Spontaneous Instability of an Ultra Thin Film.

23/03/2022
Lecture 29

Criteria based on Π or ϕ

→ Spontaneously unstable

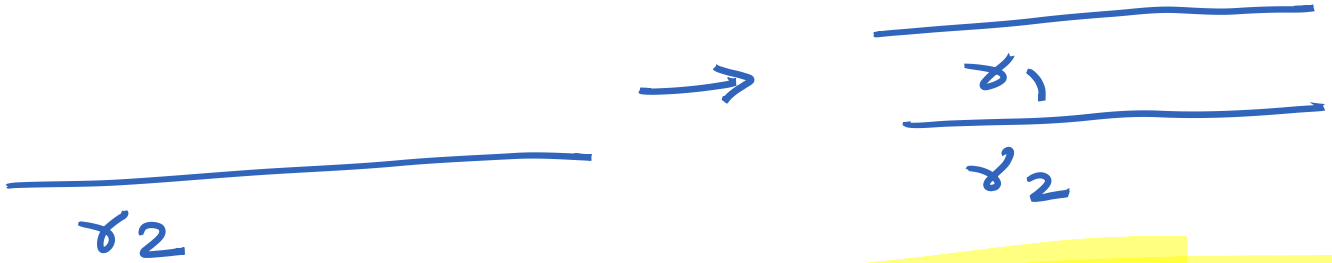
When

Strength of Disjoing Pr > Strength of Laplece Pr.

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

↳ Positive: Positive A_E

Spreading Coefficient



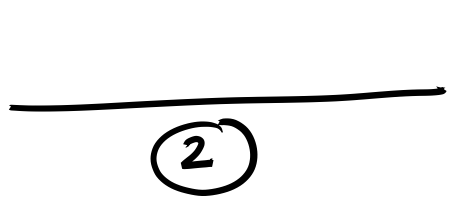
$$S_{21} = \gamma_2 - (\gamma_1 + \gamma_{12})$$

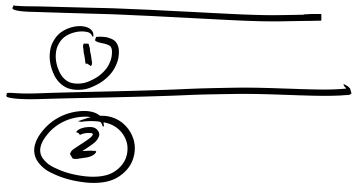
-ve S_{21} → Film NOT favored.

Consequence of "Thermodynamically not Favored" →

$$S_{21} = \gamma_2 - (\gamma_1 + \gamma_{12})$$

Negative Spreading Coeff.





↳ Film is NOT thermodynamically favored.

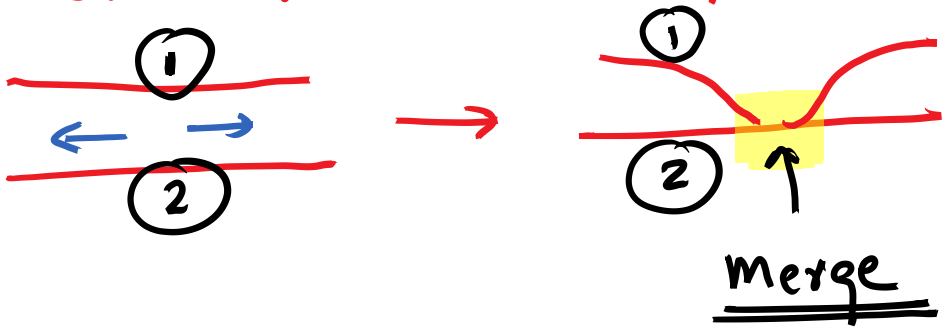
Does it mean that the film will become unstable!

S_{21} → Negative
A_E → +ve

Does both of them imply the same consequence!

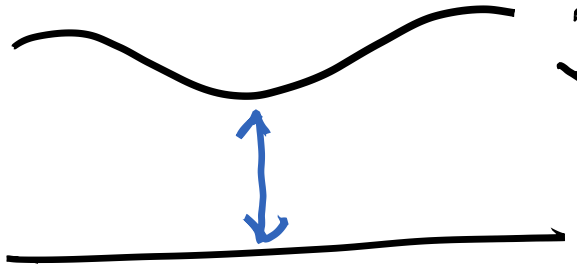
⇒ The consequence is not same

For a film to rupture → The Liquid-Air Interface and the Liquid-Solid interface must merge / touch at a point → to form a hole.



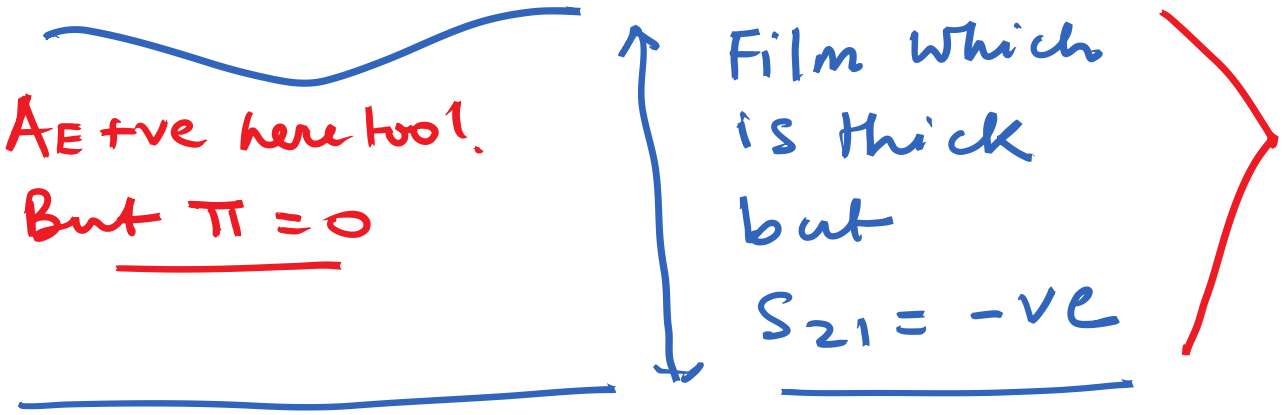
② In order for this (merging of the two interfaces) to happen

The fluctuations **MUST grow**!



↕ must grow

③ Growth of fluctuation requires active Interfacial Interaction (h is small, < 100 nm)



The growth of the fluctuations won't take place (as h > 100 nm)

So $G^{LW}_{Syst} \to 0$

If growth does not happen → Film won't rupture

* If h is high, despite being thermodynamically unfevorable, a Film will remain Intact.

$S_{21} = -ve$, but h is high (> 100 nm) $\Delta G^{Ex}_{Syst} \to 0$

→ Film will NOT Reapture

When A_E = +ve, $S_{21} \to ve$ ⟶ h is Low

Then only FILM ruptures.

What are the films that will rupture

(1) Non Zero Π. ⟶ h is Low

(2) A_E → Positive

(3) Also $S_{21} = -ve$

DO NOT ASSES THE STABILITY BASED ON S_{21} only.

Necessary Condition → (1) Non Zero disjoing Pr.

(1) Negative Disjoing Pressure

(2) Strength of Disjoing Pressure → Strength of the stabilizing effect of Laplace Pressure

Then only the Film will rupture

Typical Dewetting Experiments:-

(1) You need a ultra thin Liquid film. (*)

↓ $h < 100\,nm$

Non Zero Π.

∴ Π =

Liquid Film :-

What type of Liquid do you think is best suited for experiments.

Organic Solvent / water.

Evaporation → what is the problem →

↳ Strength of $\Pi = f(h)$

If evaporation is there → h will keep on changing during the experiments! → NOT DESIRABLE

Thin Polymer Film → Long chain polymers

Chains are long, but there is no physical cross linking between the chains.

Polymer thin Films are used.

Polymers — (1) Long Chain. → Entanglement

(Thermo Plastic)

(2) Solid at Room Temperature.

△

↓

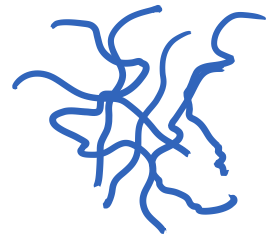
Softens

(1) At what Temp the Polymer Softens. → T_G

(2) What does softening meen to a chemical Engineer (who knows fluid dynamics)

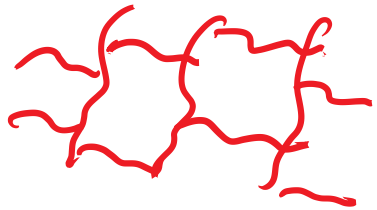
Glass Transition Temperature (T_G).

Long Chain Entangled Polymer



(Thermo Plastics)

Cross Linked Polymers



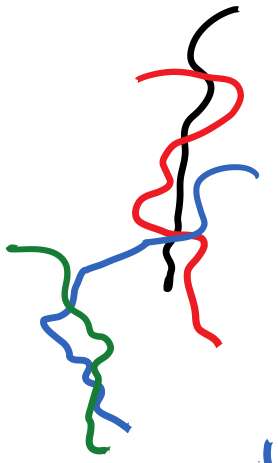
(Thermo Set Polymers)

(2) What happens for $T > T_G$

Softens.

What does it mean → Chains become mobile

↳ Viscosity decreases.



→ At room temp → the chains can't move.

→ Entanglement hinders chain movement.

→ Behaves like a Solid.

Heat up $T > T_G$ → Chains get some mobility

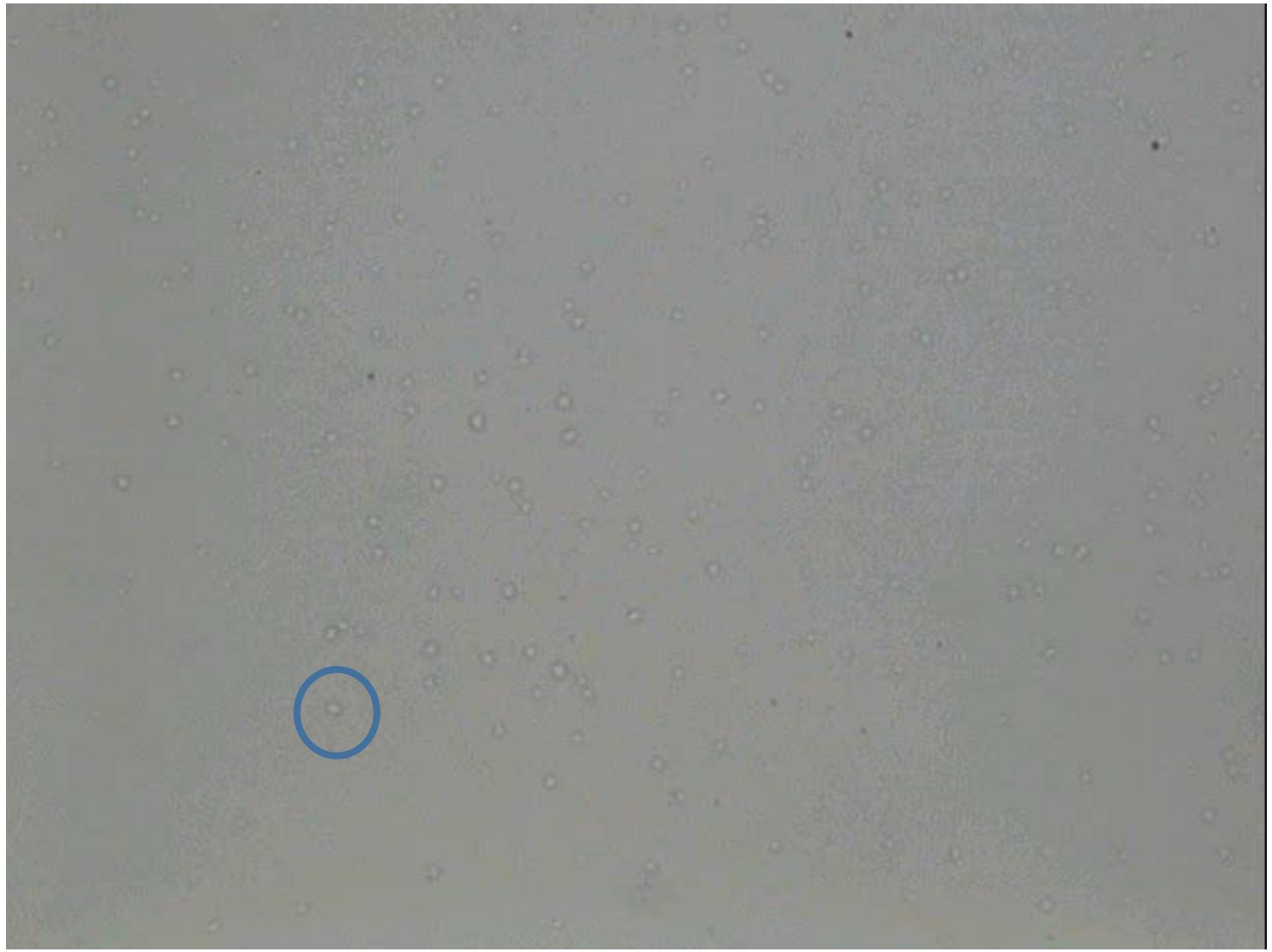
Deformable

Viscosity Decreases.

↓

As you heat up → KE of the molecules (k_BT) increases and this higher energy helps in overcoming the effect of Entanglement as well as int potential energy/ cohesive Int.

Int.



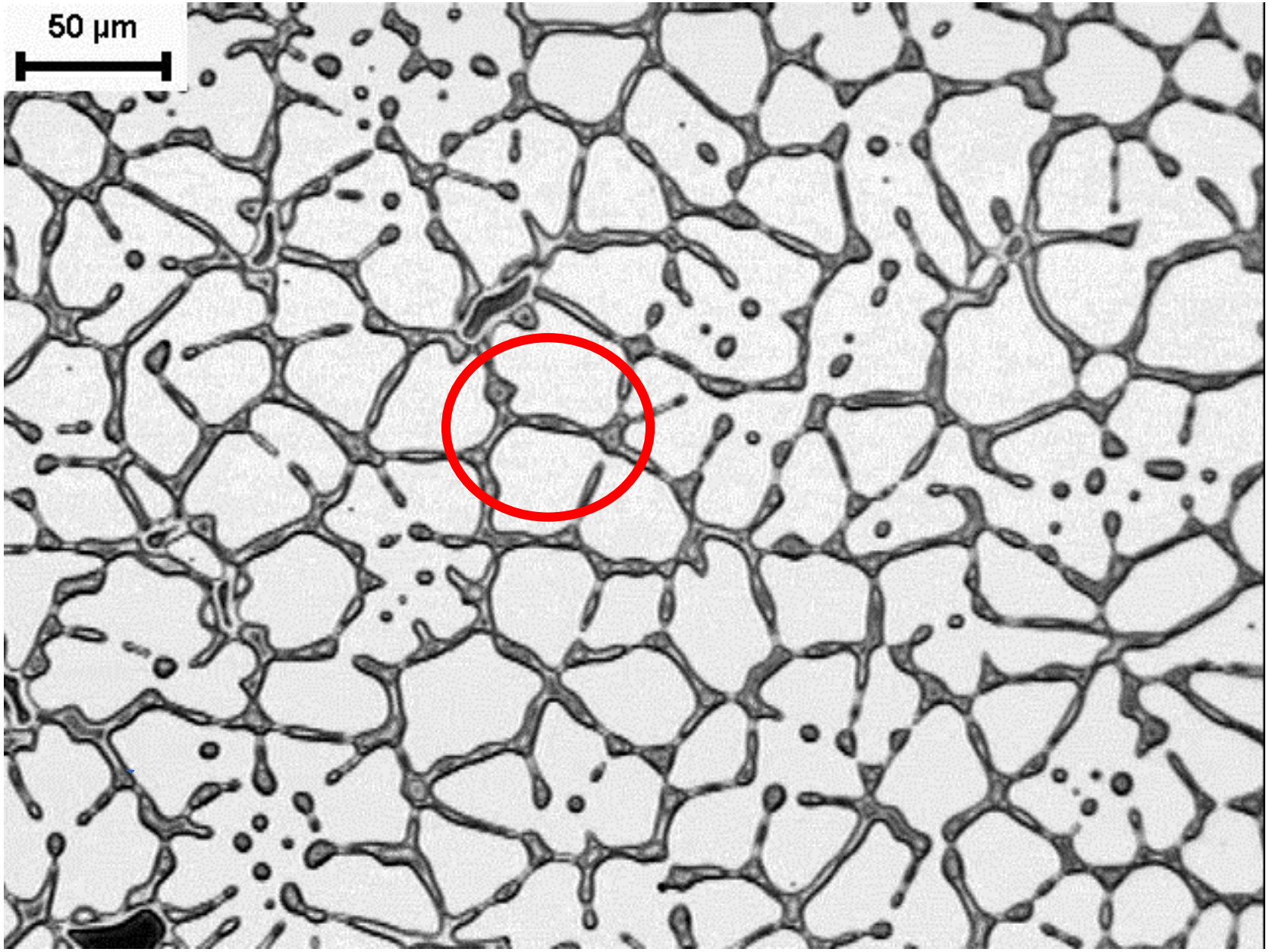
Thin Film of Polystyrene

$T_G \simeq 105^\circ C$

This film ≃ 40 nm thk

Heated to 120 °C or 80.

Rough Surface



Late Stage of Dewetting.

→ Droplets appearing.

Application (one possible) of Thin Film is functional coating on spectacle Lenses.

→ Functional coating.
(Anti scratch / Anti glare / ....)

→ Would you like to make a thick coating or a thin coating.

→ If coating is thick → Stability is guerenteed. Every material absorbs light → Thicker is your Layer, Higher is the absorbtion.

If it is thin → possibility of rupture.

Visible Light → 400 - 700 nm

UV - WL. < 400 nm

UV 400

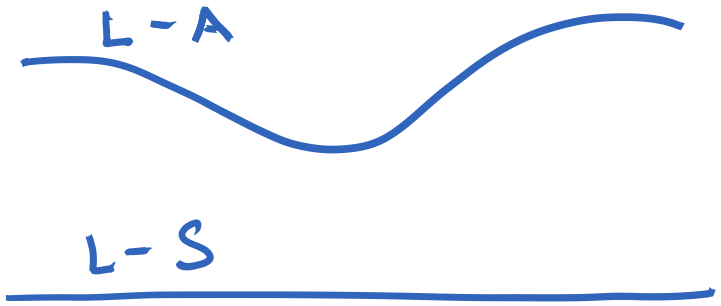
Sunglass. → Cut off all WL of Light < 400 nm. (Because Harm to UV in Sun Light).

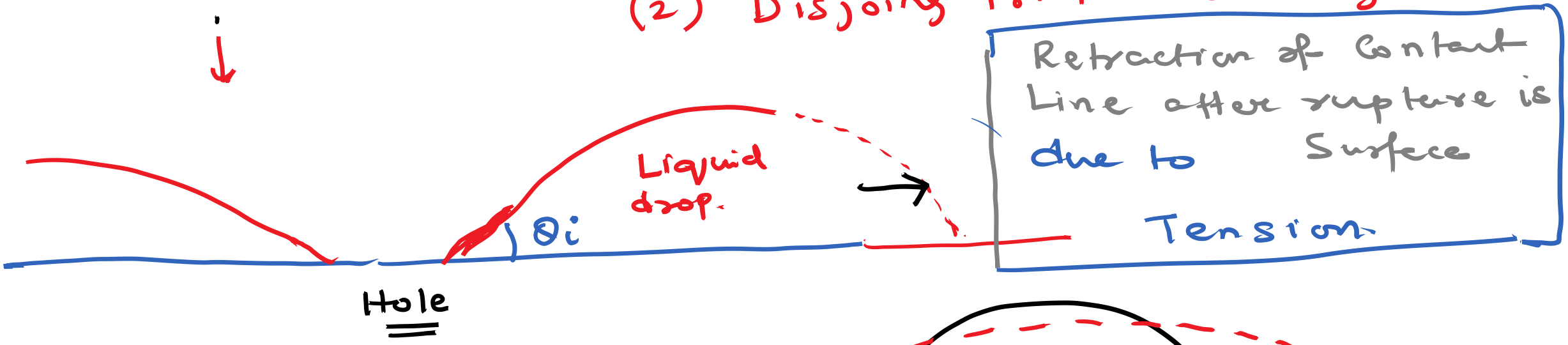
The question of UV protection becomes [more important while wearing a sunglass.

When we are Looking at the growth of an undulation,

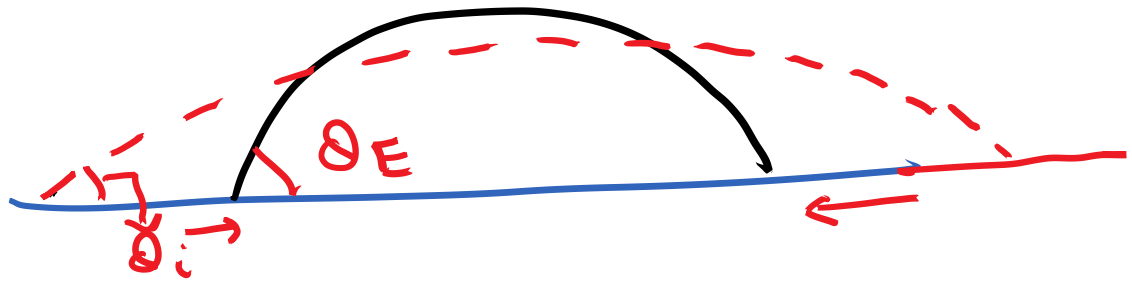
(1) Surface Tension (Laplace Pr) opposes the growth

(2) Disjoing Pr. Favors the growth.





Contact Line Further retracts (till → $\theta_i \approx \theta_E$



Surface Tension undergoes a role reversal

1) Befor rupture it tries to Stabilize the film and opposes hole formation

2) After rupture → it now favors hole growth!