

Instability and patterning in polymer thin films:

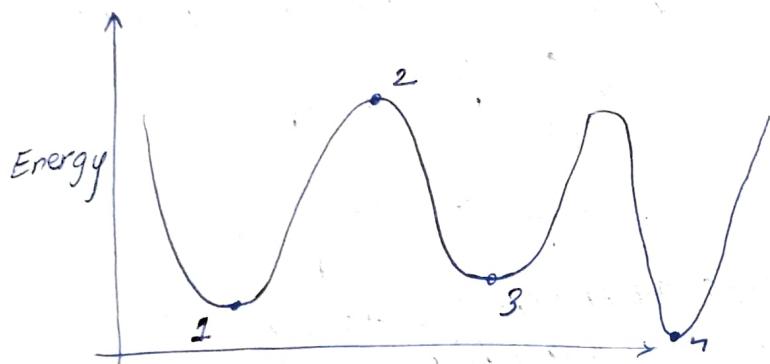
→ Application of patterned surfaces

1. Structural super hydrophobic surfaces.
2. Self cleaning surface
3. Structural color
4. reusable super adhesives
- *5. Patterning in microelectronics.

NEMS \Rightarrow nano electro mechanical systems.

Note: Concept of stability in a system is only valid when

→ Stable and unstable eq^m: system is in eq^m.



temporal / spatial / conformational
quantity.

eq^m \Rightarrow it represents
the points that
corresponds to the
extrema in the
energy landscape of
a system.

2 \Rightarrow unstable eq^m
1, 3 \Rightarrow stable eq^m

In case of multiple low energy eq^m, the eq^m which are greater than the lowest energy eq^m are termed to be in meta eq^m. (1, 3)

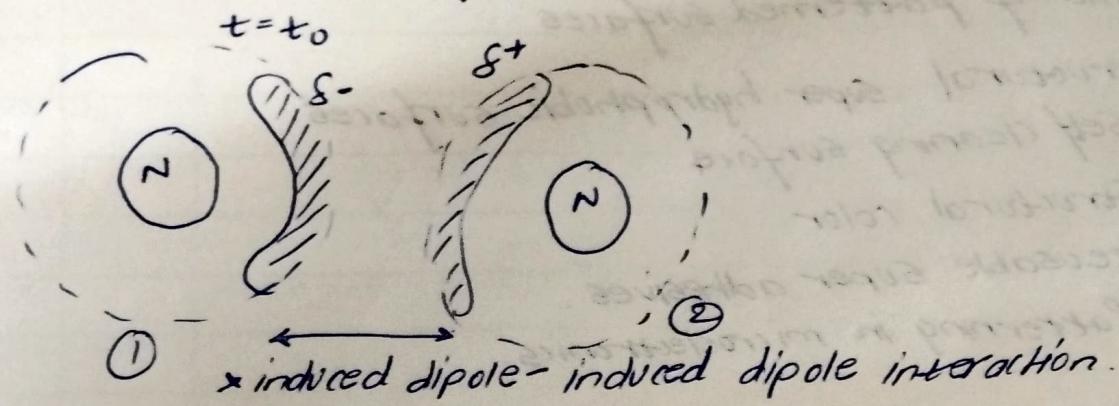
→ Stability Analysis.

for stability analysis the TE (Total energy) of a system needs to be defined.

→ At meso & nano scales ~~eff~~, intermolecular forces other than gravitational force also becomes important.

→ Molecular level forces:

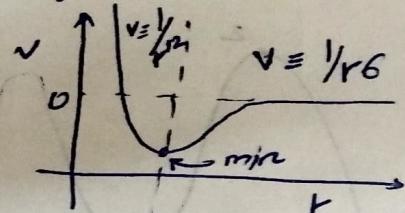
- Vander Waal's dispersion forces b/w neutral molecules.



b/cz of localisation of e^- in 1, δ^+ charge is induced in 2 and thus an attractive force is generated.

- Interaction potential is given by Lennard-Jones potential eqn

$$V = A/r^{12} - B/r^6$$



dispersion forces are always attractive between : two molecules or atoms and the interaction can stretch upto 10 nm

However, b/w 2 surfaces it can be attractive or repulsive and interaction can stretch upto 100 nm.

→ Thin films:

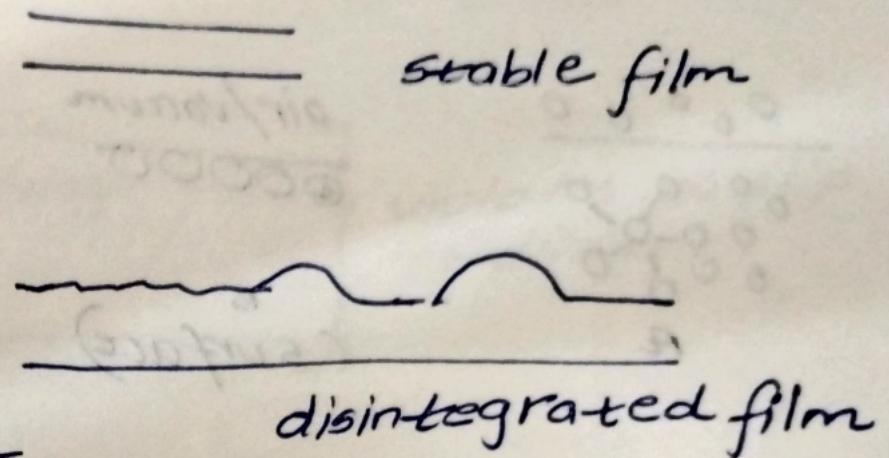
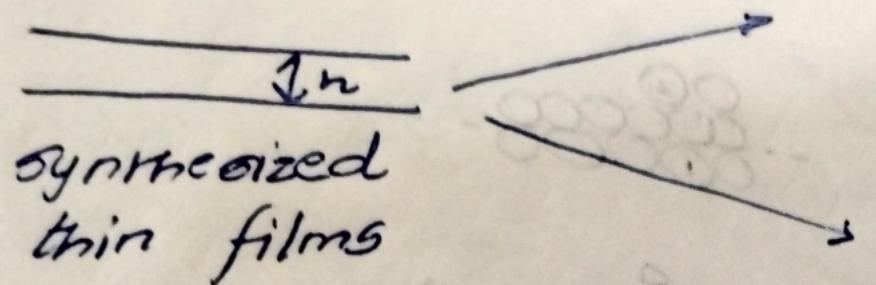
surface-1
surface-2 } film.

$$h \leq h_c$$

h_c → wif critical separation b/w two interfaces at which vw forces are active.

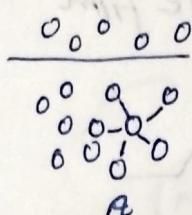
Thin films \Rightarrow $h < h_c$

vw forces are active b/w the two bounding surfaces of the film.



[Can be used for meso-scale patterning].

- surface/interface:



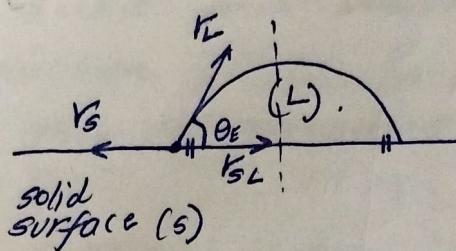
air/vacuum
@ H_2O

B
(surface)



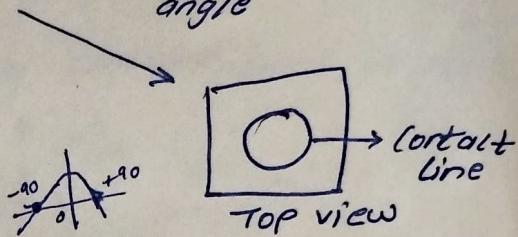
C
(interface)

- Dispensing a drop of liquid on a solid ~~surface~~ surface:



- Surface tension acts along the surface.

$\theta_E \Rightarrow$ eqm contact angle



Horizontal force balance,

Young's eqn

$$r_s = r_{SL} + r_L \cos \theta_E$$

$r_s, r_{SL}, r_L \Rightarrow$ known
 $\theta_E \Rightarrow$ contact angle

• $r_s \uparrow \theta_E \downarrow$

• $r_L \uparrow \theta_E \uparrow$

• $\theta_E < 90^\circ$ hydrophilic

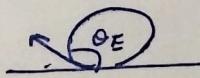
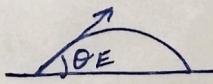
$180^\circ > \theta_E > 90^\circ$ hydrophobic.

limiting values of θ_E $0^\circ \text{ e } 180^\circ$.

$$\theta_E = 0$$

• film is formed

• complete wetting

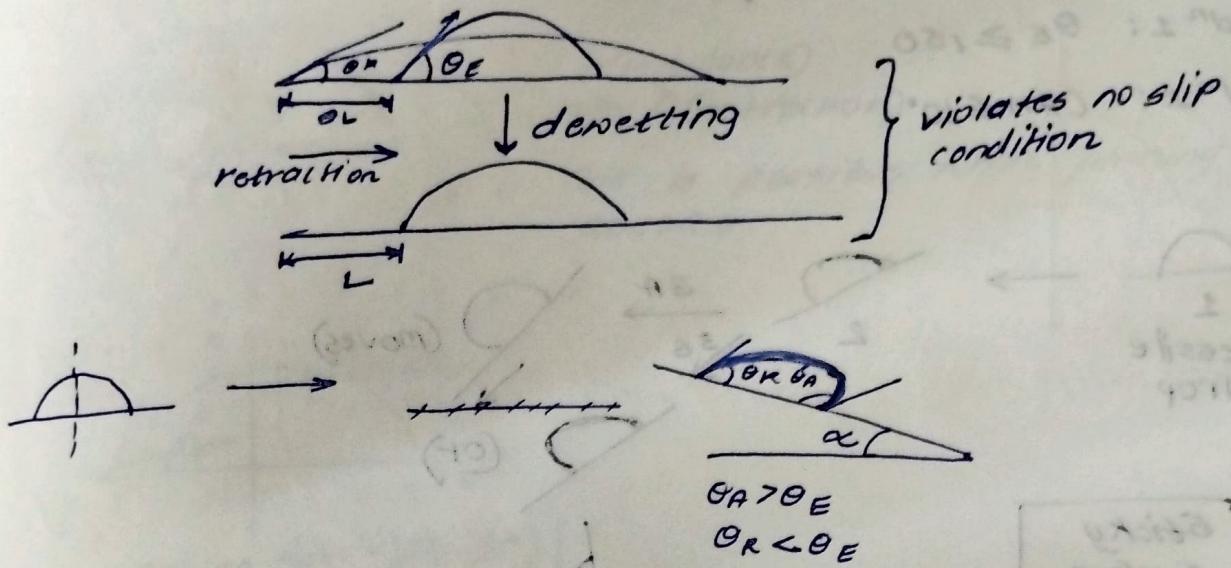


• Partial wetting.

\Rightarrow water (polar interaction (H-bonding)
+ induced dipole-induced dipole)

oil (apolar interaction (induced dipole-induced dipole))
 \therefore oil has low γ

• Fluorine is one of the lowest surface tension materials.



At some α drop will move.
→ contact angle hysteresis (CAH)

$$CAH = \theta_A - \theta_R \Big|_{\alpha=\alpha_c}$$

↑ critical α for which drop starts moving.

→ complete wetting

$$s_{SL} \text{ (spreading coefficient)} = k_s - (r_{SL} + r_L)$$

$s_{SL} > 0$ [thermodynamically favoured].

→ When drop moves it can roll or it will slide. ~~slide~~

$\theta < 90^\circ \rightarrow$ slide (no slip condn violation)

$\theta > 90^\circ \rightarrow$ hydrophobic

$\alpha_c = f(\text{drop volume}) \rightarrow$ no mathematical proof.

→ Pinning: Pinning of contact line:
Adhesion will determine pinning, α_c , CAH

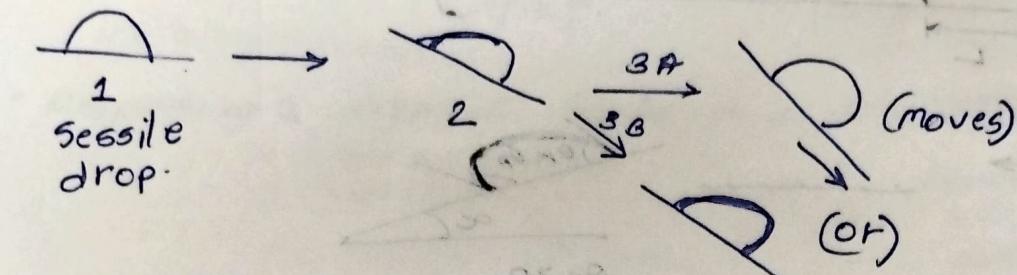
As adhesion increases $r_L \uparrow$ from Young's eqn, also α_c increases and CAH \uparrow because $\theta_A \uparrow$ $\theta_R \downarrow$

→ Super hydrophobic surface: droplet rolls down

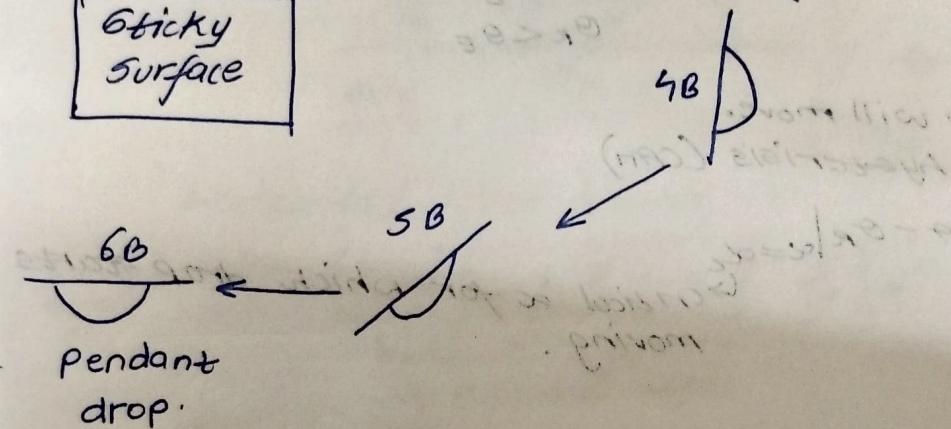
condⁿ 1: $\theta_E \geq 150^\circ$

condⁿ 2: CAH $\leq 10^\circ$

⇒

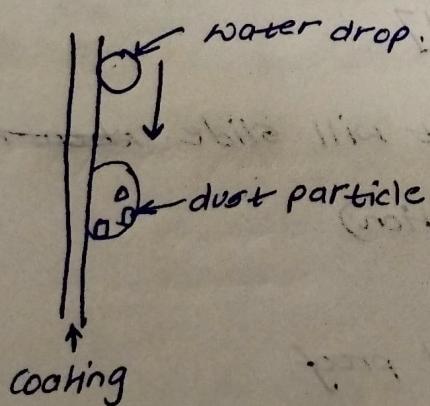


Sticky Surface



ex- rose petal [sticky hydrophobic surface].

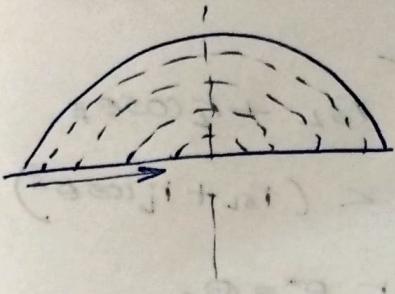
→ self cleaning surface:



1. sticky & hydrophobicity of rose petal?

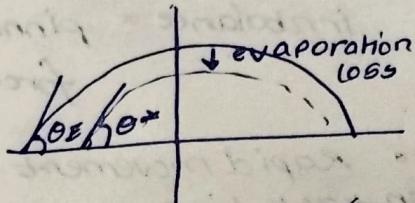
2. self-cleaning surfaces?

* What happens during evaporation?

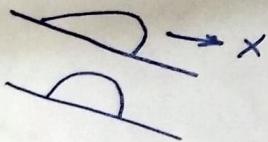


$\delta(\text{imbalance}) \Rightarrow \delta(\text{retraction})$

This is possible when pinning is absent.



$$\text{Driving force} = |\theta_E - \theta^*|$$



- 1. Contact line does not respond to small imbalance (Pinned)
- 2. Once imbalance is high, contact line moves such a surface has 'finite pinning.'

- We are looking for the evaporation of a drop on a finite pinning surface.

- * Drop evaporation on a flat horizontal surface,

→ Practical surface [exhibits pinning]

finite

infinite
(sticky)

- 1. zero/no pinning ($\alpha_c \rightarrow 0$)



- Contact line retraction is continuous
- CCA (constant contact angle) mode of evaporation

- 2. Infinite pinning

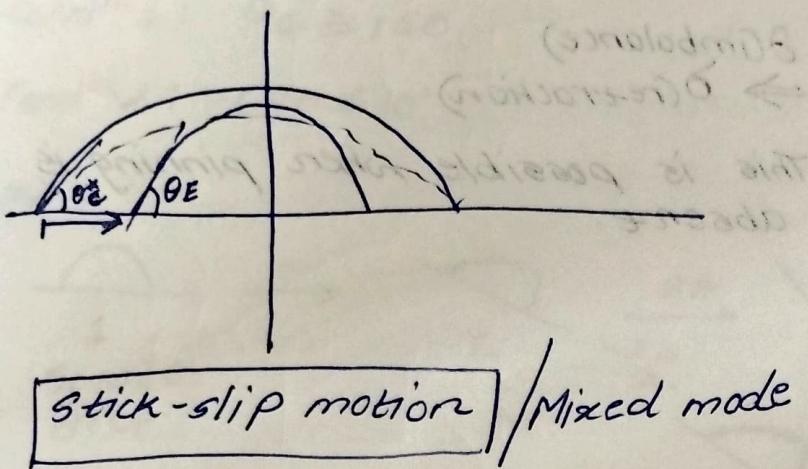


- $\theta_E \downarrow$ with time.

- CCR (constant radius) mode of evaporation
- No movement.

- 3. Finite pinning.

finite pinning: before moving the imbalance has to overcome threshold.



Stick-slip motion / Mixed mode

$$F_G = F_{GL} + F_L \cos \theta_E$$

$$F_G < (F_{GL} + F_L \cos \theta_s^*)$$

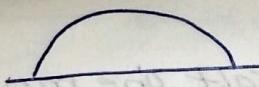
$$\text{for } \theta^* = \theta_c$$

imbalance = pinning force

Rapid movement of contact line.

Contact line retraction is discrete

low pinning



$$\theta_{c1}$$

t_d , (delay before meaning)

high pinning

$$\theta_{c2}$$

$$t_d$$

$$\theta_{c2} < \theta_{c1}$$

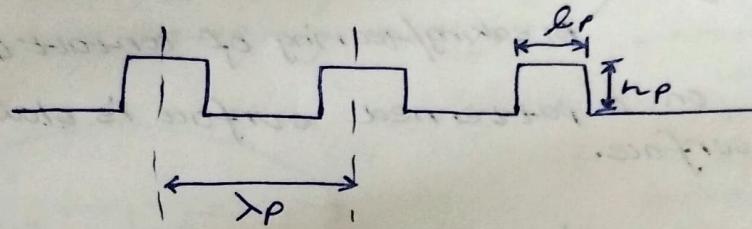
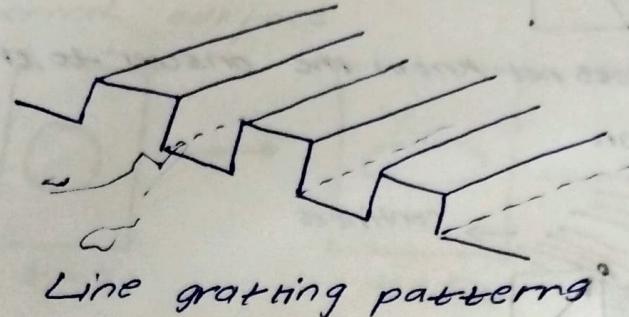
$$t_d > t_d$$

→ at infinite pinning (limiting case)

$$\theta_c \rightarrow 0$$

$$t_d \rightarrow \infty$$

* Evaporation drying of a liquid drop on a patterned surface
 → topographically patterned surface

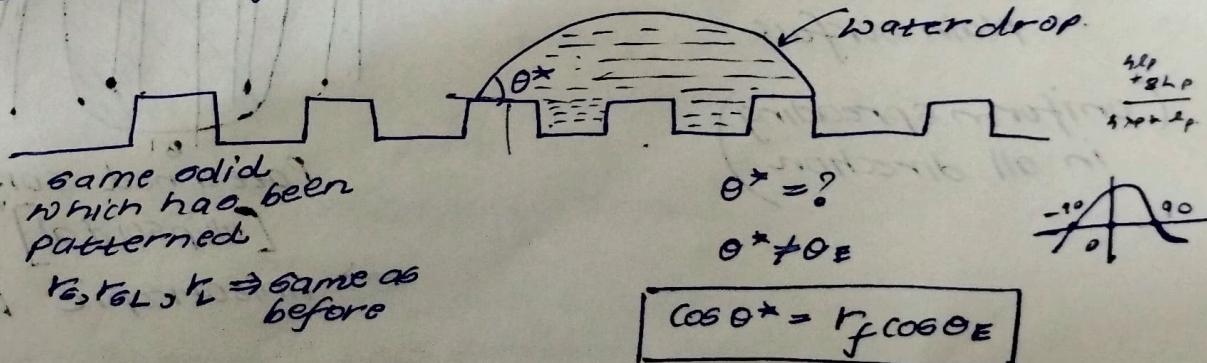


λ_p = periodicity

l_p = line width

h_p = pattern height

wenzel-state of wetting



$$r_f = \frac{(\text{Actual wetted area})}{(\text{Projected Area})}$$

$$r_f = \frac{\lambda_p + 2h_p}{\lambda_p} \rightarrow r_f > 1$$

for flat surface,

$$h_p = 0 \\ \therefore r_f = 1$$

more hydrophilic patterned surface

θ^* → apparent eqm contact angle

r_f → line roughness

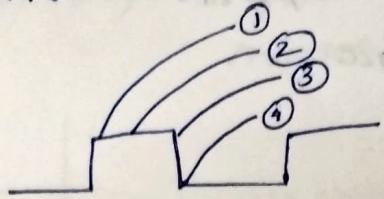
$$\theta^* > \theta_E$$

for hydrophilic surface, $\theta_E > \theta^*$

for hydrophobic surface, $\theta^* > \theta_E$

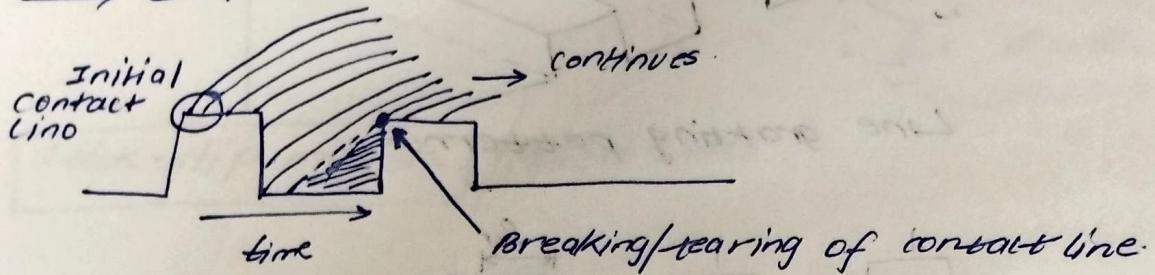
more hydrophobic patterned surface

→ Where does contact line actually start?



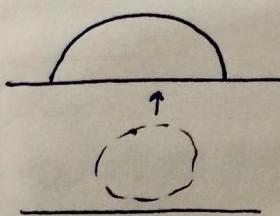
community does not know the answer to this.

→ evaporation



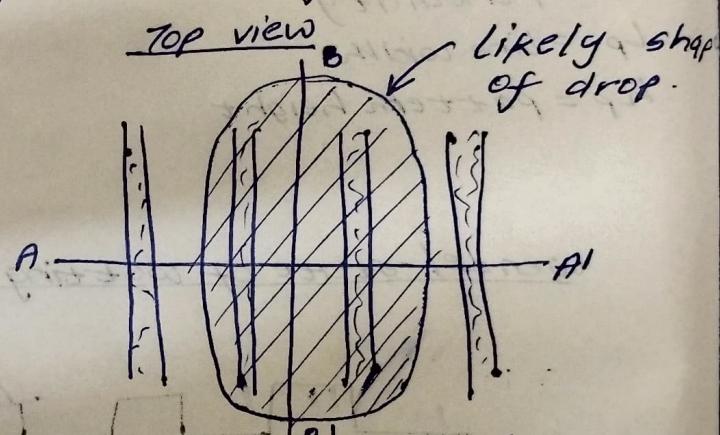
→ Retraction on a patterned surface is slower than the flat surface.

→ Shape of water drop on patterned surface?



plain surface

(uniform spreading
in all direction)



Patterned surface
[ellipsoidal]

→ Anisotropic wetting.

$\cos \theta^* = k_f \cos \theta_E$ is only valid
on section AA'

section $\Rightarrow B-B'$



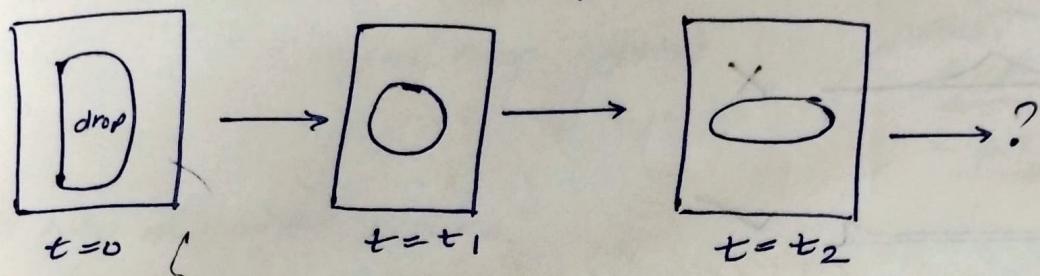
most likely,

$$\theta_1 < \theta^{*}$$

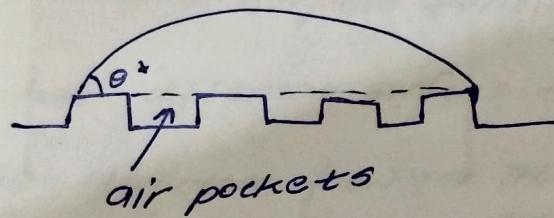
$$\theta_1 \neq \theta_E$$

During retraction
evaporation along BB' is faster than evaporation along AA'.

* Geometrically \rightarrow eccentricity will reduce.
Top view \rightarrow patterned surface



\Rightarrow Cassie-Baxter state of wetting:
[drop does not enter grooves]



Note: we get Wenzel state of wetting for hydrophobic base surface as well.

Base surface does not want the liquid to enter & the head is not enough to drive the air out.

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

f = fraction of S-L contact area (calculated along the line)

$$r_f^* > 1 \quad \& \quad f < 1$$

\rightarrow for hydrophobic base surface, $\theta_E > 90^\circ$

$$\theta^* > \theta_E$$

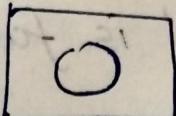
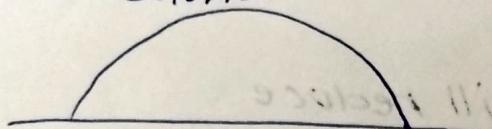
\rightarrow for hydrophilic base surface, $\theta_E < 90^\circ$

$$\text{if } (1-f) > r_f^* f^* \cos\theta_E$$

then hydrophobicity can be achieved.

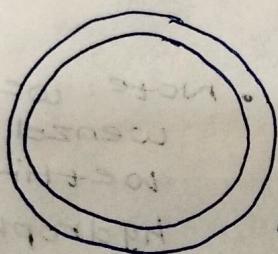
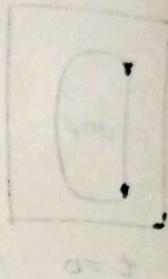
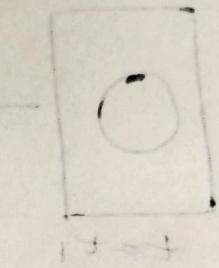
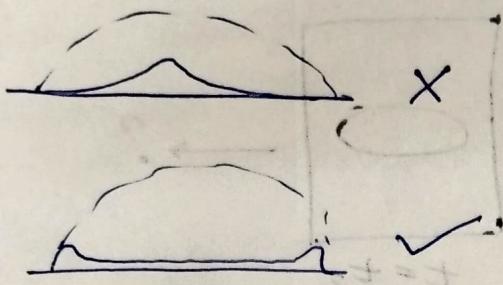
\rightarrow The distortion in the shape will not be much in Cassie state as compared to Wenzel state of wetting.

→ dilute solution



TOP view.

• On evaporation:



Ring like
deposition

Coffee ring effect

Steps:

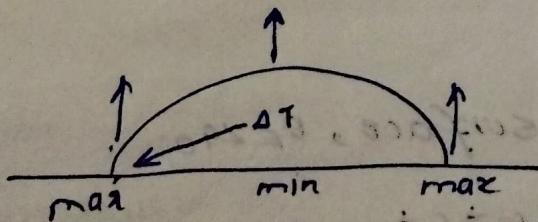
1. Evaporation

2. Deposition starts when $C_i \equiv C_{sat}$.

3. Practical surface
→ finite pinning.

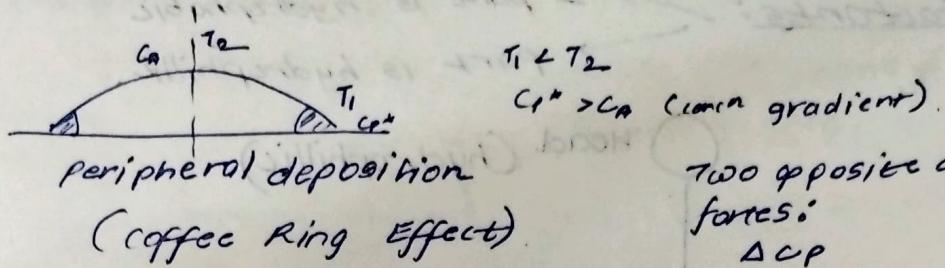
4. Rate of evaporation over a curved surface
= $f(\text{curvature})$.

Rate of evap. from periphery of a drop is maximum.



$T_1 < T_2$ (leads to convection).

⇒ solution drop evaporation drying.



- Still why deposition occurs?

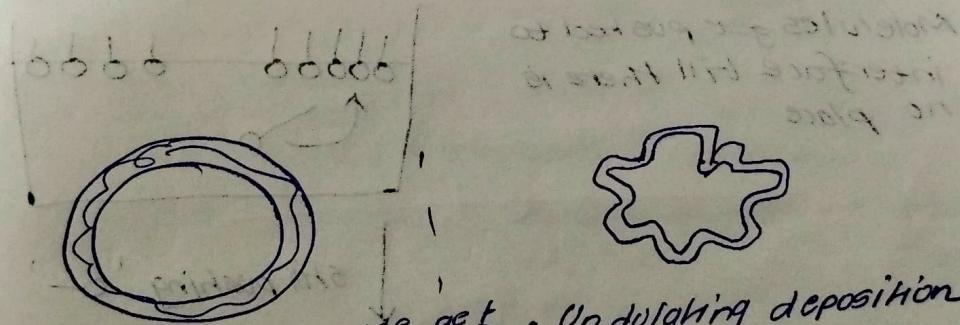
→ because saturation mediated deposition dominates.

[Concept: low resistance path is followed by solute]

- Also there is a surface tension gradient bcoz solute is deposited

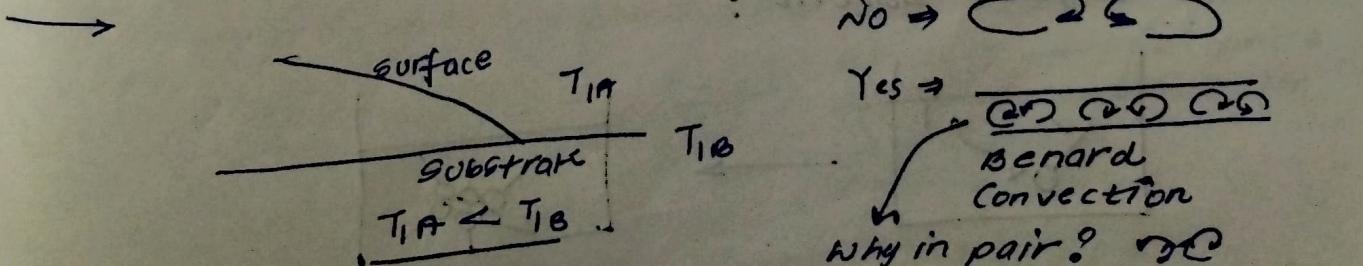
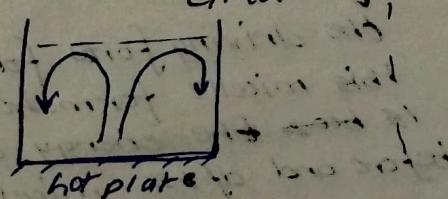
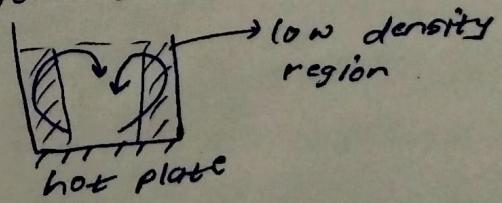
Solvent has different surface tensions.

- $\Delta r \Rightarrow$ Marangoni flow → there is a flow from low r region to high r region.
direction is case sensitive.



- Instead of clear circular deposition we get Undulating deposition

Circulation direction depends on material of walls.



No ⇒

Yes ⇒

Benard convection

Why in pair? → reduction in shear stress

→ Surfactants: → 1 part is hydrophobic
→ part is hydrophilic.

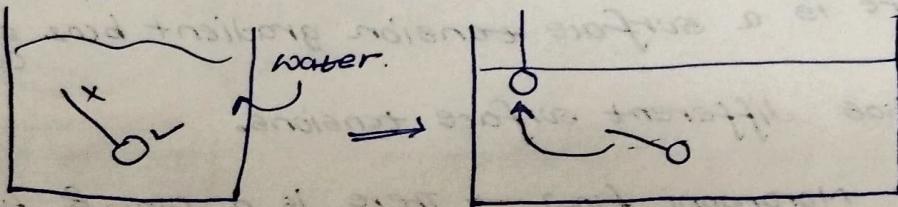
Head (hydrophilic)

Long chain hydrocarbon
(Hydrophobic part)

- Most plastics are hydrophobic.

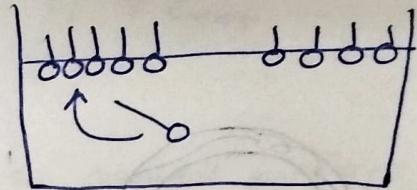
- Glass is hydrophilic

- Critical micellisation concn : CMC

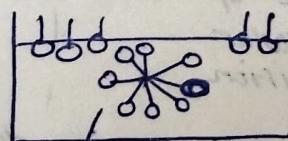


↓ increasing surfactant

Molecules get pushed to interface till there is no place

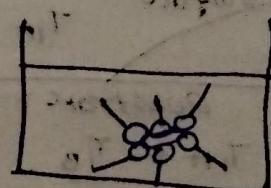
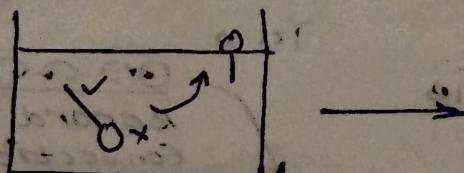


still pushing 'O'



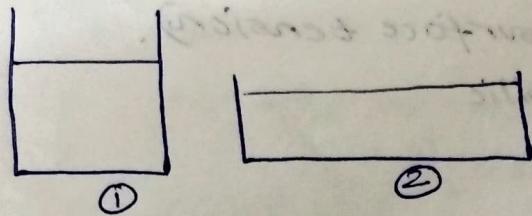
the driving force for this micelle formation is b/w the energy difference before and after micelle format.

- for organic solvent :



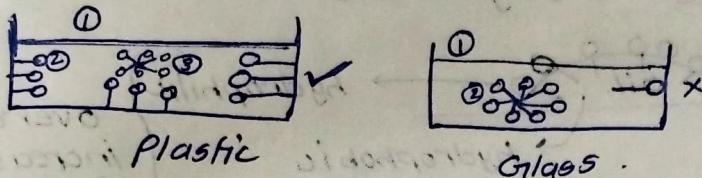
Reverse micelle (also used as nano-reactors)

- $CMC \Rightarrow f(\text{shape of vessel})$.



Same vol., same surfactant.
Different CMC.

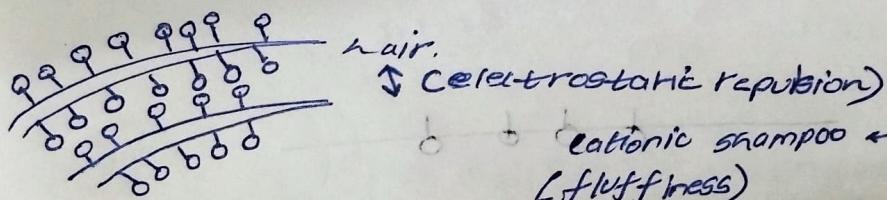
For polar solvent (H_2O):



- Types of surfactants:

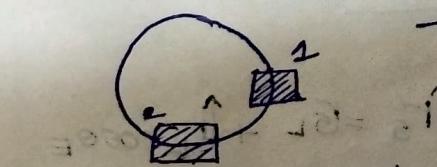
Generally classified based on nature of head.
(Inorganic)

- 1) Anionic
- 2) Cationic
- 3) Zwitterionic
- 4) Non-ionic



cationic shampoo \leftrightarrow anionic conditioner.
(fluffiness) (controllability).

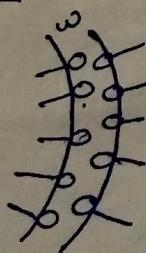
- Soap bubbles



Boundary of a soap bubble is an example of self-standing thin film.
[unsupported]

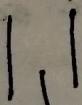
①

air



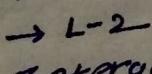
Interaction b/w adjacent molecules.

thin film.



\downarrow (body force) causes draining of the water but due to charged heads of surfactants there is repulsion and thus the film becomes stable.

②



$\rightarrow L-1$

$\rightarrow L-2$

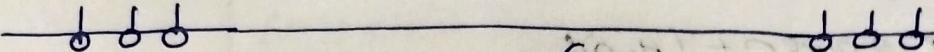
Interaction b/w molecules in L-1 & L-2.

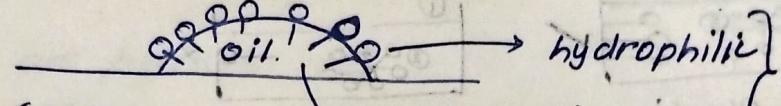
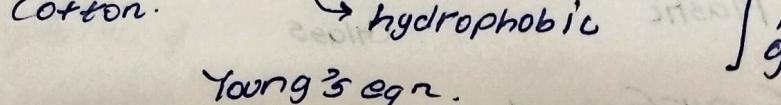
→ How surfactants clean?

Dirt (oily) → hydrophobic (low surface tension).

Cotton (cellulose) → hydrophilic

Polyester → hydrophobic.

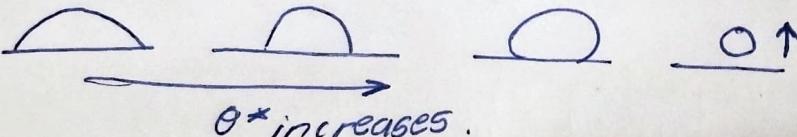
—  water + surfactant

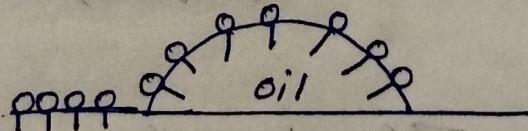

cotton. 
Young's eqn.

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

$$\gamma_L \uparrow \therefore \theta_E \uparrow$$

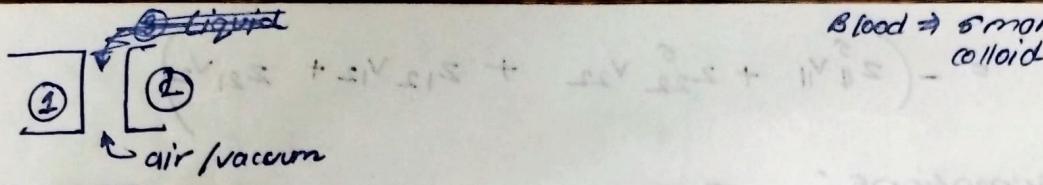
when $\theta_E \rightarrow 180^\circ$ the oil gets removed.
(detaches).


 $\theta^* \text{ increases}$.

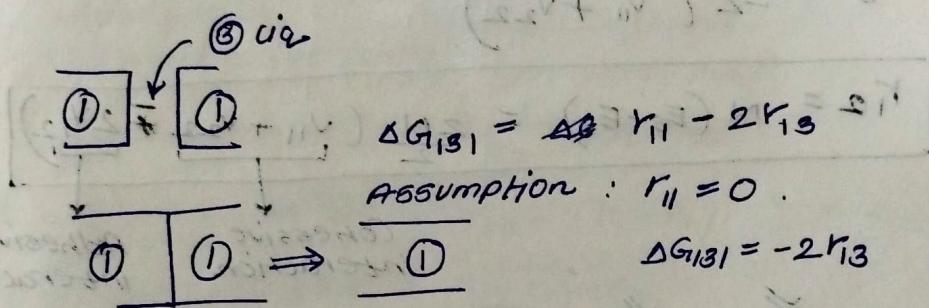
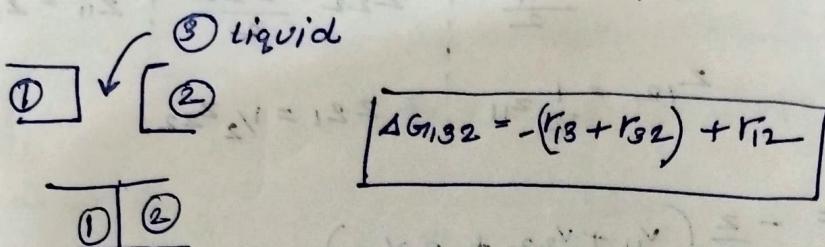


$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta_E$$

→ Dry cleaning [organic solvent is used]



$$\Delta G_i = \Delta G_{12} = G_{1F} - G_{1i} \\ = r_{12} - (r_1 + r_2)$$



$\Delta G < 0$ coagulation $\Delta G > 0$ stable dispersion.



P_{12} = (Energy of interaction of a pair of molecules at surface)

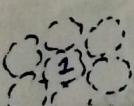
- (Energy of interaction of the same pair of molecules at the bulk)

$$P_{12} = E_S - E_b$$

N = no. of pairs of molecules at the interface per unit area.

$$\therefore \boxed{N(E_S - E_b) = r_{12}}$$

Z_{11}^S	v_{11}
Z_{22}^S	v_{22}
Z_{12}	v_{12}
Z_{21}	v_{21}
$v_{12} = v_{21}$	



$$E_b = -Z_{11}v_{11} - Z_{22}v_{22}$$

$v_{11} \rightarrow$ energy of interaction between pair of ①

$Z_{ij} \Rightarrow$ how many molecules of j are surrounding i

$Z_{11} \Rightarrow$ co-ord No. of ① in bulk.

$$E_s = - \left(z_{11}^s v_{11} + z_{22}^s v_{22} + z_{12} v_{12} + z_{21} v_{21} \right)$$

Assumptions:

$$z_{11} = z_{22} = z$$

$$\cancel{z_{11}^s} = \cancel{z_{22}^s} = z$$

$$z_{11}^s = \frac{z_{11}}{2} \quad | \quad z_{22}^s = \frac{z_{22}}{2} \quad | \quad z_{11}^s = z_{22}^s = 0.5$$

$$z_{12} = \frac{1}{2} z_{11} \quad | \quad z_{21} = \frac{1}{2} z_{22}$$

$$E_s = - \frac{z}{2} (v_{11} + v_{22} + 2v_{12})$$

$$E_b = -z (v_{11} + v_{22})$$

$$r_{12} = \frac{zN}{2} (v_{11} + v_{22} - 2v_{12})$$

Cohesive interaction

Adhesive interaction

$$v_{11} = v_{11}^{WW} + v_{11}^{AB} + v_{11}^{st}$$

Vanderwall interaction Polar steric
not included.

$$r_{12} = \frac{zN}{2} [v_{11} + v_{22} - 2v_{12}]$$

Suppose one of the phases is non-condensed, i.e., 2 is a gas.

$$v_{22} = 0$$

$$v_{12} = 0$$

$$r_{12} = r_1 = \frac{zN}{2} v_{11}$$

$$r_2 = \frac{zN}{2} v_{22}$$

$$r_{12} = r_1 + r_2 - zN v_{12}$$

$$\Delta G_{12} = [r_{12} - (r_1 + r_2)] = -zN v_{12}$$

$$\begin{array}{|c|} \hline 1 \\ \hline \end{array} \quad \begin{array}{|c|} \hline 2 \\ \hline \end{array} \quad \Delta G_{12+} = r_{12} - (r_1 + r_2) \\ r_{11} = 0.$$

$$\begin{array}{|c|} \hline 1 \\ \hline \end{array} \quad \begin{array}{|c|} \hline 2 \\ \hline \end{array} \quad P_{12} = (E_S - E_b)$$

$$E_b = -z_{11}v_{11} - z_{22}v_{22}$$

$$E_S = -z_{11S}v_{11} - z_{22S}v_{22} - z_{12}v_{12} \\ - z_{21}v_{21}$$

Ass:

$$z_{11} = z_{22} = z$$

$$z_{11S} = z_{22S} = z_{12} = z_{21} = \frac{z}{2} \quad r_{12} = \frac{zN}{2} (v_{11} + v_{22} - 2v_{12}).$$

$r_{11} = 0$ (true for liq.

assumption for solids).

$$r_{12} = r_1 + r_2 - Nz v_{12}$$

$$\Delta G_{12} = r_{12} - (r_1 + r_2)$$

$$-\Delta G_{12} = (r_1 + r_2) - r_{12}.$$

$$\Delta G_{12} = -Nz r_{12}$$

Vanderwaals interaction,

$$v_{12}^{LW} = \sqrt{v_{11}^{LW} \times v_{22}^{LW}}$$

$$\Delta G_{12} = -Nz (v_{12}^{LW} + v_{12}^{AB})$$

$$\Delta G_{12}^{LW} = -Nz v_{12}^{LW}$$

$$= -Nz \sqrt{v_{11}^{LW} \times v_{22}^{LW}}$$

$$= -2 \sqrt{\left(\frac{N}{2} v_{11}^{LW}\right) \times \left(\frac{N}{2} v_{22}^{LW}\right)}.$$

$$\Delta G_{12}^{LW} = -2 \sqrt{r_1^{LW} \times r_2^{LW}}$$

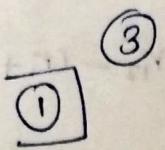
$$\Delta G_{12}^{LW} = r_{12}^{LW} - (r_1^{LW} + r_2^{LW})$$

$$\Delta G_{12}^{LW} = r_{12}^{LW} = r_1^{LW} + r_2^{LW} - 2\sqrt{r_1^{LW} r_2^{LW}}$$

$$r_{12}^{LW} = (\sqrt{r_1^{LW}} - \sqrt{r_2^{LW}})^2$$

Vanderwaals component of interfacial tension is
proportional to

→



$$\Delta G_{1B1} = r_{11} - 2r_{13}$$

$$= -2r_{13}$$

for apolar ① & ③ $r^{AB} = 0$.

$$\Delta G_{1B1} = \Delta G_{1B1}^{\text{LW}} = -2r_{13}^{\text{LW}}$$

$$r_{13}^{\text{LW}} > 0 \text{ always}$$

$$\Delta G_{1B1} < 0 \text{ always}$$

∴ the colloid will never be stable. It will coagulate

→ To quantify the AB type interaction, we define two semi-empirical parameters,

r^- → e-donor / proton acceptor parameter

r^+ → conjugate (opposite).

* Assumption:

$$1. r_i^{AB} = 2\sqrt{r_i^- r_i^+}$$

- for very few materials r_i^+ & r_i^- are same.
- for large no. of materials $r_i^+ = 0$ or $r_i^- = 0$. This type of materials are monopolar.
- $r_i^{AB} = 0$ does not mean the material is apolar. It can be monopolar.

$$2. \Delta G_{12}^{AB} = -2 \left[\sqrt{r_1^- r_2^+} + \sqrt{r_1^+ r_2^-} \right]$$

$$\rightarrow \Delta G_{12}^{AB} = r_{12}^{AB} - (r_1^{AB} + r_2^{AB})$$

$$r_{12}^{AB} = r_1^{AB} + r_2^{AB} + \Delta G_{12}^{AB}$$

$$r_{12}^{AB} = -2 \left[\sqrt{r_1^- r_2^+} + \sqrt{r_1^+ r_2^-} \right] + 2\sqrt{r_1^- r_1^+} + 2\sqrt{r_2^- r_2^+}$$

$$r_{12}^{AB} = 2 \left[\sqrt{r_1^- r_2^+} + \sqrt{r_1^+ r_2^-} - \sqrt{r_1^- r_1^+} - \sqrt{r_2^- r_2^+} \right]$$

$$r_{12} = r_{12}^{1\omega} + r_{12}^{AB}$$

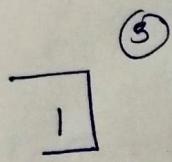
$$r_{12} = (\sqrt{r_1^{1\omega}} - \sqrt{r_2^{1\omega}})^2 + 2 \left[\frac{\sqrt{r_1+r_2^-} + \sqrt{r_2+r_1^-} - \sqrt{r_1+r_2^+}}{\sqrt{r_1+r_2^-}} \right]$$

$$\Delta G_{121} = ? = r_{11} - 2r_{13} = -2r_{13}$$

$$= -2r_{13}^{1\omega} - 2r_{13}^{AB}$$

Polarity is a necessary but not a sufficient condition for stable colloids.

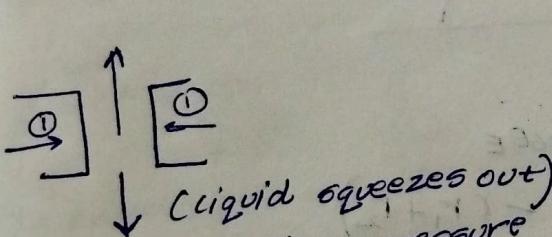
→



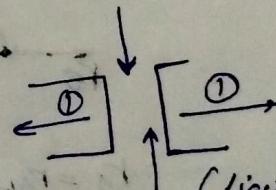
$$\Delta G_{121} = -2r_{13}$$

$$r_{13} = r_{13}^{1\omega} + r_{13}^{AB}$$

$$= (\sqrt{r_1^{1\omega}} - \sqrt{r_3^{1\omega}})^2 + 2 \left(\underbrace{\sqrt{r_1+r_3^-} + \sqrt{r_3+r_1^-}}_B - \underbrace{\sqrt{r_1+r_3^+} - \sqrt{r_1-r_3^+}}_C \right)$$



(liquid squeezes out)
hydration pressure



(liquid fills in
the void).

Hydrophobic
repulsion.

• Special cases:

- 1. Polar colloid in apolar solvent $\rightarrow r_3^+, r_3^- \Rightarrow 0$
- 2. A-polar colloid in polar solvent. $\rightarrow r_1^+, r_1^- \Rightarrow \text{non-zero}$

$$r_3^+, r_3^- \Rightarrow 0$$

$$r_1^+, r_1^- \Rightarrow \text{non-zero}$$

$$r_3^+, r_3^- \Rightarrow \text{non-zero}$$

In both 1 & 2 term C is dead.

* here coagulation is more favoured as compared to the case where both colloid and solvent are apolar.

Reason → 1 extra positive term from B.

3. Polar colloid/monopolar liq.

$$r_1^+ , r_1^- \Rightarrow \text{non zero}$$

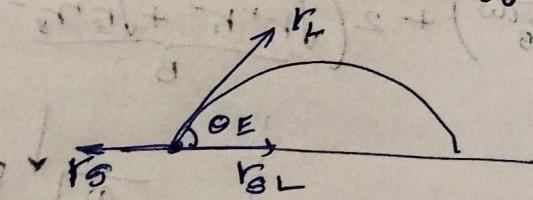
$$r_2^+ \text{ or } r_3^- \Rightarrow \text{zero}$$

4. Monopolar colloid/monopolar liq.

r_1^+	r_1^-	r_3^+	r_3^-
Coagulation ✓	0	-	0
Possibility of getting stable colloid is maximum.	-	0	-
Coagulation ✓	-	0	-

→ Use of Goniometer

1. To determine contact angle
2. To determine surface energy.



$$r_B = r_{GL} + r_L \cos \theta_E$$

$$\begin{aligned} \Delta G_{12} &= r_{12} - (r_1 + r_2) \\ &= \Delta G_{12}^{LW} + \Delta G_{12}^{AB}. \end{aligned}$$

$$\Delta G_{12}^{LW} = -2\sqrt{r_{12} r_L} \cos \theta_E$$

$$\Delta G_{12}^{AB} = -2 \left[\sqrt{r_1 + r_2} - \sqrt{r_1 - r_2} \right]$$

$$\Delta G_{12}^{SL} = r_{GL} - (r_3 + r_L)$$

$$r_{GL} = \Delta G_{SL} + (r_3 + r_L) ; r_3 = r_{3L} + r_L \cos \theta_E$$

$$r_3 - r_L \cos \theta_E = \Delta G_{SL} + r_3 + r_L$$

$$r_L = \Delta G_{SL} + (r_3 + r_L) + r_L \cos \theta_E$$

$$\Delta G_{SL} = -(1 + \cos\theta_E) r_L$$

Young-Dupre eqn.

$$(1 + \cos\theta_E) r_L = 2 \left[\sqrt{r_6^{LW} r_L^{LW}} + \sqrt{r_6^+ r_L^-} + \sqrt{r_6^- r_L^+} \right]$$

for some liq. r_6^{LW}, r_L^+, r_L^- are known.

→ Used to find surface

$$r_S = r_S^{LW} + r_S^{AB} = r_S^{LW} + 2\sqrt{r_6^+ r_6^-}$$

By using 8 liquids of known r_6^{LW}, r_L^+ & r_L^- on same solid, we can compute r_6 by solving 8 simultaneous eqns in r_S^{LW}, r_S^+, r_S^-

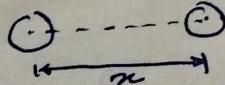
Pb:

$$r_L(1 + \cos\theta_E) = 2 \left[\sqrt{r_6^{LW} r_L^{LW}} + \sqrt{r_6^+ r_L^-} + \sqrt{r_6^- r_L^+} \right]$$

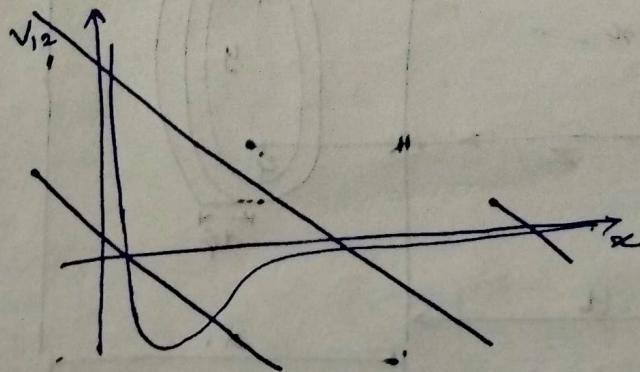
liq	θ_E	$\frac{r_L^{LW}}{50.8}$	$\frac{r_L^+}{0}$	$\frac{r_L^-}{0}$	$\frac{r_L}{50.8}$
A	39.4	50.8	0	0	50.8
B	60.9	21.8	25.5	25.5	72.8
C	63.1	34	57.4	3.2	64

→ 3eqn & 3 variables to find r_6^{LW}, r_6^+, r_6^-

$$\rightarrow V_{12}^{LW} = -\frac{\alpha}{x^6} - \frac{\beta_{12}}{x^6}$$



V_{12} ⇒ potential energy of interaction.



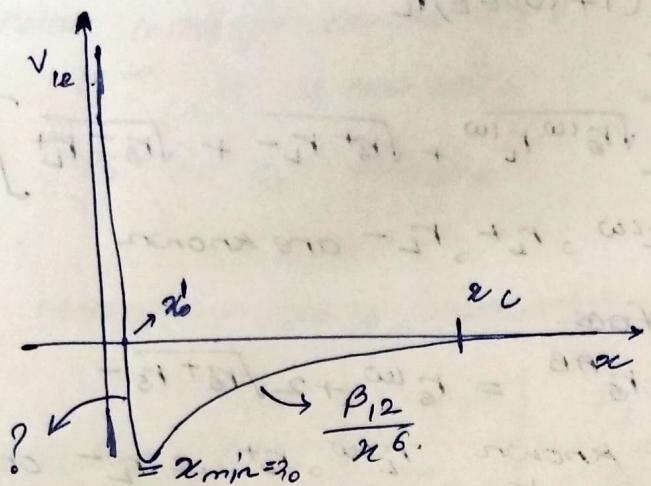
$V_{12}^{LW} \Rightarrow$ always attractive

$V_{12}^{\text{total}} \Rightarrow$ attractive + repulsive

Hard sphere model



e-cloud



$n_c \sim 10 \text{ nm}$

→ Repulsion that occurs for $x < x_{\min}$ is called Pauli's repulsion.

→ expression for repulsive part $\propto 1/x^{12}$

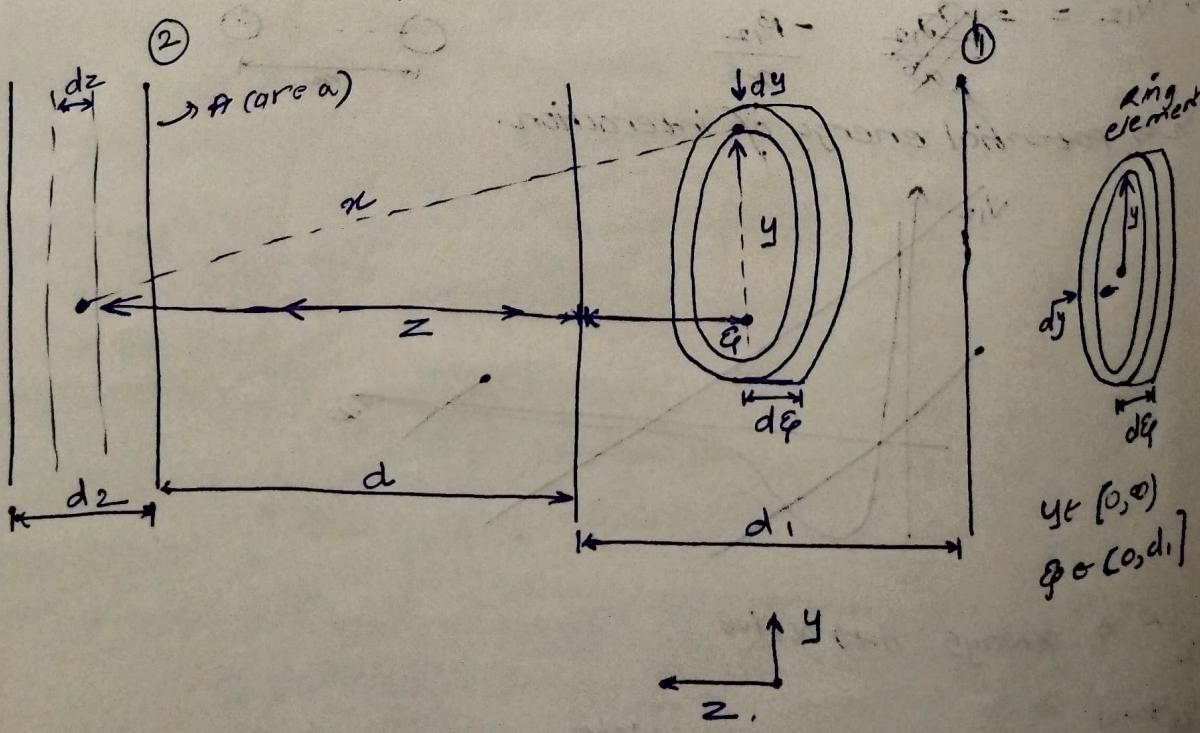
→ overall expression $\Rightarrow V_{12}^{\text{Total}} = \frac{B}{x^{12}} - \frac{A}{x^6}$

Lenard-Jones Potential

$\frac{B}{x^{12}}$ ⇒ empirical

• Separation distance at contact $\neq 0$

→ Vander Waal's interaction between 2 surfaces:
Figure-1



$$\nabla_{12}^{1\omega} = -\frac{\beta_{12}}{x^6}$$

$$\text{vol of ring} = 2\pi y dy d\varphi$$

No. of molecules in ring unit volume = no/vol

$$= \frac{\text{No.}}{\text{mole}} \times \frac{\text{mole}}{\text{mass}} \times \frac{\text{mass}}{\text{vol}}$$

$$= \frac{N_A P}{M_w} = \frac{N_A P_1}{M_1}$$

$$\text{- No. of molecules in ring} = \frac{N_A P_1}{M_1} \times 2\pi y dy d\varphi$$

Potential energy of interaction b/w the chosen molecule of ② with all molecules of ①

$$= -\frac{\beta_{12}}{x^6} \left(2\pi y dy d\varphi \cdot \frac{N_A P_1}{M_1} \right)$$

① in the ring.

$$= -\frac{\beta_{12} N_A P_1}{M_1} \left(\frac{2\pi y dy d\varphi}{x^6} \right)$$

Potential energy of interaction between the chosen molecule of ② with all molecules of ①.

$$= \int_{\epsilon=0}^{d_1} \int_{y=0}^{y=\infty} \left(-\frac{\beta_{12} N_A P_1}{M_1} \times \frac{2\pi y dy d\varphi}{x^6} \right) dy d\varphi$$

$$= -\frac{\beta_{12} N_A P_1}{M_1} \times 2\pi \int_0^{d_1} \int_0^{\infty} \frac{y dy d\varphi}{[(z+\epsilon)^2 + y^2]^3}$$

$$\int_0^{\infty} \frac{y dy}{[(z+\epsilon)^2 + y^2]^3} = \frac{1}{4(z+\epsilon)^2}$$

$$y^2 = p$$

$$2y dy = dp$$

$$\int_0^{\infty} \frac{dp}{2[(z+\epsilon)^2 + p]^3} \Rightarrow \frac{1}{2} \left[\frac{x^2 + p}{-2} \right]^{-2} \Rightarrow \frac{-1}{4} \left[\frac{1}{(z^2 + \epsilon^2)^2} \right] \Big|_0^{\infty}$$

$$\Rightarrow -\frac{1}{4} \left[\frac{1}{(z^2 + \epsilon^2)^2} \right]$$

$$= \frac{-1}{4(z+\epsilon)^2}$$