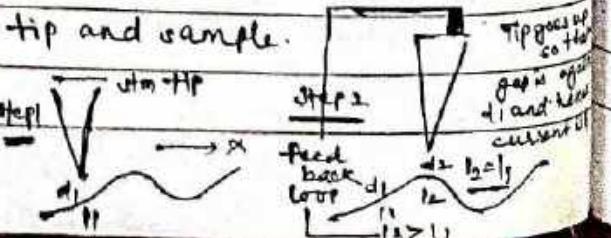
at every pt. STM measured tunnelling current L1 is true surface is mathematically created.

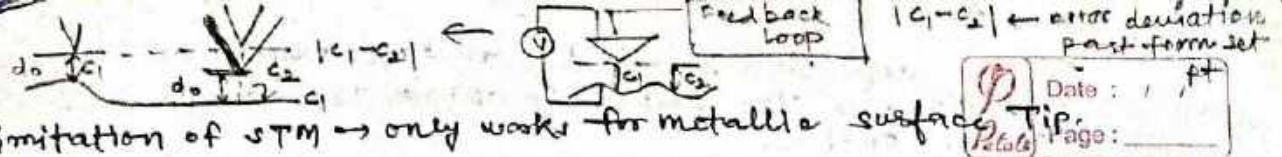
specify set pt.  $\rightarrow$  in terms of current

### constant current mode

STM uses feedback controller to keep the tunnelling current constantly adjusting the height of the scanner at each measurement point.

When the system detects  $\uparrow$  in tunnelling current, it adjusts the voltage applied to the piezoelectric scanner to  $\uparrow$  the distance b/w the tip and sample.





- ① Limitation of SPM → only works for metallic surfaces.
- Surface needs to be pretty smooth if this needs to successfully work.
  - To get rid of this limitation, we use const. current mode where our aim is to maintain current and thus we adjust the ht. of tip accordingly.

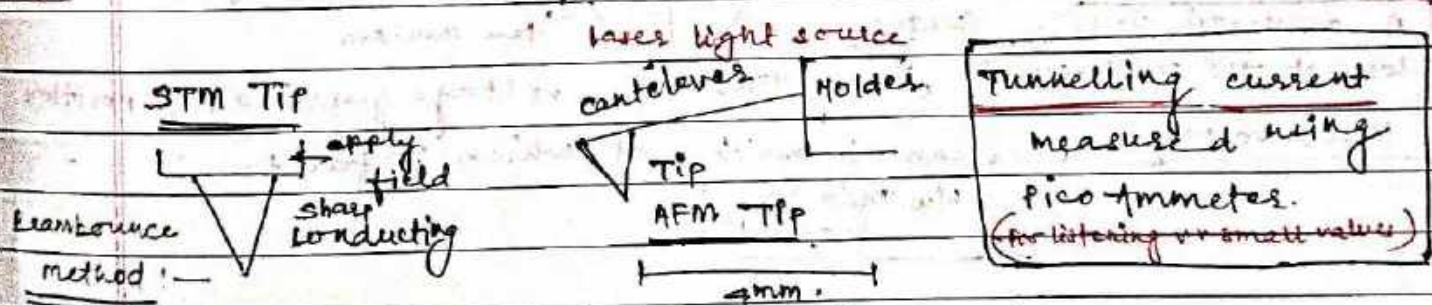
No possibility of the tip colliding with the surface or go so far such that current becomes zero. Tracking the motion of the tip synchronized / in phase to the roughness of the surface.

STM generates ~~image~~ and biggest difference as compared to the microscope is that it does not generate images.

Ques: Can STM be extended to other types of materials? How?

~~AFM has~~ Current → van der waals force [replaced]  
 AFM works on interatomic forces which is present in all types of forces. Interat (intermolecular attraction).

The imaging or inform' about the topography of a surface is done based on the modulation of interaction forces between atoms (or molecules) on the surface.



Tunnelling current measured using picoammeters.  
 (for listening very small values)

How to measure Vanderwaal forces? Universal force field, can we measure Vanderwaal forces? — such minute forces cannot be accurately measured. However, we can compare the forces. If we have feedback controller, the deviation from point to point is enough to measure change.

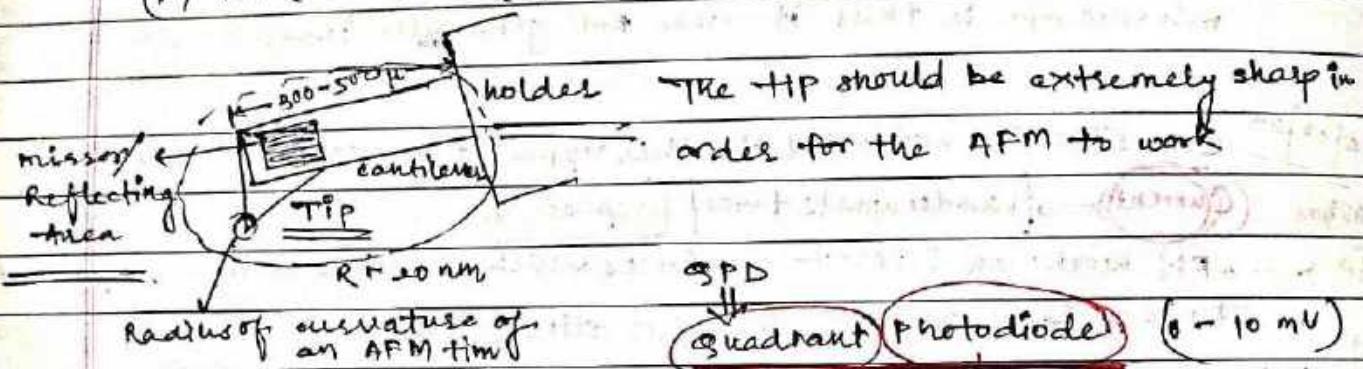
~~cantilever~~! — The cantilever moves following the contours of the sample. picks up information twice (loop). So it picks up while going (trace) and while returning (retrace).

- \* The deflection is detected and mapped as the tip scans the surface to obtain the image of the surface

What is an AFM?

- \* Variation in vdw forces to track the topography of a surface
  - \* The instrument operates based on the interaction b/w surface, the sample and the tip
  - \* The probing tip is attached to a cantilever and the force acting on the tip causes a small deflection of the cantilever
- 3 components we are going to use

(1) Tip (AFM) (2) Quadrant photodiode (3) Laser source.

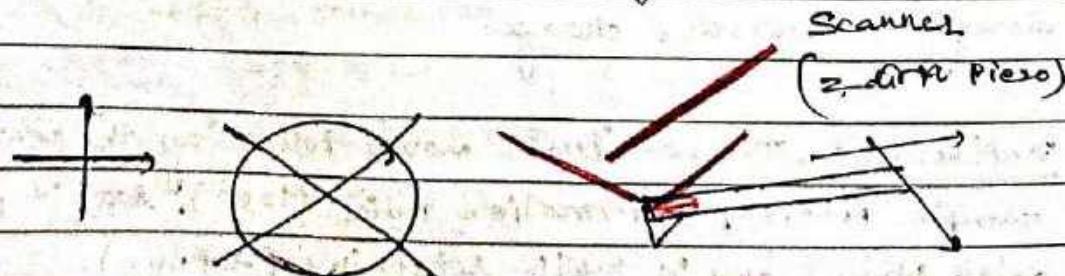


QPD (Quadrant Photodiode) ( $0 - 10 \text{ mV}$ )

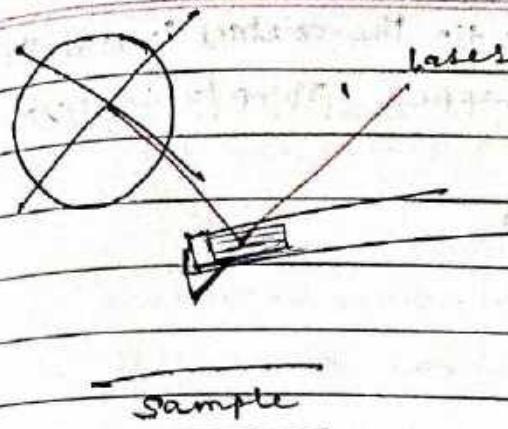
when light falls some voltage gets generated.

A concentric circle closer to the center gives  $0 \text{ mV}$ . The voltage gen. is a fn of position. As the radius  $\uparrow$  radially outward, the voltage  $\uparrow$  (outward). The laser can distinguish at which it falls b/w their x & y coordinates.

- # Laser is falling on the mirror, and the beam gets reflected back to photosensitive photodetector. But the laser and detector are not always coupled.
- # So, what we need to do is  $\Rightarrow$  Alignment



- # Half alignment bcoz we have coupled only 2 of the components



When is it aligned? reading on SPD is zero mV

Where is the sample? Sample is faraway. Alignment is done away from the sample so that the tip does not break.

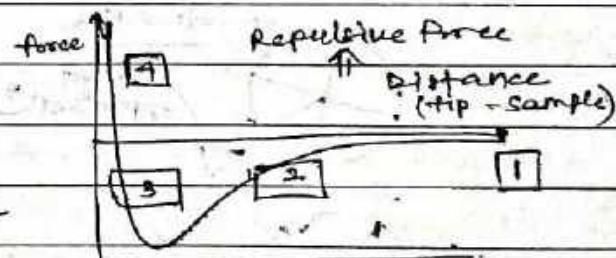
Engage the sample along B with the aligned apparatus.

In most cases, we bring the sample close to the tip mechanically using a ~~sample motor~~ stepper motor.

Where to stop? How close the sample should be brought to the tip?  $\Rightarrow$  operation is called Approach. Physically engaging sample with the aligned tip.

A change is expected between the tip and sample surface when the distance between them goes lower than order of 100 nm.

There will be diffraction in a cantilever.



What is the criteria for choosing the cantilever tip?

⑥ Cantilever should be flexible enough such that it can deform to the strength of van der waals forces. Once the tip crosses the 100 nm barrier, the interaction b/w the tip and surface starts. Eventually, the tip will touch the surface. Cantilever is optically coupled. So, once the cantilever deforms the laser beam will fall somewhere else on the SPD. The tip stoops down as well as the surface is being pushed up, they will meet midway, the contact is established at half a distance, this is known as jump to contact.

jump to whatever

contact ~~of the~~ suppose the cantilever does

not deform the surface moves and touches the tip.

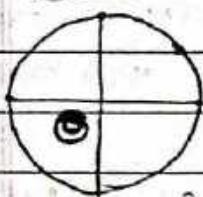
3 mV  
5 mV

- force high
- deform<sup>n</sup> high
- set pt. is further away from centre
- Radius of Curvature for Cantilever reduces

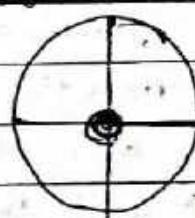
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However, due to sloping of the tip, the contact is established earlier than originally it was going to happen (Jump to contact)

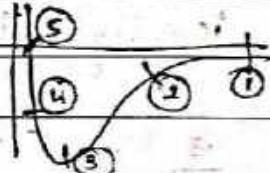
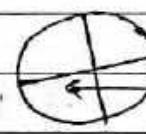
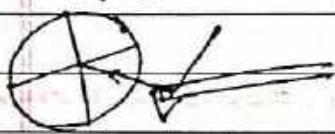
Real



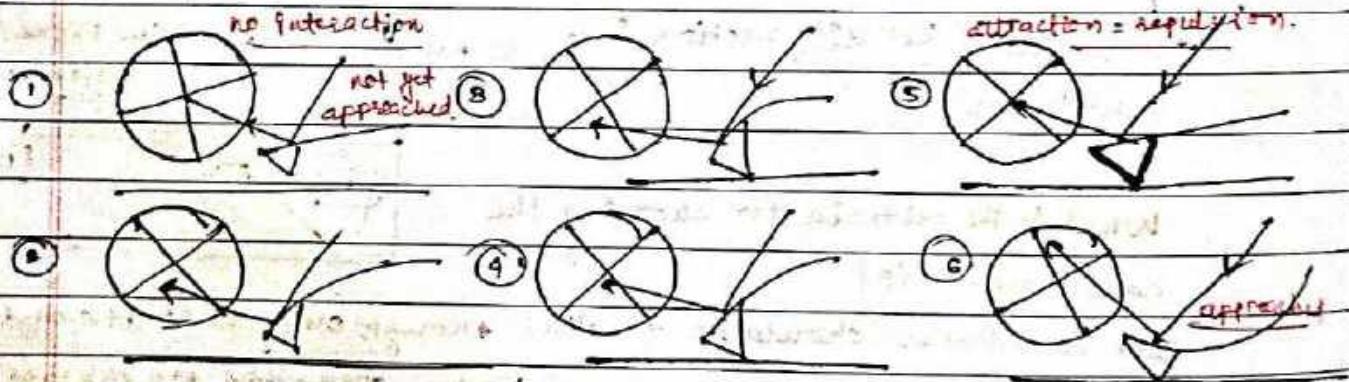
Hypothetical



The tip feels the attraction and the cantilever deforms. Since the tip is mounted on the cantilever it deforms



We continue to approach even after physical contact has been established. At the point of contact, the deformation starts to reduce then it becomes zero and after some time, the cantilever becomes a pivot and then it becomes concave.

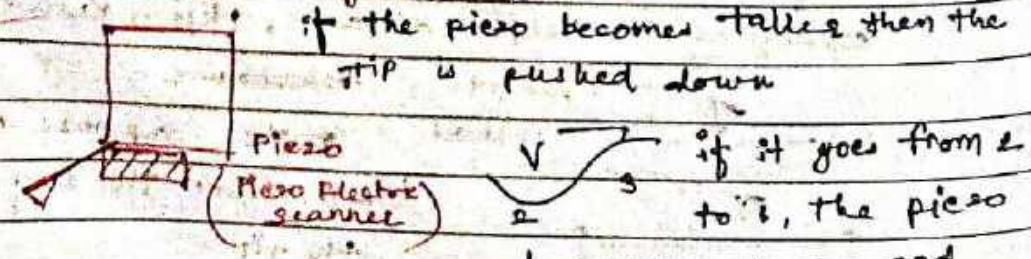


Sample is pushing the tip adequately high that the net force is repulsion. We define a setpoint ( $\pm 2 \text{ mV}$  /  $3 \text{ mV}$ ) → repulsive force is higher). The surface is moved till setpoint is reached.

18/04/23

V  $\longrightarrow$  V what exactly is a controller?

if the piezo becomes taller then the tip is pushed down



V if it goes from 2 to 3, the piezo becomes shorter and fatter

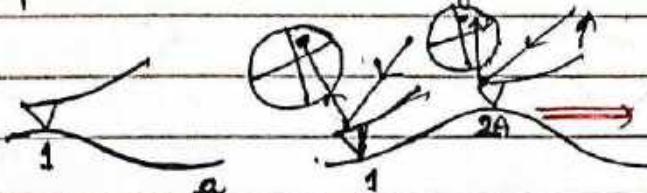
attraction  $\rightarrow$  jump to contact

condition (lower setpoint)  $\rightarrow$  concave geometry  $\rightarrow$  flat  $\rightarrow$  curvature

once we start approach, then set point is set, and it remains constant throughout the process.

$\Rightarrow$   $gmV \approx 5mV$

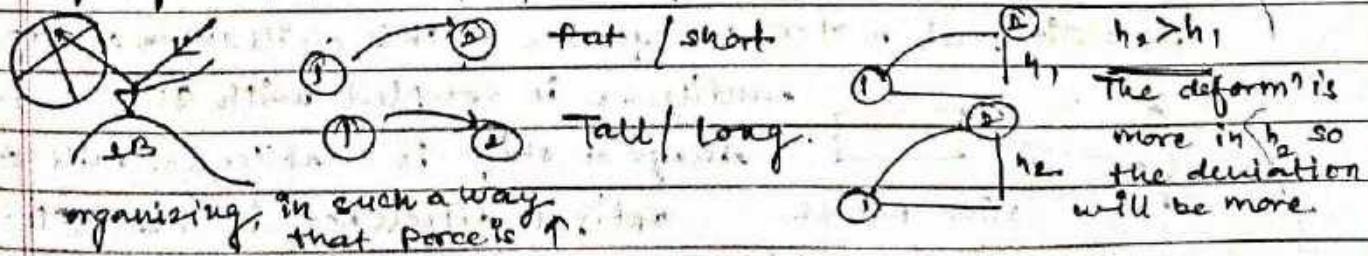
- \* higher is the set pt. more concave will be the cantilever
- \* whatever be the set pt., the jump to contact will be at the same time
- \* repulsive force is higher for higher set pt.



① Tip has to be physically moved from ① to ②. It needs to be dragged there ②

As the cantilever moves from pt. ① to pt. ② what will happen?

- The tip obeys the contours of the sample.
- Light will not fall on the set pt. It will fall somewhere else so we get an error. The error is fed to the controller (piezo). So now, the piezo should become fat & short. Every subsequent step, the error to the piezo is then resolved in such a way that the pt. in SPD again reaches the set point.
- If deform<sup>n</sup> ↑, the force is going to ↑ and voltage ↑.



### Contact Mode of AFM

The set point is in terms of the force of the cantilever. Cantilever deflected under hook's law  $F = -kx$  where  $k$  is cantilever spring constant. The scanner moves along the surface (always in constant). Scanning is done in the repulsive interaction regime. Along with the surface profile (topography) the force on the cantilever will change. Feedback loop activated due to error in force set point.

The tip has to be small as well as the spring constant should be as small as possible. A stiff cantilever will not respond to very small force.  
mode of operation : contact mode: low force constant  
Non contact mode: high force constant

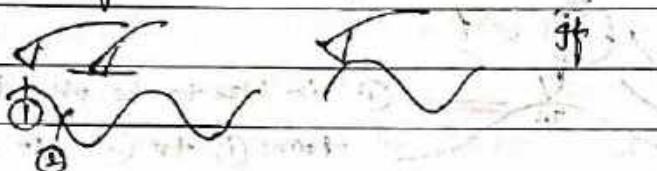


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- The vision of interest is a square area.
- ⇒ The most imp. part of an AFM generated image is the vertical bar bcoz without it we won't be able to get the idea of the depth of the structures as the images are later converted into grayscale & there is normalization of the points. So, there is no other way to know the surface depth & topography of the surface.

Why we don't scan in non-contact mode?

The sensitivity will be very very less and there is always a possibility that if the end pt. is adequately low there will be no deformn.

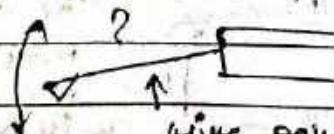


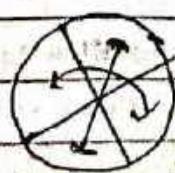
Limitations! → Due to which conditions we have

- ① We can't measure the topography for soft surface.
- ② friction b/w tip & surface is very high. So, tip becomes ~~more~~ blunt as a result of very fast tip wear erosion.
- ③ Resolution depends on how sharp the tip is.

How to overcome the limitations?

Cantilever can be used as a spring if oscillation from outside by an additional motor. consequence of this oscillation on SPD bcoz

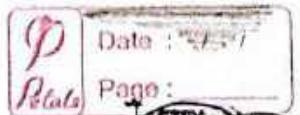
 cantilever is coupled with SPD. So any change or shift in cantilever will show an optical difference in the SPD. The movement of the pt. on SPD will be simple harmonic motion (SHM) as a result.



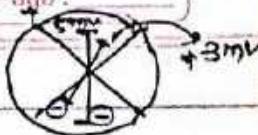
How to fix the oscillation?

The unit of oscillation will be in terms of Volts

extent of lateral deform different due to material prop. (friction coeff.)



2 operators → chosen amplitude →  $5 \text{ mV}$  &  $5 \text{ mV}$

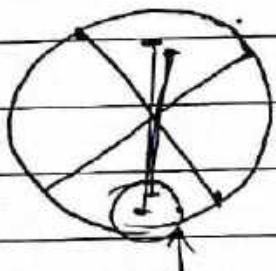


non qu<sub>1</sub>, contact mode, we first align & then choose free amplitude.

What is the setpoint analog?

in the previous case, static cantilever was approaching and in this one, an oscillating cantilever is approaching. This oscillating cantilever comes to approach, slowly, the surface comes close, it starts to tap on the surface bcoz of which one side of the solid gets truncated. intermittent contact or tapping mode

inter b/w tip and surface ↑ Amplitude ↓



When to stop? What is the set point?

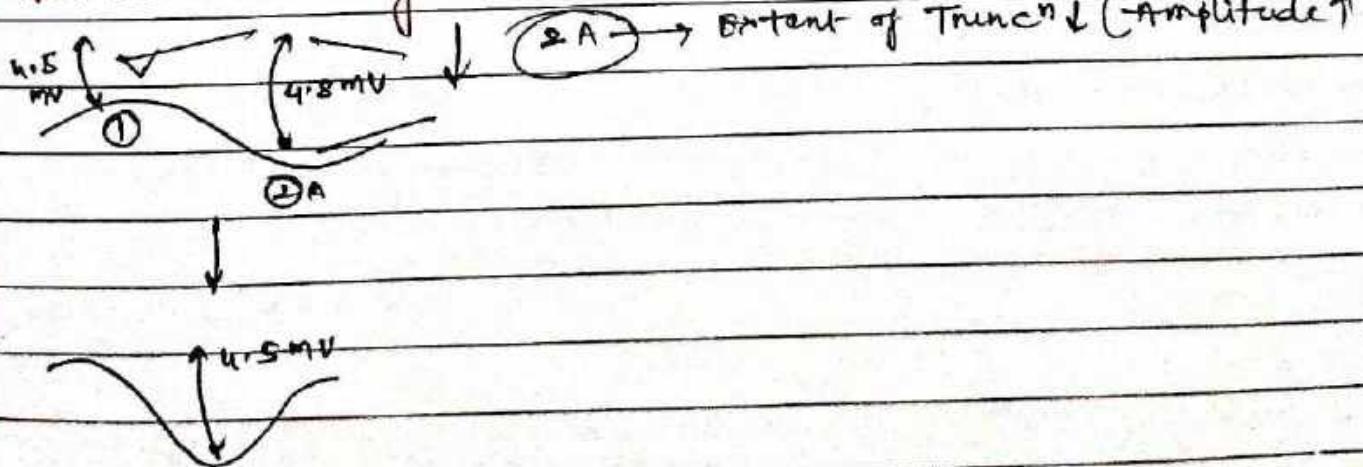
here we choose the set point on percentage truncation. We stop at 90%. means the truncation is 10%.

$$\text{effective Truncated amplitude} = 5 - (0.1)(5)$$

extent of truncn↑. (if set pt.  $5 \text{ mV}$ )

$$= 4.5 \text{ mV}$$

How the scans are generated in this mode?



Tip convolution :-